

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 November 2011 (24.11.2011)

(10) International Publication Number
WO 2011/144907 A2

(51) International Patent Classification:

C09K 3/30 (2006.01)

(21) International Application Number:

PCT/GB2011/000770

(22) International Filing Date:

20 May 2011 (20.05.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1008438.2	20 May 2010 (20.05.2010)	GB
1010057.6	16 June 2010 (16.06.2010)	GB
1020624.1	6 December 2010 (06.12.2010)	GB
1102556.6	14 February 2011 (14.02.2011)	GB

(71) Applicant (for all designated States except US): **MEXI-CHEM AMANCO HOLDING S.A. DE C.V.** [MX/MX]; Rio San Javier No. 10, Fraccionamiento, Viveros del Rio, Tlalnepantla, Estado de Mexico 54060 (MX).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **LOW, Robert, E.** [GB/GB]; Mexichem UK Limited, PO Box 13, The Heath, Runcorn, Cheshire WA7 4QF (GB).

(74) Agent: **PUGH, Robert**; Potter Clarkson LLP, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))



WO 2011/144907 A2

(54) Title: HEAT TRANSFER COMPOSITIONS

(57) Abstract: The invention provides a heat transfer composition comprising (i) a first component selected from *trans*-1, 3,3,3-tetrafluoropropene (R-1234ze(E)), *cis*-1, 3,3,3-tetrafluoropropene (R-1234ze(Z)) and mixtures thereof; (ii) carbon dioxide (R-744); and (iii) a third component selected from 1,1,1-trifluoropropane (R-263fb), 1,1,1,2,3-pentafluoropropane (R-245eb), ammonia (R-717) and mixtures thereof.

HEAT TRANSFER COMPOSITIONS

The invention relates to heat transfer compositions, and in particular to heat transfer compositions which may be suitable as replacements for existing refrigerants such as R-5 134a, R-152a, R-1234yf, R-22, R-410A, R-407A, R-407B, R-407C, R507 and R-404a.

The listing or 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.

10

Mechanical refrigeration systems and related heat transfer devices such as heat pumps and air-conditioning systems are well known. In such systems, a refrigerant liquid evaporates at low pressure taking heat from the surrounding zone. The resulting vapour is then compressed and passed to a condenser where it condenses and gives off heat to 15 a second zone, the condensate being returned through an expansion valve to the evaporator, so completing the cycle. Mechanical energy required for compressing the vapour and pumping the liquid is provided by, for example, an electric motor or an internal combustion engine.

20

In addition to having a suitable boiling point and a high latent heat of vaporisation, the properties preferred in a refrigerant include low toxicity, non-flammability, non-corrosivity, high stability and freedom from objectionable odour. Other desirable properties are ready compressibility at pressures below 25 bars, low discharge temperature on compression, high refrigeration capacity, high efficiency (high coefficient of performance) and an 25 evaporator pressure in excess of 1 bar at the desired evaporation temperature.

Dichlorodifluoromethane (refrigerant R-12) possesses a suitable combination of properties and was for many years the most widely used refrigerant. Due to international 30 concern that fully and partially halogenated chlorofluorocarbons were damaging the earth's protective ozone layer, there was general agreement that their manufacture and use should be severely restricted and eventually phased out completely. The use of dichlorodifluoromethane was phased out in the 1990's.

Chlorodifluoromethane (R-22) was introduced as a replacement for R-12 because of its 35 lower ozone depletion potential. Following concerns that R-22 is a potent greenhouse gas, its use is also being phased out.

Whilst heat transfer devices of the type to which the present invention relates are essentially closed systems, loss of refrigerant to the atmosphere can occur due to leakage during operation of the equipment or during maintenance procedures. It is 5 important, therefore, to replace fully and partially halogenated chlorofluorocarbon refrigerants by materials having zero ozone depletion potentials.

In addition to the possibility of ozone depletion, it has been suggested that significant 10 concentrations of halocarbon refrigerants in the atmosphere might contribute to global warming (the so-called greenhouse effect). It is desirable, therefore, to use refrigerants which have relatively short atmospheric lifetimes as a result of their ability to react with other atmospheric constituents such as hydroxyl radicals, or as a result of ready degradation through photolytic processes.

15 R-410A and R-407 refrigerants (including R-407A, R-407B and R-407C) have been introduced as a replacement refrigerant for R-22. However, R-22, R-410A and the R-407 refrigerants all have a high global warming potential (GWP, also known as greenhouse warming potential).

20 1,1,1,2-tetrafluoroethane (refrigerant R-134a) was introduced as a replacement refrigerant for R-12. R-134a is an energy efficient refrigerant, used currently for automotive air conditioning. However it is a greenhouse gas with a GWP of 1430 relative to CO₂ (GWP of CO₂ is 1 by definition). The proportion of the overall environmental impact of automotive air conditioning systems using this gas, which may be attributed to 25 the direct emission of the refrigerant, is typically in the range 10-20%. Legislation has now been passed in the European Union to rule out use of refrigerants having GWP of greater than 150 for new models of car from 2011. The car industry operates global technology platforms, and in any event emission of greenhouse gas has global impact, thus there is a need to find fluids having reduced environmental impact (e.g. reduced 30 GWP) compared to HFC-134a.

R-152a (1,1-difluoroethane) has been identified as an alternative to R-134a. It is somewhat more efficient than R-134a and has a greenhouse warming potential of 120. However the flammability of R-152a is judged too high, for example to permit its safe use 35 in mobile air conditioning systems. In particular it is believed that its lower flammable limit in air is too low, its flame speeds are too high, and its ignition energy is too low.

Thus there is a need to provide alternative refrigerants having improved properties such as low flammability. Fluorocarbon combustion chemistry is complex and unpredictable. It is not always the case that mixing a non-flammable fluorocarbon with a flammable 5 fluorocarbon reduces the flammability of the fluid or reduces the range of flammable compositions in air. For example, the inventors have found that if non-flammable R-134a is mixed with flammable R-152a, the lower flammable limit of the mixture alters in a manner which is not predictable. The situation is rendered even more complex and less predictable if ternary or quaternary compositions are considered.

10

There is also a need to provide alternative refrigerants that may be used in existing devices such as refrigeration devices with little or no modification.

15 R-1234yf (2,3,3,3-tetrafluoropropene) has been identified as a candidate alternative refrigerant to replace R-134a in certain applications, notably the mobile air conditioning or heat pumping applications. Its GWP is about 4. R-1234yf is flammable but its flammability characteristics are generally regarded as acceptable for some applications including mobile air conditioning or heat pumping. In particular, when compared with R-152a, its lower flammable limit is higher, its minimum ignition energy is higher and the 20 flame speed in air is significantly lower than that of R-152a.

25 The environmental impact of operating an air conditioning or refrigeration system, in terms of the emissions of greenhouse gases, should be considered with reference not only to the so-called "direct" GWP of the refrigerant, but also with reference to the so-called "indirect" emissions, meaning those emissions of carbon dioxide resulting from consumption of electricity or fuel to operate the system. Several metrics of this total GWP impact have been developed, including those known as Total Equivalent Warming Impact (TEWI) analysis, or Life-Cycle Carbon Production (LCCP) analysis. Both of these 30 measures include estimation of the effect of refrigerant GWP and energy efficiency on overall warming impact. Emissions of carbon dioxide associated with manufacture of the refrigerant and system equipment should also be considered.

35 The energy efficiency and refrigeration capacity of R-1234yf have been found to be significantly lower than those of R-134a and in addition the fluid has been found to exhibit increased pressure drop in system pipework and heat exchangers. A consequence of this is that to use R-1234yf and achieve energy efficiency and cooling

performance equivalent to R-134a, increased complexity of equipment and increased size of pipework is required, leading to an increase in indirect emissions associated with equipment. Furthermore, the production of R-1234yf is thought to be more complex and less efficient in its use of raw materials (fluorinated and chlorinated) than R-134a.

5 Current projections of long term pricing for R-1234yf is in the range 10-20 times greater than R-134a. This price differential and the need for extra expenditure on hardware will limit the rate at which refrigerants are changed and hence limit the rate at which the overall environmental impact of refrigeration or air conditioning may be reduced. In summary, the adoption of R-1234yf to replace R-134a will consume more raw materials

10 and result in more indirect emissions of greenhouse gases than does R-134a.

Some existing technologies designed for R-134a may not be able to accept even the reduced flammability of some heat transfer compositions (any composition having a GWP of less than 150 is believed to be flammable to some extent).

15 A principal object of the present invention is therefore to provide a heat transfer composition which is usable in its own right or suitable as a replacement for existing refrigeration usages which should have a reduced GWP, yet have a capacity and energy efficiency (which may be conveniently expressed as the "Coefficient of Performance")

20 ideally within 10% of the values, for example of those attained using existing refrigerants (e.g. R-134a, R-152a, R-1234yf, R-22, R-410A, R-407A, R-407B, R-407C, R507 and R-404a), and preferably within less than 10% (e.g. about 5%) of these values. It is known in the art that differences of this order between fluids are usually resolvable by redesign of equipment and system operational features. The composition should also ideally have

25 reduced toxicity and acceptable flammability.

The subject invention addresses the above deficiencies by the provision of a heat transfer composition comprising (i) a first component selected from *trans*-1,3,3,3-tetrafluoropropene (R-1234ze(E)), *cis*-1,3,3,3-tetrafluoropropene (R-1234ze(Z)) and mixtures thereof; (ii) carbon dioxide (CO₂ or R-744); and (iii) a third component selected from 1,1,1-trifluoropropane (R-263fb), 1,1,1,2,3-pentafluoropropane (R-245eb), ammonia (R-717) and mixtures thereof.

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

Typically, the compositions of the invention contain *trans*-1,3,3,3-tetrafluoropropene (R-1234ze(E)). The majority of the specific compositions described herein contain R-1234ze(E). It is to be understood, of course, that some or all of the R-1234ze(E) in such compositions can be replaced by R-1234ze(Z). The *trans* isomer is currently preferred, 5 however.

Typically, the composition of the invention contain at least about 5 % by weight R-1234ze(E), preferably at least about 15 % by weight. In one embodiment, the compositions of the invention contain at least about 45 % by weight R-1234ze(E), for 10 example from about 50 to about 98 % by weight.

The preferred amounts and choice of components for the invention are determined by a combination of properties:

15 (a) Flammability: non-flammable or weakly flammable compositions are preferred.
(b) Effective operating temperature of the refrigerant in an air conditioning system evaporator.
(c) Temperature "glide" of the mixture and its effect on heat exchanger performance.
(d) Critical temperature of the composition. This should be higher than the maximum 20 expected condenser temperature.

The effective operating temperature in an air conditioning cycle, especially automotive air conditioning, is limited by the need to avoid ice formation on the air-side surface of the refrigerant evaporator. Typically air conditioning systems must cool and dehumidify 25 humid air; so liquid water will be formed on the air-side surface. Most evaporators (without exception for the automotive application) have finned surfaces with narrow fin spacing. If the evaporator is too cold then ice can be formed between the fins, restricting the flow of air over the surface and reducing overall performance by reducing the working area of the heat exchanger.

30 It is known for automotive air-conditioning applications (*Modern Refrigeration and Air Conditioning* by AD Althouse et al, 1988 edition, Chapter 27, which is incorporated herein by reference) that refrigerant evaporation temperatures of -2 °C or higher are preferred to ensure that the problem of ice formation is thereby avoided.

It is also known that non-azeotropic refrigerant mixtures exhibit temperature "glide" in evaporation or condensation. In other words, as the refrigerant is progressively vaporised or condensed at constant pressure, the temperature rises (in evaporation) or drops (in condensation), with the total temperature difference (inlet to outlet) being 5 referred to as the temperature glide. The effect of glide on evaporation and condensation temperature must also be considered.

The critical temperature of a heat transfer composition should be higher than the maximum expected condenser temperature. This is because the cycle efficiency drops 10 as critical temperature is approached. As this happens, the latent heat of the refrigerant is reduced and so more of the heat rejection in the condenser takes place by cooling gaseous refrigerant; this requires more area per unit heat transferred.

R-410A is commonly used in building and domestic heat pump systems and by way of 15 illustration its critical temperature of about 71 °C is higher than the highest normal condensing temperature required to deliver useful warm air at about 50 °C. The automotive duty requires air at about 50 °C so the critical temperature of the fluids of the invention should be higher than this if a conventional vapour compression cycle is to be utilised. Critical temperature is preferably at least 15K higher than the maximum air 20 temperature.

In one aspect, the compositions of the invention have a critical temperature of greater than about 65 °C, preferably greater than about 70 °C.

25 The carbon dioxide content of the compositions of the invention is limited primarily by considerations (b) and/or (c) and/or (d) above. Conveniently, the compositions of the invention typically contain up to about 35 % by weight R-744, preferably up to about 30 % by weight.

30 In a preferred aspect, the compositions of the invention contain from about 4 to about 30 % R-744 by weight, preferably from about 4 to about 28 % by weight, or from about 8 to about 30 % by weight, or from about 10 to about 30 % by weight.

35 The content of the third component, which may include flammable compounds such as R263fb, is selected so that even in the absence of the carbon dioxide element of the composition, the residual fluorocarbon mixture has a lower flammable limit in air at

ambient temperature (e.g. 23°C) (as determined in the ASHRAE-34 12 litre flask test apparatus) which is greater than 5% v/v, preferably greater than 6% v/v, most preferably such that the mixture is non-flammable. The issue of flammability is discussed further later in this specification.

5

Typically, the compositions of the invention contain up to about 60 % by weight of the third component. Preferably, the compositions of the invention contain up to about 50 % by weight of the third component. Conveniently, the compositions of the invention contain up to about 45 % by weight of the third component. In one aspect, the compositions of the invention contain from about 1 to about 40 % by weight of the third component.

