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(54) Title: CASCADE REFRIGERATION SYSTEM WITH FLUOROOLEFIN REFRIGERANT

(57) Abstract: The present invention relates to a cascade refrigeration system which circulates a refrigerant comprising a fluoroolefin therethrough. The cascade refrigeration system includes a low temperature refrigeration loop and a medium temperature refrigeration loop. The fluoroolefin circulates through either loop, or both. In a particular embodiment, the fluoroolefin circulates through the medium temperature loop. In a particular embodiment, where the cascade refrigeration system includes a first and a second cascade heat exchanger, and a secondary heat transfer loop which extends between the first and second cascade heat exchangers, either the first and/or second refrigerant may be, but need not necessarily be, a fluoroolefin.

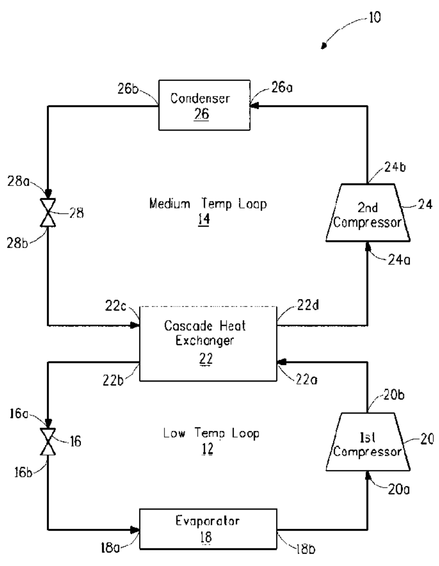

FIG. 1

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TITLE

CASCADE REFRIGERATION SYSTEM
WITH FLUOROOLEFIN REFRIGERANT

BACKGROUND

1. Field of the Disclosure.

The present disclosure relates to a cascade refrigeration system which circulates a refrigerant comprising a fluoroolefin therethrough. In particular, such a cascade system includes a medium temperature loop and a low temperature loop, and a fluoroolefin refrigerant may be used in either loop, or both.

2. Description of Related Art.

Cascade refrigeration systems are known in the art, see for example, ICR07-B2-358, "CO_2-DX Systems for Medium-and Low-Temperature Refrigeration in Supermarket Applications", T. Sienel, O. Finckh, International Congress of Refrigeration, 2007, Beijing. Such a system typically uses a refrigerant such as 1,1,1,2-tetrafluoroethane (R134a) or blends thereof with HFC-125 and HFC-143a (i.e., R404A) in the medium temperature loop and carbon dioxide (CO_2) in the low temperature loop to provide cooling to display cases, for instance, in supermarkets.

The refrigeration industry has been working for the past few decades to find replacement refrigerants for the ozone-depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being phased out as a result of the Montreal Protocol. The solution for most refrigerant producers has been the commercialization of hydrofluorocarbon (HFC) refrigerants. The new HFC refrigerants, HFC-134a being the most widely used at this time, have zero ozone depletion potential and thus are not affected by the current regulatory phase out as a result of the Montreal Protocol.

2010315264 02 Nov 2015

Further environmental regulations may ultimately cause global phase out of certain HFC refrigerants. Currently, the automobile industry is facing regulations relating to global warming potential for refrigerants used in mobile air-conditioning. Therefore, there is a great current need to identify new refrigerants with reduced global warming potential for the mobile air-conditioning market. Should the regulations be more broadly applied in the future, for instance for stationary air conditioning and refrigeration systems, an even greater need will be felt for refrigerants that can be used in all areas of the refrigeration and air-conditioning industry.

Currently proposed replacement refrigerants for HFC-134a include HFC-152a, pure hydrocarbons such as butane or propane, or "natural" refrigerants such as CO_2. Many of these suggested replacements are toxic, flammable, and/or have low energy efficiency. New replacements are also being proposed for HCFC-22, R404A, R407C and R410A, among others. As these replacements are found, new uses of such alternative refrigerants are being sought in order to take advantage of their low or zero ozone depletion potential and lower global warming potential.

SUMMARY OF THE INVENTION

The present disclosure describes cascade refrigeration systems which use refrigerant compositions which have unique characteristics to meet the demands of low or zero ozone depletion potential and lower global warming potential as compared to current refrigerants.