10 In one embodiment, the compositions of the invention comprise from about 10 to about 95 % R-1234ze(E) by weight, from about 2 to about 30 % by weight R-744, and from 15 about 3 to about 60 % by weight of the third component.

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

20 For the avoidance of doubt, it is to be understood that the stated upper and lower values for ranges of amounts 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.

25 In one embodiment, the compositions of the invention consist essentially of (or consist of) the first component (e.g. R-1234ze(E)), R-744 and the third component.

30 By the term "consist essentially of", we mean 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. We include the term "consist of" within the meaning of "consist essentially of".

35 For the avoidance of doubt, any of the compositions of the invention described herein, including those with specifically defined compounds and amounts of compounds or

components, may consist essentially of (or consist of) the compounds or components defined in those compositions.

The third component is selected from R-263fb, R-245eb, ammonia, and mixtures thereof.

5 In one aspect, the third component contains only one of the listed components. For example, the third component may contain only one of R-263fb, R-245eb or ammonia. Thus, the compositions of the invention may be ternary blends of R-1234ze(E), R-744 and one of the listed third components (e.g. R-263fb or R-245eb).

10 However, mixtures R-263fb, R-245eb and ammonia can be used as the third component.

The invention contemplates compositions in which additional compounds are included in the third component. Example of such compounds include difluoromethane (R-32), 1,1-difluoroethane (R-152a), fluoroethane (R-161), 1,1,1,2-tetrafluoroethane (R-134a), 15 2,3,3,3-tetrafluoropropene (R-1234yf), 3,3,3-trifluoropropene (R-1243zf), propylene (R-1270), propane (R-290), n-butane (R-600), isobutane (R-600a), and mixtures thereof.

For example, the compositions of the invention may include R-134a. If present, the R-134a typically is present in an amount of from about 2 to about 50 % by weight, such as 20 from about 5 to about 40 % by weight (e.g. from about 5 to about 20 % by weight).

Preferably, the compositions of the invention which contain R-134a 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 25 temperature between about -20°C and 60°C are also non-flammable.

In one embodiment, the third component comprises R-263fb. The third component may consist essentially of (or consist of) R-263fb. Compositions of the invention which contain R-263fb typically contain it in an amount of up to about 50 % by weight, 30 preferably up to 40 % by weight, for example up to 30 % by weight.

Preferred compositions of the invention contain from about 30 to about 94 % R-1234ze(E), from about 4 to about 30 % by weight R-744 and from about 2 to about 40 % by weight R-263fb. For example, such compositions may comprise from about 37 to 35 about 92 % R-1234ze(E), from about 4 to about 28 % by weight R-744 and from about 4 to about 35 % by weight R-263fb.

Further preferred compositions of the invention contain from about 42 to about 91 % R-1234ze(E), from about 4 to about 28 % by weight R-744 and from about 5 to about 30 % by weight R-263fb. For example, such compositions may comprise from about 42 to about 85 % R-1234ze(E), from about 10 to about 28 % by weight R-744 and from about 5 to about 30 % by weight R-263fb.

5 In one embodiment, the third component comprises R-245eb. The third component may consist essentially of (or consist of) R-245eb. Compositions of the invention which contain R-245eb typically contain it in an amount of up to about 30 % by weight.

10

Preferred compositions of the invention contain from about 42 to about 91 % R-1234ze(E), from about 4 to about 28 % by weight R-744 and from about 5 to about 30 % by weight R-245eb. For example, such compositions may comprise from about 42 to about 85 % by weight R-1234ze(E), from about 10 to about 28 % by weight R-744 and 15 from about 5 to about 30 % by weight R-245eb.

In one embodiment, the third component comprises ammonia. The third component may consist essentially of (or consist of) ammonia. Compositions of the invention which contain ammonia typically contain it in an amount of up to about 30 % by weight.

20

The compositions of the invention may further contain pentafluoroethane (R-125). If present, R-125 typically is present in amounts up to about 40 % by weight, preferably from about 2 to about 20 % by weight.

25

Compositions according to the invention conveniently comprise substantially no R-1225 (pentafluoropropene), conveniently substantially no R-1225ye (1,2,3,3,3-pentafluoropropene) or R-1225zc (1,1,3,3,3-pentafluoropropene), which compounds may have associated toxicity issues.

30

By "substantially no", we include the meaning that the compositions of the invention contain 0.5% by weight or less of the stated component, preferably 0.1% or less, based on the total weight of the composition.

Certain compositions of the invention may contain substantially no:

35 (i) 2,3,3,3-tetrafluoropropene (R-1234yf),
(ii) *cis*-1,3,3,3-tetrafluoropropene (R-1234ze(Z)), and/or

(iii) 3,3,3-trifluoropropene (R-1243zf).

The compositions of the invention have zero ozone depletion potential.

5 Typically, the compositions of the invention have a GWP that is less than 1300, preferably less than 1000, more preferably less than 800, 500, 400, 300 or 200, especially less than 150 or 100, even less than 50 in some cases. Unless otherwise stated, IPCC (Intergovernmental Panel on Climate Change) TAR (Third Assessment Report) values of GWP have been used herein.

10

Advantageously, the compositions are of reduced flammability hazard when compared to the third component(s) alone, e.g. R-263fb or R-245eb. Preferably, the compositions are of reduced flammability hazard when compared to R-1234yf.

15 In one aspect, the compositions have one or more of (a) a higher lower flammable limit; (b) a higher ignition energy; or (c) a lower flame velocity compared to the third component(s) such as R-263fb or R245eb. In a preferred embodiment, the compositions of the invention are non-flammable. Advantageously, the mixtures of vapour that exist in equilibrium with the compositions of the invention at any temperature between about –
20 20°C and 60°C are also non-flammable.

Flammability may be determined in accordance with ASHRAE Standard 34 incorporating the ASTM Standard E-681 with test methodology as per Addendum 34p dated 2004, the entire content of which is incorporated herein by reference.

25

In some applications it may not be necessary for the formulation to be classed as non-flammable by the ASHRAE-34 methodology; it is possible to develop fluids whose flammability limits will be sufficiently reduced in air to render them safe for use in the application, for example if it is physically not possible to make a flammable mixture by 30 leaking the refrigeration equipment charge into the surrounds.

R-1234ze(E) is non-flammable in air at 23°C, although it exhibits flammability at higher temperatures in humid air. We have determined by experimentation that mixtures of R-1234ze(E) with flammable fluorocarbons such as R-32, R-152a or R-161 will remain non-flammable in air at 23 °C if the “fluorine ratio” R_f of the mixture is greater than about 0.57, where R_f is defined per gram-mole of the overall refrigerant mixture as:

$$R_f = (\text{gram-moles of fluorine}) / (\text{gram-moles fluorine} + \text{gram-moles hydrogen})$$

Thus for R-161, $R_f = 1/(1+5) = 1/6$ (0.167) and it is flammable, in contrast R-1234ze(E)

5 has $R_f = 4/6$ (0.667) and it is non-flammable. We found by experiment that a 20% v/v mixture of R-161 in R-1234ze(E) was similarly non-flammable. The fluorine ratio of this non-flammable mixture is $0.2*(1/6) + 0.8*(4/6) = 0.567$.

The validity of this relationship between flammability and fluorine ratio of 0.57 or higher

10 has thusfar been experimentally proven for HFC-32, HFC-152a and mixtures of HFC-32 with HFC-152a.

Takizawa et al, *Reaction Stoichiometry for Combustion of Fluoroethane Blends*,

ASHRAE Transactions 112(2) 2006 (which is incorporated herein by reference), shows

15 that there exists a near-linear relationship between this ratio and the flame speed of mixtures comprising R-152a, with increasing fluorine ratio resulting in lower flame speeds. The data in this reference teach that the fluorine ratio needs to be greater than about 0.65 for the flame speed to drop to zero, in other words, for the mixture to be non-flammable.

20

Similarly, Minor et al (Du Pont Patent Application WO2007/053697) provide teaching on the flammability of many hydrofluoroolefins, showing that such compounds could be expected to be non-flammable if the fluorine ratio is greater than about 0.7.

25 In view of this prior art teaching, it is unexpected that that mixtures of R-1234ze(E) with flammable fluorocarbons will remain non-flammable in air at 23 °C if the fluorine ratio R_f of the mixture is greater than about 0.57.

Furthermore, we identified that if the fluorine ratio is greater than about 0.46 then the

30 composition can be expected to have a lower flammable limit in air of greater than 6% v/v at room temperature.

35 By producing low- or non-flammable R-744/third component/R-1234ze(E) blends containing unexpectedly low amounts of R-1234ze(E), the amounts of the third component, in particular, in such compositions are increased. This is believed to result in heat transfer compositions exhibiting increased cooling capacity and/or decreased

pressure drop, compared to equivalent compositions containing higher amounts of (e.g. almost 100 %) R-1234ze(E).

Thus, the compositions of the invention exhibit a completely unexpected combination of 5 low-/non-flammability, low GWP and improved refrigeration performance properties. Some of these refrigeration performance properties are explained in more detail below.

Temperature glide, which can be thought of as the difference between bubble point and 10 dew point temperatures of a zeotropic (non-azeotropic) mixture at constant pressure, is a characteristic of a refrigerant; if it is desired to replace a fluid with a mixture then it is often preferable to have similar or reduced glide in the alternative fluid. In an embodiment, the compositions of the invention are zeotropic.

Advantageously, the volumetric refrigeration capacity of the compositions of the invention 15 is at least 85% of the existing refrigerant fluid it is replacing, preferably at least 90% or even at least 95%.

The compositions of the invention typically have a volumetric refrigeration capacity that is 20 at least 90% of that of R-1234yf. Preferably, the compositions of the invention have a volumetric refrigeration capacity that is at least 95% of that of R-1234yf, for example from about 95% to about 120% of that of R-1234yf.

In one embodiment, the cycle efficiency (Coefficient of Performance, COP) of the compositions of the invention is within about 5% or even better than the existing 25 refrigerant fluid it is replacing

Conveniently, the compressor discharge temperature of the compositions of the invention is within about 15K of the existing refrigerant fluid it is replacing, preferably about 10K or even about 5K.

30 The compositions of the invention preferably have energy efficiency at least 95% (preferably at least 98%) of R-134a under equivalent conditions, while having reduced or equivalent pressure drop characteristics and cooling capacity at 95% or higher of R-134a values. Advantageously the compositions have higher energy efficiency and lower 35 pressure drop characteristics than R-134a under equivalent conditions. The

compositions also advantageously have better energy efficiency and pressure drop characteristics than R-1234yf alone.

5 The heat transfer compositions of the invention are suitable for use in existing designs of equipment, and are compatible with all classes of lubricant currently used with established HFC refrigerants. They may be optionally stabilized or compatibilized with mineral oils by the use of appropriate additives.

10 Preferably, when used in heat transfer equipment, the composition of the invention is combined with a lubricant.

15 Conveniently, the lubricant is selected from the group consisting 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.

Advantageously, the lubricant further comprises a stabiliser.

20 Preferably, the stabiliser is selected from the group consisting of diene-based compounds, phosphates, phenol compounds and epoxides, and mixtures thereof.

Conveniently, the composition of the invention may be combined with a flame retardant.

25 Conveniently, the flame retardant is selected from the group consisting of tri-(2-chloroethyl)-phosphate, (chloropropyl) phosphate, tri-(2,3-dibromopropyl)-phosphate, tri-(1,3-dichloropropyl)-phosphate, diammonium phosphate, various halogenated aromatic compounds, antimony oxide, aluminium trihydrate, polyvinyl chloride, a fluorinated iodocarbon, a fluorinated bromocarbon, trifluoro iodomethane, perfluoroalkyl amines, bromo-fluoroalkyl amines and mixtures thereof.

30

Preferably, the heat transfer composition is a refrigerant composition.

In one embodiment, the invention provides a heat transfer device comprising a composition of the invention.

35

Preferably, the heat transfer device is a refrigeration device.

Conveniently, the heat transfer device is selected from the group consisting of automotive air conditioning systems, residential air conditioning systems, commercial air conditioning systems, residential refrigerator systems, residential freezer systems, 5 commercial refrigerator systems, commercial freezer systems, chiller air conditioning systems, chiller refrigeration systems, and commercial or residential heat pump systems. Preferably, the heat transfer device is a refrigeration device or an air-conditioning system.

10 The compositions of the invention are particularly suitable for use in mobile air-conditioning applications, such as automotive air-conditioning systems (e.g. heat pump cycle for automotive air-conditioning).

Advantageously, the heat transfer device contains a centrifugal-type compressor.

15 The invention also provides the use of a composition of the invention in a heat transfer device as herein described.

20 According to a further aspect of the invention, there is provided a blowing agent comprising a composition of the invention.

According to another aspect of the invention, there is provided a foamable composition comprising one or more components capable of forming foam and a composition of the invention.

25 Preferably, the one or more components capable of forming foam are selected from polyurethanes, thermoplastic polymers and resins, such as polystyrene, and epoxy resins.

30 According to a further aspect of the invention, there is provided a foam obtainable from the foamable composition of the invention.

Preferably the foam comprises a composition of the invention.

According to another aspect of the invention, there is provided a sprayable composition comprising a material to be sprayed and a propellant comprising a composition of the invention.

5 According to a further aspect of the invention, there is provided a method for cooling an article which comprises condensing a composition of the invention and thereafter evaporating said composition in the vicinity of the article to be cooled.

10 According to another aspect of the invention, there is provided a method for heating an article which comprises condensing a composition of the invention in the vicinity of the article to be heated and thereafter evaporating said composition.

15 According to a further aspect of the invention, there is provided a method for extracting a substance from biomass comprising contacting the biomass with a solvent comprising a composition of the invention, and separating the substance from the solvent.

According to another aspect of the invention, there is provided a method of cleaning an article comprising contacting the article with a solvent comprising a composition of the invention.

20 According to a further aspect of the invention, there is provided a method for extracting a material from an aqueous solution comprising contacting the aqueous solution with a solvent comprising a composition of the invention, and separating the material from the solvent.

25 According to another aspect of the invention, there is provided a method for extracting a material from a particulate solid matrix comprising contacting the particulate solid matrix with a solvent comprising a composition of the invention, and separating the material from the solvent.

30 According to a further aspect of the invention, there is provided a mechanical power generation device containing a composition of the invention.

35 Preferably, the mechanical power generation device is adapted to use a Rankine Cycle or modification thereof to generate work from heat.

According to another aspect of the invention, there is provided a method of retrofitting a heat transfer device comprising the step of removing an existing heat transfer fluid, and introducing a composition of the invention. Preferably, the heat transfer device is a refrigeration device or (a static) air conditioning system. Advantageously, the method 5 further comprises the step of obtaining an allocation of greenhouse gas (e.g. carbon dioxide) emission credit.

In accordance with the retrofitting method described above, an existing heat transfer fluid can be fully removed from the heat transfer device before introducing a composition of 10 the invention. An existing heat transfer fluid can also be partially removed from a heat transfer device, followed by introducing a composition of the invention.

In another embodiment wherein the existing heat transfer fluid is R-134a, and the composition of the invention contains R134a, R-1234ze(E), R-744, the third component 15 and any R-125 present (and optional components such as a lubricant, a stabiliser or an additional flame retardant), R-1234ze(E) and R-744, etc, can be added to the R-134a in the heat transfer device, thereby forming the compositions of the invention, and the heat transfer device of the invention, *in situ*. Some of the existing R-134a may be removed 20 from the heat transfer device prior to adding the R-1234ze(E), R-744, etc, to facilitate providing the components of the compositions of the invention in the desired proportions.

Thus, the invention provides a method for preparing a composition and/or heat transfer device of the invention comprising introducing R-1234ze(E), R-744, the third component, any R-125 desired, and optional components such as a lubricant, a stabiliser or an 25 additional flame retardant, into a heat transfer device containing an existing heat transfer fluid which is R-134a. Optionally, at least some of the R-134a is removed from the heat transfer device before introducing the R-1234ze(E), R-744, etc.

Of course, the compositions of the invention may also be prepared simply by mixing the 30 R-1234ze(E), R-744, the third component, any R-125 desired (and optional components such as a lubricant, a stabiliser or an additional flame retardant) in the desired proportions. The compositions can then be added to a heat transfer device (or used in any other way as defined herein) that does not contain R-134a or any other existing heat transfer 35 fluid, such as a device from which R-134a or any other existing heat transfer fluid have been removed.

In a further aspect of the invention, there is provided a method for reducing the environmental impact arising from operation of a product comprising an existing compound or composition, the method comprising replacing at least partially the existing compound or composition with a composition of the invention. Preferably, this method 5 comprises the step of obtaining an allocation of greenhouse gas emission credit.

By environmental impact we include the generation and emission of greenhouse warming gases through operation of the product.

10 As mentioned above, this environmental impact can be considered as including not only those emissions of compounds or compositions having a significant environmental impact from leakage or other losses, but also including the emission of carbon dioxide arising from the energy consumed by the device over its working life. Such environmental impact may be quantified by the measure known as Total Equivalent 15 Warming Impact (TEWI). This measure has been used in quantification of the environmental impact of certain stationary refrigeration and air conditioning equipment, including for example supermarket refrigeration systems (see, for example, http://en.wikipedia.org/wiki/Total_equivalent_warming_impact).

20 The environmental impact may further be considered as including the emissions of greenhouse gases arising from the synthesis and manufacture of the compounds or compositions. In this case the manufacturing emissions are added to the energy consumption and direct loss effects to yield the measure known as Life-Cycle Carbon Production (LCCP, see for example 25 <http://www.sae.org/events/aars/presentations/2007papasavva.pdf>). The use of LCCP is common in assessing environmental impact of automotive air conditioning systems.

30 Emission credit(s) are awarded for reducing pollutant emissions that contribute to global warming and may, for example, be banked, traded or sold. They are conventionally expressed in the equivalent amount of carbon dioxide. Thus if the emission of 1 kg of R-134a is avoided then an emission credit of $1 \times 1300 = 1300$ kg CO₂ equivalent may be awarded.

35 In another embodiment of the invention, there is provided a method for generating greenhouse gas emission credit(s) comprising (i) replacing an existing compound or composition with a composition of the invention, wherein the composition of the invention

has a lower GWP than the existing compound or composition; and (ii) obtaining greenhouse gas emission credit for said replacing step.

In a preferred embodiment, the use of the composition of the invention results in the equipment having a lower Total Equivalent Warming Impact, and/or a lower Life-Cycle Carbon Production than that which would be attained by use of the existing compound or composition.

These methods may be carried out on any suitable product, for example in the fields of air-conditioning, refrigeration (e.g. low and medium temperature refrigeration), heat transfer, blowing agents, aerosols or sprayable propellants, gaseous dielectrics, cryosurgery, veterinary procedures, dental procedures, fire extinguishing, flame suppression, solvents (e.g. carriers for flavorings and fragrances), cleaners, air horns, pellet guns, topical anesthetics, and expansion applications. Preferably, the field is air-conditioning or refrigeration.

Examples of suitable products include heat transfer devices, blowing agents, foamable compositions, sprayable compositions, solvents and mechanical power generation devices. In a preferred embodiment, the product is a heat transfer device, such as a refrigeration device or an air-conditioning unit.

The existing compound or composition has an environmental impact as measured by GWP and/or TEWI and/or LCCP that is higher than the composition of the invention which replaces it. The existing compound or composition may comprise a fluorocarbon compound, such as a perfluoro-, hydrofluoro-, chlorofluoro- or hydrochlorofluoro-carbon compound or it may comprise a fluorinated olefin

Preferably, the existing compound or composition is a heat transfer compound or composition such as a refrigerant. Examples of refrigerants that may be replaced include R-134a, R-152a, R-1234yf, R-410A, R-407A, R-407B, R-407C, R507, R-22 and R-404A. The compositions of the invention are particularly suited as replacements for R-134a, R-152a or R-1234yf, especially R-134a or R-1234yf.

Any amount of the existing compound or composition may be replaced so as to reduce the environmental impact. This may depend on the environmental impact of the existing compound or composition being replaced and the environmental impact of the

replacement composition of the invention. Preferably, the existing compound or composition in the product is fully replaced by the composition of the invention.

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

5

Examples

Modelled Performance Data

10 **Generation of accurate physical property model**

The physical properties of R-1234yf and R-1234ze(E) required to model refrigeration cycle performance, namely critical point, vapour pressure, liquid and vapour enthalpy, liquid and vapour density and heat capacities of vapour and liquid were accurately 15 determined by experimental methods over the pressure range 0-200bar and temperature range -40 to 200°C, and the resulting data used to generate Helmholtz free energy equation of state models of the Span-Wagner type for the fluid in the NIST REFPROP Version 8.0 software, which is more fully described in the user guide www.nist.gov/srd/PDFfiles/REFPROP8.PDF, and is incorporated herein by reference. 20 The variation of ideal gas enthalpy of both fluids with temperature was estimated using molecular modelling software Hyperchem v7.5 (which is incorporated herein by reference) and the resulting ideal gas enthalpy function was used in the regression of the equation of state for these fluids. The predictions of this model for R1234yf and R1234ze(E) were compared to the predictions yielded by use of the standard files for 25 R1234yf and R1234ze(E) included in REFPROP Version 9.0 (incorporated herein by reference). It was found that close agreement was obtained for each fluid's properties.

The vapour liquid equilibrium behaviour of R-1234ze(E) was studied in a series of binary pairs with carbon dioxide, R-32, R-125, R-134a, R-152a, R-161, propane and propylene 30 over the temperature range -40 to +60°C, which encompasses the practical operating range of most refrigeration and air conditioning systems. The composition was varied over the full compositional space for each binary in the experimental programme. Mixture parameters for each binary pair were regressed to the experimentally obtained data and the parameters were also incorporated into the REFPROP software model. The 35 academic literature was next searched for data on the vapour liquid equilibrium behaviour of carbon dioxide with the hydrofluorocarbons R-32, R-125, R-152a, R-161

and R-152a. The VLE data obtained from sources referenced in the article *Applications of the simple multi-fluid model to correlations of the vapour-liquid equilibrium of refrigerant mixtures containing carbon dioxide*, by R. Akasaka, Journal of Thermal Science and Technology, 159-168, 4, 1, 2009 (which is incorporated herein by reference) 5 were then used to generate mixing parameters for the relevant binary mixtures and these were then also incorporated into the REFPROP model. The standard REFPROP mixing parameters for carbon dioxide with propane and propylene were also incorporated to this model.

10 The resulting software model was used to compare the performance of selected fluids of the invention with R-134a in a heat pumping cycle application.

Heat pumping cycle comparison

15 In a first comparison the behaviour of the fluids was assessed for a simple vapour compression cycle with conditions typical of automotive heat pumping duty in low winter ambient temperatures. In this comparison pressure drop effects were included in the model by assignation of a representative expected pressure drop to the reference fluid (R-134a) followed by estimation of the equivalent pressure drop for the mixed refrigerant 20 of the invention in the same equipment at the same heating capacity. The comparison was made on the basis of equal heat exchanger area for the reference fluid (R-134a) and for the mixed fluids of the invention. The methodology used for this model was derived using the assumptions of equal effective overall heat transfer coefficient for refrigerant condensation, refrigerant evaporation, refrigerant liquid subcooling and refrigerant 25 vapour superheating processes to derive a so-called *UA* model for the process. The derivation of such a model for nonazeotropic refrigerant mixtures in heat pump cycles is more fully explained in the reference text *Vapor Compression Heat Pumps with refrigerant mixtures* by R Radermacher & Y Hwang (pub Taylor & Francis 2005) Chapter 3, which is incorporated herein by reference.

30 Briefly, the model starts with an initial estimate of the condensing and evaporating pressures for the refrigerant mixture and estimates the corresponding temperatures at the beginning and end of the condensation process in the condenser and the evaporation process in the evaporator. These temperatures are then used in conjunction 35 with the specified changes in air temperatures over condenser and evaporator to estimate a required overall heat exchanger area for each of the condenser and

evaporator. This is an iterative calculation: the condensing and evaporating pressures are adjusted to ensure that the overall heat exchanger areas are the same for reference fluid and for the mixed refrigerant.

5 For the comparison the worst case for heat pumping in automotive application was assumed with the following assumptions for air temperature and for R-134a cycle conditions.

Cycle conditions

10

Ambient air temperature on to condenser and evaporator -15°C

Air temperature leaving evaporator: -25°C

Air temperature leaving condenser (passenger air) +45°C

R134a evaporating temperature -30°C

15

R-134a condensing temperature +50°C

Subcooling of refrigerant in condenser 1K

Superheating of refrigerant in evaporator 5K

Compressor suction temperature 0°C

Compressor isentropic efficiency 66%

20

Passenger air heating load 2kW

Pressure drop in evaporator for R-134a 0.03bar

Pressure drop in condenser for R-134a 0.03bar

Pressure drop in suction line for R-134a 0.03bar

25

The model assumed countercurrent flow for each heat exchanger in its calculation of effective temperature differences for each of the heat transfer processes.

Condensing and evaporating temperatures for compositions was adjusted to give equivalent usage of heat exchange area as reference fluid. The following input

30

parameters were used.

Parameter		Reference
Refrigerant		R134a
Mean condenser temperature	°C	50
Mean evaporator temperature	°C	-30
Condenser subcooling	K	1
Evaporator superheat	K	5
Suction diameter	mm	16.2

Heating capacity	kW	2
Evaporator pressure drop	bar	0.03
Suction line pressure drop	bar	0.03
Condenser pressure drop	bar	0.03
Compressor suction temperature	°C	0
Isentropic efficiency		66%
Evaporator air on	°C	-15.00
Evaporator air off	°C	-25.00
Condenser air on	°C	-15.00
Condenser air off	°C	45.00
Condenser area	100.0%	100.0%
Evaporator area	100.0%	100.0%

Using the above model, the performance data for the reference R-134a is shown below.

COP (heating)		2.11
COP (heating) relative to Reference		100.0%
Volumetric heating capacity at suction	kJ/m ³	879
Capacity relative to Reference		100.0%
Critical temperature	°C	101.06
Critical pressure	bar	40.59
Condenser enthalpy change	kJ/kg	237.1
Pressure ratio		16.36
Refrigerant mass flow	kg/hr	30.4
Compressor discharge temperature	°C	125.5
Evaporator inlet pressure	bar	0.86
Condenser inlet pressure	bar	13.2
Evaporator inlet temperature	°C	-29.7
Evaporator dewpoint	°C	-30.3
Evaporator exit gas temperature	°C	-25.3
Evaporator mean temperature	°C	-30.0
Evaporator glide (out-in)	K	-0.6
Compressor suction pressure	bar	0.81
Compressor discharge pressure	bar	13.2
Suction line pressure drop	Pa/m	292
Pressure drop relative to reference		100.0%
Condenser dew point	°C	50.0
Condenser bubble point	°C	50.0
Condenser exit liquid temperature	°C	49.0
Condenser mean temperature	°C	50.0
Condenser glide (in-out)	K	0.1

The generated performance data for selected compositions of the invention is set out in the following Tables. The tables show key parameters of the heat pump cycle, including operating pressures, volumetric heating capacity, energy efficiency (expressed as coefficient of performance for heating COP) compressor discharge temperature and

pressure drops in pipework. The volumetric heating capacity of a refrigerant is a measure of the amount of heating which can be obtained for a given size of compressor operating at fixed speed. The coefficient of performance (COP) is the ratio of the amount of heat energy delivered in the condenser of the heat pump cycle to the amount of work consumed by the compressor.