In addition to lower global warming potential advantages, the cascade refrigeration systems of the present invention may have higher energy efficiency and capacity than currently used cascade refrigeration systems.

Therefore, in accordance with the present invention there is provided a cascade refrigeration system having at least two refrigeration loops, each circulating a refrigerant therethrough, comprising:

(a) a first expansion device for reducing the pressure and temperature of a first refrigerant liquid;

(b) an evaporator having an inlet and an outlet, wherein the first refrigerant liquid from the first expansion device enters the evaporator through the evaporator inlet and is evaporated in the evaporator to form a first refrigerant vapor, thereby producing cooling, and circulates to the outlet;

(c) a first compressor having an inlet and an outlet, wherein the first refrigerant vapor from the evaporator circulates to the inlet of the first compressor and is compressed, thereby increasing the pressure and the temperature of the first refrigerant vapor, and the compressed first refrigerant vapor circulates to the outlet of the first compressor;

(d) a cascade heat exchanger system having:

   (i) a first inlet and a first outlet, wherein the first refrigerant vapor circulates from the first inlet to the first outlet and is condensed in the cascade heat exchanger system to form a first refrigerant liquid, thereby rejecting heat, and

   (ii) a second inlet and a second outlet, wherein a second refrigerant liquid circulates from the second inlet to the second outlet and absorbs the heat rejected by the first refrigerant and forms a second refrigerant vapor;

(e) a second compressor having an inlet and an outlet, wherein the second refrigerant vapor from the cascade heat exchanger system is drawn into the second compressor and is compressed, thereby increasing the pressure and temperature of the second refrigerant vapor;

(f) a condenser having an inlet and an outlet for circulating the second refrigerant vapor therethrough and for condensing the second refrigerant vapor from the second compressor to form a second refrigerant liquid, wherein the second refrigerant liquid exits the condenser through the condenser outlet; and

(g) a second expansion device for reducing the pressure and temperature of the second refrigerant liquid exiting the condenser and entering the second inlet of the cascade heat exchanger system.

wherein the first refrigerant is CO_2 and the second refrigerant comprises at least one fluoroolefin selected from the group consisting of HFO-1234yf, trans-HFO-1234ze, and mixtures thereof.

The present invention also provides a cascade refrigeration system having at least two refrigeration loops, each circulating a refrigerant therethrough, comprising:

(a) a first expansion device for reducing the pressure and temperature of a first refrigerant liquid;

(b) an evaporator having an inlet and an outlet, wherein the first refrigerant liquid from the first expansion device enters the evaporator through the evaporator inlet and is evaporated in the evaporator to form a first refrigerant vapor, thereby producing cooling, and circulates to the outlet;

(c) a first compressor having an inlet and an outlet, wherein the first refrigerant vapor from the evaporator circulates to the inlet of the first compressor and is compressed, thereby increasing the pressure and the temperature of the first refrigerant vapor, and the compressed first refrigerant vapor circulates to the outlet of the first compressor;

(d) a cascade heat exchanger system comprising:

(i) a first cascade heat exchanger having:

(A) a first inlet and a first outlet, wherein the first refrigerant vapor from the evaporator circulates from the first inlet to the first outlet and is condensed in the first cascade heat exchanger to form a first refrigerant liquid, thereby rejecting heat, and

(B) a second inlet and a second outlet, wherein a heat transfer fluid circulates from the second inlet to the second outlet, wherein the heat rejected by the first refrigerant vapor as it is condensed is absorbed by the heat transfer fluid,

(ii) a second cascade heat exchanger having:

(A) a first inlet and a first outlet, wherein the heat transfer fluid from the first cascade heat exchanger circulates from the first inlet to the first outlet and rejects the heat absorbed in the first cascade heat exchanger, and

(B) a second inlet and a second outlet, wherein a second refrigerant liquid circulates from the second inlet to the second outlet and absorbs the heat rejected by the heat transfer fluid and forms a second refrigerant vapor;

(e) a second compressor having an inlet and an outlet, wherein the second refrigerant vapor from the second cascade heat exchanger is drawn into the second compressor and is compressed, thereby increasing the pressure and temperature of the second refrigerant vapor;

(f) a condenser having an inlet and an outlet for circulating the second refrigerant vapor therethrough and for condensing the second refrigerant vapor from the second compressor to form a second refrigerant liquid, wherein the second refrigerant liquid exits the condenser through the outlet; and

(g) a second expansion device for reducing the pressure and temperature of the second refrigerant liquid exiting the condenser and entering the second inlet of the second cascade heat exchanger;

wherein the first refrigerant is CO_2 and the second refrigerant comprises at least one fluoroolefin selected from the group consisting of HFO-1234yf, trans-HFO-1234ze, and mixtures thereof.