5 The performance of R-134a is taken as the reference point for comparison of heating capacity, energy efficiency and pressure drop. This fluid is used as a reference for comparison of the ability of the fluids of the invention to be used in the heat pump mode 10 of an automotive combined air conditioning and heat pump system.

It should be noted in passing that the utility of fluids of the invention is not limited to 15 automotive systems. Indeed these fluids can be used in so-called stationary (residential or commercial) equipment. Currently the main fluids used in such stationary equipment are R-410A (having a GWP of 2100) or R22 (having a GWP of 1800 and an ozone depletion potential of 0.05). The use of the fluids of the invention in such stationary equipment offers the ability to realise similar utility but with fluids having no ozone depletion potential and significantly reduced GWP compared to R410A.

20 It is evident that fluids of the invention can provide improved energy efficiency compared to R-134a or R-410A. It is unexpectedly found that the addition of carbon dioxide to the refrigerants of the invention can increase the COP of the resulting cycle above that of R-134a, even in case where admixture of the other mixture components would result in a fluid having worse energy efficiency than R-134a.

25 It is further found for all the fluids of the invention that compositions up to about 30% w/w of CO₂ can be used which yield refrigerant fluids whose critical temperature is about 70 °C or higher. This is particularly significant for stationary heat pumping applications 30 where R-410A is currently used. The fundamental thermodynamic efficiency of a vapour compression process is affected by proximity of the critical temperature to the condensing temperature. R-410A has gained acceptance and can be considered an acceptable fluid for this application; its critical temperature is 71 °C. It has unexpectedly been found that significant quantities of CO₂ (critical temperature 31 °C) can be incorporated in fluids of the invention to yield mixtures having similar or higher critical 35 temperature to R-410A. Preferred compositions of the invention therefore have critical temperatures are about 70 °C or higher.

The heating capacity of the preferred fluids of the invention typically exceeds that of R134a. It is thought that R-134a alone, operated in an automotive a/c and heat pump system, cannot provide all of the potential passenger air heating demand in heat pump mode. Therefore higher heating capacities than R-134a are preferred for potential use in an automotive a/c and heat pump application. The fluids of the invention offer the ability to optimise fluid capacity and energy efficiency for both air conditioning and cooling modes so as to provide an improved overall energy efficiency for both duties.

10 For reference, the heating capacity of R-410A in the same cycle conditions was estimated at about 290% of the R-134a value and the corresponding energy efficiency was found to be about 106% of the R-134a reference value.

15 It is evident by inspection of the tables that fluids of the invention have been discovered having comparable heating capacities and energy efficiencies to R-410A, allowing adaption of existing R-410A technology to use the fluids of the invention if so desired.

Some further benefits of the fluids of the invention are described in more detail below.

20 At equivalent cooling capacity the compositions of the invention offer reduced pressure drop compared to R-134a. This reduced pressure drop characteristic is believed to result in further improvement in energy efficiency (through reduction of pressure losses) in a real system. Pressure drop effects are of particular significance for automotive air conditioning and heat pump applications so these fluids offer particular advantage for this 25 application.

30 The performance of fluids of the invention were compared to binary mixtures of CO₂/R1234ze(E). For all the ternary compositions of the invention the energy efficiency of the ternary mixtures was increased relative to the binary mixture having equivalent CO₂ content. These mixtures therefore represent an improved solution relative to the CO₂/R1234ze(E) binary refrigerant mixture, at least for CO₂ content less than 30% w/w.

Table 1: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 5 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	0/5/95	2/5/93	4/5/91	6/5/89	8/5/87	10/5/85	12/5/83	14/5/81
COP (heating)	1.99	2.05	2.10	2.13	2.16	2.18	2.19	2.21
COP relative to Reference	94.1%	97.2%	99.5%	101.1%	102.4%	103.3%	104.1%	104.7%
Volumetric heating capacity at suction	622	704	788	875	965	1058	1153	1252
Capacity relative to Reference	70.8%	80.1%	89.7%	99.5%	109.8%	120.4%	131.3%	142.5%
Critical temperature	°C	110.82	106.85	103.13	99.62	96.30	93.17	90.20
Critical pressure	bar	37.25	38.08	38.90	39.72	40.53	41.34	42.14
Condenser enthalpy change	kJ/kg	210.3	224.1	235.6	245.3	253.6	261.0	267.5
Pressure ratio	kg/hr	18.51	18.81	18.90	18.81	18.59	18.27	17.88
Refrigerant mass flow	°C	34.2	32.1	30.6	29.4	28.4	27.6	26.9
Compressor discharge temperature	bar	112.2	116.6	120.5	124.1	127.4	130.4	133.2
Evaporator inlet pressure	bar	0.66	0.70	0.76	0.82	0.89	0.96	1.04
Condenser inlet pressure	bar	10.8	12.0	13.2	14.4	15.6	16.8	18.0
Evaporator inlet temperature	°C	-28.9	-29.6	-30.3	-31.1	-31.9	-32.7	-33.6
Evaporator dewpoint	°C	-30.2	-29.7	-29.0	-28.2	-27.4	-26.6	-25.8
Evaporator exit gas temperature	°C	-25.2	-24.7	-24.0	-23.2	-22.4	-21.6	-20.8
Evaporator mean temperature	°C	-29.6	-29.6	-29.7	-29.6	-29.6	-29.7	-29.8
Evaporator glide (out-in)	K	-1.3	0.0	1.3	2.8	4.4	6.1	7.8
Compressor suction pressure	bar	0.58	0.64	0.70	0.77	0.84	0.92	1.01
Compressor discharge pressure	bar	10.8	12.0	13.2	14.4	15.6	16.8	18.0
Suction line pressure drop	Pa/m	457	385	331	289	256	229	206
Pressure drop relative to reference	156.3%	131.8%	113.4%	99.1%	87.6%	78.3%	70.4%	63.9%
Condenser dew point	°C	53.3	55.3	57.0	58.4	59.4	60.2	60.8
Condenser bubble point	°C	53.1	47.1	42.4	38.8	35.9	33.6	31.8
Condenser exit liquid temperature	°C	52.1	46.1	41.4	37.8	34.9	32.6	30.8
Condenser mean temperature	°C	53.2	51.2	49.7	48.6	47.7	46.9	45.7
Condenser glide (in-out)	K	0.1	8.2	14.5	19.6	23.5	26.6	30.9

Table 2: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 5 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	16/5/79	18/5/77	20/5/75	22/5/73	24/5/71	26/5/69	28/5/67	30/5/65
COP (heating)	2.22	2.22	2.23	2.23	2.24	2.24	2.24	2.23
COP relative to Reference	105.1%	105.5%	105.7%	105.9%	106.0%	106.0%	106.0%	105.9%
Volumetric heating capacity at suction	1352	1455	1559	1665	1771	1878	1986	2093
Capacity relative to Reference	153.9%	165.6%	177.5%	189.5%	201.6%	213.8%	226.0%	238.2%
Critical temperature	84.72	82.18	79.76	77.46	75.26	73.16	71.15	69.22
Critical pressure	43.73	44.53	45.32	46.10	46.88	47.66	48.44	49.22
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature								
Evaporator inlet pressure								
Condenser inlet pressure								
Evaporator inlet temperature								
Evaporator dewpoint								
Evaporator exit gas temperature								
Evaporator mean temperature								
Evaporator glide (out-in)								
Compressor suction pressure								
Compressor discharge pressure								
Suction line pressure drop								
Pressure drop relative to reference								
Condenser dew point								
Condenser bubble point								
Condenser exit liquid temperature								
Condenser mean temperature								
Condenser glide (in-out)								

Table 3: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 7 % R-263fb Composition CO₂/R-263fb/R-1234ze(E) % by weight ▲

	0/7/93	2/7/91	4/7/89	6/7/87	8/7/85	10/7/83	12/7/81	14/7/79
COP (heating)	1.98	2.05	2.10	2.13	2.16	2.18	2.19	2.21
COP relative to Reference	94.1%	97.2%	99.4%	101.1%	102.3%	103.3%	104.0%	104.6%
Volumetric heating capacity at suction	625	707	791	878	969	1062	1158	1256
Capacity relative to Reference	71.1%	80.4%	90.0%	100.0%	110.2%	120.9%	131.8%	143.0%
Critical temperature	°C	111.18	107.22	103.50	99.99	96.67	93.54	90.57
Critical pressure	bar	37.49	38.35	39.19	40.03	40.86	41.69	42.51
Condenser enthalpy change	kJ/kg	210.4	224.3	235.9	245.6	253.9	261.2	267.7
Pressure ratio		18.43	18.74	18.84	18.77	18.54	18.23	17.85
Refrigerant mass flow	kg/hr	34.2	32.1	30.5	29.3	28.4	27.6	26.9
Compressor discharge temperature	°C	112.0	116.4	120.4	124.0	127.2	130.2	133.0
Evaporator inlet pressure	bar	0.66	0.71	0.76	0.82	0.89	0.97	1.05
Condenser inlet pressure	bar	10.8	12.0	13.3	14.5	15.7	16.9	18.1
Evaporator inlet temperature	°C	-28.9	-29.6	-30.3	-31.1	-31.9	-32.7	-33.6
Evaporator dewpoint	°C	-30.2	-29.6	-29.0	-28.2	-27.4	-26.6	-25.8
Evaporator exit gas temperature	°C	-25.2	-24.6	-24.0	-23.2	-22.4	-21.6	-20.8
Evaporator mean temperature	°C	-29.5	-29.6	-29.6	-29.6	-29.6	-29.6	-29.7
Evaporator glide (out-in)	K	-1.2	0.0	1.4	2.9	4.5	6.1	7.8
Compressor suction pressure	bar	0.59	0.64	0.70	0.77	0.85	0.93	1.01
Compressor discharge pressure	bar	10.8	12.0	13.3	14.5	15.7	16.9	18.1
Suction line pressure drop	Pa/m	455	383	330	288	255	227	205
Pressure drop relative to reference		155.6%	131.2%	112.9%	98.6%	87.2%	77.9%	70.1%
Condenser dew point	°C	53.3	55.4	57.1	58.5	59.5	60.3	61.3
Condenser bubble point	°C	53.2	47.1	42.4	38.7	35.9	33.6	31.7
Condenser exit liquid temperature	°C	52.2	46.1	41.4	37.7	34.9	32.6	30.7
Condenser mean temperature	°C	53.2	51.2	49.7	48.6	47.7	46.9	45.7
Condenser glide (in-out)	K	0.1	8.3	14.7	19.7	23.7	26.8	31.0

Table 4: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 7 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	16/7/77	18/7/75	20/7/73	22/7/71	24/7/69	26/7/67	28/7/65	30/7/63
COP (heating)	2.21	2.22	2.23	2.23	2.23	2.23	2.23	2.23
COP relative to Reference	105.0%	105.4%	105.6%	105.8%	105.9%	105.9%	105.9%	105.8%
Volumetric heating capacity at suction	1357	1460	1564	1670	1776	1883	1991	2099
Capacity relative to Reference	154.5%	166.1%	178.0%	190.0%	202.2%	214.4%	226.6%	238.9%
Critical temperature	85.08	82.54	80.11	77.81	75.60	73.50	71.49	69.56
Critical pressure	bar 44.13	bar 44.94	bar 45.74	bar 46.53	bar 47.33	bar 48.12	bar 48.90	bar 49.69
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature								
Evaporator inlet pressure								
Condenser inlet pressure								
Evaporator inlet temperature								
Evaporator dewpoint								
Evaporator exit gas temperature								
Evaporator mean temperature								
Evaporator glide (out-in)								
Compressor suction pressure								
Compressor discharge pressure								
Suction line pressure drop								
Pressure drop relative to reference								
Condenser dew point	°C 61.4	°C 61.5	°C 61.4	°C 61.2	°C 60.9	°C 60.5	°C 60.0	°C 59.5
Condenser bubble point	°C 29.0	°C 27.9	°C 27.1	°C 26.3	°C 25.7	°C 25.1	°C 24.7	°C 24.3
Condenser exit liquid temperature	°C 28.0	°C 26.9	°C 26.1	°C 25.3	°C 24.7	°C 24.1	°C 23.7	°C 23.3
Condenser mean temperature	°C 45.2	°C 44.7	°C 44.2	°C 43.3	°C 42.8	°C 42.3	°C 41.9	°C 41.9
Condenser glide (in-out)	K 32.5	K 33.6	K 34.3	K 35.2	K 35.4	K 35.3	K 35.2	K 35.2

Table 5: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 10 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	0/10/90	2/10/88	4/10/86	6/10/84	8/10/82	10/10/80	12/10/78	14/10/76
COP (heating)	1.98	2.05	2.10	2.13	2.16	2.18	2.19	2.20
COP relative to Reference	93.9%	97.1%	99.4%	101.0%	102.2%	103.2%	103.9%	104.5%
Volumetric heating capacity at suction	628	711	796	883	974	1067	1164	1262
Capacity relative to Reference	71.5%	80.9%	90.6%	100.5%	110.8%	121.5%	132.4%	143.7%
Critical temperature	°C	111.73	107.77	104.04	100.53	97.22	94.08	91.11
Critical pressure	bar	37.83	38.72	39.60	40.47	41.33	42.19	43.03
Condenser enthalpy change	kJ/kg	210.6	224.7	236.3	246.1	254.4	261.7	268.1
Pressure ratio	kg/hr	18.31	18.65	18.77	18.71	18.50	18.18	17.81
Refrigerant mass flow	°C	34.2	32.0	30.5	29.3	28.3	27.5	26.9
Compressor discharge temperature	bar	111.7	116.1	120.1	123.7	127.0	129.9	132.7
Evaporator inlet pressure	bar	0.67	0.71	0.77	0.83	0.90	0.97	1.05
Condenser inlet pressure	bar	10.8	12.1	13.3	14.6	15.8	17.0	18.1
Evaporator inlet temperature	°C	-28.9	-29.6	-30.3	-31.1	-31.9	-32.7	-33.6
Evaporator dewpoint	°C	-30.1	-29.6	-29.0	-28.2	-27.4	-26.6	-25.8
Evaporator exit gas temperature	°C	-25.1	-24.6	-24.0	-23.2	-22.4	-21.6	-20.8
Evaporator mean temperature	°C	-29.5	-29.6	-29.6	-29.6	-29.6	-29.6	-29.7
Evaporator glide (out-in)	K	-1.2	0.0	1.4	2.9	4.5	6.1	7.8
Compressor suction pressure	bar	0.59	0.65	0.71	0.78	0.85	0.93	1.02
Compressor discharge pressure	bar	10.8	12.1	13.3	14.6	15.8	17.0	18.1
Suction line pressure drop	Pa/m	452	381	327	286	253	226	204
Pressure drop relative to reference		154.7%	130.3%	112.0%	97.9%	86.6%	77.4%	69.7%
Condenser dew point	°C	53.4	55.5	57.2	58.6	59.7	60.5	61.1
Condenser bubble point	°C	53.3	47.1	42.3	38.6	35.7	33.4	31.6
Condenser exit liquid temperature	°C	52.3	46.1	41.3	37.6	34.7	32.4	30.6
Condenser mean temperature	°C	53.3	51.3	49.8	48.6	47.7	47.0	46.3
Condenser glide (in-out)	K	0.1	8.4	14.9	20.0	24.0	27.1	29.5

Table 6: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 10 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	16/10/74	18/10/72	20/10/70	22/10/68	24/10/66	26/10/64	28/10/62	30/10/60
COP (heating)	2.21	2.22	2.22	2.23	2.23	2.23	2.23	2.23
COP relative to Reference	104.9%	105.2%	105.5%	105.7%	105.8%	105.7%	105.7%	105.6%
Volumetric heating capacity at suction	1363	1466	1571	1676	1783	1890	1998	2105
Capacity relative to Reference	155.1%	166.9%	178.7%	190.8%	202.9%	215.1%	227.4%	239.6%
Critical temperature	85.61	83.07	80.64	78.33	76.12	74.02	72.00	70.07
Critical pressure	bar 44.70	bar 45.53	bar 46.34	bar 47.16	bar 47.97	bar 48.77	bar 49.57	bar 50.37
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature	kg/hr 25.8	kg/hr 25.3	kg/hr 24.9	kg/hr 24.6	kg/hr 24.2	kg/hr 23.9	kg/hr 23.6	kg/hr 23.3
Evaporator inlet pressure	°C 137.7	°C 140.0	°C 142.2	°C 144.4	°C 146.6	°C 148.7	°C 150.9	°C 153.0
Condenser inlet pressure	bar 1.23	bar 1.33	bar 1.43	bar 1.53	bar 1.64	bar 1.75	bar 1.86	bar 1.98
Evaporator inlet temperature	bar 20.4	bar 21.5	bar 22.6	bar 23.7	bar 24.8	bar 25.8	bar 26.8	bar 27.9
Evaporator dewpoint	°C -35.5	°C -36.6	°C -37.6	°C -38.7	°C -39.8	°C -40.9	°C -42.0	°C -43.0
Evaporator exit gas temperature	°C -24.3	°C -23.6	°C -23.0	°C -22.4	°C -21.9	°C -21.5	°C -21.1	°C -20.9
Evaporator mean temperature	°C -19.3	°C -18.6	°C -18.0	°C -17.4	°C -16.9	°C -16.5	°C -16.1	°C -15.9
Evaporator glide (out-in)	°C -29.9	°C -30.1	°C -30.3	°C -30.6	°C -30.9	°C -31.2	°C -31.6	°C -31.9
Compressor suction pressure	K 11.3	K 13.0	K 14.6	K 16.3	K 17.9	K 19.4	K 20.8	K 22.2
Compressor discharge pressure	bar 20.4	bar 21.5	bar 22.6	bar 23.7	bar 24.8	bar 25.8	bar 26.8	bar 27.9
Suction line pressure drop	Pa/m 169	Pa/m 155	Pa/m 143	Pa/m 132	Pa/m 123	Pa/m 115	Pa/m 107	Pa/m 101
Pressure drop relative to reference								
Condenser dew point	°C 61.6	°C 61.6	°C 61.5	°C 61.3	°C 61.0	°C 60.6	°C 60.1	°C 59.5
Condenser bubble point	°C 28.9	°C 27.8	°C 27.0	°C 26.3	°C 25.6	°C 25.1	°C 24.7	°C 24.3
Condenser exit liquid temperature	°C 27.9	°C 26.8	°C 26.0	°C 25.3	°C 24.6	°C 24.1	°C 23.7	°C 23.3
Condenser mean temperature	°C 45.2	°C 44.7	°C 44.3	°C 43.8	°C 43.3	°C 42.8	°C 42.4	°C 41.9
Condenser glide (in-out)	K 32.7	K 33.8	K 34.5	K 35.0	K 35.3	K 35.4	K 35.4	K 35.2

Table 7: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 12 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	0/12/88	2/12/86	4/12/84	6/12/82	8/12/80	10/12/78	12/12/76	14/12/74
COP (heating)	1.98	2.05	2.09	2.13	2.15	2.17	2.19	2.20
COP relative to Reference	93.9%	97.1%	99.3%	101.0%	102.2%	103.1%	103.9%	104.4%
Volumetric heating capacity at suction	630	713	798	886	977	1071	1167	1266
Capacity relative to Reference	71.7%	81.1%	90.8%	100.9%	111.2%	121.9%	132.8%	144.1%
Critical temperature	112.09	108.13	104.41	100.89	97.58	94.44	91.47	88.65
Critical pressure	38.05	38.96	39.86	40.75	41.63	42.50	43.36	44.22
Condenser enthalpy change								
Pressure ratio	210.8	225.0	236.7	246.5	254.8	262.0	268.4	274.2
Refrigerant mass flow	18.24	18.60	18.74	18.68	18.47	18.16	17.78	17.37
Compressor discharge temperature	34.2	32.0	30.4	29.2	28.3	27.5	26.8	26.3
Evaporator inlet pressure	111.5	115.9	119.9	123.6	126.8	129.8	132.5	135.0
Condenser inlet pressure	0.67	0.72	0.77	0.83	0.90	0.98	1.06	1.15
Evaporator inlet temperature	10.9	12.1	13.4	14.6	15.8	17.0	18.2	19.3
Evaporator dewpoint	-28.9	-29.6	-30.3	-31.1	-31.9	-32.7	-33.6	-34.6
Evaporator exit gas temperature	-30.1	-29.6	-28.9	-28.2	-27.4	-26.6	-25.8	-25.0
Evaporator mean temperature	-25.1	-24.6	-23.9	-23.2	-22.4	-21.6	-20.8	-20.0
Evaporator glide (out-in)	-29.5	-29.6	-29.6	-29.6	-29.6	-29.6	-29.7	-29.8
Compressor suction pressure	-1.2	0.0	1.4	2.9	4.5	6.1	7.8	9.6
Compressor discharge pressure	0.60	0.65	0.71	0.78	0.86	0.94	1.02	1.11
Suction line pressure drop	450	379	326	285	252	225	203	184
Pressure drop relative to reference	154.2%	129.8%	111.6%	97.5%	86.2%	77.1%	69.4%	63.0%
Condenser dew point	53.5	55.6	57.4	58.8	59.9	60.7	61.2	61.6
Condenser bubble point	53.3	47.1	42.2	38.5	35.6	33.3	31.5	30.0
Condenser exit liquid temperature	52.3	46.1	41.2	37.5	34.6	32.3	30.5	29.0
Condenser mean temperature	53.4	51.3	49.8	48.6	47.7	47.0	46.4	45.8
Condenser glide (in-out)	0.1	8.5	15.1	20.3	24.2	27.3	29.7	31.5

Table 8: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 12 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	16/12/72	18/12/70	20/12/68	22/12/66	24/12/64	26/12/62	28/12/60	30/12/58
COP (heating)	2.21	2.22	2.22	2.23	2.23	2.23	2.23	2.22
COP relative to Reference	104.8%	105.2%	105.4%	105.6%	105.6%	105.7%	105.6%	105.5%
Volumetric heating capacity at suction	1367	1470	1574	1680	1786	1894	2001	2109
Capacity relative to Reference	155.5%	167.3%	179.1%	191.2%	203.3%	215.5%	227.8%	240.0%
Critical temperature	85.97	83.42	80.99	78.68	76.47	74.36	72.34	70.41
Critical pressure	45.06	45.90	46.73	47.56	48.38	49.19	50.00	50.81
Condenser enthalpy change								
Pressure ratio	279.5	284.4	289.0	293.4	297.6	301.7	305.7	309.6
Refrigerant mass flow	16.94	16.50	16.07	15.65	15.25	14.88	14.52	14.19
Compressor discharge temperature	25.8	25.3	24.9	24.5	24.2	23.9	23.6	23.3
Evaporator inlet pressure	137.5	139.8	142.0	144.2	146.3	148.4	150.5	152.6
Condenser inlet pressure	1.24	1.33	1.44	1.54	1.65	1.76	1.87	1.98
Evaporator inlet temperature	20.5	21.6	22.7	23.8	24.8	25.9	26.9	27.9
Evaporator inlet temperature	-35.5	-36.6	-37.6	-38.7	-39.8	-40.9	-42.0	-43.1
Evaporator dewpoint	-24.3	-23.6	-23.0	-22.4	-21.9	-21.5	-21.1	-20.8
Evaporator exit gas temperature	-19.3	-18.6	-18.0	-17.4	-16.9	-16.5	-16.1	-15.8
Evaporator mean temperature	-29.9	-30.1	-30.3	-30.6	-30.9	-31.2	-31.6	-32.0
Evaporator glide (out-in)	K	11.3	13.0	14.7	16.3	17.9	19.4	20.9
Compressor suction pressure	bar	1.21	1.31	1.41	1.52	1.63	1.74	1.85
Compressor discharge pressure	bar	20.5	21.6	22.7	23.8	24.8	25.9	26.9
Suction line pressure drop	Pa/m	168	154	142	132	123	115	107
Pressure drop relative to reference		57.5%	52.8%	48.7%	45.1%	42.0%	39.2%	34.5%
Condenser dew point	°C	61.7	61.7	61.6	61.4	61.0	60.6	60.1
Condenser bubble point	°C	28.8	27.8	26.9	26.2	25.6	25.1	24.6
Condenser exit liquid temperature	°C	27.8	26.8	25.9	25.2	24.6	24.1	23.6
Condenser mean temperature	°C	45.3	44.8	44.3	43.8	43.3	42.9	41.9
Condenser glide (in-out)	K	32.9	34.0	34.7	35.2	35.4	35.5	35.3

Table 9: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 15 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	0/15/85	2/15/83	4/15/81	6/15/79	8/15/77	10/15/75	12/15/73	14/15/71
COP (heating)	1.98	2.05	2.09	2.13	2.15	2.17	2.19	2.20
COP relative to Reference	93.8%	97.0%	99.3%	100.9%	102.2%	103.1%	103.8%	104.3%
Volumetric heating capacity at suction	632	716	802	890	981	1075	1171	1270
Capacity relative to Reference	72.0%	81.5%	91.2%	101.3%	111.7%	122.3%	133.3%	144.5%
Critical temperature	112.62	108.67	104.94	101.43	98.12	94.98	92.00	89.18
Critical pressure	bar 38.34	39.29	40.23	41.15	42.06	42.95	43.84	44.72
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature								
Evaporator inlet pressure								
Condenser inlet pressure								
Evaporator inlet temperature								
Evaporator dewpoint								
Evaporator exit gas temperature								
Evaporator mean temperature								
Evaporator glide (out-in)								
Compressor suction pressure								
Compressor discharge pressure								
Suction line pressure drop								
Pressure drop relative to reference								
Condenser dew point	°C 53.5	55.7	57.5	59.0	60.1	60.9	61.4	61.8
Condenser bubble point	°C 53.4	47.0	42.1	38.4	35.5	33.2	31.3	29.9
Condenser exit liquid temperature	°C 52.4	46.0	41.1	37.4	34.5	32.2	30.3	28.9
Condenser mean temperature	°C 53.5	51.4	49.8	48.7	47.8	47.0	46.4	45.8
Condenser glide (in-out)	K 0.1	8.7	15.4	20.6	24.6	27.7	30.1	31.9