2010315264 24 Feb 2016

In a particular embodiment, the cascade heat exchanger system may include a first and a second cascade heat exchanger, and a secondary heat transfer loop which extends between the first and the second cascade heat exchanger. In this embodiment, the second refrigerant liquid indirectly absorbs the heat rejected by the first refrigerant vapor through a heat transfer fluid which circulates between the first cascade heat exchanger and the second cascade heat exchanger through the secondary heat transfer loop. The first cascade heat exchanger has a first inlet and a first outlet, and a second inlet and a second outlet, wherein the first refrigerant vapor circulates from the first inlet to the first outlet and rejects heat and is condensed, and a secondary heat transfer fluid circulates from the second inlet to the second outlet and absorbs the heat rejected from the first refrigerant vapor and circulates to the second cascade heat exchanger. The second cascade heat exchanger has a first inlet and a first outlet, and a second inlet and a second outlet, wherein the heat transfer fluid circulates from the second outlet of the first cascade heat exchanger to the first inlet of the second cascade heat exchanger and to the first outlet of the second cascade heat exchanger and rejects the heat absorbed from the first refrigerant. The second refrigerant liquid circulates from the second inlet to the second outlet of the second cascade heat exchanger and absorbs the heat rejected by the heat transfer fluid and forms a second refrigerant vapor. In this embodiment, either the first and/or second refrigerant may be, but need not necessarily be, a fluoroolefin.

Further in accordance with the present invention, there is provided a method of exchanging heat between at least two refrigeration loops, comprising:

(a) absorbing heat from a body to be cooled in a first refrigeration loop and rejecting this heat to a second refrigeration loop; and

(b) absorbing the heat from the first refrigeration loop in the second refrigeration loop and rejecting this heat to ambient, wherein the first refrigerant is CO_2 and the second refrigerant comprises at least one

2010315264 24 Feb 2016

fluoroolefin selected from the group consisting of HFO-1234yf, trans-HFO-1234ze, and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention may be better understood with reference to the following Figures, wherein:

FIG.1 is a schematic diagram of a cascade refrigeration system according to one embodiment of the present invention.

FIG. 2 is a schematic diagram of another embodiment of the cascade refrigeration system of the present invention.

FIG. 3 is a schematic diagram of a further embodiment of the present invention which shows a cascade refrigeration system with a secondary heat transfer loop which transfers heat from a lower temperature loop to a higher temperature loop.

FIG. 4 is a schematic diagram of yet another embodiment of the cascade refrigeration system of the present invention which has multiple low temperature loops.

FIG. 5 is a graph of the cooling capacity and COP for a refrigerant composition comprising HFO-1234yf and HFC-134a versus the weight percent of HFO-1234yf in the composition.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Before addressing details of embodiments described below, some terms are defined or clarified.

Refrigeration capacity (also referred to as cooling capacity) is a term to define the change in enthalpy of a refrigerant in an evaporator per unit mass of refrigerant circulated, or the heat removed by the refrigerant in the evaporator per unit volume of refrigerant vapor exiting the evaporator (volumetric capacity). The refrigeration capacity is a measure of the ability of a refrigerant or heat transfer composition to produce cooling. Therefore, the higher the capacity, the greater the cooling that is produced for a given refrigerant circulation rate. Cooling rate refers to the heat removed by the refrigerant in the evaporator per unit time.

Coefficient of performance (COP) is the amount of heat removed from a body to be cooled divided by the required energy input to operate the cycle over a given time interval. The higher the COP, the higher is the energy efficiency. COP is directly related to the energy efficiency ratio (EER) that is the efficiency rating for refrigeration or air conditioning equipment at a specific set of internal and external temperatures.

Global warming potential (GWP) is an index for estimating relative global warming contribution due to atmospheric emission of a kilogram of a particular greenhouse gas compared to emission of a kilogram of carbon dioxide. GWP can be calculated for different time horizons showing the effect of atmospheric lifetime for a given gas. The GWP for the 100 year time horizon is commonly the value referenced. For mixtures, a mass-fraction weighted average can be calculated based on the individual GWPs for each component.