Table 10: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 15 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▶	16/15/69	18/15/67	20/15/65	22/15/63	24/15/61	26/15/59	28/15/57	30/15/55
COP (heating)	2.21	2.22	2.22	2.22	2.22	2.22	2.22	2.22
COP relative to Reference	104.7%	105.1%	105.3%	105.4%	105.5%	105.5%	105.4%	105.3%
Volumetric heating capacity at suction	1371	1474	1578	1684	1790	1897	2005	2112
Capacity relative to Reference	156.0%	167.7%	179.6%	191.6%	203.8%	215.9%	228.1%	240.3%
Critical temperature	86.50	83.95	81.52	79.20	76.98	74.87	72.84	70.91
Critical pressure	45.58	46.44	47.29	48.13	48.97	49.80	50.62	51.44
Condenser enthalpy change								
Pressure ratio	279.9	284.8	289.3	293.6	297.8	301.8	305.7	309.6
Refrigerant mass flow	16.92	16.48	16.05	15.63	15.23	14.85	14.50	14.17
Compressor discharge temperature	25.7	25.3	24.9	24.5	24.2	23.9	23.5	23.3
Evaporator inlet pressure	137.2	139.5	141.7	143.8	145.9	148.0	150.1	152.2
Condenser inlet pressure	bar 1.24	bar 1.34	bar 1.44	bar 1.55	bar 1.66	bar 1.77	bar 1.88	bar 1.99
Evaporator inlet temperature	20.6	21.7	22.8	23.8	24.9	25.9	27.0	28.0
Evaporator inlet temperature	°C -35.6	°C -36.6	°C -37.7	°C -38.8	°C -39.9	°C -41.0	°C -42.1	°C -43.2
Evaporator dewpoint	°C -24.2	°C -23.6	°C -22.9	°C -22.4	°C -21.9	°C -21.5	°C -21.1	°C -20.8
Evaporator exit gas temperature	°C -19.2	°C -18.6	°C -17.9	°C -17.4	°C -16.9	°C -16.5	°C -16.1	°C -15.8
Evaporator mean temperature	°C -29.9	°C -30.1	°C -30.3	°C -30.6	°C -30.9	°C -31.2	°C -31.6	°C -32.0
Evaporator glide (out-in)	K 11.3	K 13.0	K 14.7	K 16.4	K 18.0	K 19.5	K 21.0	K 22.4
Compressor suction pressure	bar 1.22	bar 1.32	bar 1.42	bar 1.53	bar 1.63	bar 1.75	bar 1.86	bar 1.98
Compressor discharge pressure	bar 20.6	bar 21.7	bar 22.8	bar 23.8	bar 24.9	bar 25.9	bar 27.0	bar 28.0
Suction line pressure drop	Pa/m 167	Pa/m 154	Pa/m 142	Pa/m 131	Pa/m 122	Pa/m 114	Pa/m 107	Pa/m 101
Pressure drop relative to reference	57.3%	52.6%	48.5%	45.0%	41.9%	39.1%	36.7%	34.5%
Condenser dew point	°C 61.9	°C 61.9	°C 61.8	°C 61.5	°C 61.2	°C 60.7	°C 60.2	°C 59.6
Condenser bubble point	°C 28.7	°C 27.7	°C 26.8	°C 26.1	°C 25.5	°C 25.0	°C 24.6	°C 24.2
Condenser exit liquid temperature	°C 27.7	°C 26.7	°C 25.8	°C 25.1	°C 24.5	°C 24.0	°C 23.6	°C 23.2
Condenser mean temperature	°C 45.3	°C 44.8	°C 44.3	°C 43.8	°C 43.4	°C 42.9	°C 42.4	°C 41.9
Condenser glide (in-out)	K 33.3	K 34.3	K 35.0	K 35.4	K 35.7	K 35.6	K 35.6	K 35.4

Table 11: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 18 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	0/18/82	2/18/80	4/18/78	6/18/76	8/18/74	10/18/72	12/18/70	14/18/68
COP (heating)	1.98	2.04	2.09	2.13	2.15	2.17	2.19	2.20
COP relative to Reference	93.7%	97.0%	99.3%	100.9%	102.1%	103.0%	103.7%	104.2%
Volumetric heating capacity at suction	634	718	804	893	984	1078	1175	1273
Capacity relative to Reference	72.1%	81.7%	91.5%	101.6%	112.0%	122.7%	133.7%	144.9%
Critical temperature	1113.15	109.20	105.48	101.97	98.65	95.51	92.53	89.71
Critical pressure	38.60	39.59	40.56	41.51	42.45	43.38	44.29	45.19
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature								
Evaporator inlet pressure								
Condenser inlet pressure								
Evaporator inlet temperature								
Evaporator dewpoint								
Evaporator exit gas temperature								
Evaporator mean temperature								
Evaporator glide (out-in)								
Compressor suction pressure								
Compressor discharge pressure								
Suction line pressure drop								
Pressure drop relative to reference								
Condenser dew point	53.6	55.9	57.7	59.2	60.3	61.1	61.7	62.0
Condenser bubble point	53.5	47.0	42.0	38.2	35.3	33.0	31.2	29.7
Condenser exit liquid temperature	52.5	46.0	41.0	37.2	34.3	32.0	30.2	28.7
Condenser mean temperature	53.5	51.4	49.8	48.7	47.8	47.0	46.4	45.8
Condenser glide (in-out)	0.2	8.9	15.7	21.0	25.0	28.1	30.5	32.3

Table 12: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 18 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	16/18/66	18/18/64	20/18/62	22/18/60	24/18/58	26/18/56	28/18/54	30/18/52
COP (heating)	2.21	2.21	2.22	2.22	2.22	2.22	2.22	2.22
COP relative to Reference	104.7%	105.0%	105.2%	105.3%	105.4%	105.3%	105.3%	105.1%
Volumetric heating capacity at suction	K/m ³	1374	1477	1581	1686	1792	1899	2006
Capacity relative to Reference		156.4%	168.1%	179.9%	191.9%	204.0%	216.1%	228.3%
Critical temperature	°C	87.02	84.47	82.03	79.71	77.49	75.37	73.35
Critical pressure	bar	46.07	46.95	47.82	48.68	49.53	50.38	51.21
Condenser enthalpy change	kJ/kg	280.6	285.3	289.8	294.1	298.2	302.1	306.0
Pressure ratio	kg/hr	16.91	16.47	16.04	15.62	15.22	14.84	14.49
Refrigerant mass flow	°C	25.7	25.2	24.8	24.5	24.1	23.8	23.5
Compressor discharge temperature	bar	137.0	139.2	141.4	143.5	145.6	147.7	149.7
Evaporator inlet pressure	bar	1.25	1.35	1.45	1.55	1.66	1.77	1.88
Condenser inlet pressure	bar	20.6	21.7	22.8	23.9	25.0	26.0	27.0
Evaporator inlet temperature	°C	-35.6	-36.6	-37.7	-38.8	-39.9	-41.1	-42.2
Evaporator dewpoint	°C	-24.2	-23.5	-22.9	-22.3	-21.8	-21.4	-21.1
Evaporator exit gas temperature	°C	-19.2	-18.5	-17.9	-17.3	-16.8	-16.4	-16.1
Evaporator mean temperature	°C	-29.9	-30.1	-30.3	-30.6	-30.9	-31.2	-31.6
Evaporator glide (out-in)	K	11.4	13.1	14.8	16.5	18.1	19.7	21.1
Compressor suction pressure	bar	1.22	1.32	1.42	1.53	1.64	1.75	1.87
Compressor discharge pressure	bar	20.6	21.7	22.8	23.9	25.0	26.0	27.0
Suction line pressure drop	Pa/m	167	153	141	131	122	114	107
Pressure drop relative to reference	Pa/m	57.0%	52.4%	48.4%	44.9%	41.8%	39.1%	36.6%
Condenser dew point	°C	62.1	62.1	62.0	61.7	61.3	60.9	60.3
Condenser bubble point	°C	28.5	27.5	26.7	26.0	25.4	24.9	24.5
Condenser exit liquid temperature	°C	27.5	26.5	25.7	25.0	24.4	23.9	23.5
Condenser mean temperature	°C	45.3	44.8	44.3	43.9	43.4	42.9	41.9
Condenser glide (in-out)	K	33.6	34.6	35.3	35.7	35.9	36.0	35.8

Table 13: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 20 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▶	0/20/80	2/20/78	4/20/76	6/20/74	8/20/72	10/20/70	12/20/68	14/20/66
COP (heating)	1.97	2.04	2.09	2.13	2.15	2.17	2.19	2.20
COP relative to Reference	93.6%	97.0%	99.3%	100.9%	102.1%	103.0%	103.7%	104.2%
Volumetric heating capacity at suction	634	719	806	894	986	1080	1176	1275
Capacity relative to Reference	72.2%	81.8%	91.7%	101.8%	112.2%	122.9%	133.9%	145.1%
Critical temperature	113.50	109.55	105.83	102.32	99.00	95.86	92.88	90.06
Critical pressure	38.76	39.78	40.77	41.74	42.70	43.64	44.57	45.48
Condenser enthalpy change								
Pressure ratio	kg/kg	211.8	226.6	238.7	248.6	256.9	264.1	270.3
Refrigerant mass flow	kg/hr	18.01	18.45	18.65	18.63	18.44	18.14	17.77
Compressor discharge temperature	°C	34.0	31.8	30.2	29.0	28.0	27.3	26.6
Evaporator inlet pressure	bar	110.8	115.3	119.4	123.1	126.3	129.3	132.0
Condenser inlet pressure	bar	0.68	0.72	0.78	0.84	0.91	0.99	1.07
Evaporator inlet temperature	°C	-28.9	-29.6	-30.3	-31.1	-31.9	-32.7	-33.6
Evaporator dewpoint	°C	-30.1	-29.6	-28.9	-28.2	-27.3	-26.5	-25.7
Evaporator exit gas temperature	°C	-25.1	-24.6	-23.9	-23.2	-22.3	-21.5	-20.7
Evaporator mean temperature	°C	-29.5	-29.6	-29.6	-29.6	-29.6	-29.6	-29.7
Evaporator glide (out-in)	K	-1.2	0.0	1.4	2.9	4.5	6.2	7.9
Compressor suction pressure	bar	0.60	0.66	0.72	0.79	0.87	0.95	1.03
Compressor discharge pressure	bar	10.9	12.2	13.5	14.7	16.0	17.2	18.4
Suction line pressure drop	Pa/m	446	374	321	280	248	222	200
Pressure drop relative to reference		152.6%	128.0%	109.9%	96.0%	84.9%	76.0%	68.5%
Condenser dew point	°C	53.7	56.0	57.8	59.3	60.5	61.3	61.8
Condenser bubble point	°C	53.5	46.9	41.9	38.1	35.1	32.8	31.0
Condenser exit liquid temperature	°C	52.5	45.9	40.9	37.1	34.1	31.8	30.0
Condenser mean temperature	°C	53.6	51.4	49.9	48.7	47.8	47.1	46.4
Condenser glide (in-out)	K	0.2	9.0	16.0	21.3	25.3	28.4	30.8

Table 14: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 20 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▶	16/20/64	18/20/62	20/20/60	22/20/58	24/20/56	26/20/54	28/20/52	30/20/50
COP (heating)	2.21	2.21	2.22	2.22	2.22	2.22	2.22	2.21
COP relative to Reference	104.6%	104.9%	105.1%	105.2%	105.3%	105.2%	105.2%	105.0%
Volumetric heating capacity at suction	1376	1478	1582	1687	1793	1899	2005	2111
Capacity relative to Reference	156.6%	168.2%	180.0%	192.0%	204.0%	216.1%	228.2%	240.2%
Critical temperature	87.37	84.81	82.38	80.05	77.83	75.71	73.68	71.73
Critical pressure	bar 46.39	47.28	48.16	49.03	49.89	50.75	51.59	52.43
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature								
Evaporator inlet pressure								
Condenser inlet pressure								
Evaporator inlet temperature								
Evaporator dewpoint								
Evaporator exit gas temperature								
Evaporator mean temperature								
Evaporator glide (out-in)								
Compressor suction pressure								
Compressor discharge pressure								
Suction line pressure drop								
Pressure drop relative to reference								
Condenser dew point	°C 62.3	62.3	62.1	61.8	61.5	61.0	60.4	59.8
Condenser bubble point	°C 28.4	27.4	26.6	25.9	25.3	24.8	24.4	24.1
Condenser exit liquid temperature	°C 27.4	26.4	25.6	24.9	24.3	23.8	23.4	23.1
Condenser mean temperature	°C 45.3	44.8	44.4	43.9	43.4	42.9	42.4	41.9
Condenser glide (in-out)	K 33.9	34.9	35.5	35.9	36.1	36.2	36.0	35.8

Table 15: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 22 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▶	0/22/78	2/22/76	4/22/74	6/22/72	8/22/70	10/22/68	12/22/66	14/22/64
COP (heating)	1.97	2.04	2.09	2.13	2.15	2.17	2.19	2.20
COP relative to Reference	93.6%	96.9%	99.3%	100.9%	102.1%	103.0%	103.6%	104.2%
Volumetric heating capacity at suction	635	720	807	896	987	1081	1177	1276
Capacity relative to Reference	72.3%	81.9%	91.8%	101.9%	112.3%	123.0%	134.0%	145.2%
Critical temperature	113.85	109.90	106.18	102.67	99.35	96.21	93.23	90.41
Critical pressure	38.91	39.95	40.96	41.96	42.93	43.89	44.84	45.77
Condenser enthalpy change								
Pressure ratio	212.1	227.1	239.3	249.3	257.6	264.7	270.9	276.5
Refrigerant mass flow	17.97	18.43	18.64	18.84	18.45	18.16	17.79	17.37
Compressor discharge temperature	33.9	31.7	30.1	28.9	28.0	27.2	26.6	26.0
Evaporator inlet pressure	110.6	115.2	119.4	123.0	126.3	129.2	131.9	134.4
Condenser inlet pressure	0.68	0.72	0.78	0.84	0.91	0.99	1.07	1.16
Evaporator inlet temperature	10.9	12.2	13.5	14.8	16.0	17.2	18.4	19.6
Evaporator dewpoint	-28.9	-29.6	-30.3	-31.1	-31.9	-32.7	-33.7	-34.6
Evaporator exit gas temperature	-30.1	-29.6	-28.9	-28.2	-27.3	-26.5	-25.7	-24.9
Evaporator mean temperature	-25.1	-24.6	-23.9	-23.2	-22.3	-21.5	-20.7	-19.9
Evaporator glide (out-in)	-29.5	-29.6	-29.6	-29.6	-29.6	-29.6	-29.7	-29.8
Compressor suction pressure	K	-1.2	0.0	1.4	2.9	4.6	6.2	8.0
Compressor discharge pressure	bar	0.61	0.66	0.72	0.79	0.87	0.95	1.04
Suction line pressure drop	bar	10.9	12.2	13.5	14.8	16.0	17.2	18.4
Pressure drop relative to reference	Pa/m	445	373	320	279	247	221	200
Condenser dew point	°C	53.7	56.1	58.0	59.5	60.6	61.5	62.3
Condenser bubble point	°C	53.6	46.8	41.8	37.9	35.0	32.7	30.9
Condenser exit liquid temperature	°C	52.6	45.8	40.8	36.9	34.0	31.7	29.9
Condenser mean temperature	°C	53.6	51.5	49.9	48.7	47.8	47.1	45.9
Condenser glide (in-out)	K	0.2	9.2	16.2	21.6	25.7	28.8	32.9

Table 16: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 22 % R-263fb

Composition CO₂/R-263fb/R-1234ze(E) % by weight ▲

	16/22/62	18/22/60	20/22/58	22/22/56	24/22/54	26/22/52	28/22/50	30/22/48
COP (heating)	2.20	2.21	2.21	2.22	2.22	2.22	2.22	2.21
COP relative to Reference	104.5%	104.8%	105.0%	105.1%	105.2%	105.2%	105.1%	104.9%
Volumetric heating capacity at suction	kJ/m ³	1376	1479	1582	1687	1792	1898	2003
Capacity relative to Reference	156.6%	168.3%	180.1%	192.0%	204.0%	216.0%	228.0%	239.9%
Critical temperature	°C	87.72	85.16	82.72	80.39	78.17	76.04	74.01
Critical pressure	bar	46.69	47.59	48.48	49.37	50.24	51.11	51.96
Condenser enthalpy change	kJ/kg	281.6	286.3	290.7	294.9	298.9	302.8	306.6
Pressure ratio	kg/hr	16.94	16.50	16.06	15.64	15.24	14.86	14.51
Refrigerant mass flow	°C	136.7	139.0	141.1	143.2	145.3	147.3	149.4
Compressor discharge temperature	bar	1.25	1.35	1.45	1.56	1.66	1.77	1.89
Evaporator inlet pressure	bar	20.7	21.8	22.9	24.0	25.0	26.1	27.1
Condenser inlet pressure	°C	-35.6	-36.7	-37.8	-38.9	-40.1	-41.2	-42.4
Evaporator inlet temperature	°C	-24.2	-23.5	-22.8	-22.3	-21.8	-21.3	-21.0
Evaporator dewpoint	°C	-19.2	-18.5	-17.8	-17.3	-16.8	-16.3	-16.0
Evaporator exit gas temperature	°C	-29.9	-30.1	-30.3	-30.6	-30.9	-31.3	-31.7
Evaporator mean temperature	K	11.5	13.2	14.9	16.6	18.3	19.9	21.4
Evaporator glide (out-in)	bar	1.22	1.32	1.43	1.53	1.64	1.75	1.87
Compressor suction pressure	bar	20.7	21.8	22.9	24.0	25.0	26.1	27.1
Compressor discharge pressure	Pa/m	166	153	141	131	122	114	107
Suction line pressure drop	Pa/m	56.8%	52.2%	48.2%	44.8%	41.7%	39.0%	36.6%
Pressure drop relative to reference	°C	62.5	62.4	62.3	62.0	61.6	61.1	60.6
Condenser dew point	°C	28.2	27.3	26.5	25.8	25.2	24.7	24.3
Condenser bubble point	°C	27.2	26.3	25.5	24.8	24.2	23.7	23.3
Condenser exit liquid temperature	°C	45.4	44.9	44.4	43.9	43.4	42.9	42.4
Condenser mean temperature	K	34.2	35.2	35.8	36.2	36.4	36.2	35.9

Table 17: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 25 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▲	0/25/75	2/25/73	4/25/71	6/25/69	8/25/67	10/25/65	12/25/63	14/25/61
COP (heating)	1.97	2.04	2.09	2.13	2.15	2.17	2.18	2.20
COP relative to Reference	93.5%	96.9%	99.3%	100.9%	102.1%	103.0%	103.6%	104.1%
Volumetric heating capacity at suction	635	720	808	897	988	1082	1178	1277
Capacity relative to Reference	72.3%	82.0%	91.9%	102.1%	112.5%	123.2%	134.1%	145.3%
Critical temperature	114.37	110.42	106.71	103.20	99.88	96.73	93.75	90.92
Critical pressure	39.12	40.19	41.24	42.26	43.27	44.25	45.22	46.17
Condenser enthalpy change								
Pressure ratio	212.6	228.0	240.3	250.3	258.7	265.8	272.0	277.5
Refrigerant mass flow	17.91	18.41	18.65	18.66	18.48	18.19	17.82	17.41
Compressor discharge temperature	33.9	31.6	30.0	28.8	27.8	27.1	26.5	25.9
Evaporator inlet pressure	110.4	115.1	119.3	122.9	126.2	129.1	131.8	134.3
Condenser inlet pressure	0.68	0.73	0.78	0.84	0.91	0.99	1.07	1.16
Evaporator inlet temperature	10.9	12.2	13.5	14.8	16.1	17.3	18.5	19.7
Evaporator dewpoint	-28.9	-29.6	-30.3	-31.1	-31.9	-32.8	-33.7	-34.7
Evaporator exit gas temperature	-30.1	-29.6	-28.9	-28.1	-27.3	-26.5	-25.6	-24.9
Evaporator mean temperature	-25.1	-24.6	-23.9	-23.1	-22.3	-21.5	-20.6	-19.9
Evaporator glide (out-in)	-29.5	-29.6	-29.6	-29.6	-29.6	-29.6	-29.7	-29.8
Compressor suction pressure	K	-1.2	0.0	1.4	2.9	4.6	6.3	8.0
Compressor discharge pressure	bar	0.61	0.66	0.72	0.79	0.87	0.95	1.04
Suction line pressure drop	bar	10.9	12.2	13.5	14.8	16.1	17.3	18.5
Pressure drop relative to reference	Pa/m	444	371	318	278	246	220	199
Condenser dew point	°C	53.8	56.2	58.2	59.7	60.9	61.7	62.3
Condenser bubble point	°C	53.6	46.8	41.6	37.7	34.7	32.4	30.6
Condenser exit liquid temperature	°C	52.6	45.8	40.6	36.7	33.7	31.4	29.6
Condenser mean temperature	°C	53.7	51.5	49.9	48.7	47.8	47.1	46.5
Condenser glide (in-out)	K	0.2	9.5	16.6	22.1	26.2	29.3	33.4

Table 18: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 25 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▶	16/25/59	18/25/57	20/25/55	22/25/53	24/25/51	26/25/49	28/25/47	30/25/45
COP (heating)	2.20	2.21	2.21	2.21	2.21	2.21	2.21	2.21
COP relative to Reference	104.5%	104.7%	104.9%	105.0%	105.0%	105.0%	104.9%	104.7%
Volumetric heating capacity at suction	1377	1478	1581	1685	1789	1894	1998	2101
Capacity relative to Reference	156.7%	168.2%	179.9%	191.8%	203.6%	215.5%	227.4%	239.1%
Critical temperature	88.23	85.67	83.23	80.90	78.67	76.54	74.50	72.55
Critical pressure	47.11	48.04	48.95	49.85	50.74	51.62	52.49	53.35
Condenser enthalpy change								
Pressure ratio	282.5	287.2	291.5	295.7	299.7	303.5	307.3	311.1
Refrigerant mass flow	16.97	16.53	16.10	15.68	15.28	14.90	14.55	14.23
Compressor discharge temperature	25.5	25.1	24.7	24.4	24.0	23.7	23.4	23.1
Evaporator inlet pressure	136.6	138.8	141.0	143.1	145.1	147.2	149.2	151.3
Condenser inlet pressure	1.25	1.35	1.45	1.56	1.66	1.77	1.88	1.99
Evaporator inlet temperature	20.8	21.9	23.0	24.0	25.1	26.1	27.1	28.1
Evaporator dewpoint	-35.7	-36.7	-37.9	-39.0	-40.2	-41.4	-42.6	-43.8
Evaporator exit gas temperature	-24.1	-23.4	-22.8	-22.2	-21.7	-21.3	-20.9	-20.6
Evaporator mean temperature	-19.1	-18.4	-17.8	-17.2	-16.7	-16.3	-15.9	-15.6
Evaporator glide (out-in)	-29.9	-30.1	-30.3	-30.6	-31.0	-31.3	-31.8	-32.2
Compressor suction pressure	11.6	13.3	15.1	16.8	18.5	20.1	21.6	23.1
Compressor discharge pressure	1.22	1.32	1.43	1.53	1.64	1.75	1.86	1.98
Suction line pressure drop	20.8	21.9	23.0	24.0	25.1	26.1	27.1	28.1
Pressure drop relative to reference	165	152	141	131	122	114	107	101
Condenser dew point	56.6%	52.1%	48.2%	44.7%	41.7%	39.0%	36.6%	34.5%
Condenser bubble point	62.7	62.7	62.5	62.2	61.8	61.3	60.8	60.1
Condenser exit liquid temperature	28.0	27.1	26.3	25.6	25.0	24.6	24.2	23.8
Condenser mean temperature	27.0	26.1	25.3	24.6	24.0	23.6	23.2	22.8
Condenser glide (in-out)	45.4	44.9	44.4	43.9	43.4	43.0	42.5	42.0
	34.7	35.7	36.3	36.6	36.8	36.6	36.6	36.3

Table 19: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 0-14 % R-744 and 32 % R-263fb

Composition CO ₂ /R-263fb/R-1234ze(E) % by weight ▶	0/32/68	2/32/66	4/32/64	6/32/62	8/32/60	10/32/58	12/32/56	14/32/54
COP (heating)	1.97	2.04	2.10	2.13	2.15	2.17	2.18	2.19
COP relative to Reference	93.4%	97.0%	99.4%	101.0%	102.1%	103.0%	103.6%	104.0%
Volumetric heating capacity at suction	633	719	807	897	988	1081	1177	1273
Capacity relative to Reference	72.0%	81.9%	91.9%	102.0%	112.5%	123.1%	133.9%	144.9%
Critical temperature	115.56	111.62	107.91	104.40	101.08	97.94	94.95	92.12
Critical pressure	39.49	40.65	41.77	42.87	43.94	44.99	46.01	47.02
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature								
Evaporator inlet pressure								
Condenser inlet pressure								
Evaporator inlet temperature								
Evaporator dewpoint								
Evaporator exit gas temperature								
Evaporator mean temperature								
Evaporator glide (out-in)								
Compressor suction pressure								
Compressor discharge pressure								
Suction line pressure drop								
Pressure drop relative to reference								
Condenser dew point	54.0	56.6	58.7	60.4	61.6	62.5	63.1	63.4
Condenser bubble point	53.7	46.5	41.1	37.0	34.0	31.7	29.9	28.5
Condenser exit liquid temperature	52.7	45.5	40.1	36.0	33.0	30.7	28.9	27.5
Condenser mean temperature	53.9	51.5	49.9	48.7	47.8	47.1	46.5	45.9
Condenser glide (in-out)	0.3	10.2	17.7	23.4	27.6	30.8	33.1	34.9

Table 20: Theoretical Performance Data of Selected R-744/R-263fb/R-1234ze(E) blends containing 16-30 % R-744 and 32 % R-263fb

Composition $\text{CO}_2/\text{R-263fb/R-1234ze(E)}$ % by weight ▲	16/32/52	18/32/50	20/32/48	22/32/46	24/32/44	26/32/42	28/32/40	30/32/38
COP (heating)	2.20	2.20	2.21	2.21	2.21	2.21	2.20	2.20
COP relative to Reference	104.3%	104.6%	104.7%	104.8%	104.7%	104.7%	104.5%	104.3%
Volumetric heating capacity at suction	1372	1471	1572	1673	1774	1875	1974	2071
Capacity relative to Reference	156.1%	167.5%	178.9%	190.4%	201.9%	213.4%	224.7%	235.8%
Critical temperature	89.42	86.85	84.40	82.06	79.83	77.69	75.65	73.68
Critical pressure	bar 48.01	bar 48.98	bar 49.94	bar 50.88	bar 51.81	bar 52.72	bar 53.63	bar 54.52
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature								
Evaporator inlet pressure								
Condenser inlet pressure								
Evaporator inlet temperature								
Evaporator dewpoint								
Evaporator exit gas temperature								
Evaporator mean temperature								
Evaporator glide (out-in)								
Compressor suction pressure								
Compressor discharge pressure								
Suction line pressure drop								
Pressure drop relative to reference								
Condenser dew point								
Condenser bubble point								
Condenser exit liquid temperature								
Condenser mean temperature								
Condenser glide (in-out)								

Table 21: Theoretical Performance Data of Selected R-744/R-1234ze(E) blends containing 0-14 % R-744

Composition CO ₂ /R-1234ze(E) % by weight ▶	0/100	2/98	4/96	6/94	8/92	10/90	12/88	14/86
COP (heating)	1.99	2.05	2.10	2.14	2.16	2.18	2.20	2.21
COP (heating) relative to Reference	94.4% 615 70.0%	97.4% 695 79.1%	99.6% 778 88.6%	101.3% 864 98.3%	102.5% 953 108.5%	103.5% 1046 119.0%	104.3% 1141 129.8%	104.9% 1239 141.0%
Volumetric heating capacity at suction								
Capacity relative to Reference								
Critical temperature	109.89	105.93	102.20	98.69	95.38	92.25	89.29	86.48
Critical pressure	36.57	37.34	38.10	38.87	39.63	40.40	41.16	41.92
Condenser enthalpy change								
Pressure ratio								
Refrigerant mass flow								
Compressor discharge temperature								
Evaporator inlet pressure								
Condenser inlet pressure								
Evaporator inlet temperature								
Evaporator dewpoint								
Evaporator exit gas temperature								
Evaporator mean temperature								
Evaporator glide (out-in)								
Compressor suction pressure								
Compressor discharge pressure								
Suction line pressure drop								
Pressure drop relative to reference								
Condenser dew point								
Condenser bubble point								
Condenser exit liquid temperature								
Condenser mean temperature								
Condenser glide (in-out)								

Table 22: Theoretical Performance Data of Selected R-744/R-1234ze(E) blends containing 16-30 % R-744

Composition CO ₂ /R-1234ze(E) % by weight ▶	16/84	18/82	20/80	22/78	24/76	26/74	28/72	30/70
COP (heating)	2.22	2.23	2.23	2.24	2.24	2.24	2.24	2.24
COP (heating) relative to Reference	105.4%	105.7%	106.0%	106.2%	106.3%	106.3%	106.3%	106.2%
Volumetric heating capacity at suction	1339	1441	1545	1650	1756	1862	1969	2076
Capacity relative to Reference	152.4%	164.0%	175.8%	187.7%	199.8%	211.9%	224.1%	236.3%
Critical temperature	°C	83.81	81.28	78.87	76.57	74.38	72.28	70.28
Critical pressure	bar	42.68	43.44	44.20	44.96	45.72	46.47	47.23
Condenser enthalpy change	kJ/kg	278.7	283.9	288.9	293.6	298.1	302.5	306.8
Pressure ratio		17.15	16.72	16.29	15.88	15.49	15.12	14.77
Refrigerant mass flow	kg/hr	25.8	25.4	24.9	24.5	24.2	23.8	23.5
Compressor discharge temperature	°C	139.0	141.4	143.8	146.1	148.4	150.6	152.9
Evaporator inlet pressure	bar	1.20	1.29	1.39	1.49	1.60	1.70	1.81
Condenser inlet pressure	bar	20.1	21.2	22.3	23.3	24.4	25.4	26.5
Evaporator inlet temperature	°C	-35.5	-36.5	-37.6	-38.7	-39.7	-40.8	-41.9
Evaporator dewpoint	°C	-24.4	-23.7	-23.1	-22.5	-22.0	-21.6	-21.2
Evaporator exit gas temperature	°C	-19.4	-18.7	-18.1	-17.5	-17.0	-16.6	-16.2
Evaporator mean temperature	°C	-29.9	-30.1	-30.3	-30.6	-30.9	-31.2	-31.5
Evaporator glide (out-in)	K	11.2	12.9	14.5	16.2	17.7	19.2	20.7
Compressor suction pressure	bar	1.17	1.27	1.37	1.47	1.57	1.68	1.79
Compressor discharge pressure	bar	20.1	21.2	22.3	23.3	24.4	25.4	26.5
Suction line pressure drop	Pa/m	172	157	145	134	125	116	109
Pressure drop relative to reference		58.8%	53.9%	49.7%	45.9%	42.7%	39.8%	37.2%
Condenser dew point	°C	61.2	61.2	61.2	61.0	60.8	60.4	60.0
Condenser bubble point	°C	29.1	28.0	27.1	26.3	25.7	25.1	24.6
Condenser exit liquid temperature	°C	28.1	27.0	26.1	25.3	24.7	24.1	23.6
Condenser mean temperature	°C	45.1	44.6	44.1	43.7	43.2	42.7	42.3
Condenser glide (in-out)	K	32.1	33.2	34.1	34.7	35.1	35.3	35.4

In summary, the invention provides new compositions that exhibit a surprising combination of advantageous properties including good refrigeration performance, low flammability, low GWP, and/or miscibility with lubricants compared to existing refrigerants such as R-134a and the proposed refrigerant R-1234yf.

5

The invention is defined by the following claims.

CLAIMS

1. A heat transfer composition comprising:
 - (i) a first component selected from *trans*-1,3,3,3-tetrafluoropropene (R-1234ze(E)),
5 *cis*-1,3,3,3-tetrafluoropropene (R-1234ze(Z)) and mixtures thereof;
 - (ii) carbon dioxide (R-744); and
 - (iii) a third component selected from 1,1,1-trifluoropropane (R-263fb), 1,1,1,2,3-pentafluoropropane (R-245eb), ammonia (R-717) and mixtures thereof.
- 10 2. A composition according to claim 1 wherein the first component comprises R-1234ze(E).
3. A composition according to claim 1 or 2 comprising at least about 15 % by weight R-1234ze(E).
- 15 4. A composition according to any of the preceding claims comprising up to about 35 % by weight R-744, preferably about 30 % by weight R-744.
5. A composition according to claim 4 comprising from about 4 to about 30 % R-744
20 by weight, preferably from about 4 to about 28 % by weight, or from about 8 to about 30 % by weight, or from about 10 to about 30 % by weight.
6. A composition according to any of the preceding claims comprising up to about 60 % by weight of the third component, preferably up to about 50 % by weight.
- 25 7. A composition according to any of the preceding claims comprising from about 10 to about 95 % R-1234ze(E) by weight, from about 2 to about 30 % by weight R-744, and from about 3 to about 60 % by weight of the third component.
- 30 8. A composition according to any of the preceding claims which has a critical temperature of greater than about 65 °C, preferably greater than about 70 °C.
9. A composition according to any of claims 1 to 8 wherein the third component comprises R-263fb, preferably in an amount up to about 50 % by weight.

10. A composition according to claim 9 comprising from about 30 to about 94 % by weight R-1234ze(E), from about 4 to about 30 % by weight R-744 and from about 2 to about 40 % by weight R-263fb.

5 11. A composition according to claim 10 comprising from about 37 to about 92 % by weight R-1234ze(E), from about 4 to about 28 % by weight R-744 and from about 4 to about 35 % by weight R-263fb

10 12. A composition according to claim 11 comprising from about 42 to about 91 % by weight R-1234ze(E), from about 4 to about 28 % by weight R-744 and from about 5 to about 30 % by weight R-263fb.

15 13. A composition according to claim 12 comprising from about 42 to about 85 % by weight R-1234ze(E), from about 10 to about 28 % by weight R-744 and from about 5 to about 30 % by weight R-263fb.

14. A composition according to any of claims 1 to 8 wherein the third component comprises R-245eb, preferably in an amount up to 30 % by weight.

20 15. A composition according to claim 14 comprising from about 42 to about 91 % by weight R-1234ze(E), from about 4 to about 28 % by weight R-744 and from about 5 to about 30 % by weight R-245eb.

25 16. A composition according to claim 15 comprising from about 42 to about 85 % by weight R-1234ze(E), from about 10 to about 28 % by weight R-744 and from about 5 to about 30 % by weight R-245eb.

17. A composition according to any of claims 1 to 8 wherein the third component comprises ammonia, preferably in an amount up to about 30 % by weight.

30 18. A composition according to any of the preceding claims consisting essentially of R-1234ze(E), R-744 and the third component.

19. A composition according to any of claims 1 to 17, further comprising pentafluoroethane (R-125).

20. A composition according to any of the preceding claims, wherein the composition has a GWP of less than 1000, preferably less than 150.

21. A composition according to any of the preceding claims, wherein the composition 5 has a volumetric refrigeration capacity within about 15%, preferably within about 10% of the existing refrigerant that it is intended to replace.

23. A composition according to any of the preceding claims, wherein the composition is less flammable than R-263fb alone, R-245eb alone or R-1234yf alone.

10

24. A composition according to claim 23 wherein the composition has:

- (a) a higher flammable limit;
- (b) a higher ignition energy; and/or
- (c) a lower flame velocity

15 compared to R-263fb alone, R-245eb alone or R-1234yf alone.

25. A composition according to any of the preceding claims which has a fluorine ratio (F/(F+H)) of from about 0.42 to about 0.7, preferably from about 0.44 to about 0.67.

20 26. A composition according to any of the preceding claims which is non-flammable.

27. A composition according to any of the preceding claims, wherein the composition has a cycle efficiency within about 5% of the existing refrigerant that it is intended to replace.

25

28. A composition according to any of the preceding claims, wherein the composition has a compressor discharge temperature within about 15K, preferably within about 10K, of the existing refrigerant that it is intended to replace.

30 29. A composition comprising a lubricant and a composition according to any of the preceding claims.

35 30. A composition according to claim 56, wherein the lubricant is selected from 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.

31. A composition according to claim 29 or 30 further comprising a stabiliser.
32. A composition according to claim 31, wherein the stabiliser is selected from diene-based compounds, phosphates, phenol compounds and epoxides, and mixtures thereof.
33. A composition comprising a flame retardant and a composition according to any of the preceding claims.

10

34. A composition according to claim 33, wherein the flame retardant is selected from the group consisting of tri-(2-chloroethyl)-phosphate, (chloropropyl) phosphate, tri-(2,3-dibromopropyl)-phosphate, tri-(1,3-dichloropropyl)-phosphate, diammonium phosphate, various halogenated aromatic compounds, antimony oxide, aluminium trihydrate, polyvinyl chloride, a fluorinated iodocarbon, a fluorinated bromocarbon, trifluoro iodomethane, perfluoroalkyl amines, bromo-fluoroalkyl amines and mixtures thereof.
35. A composition according to any of the preceding claims which is a refrigerant composition.

20

36. A heat transfer device containing a composition as defined in any one of claims 1 to 35.

25

37. Use of a composition defined in any of claims 1 to 35 in a heat transfer device.
38. A heat transfer device according to claim 36 or 37 which is a refrigeration device.

30

39. A heat transfer device according to claim 38 which is selected from group consisting of automotive air conditioning systems, residential air conditioning systems, commercial air conditioning systems, residential refrigerator systems, residential freezer systems, commercial refrigerator systems, commercial freezer systems, chiller air conditioning systems, chiller refrigeration systems, and commercial or residential heat pump systems, preferably wherein the heat transfer device is an automobile air-conditioning system.

35

40. A heat transfer device according to claim 38 or 39 which contains a compressor.
41. A blowing agent comprising a composition as defined in any of claims 1 to 35.
- 5 42. A foamable composition comprising one or more components capable of forming foam and a composition as defined in any of claims 1 to 35, wherein the one or more components capable of forming foam are selected from polyurethanes, thermoplastic polymers and resins, such as polystyrene, and epoxy resins, and mixtures thereof.
- 10 43. A foam obtainable from the foamable composition as defined in claim 42.
44. A foam according to claim 43 comprising a composition as defined in any one of claims 1 to 62.
- 15 45. A sprayable composition comprising material to be sprayed and a propellant comprising a composition as defined in any of claims 1 to 35.
46. A method for cooling an article which comprises condensing a composition defined in any of claims 1 to 35 and thereafter evaporating the composition in the vicinity 20 of the article to be cooled.
47. A method for heating an article which comprises condensing a composition as defined in any one of claims 1 to 35 in the vicinity of the article to be heated and thereafter evaporating the composition.
- 25 48. A method for extracting a substance from biomass comprising contacting biomass with a solvent comprising a composition as defined in any of claims 1 to 35, and separating the substance from the solvent.
- 30 49. A method of cleaning an article comprising contacting the article with a solvent comprising a composition as defined in any of claims 1 to 35.
50. A method of extracting a material from an aqueous solution comprising contacting the aqueous solution with a solvent comprising a composition as defined in any of claims 35 1 to 35, and separating the substance from the solvent.

51. A method for extracting a material from a particulate solid matrix comprising contacting the particulate solid matrix with a solvent comprising a composition as defined in any of claims 1 to 35, and separating the material from the solvent.

5 52. A mechanical power generation device containing a composition as defined in any of claims 1 to 35.

53. A mechanical power generating device according to claim 52 which is adapted to use a Rankine Cycle or modification thereof to generate work from heat.

10 54. A method of retrofitting a heat transfer device comprising the step of removing an existing heat transfer fluid, and introducing a composition as defined in any one of claims 1 to 35.

15 55. A method of claim 54 wherein the heat transfer device is a refrigeration device.

56. A method according to claim 55 wherein the heat transfer device is an air conditioning system.

20 57. A method for reducing the environmental impact arising from the operation of a product comprising an existing compound or composition, the method comprising replacing at least partially the existing compound or composition with a composition as defined in any one of claims 1 to 35.

25 58. A method for preparing a composition as defined in any of claims 1 to 35, and/or a heat transfer device as defined in any of claims 36 or 38 to 40, which composition or heat transfer device contains R-134a, the method comprising introducing R-1234ze(E), R-744, the third component, and optionally any R-125, a lubricant, a stabiliser and/or a flame retardant, into a heat transfer device containing an existing heat transfer fluid which is R-134a.

30 59. A method according to claim 58 comprising the step of removing at least some of the existing R-134a from the heat transfer device before introducing the R-1234ze(E), R-744, the third component, and optionally the R-125, the lubricant, the stabiliser and/or the flame retardant.

60. A method for generating greenhouse gas emission credit comprising (i) replacing an existing compound or composition with a composition as defined in any one of claims 1 to 35, wherein the composition as defined in any one of claims 1 to 35 has a lower GWP than the existing compound or composition; and (ii) obtaining greenhouse gas emission credit for said replacing step.

5
61. A method of claim 60 wherein the use of the composition of the invention results in a lower Total Equivalent Warming Impact, and/or a lower Life-Cycle Carbon Production than is attained by use of the existing compound or composition.

10
62. A method of claim 60 or 61 carried out on a product from the fields of air-conditioning, refrigeration, heat transfer, blowing agents, aerosols or sprayable propellants, gaseous dielectrics, cryosurgery, veterinary procedures, dental procedures, fire extinguishing, flame suppression, solvents, cleaners, air horns, pellet guns, topical anesthetics, and expansion applications.

15
63. A method according to claim 57 or 62 wherein the product is selected from a heat transfer device, a blowing agent, a foamable composition, a sprayable composition, a solvent or a mechanical power generation device.

20
64. A method according to claim 63 wherein the product is a heat transfer device.

65. A method according to any one of claims 55 or 58 to 62 wherein the existing compound or composition is a heat transfer composition.

25
66. A method according to claim 65 wherein the heat transfer composition is a refrigerant selected from R-134a, R-1234yf, R-152a, R-404A, R-410A, R-507, R-407A, R-407B, R-407D, R-407E and R-407F.

30
67. Any novel heat transfer composition substantially as hereinbefore described, optionally with reference to the examples.