Ozone depletion potential (ODP) is a number that refers to the amount of stratospheric ozone depletion caused by a substance. The ODP is the ratio of the impact on stratospheric ozone of a chemical compared to the impact of a similar mass of CFC-11 (fluorotrichloromethane). Thus, the ODP of CFC-11 is defined to be 1.0. Other CFCs and HCFCs have ODPs that range from 0.01 to 1.0. HFCs have zero ODP because they do not contain chlorine.

As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

The transitional phrase "consisting of" excludes any element, step, or ingredient not specified. If in the claim such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consists of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

The transitional phrase "consisting essentially of" is used to define a composition, method or apparatus that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do materially affect the basic and novel characteristic(s) of the claimed invention. The term 'consisting essentially of' occupies a middle ground between “comprising” and 'consisting of'.

Where applicants have defined an invention or a portion thereof with an open-ended term such as "comprising," it should be readily understood that (unless otherwise stated) the description should be interpreted to also describe such an invention using the terms "consisting essentially of" or "consisting of."

Also, use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the disclosed compositions, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety, unless a particular passage is cited. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

In accordance with the present invention, there is provided a cascade refrigeration system having at least two refrigeration loops for circulating a refrigerant through each loop. Such a cascade system is shown generally at 10 in Fig. 1. The cascade refrigeration system of the present invention has at least two refrigeration loops, including a first, or lower loop 12 as shown in FIG. 1, which is a low temperature loop, and a second, or upper loop 14 as shown in FIG. 1, which is a medium temperature loop 14. Each circulates a refrigerant therethrough.

As shown in FIG. 1, the cascade refrigeration system of the present invention includes a first expansion device 16. The first expansion device has an inlet 16a and an outlet 16b. The first expansion device reduces the pressure and temperature of a first refrigerant liquid which circulates through the first or low temperature loop.

The cascade refrigeration system of the present invention also includes an evaporator 18 as shown in FIG. 1. The evaporator has an inlet 18a and an outlet 18b. The first refrigerant liquid from the first expansion device enters the evaporator through the evaporator inlet and is evaporated in the evaporator to form a first refrigerant vapor. This produces cooling in the first, or low temperature circuit at a body to be cooled, such as food in a low temperature display case. The first refrigerant vapor then circulates to the outlet of the evaporator.

The cascade refrigeration system of the present invention also includes a first compressor 20. The first compressor has an inlet 20a and an outlet 20b. The first refrigerant vapor from the evaporator circulates to the inlet of the first compressor and is compressed, thereby increasing the pressure and the temperature of the first refrigerant vapor. The compressed first refrigerant vapor then circulates to the outlet of the first compressor.

The cascade refrigeration system of the present invention also includes a cascade heat exchanger system 22. The heat exchanger has a first inlet 22a and a first outlet 22b. The first refrigerant vapor from the first compressor enters the first inlet of the heat exchanger and is condensed in the heat exchanger to form a first refrigerant liquid, thereby rejecting heat. The first refrigerant liquid then circulates to the first outlet of the heat exchanger. The heat exchanger also includes a second inlet 22c and a second outlet 22d. A second refrigerant liquid circulates from the second inlet to the second outlet of the heat exchanger and is evaporated to form a second refrigerant vapor, thereby absorbing the heat rejected by the first refrigerant (as it is condensed). This heat is rejected to ambient. The second refrigerant vapor then circulates to the second outlet of the heat exchanger. Thus, in the embodiment of Fig. 1, the heat rejected by the first refrigerant is directly absorbed by the second refrigerant, and this heat is rejected to ambient.

The cascade refrigeration system of the present invention also includes a second compressor 24 as shown in FIG. 1. The second compressor has an inlet 24a and an outlet 24b. The second refrigerant vapor from the cascade heat exchanger is drawn into the compressor through the inlet and is compressed, thereby increasing the pressure and temperature of the second refrigerant vapor. The second refrigerant vapor then circulates to the outlet of the second compressor.

The cascade refrigeration system of the present invention also includes a condenser 26 having an inlet 26a and an outlet 26b. The second refrigerant from the second compressor circulates from the inlet and is condensed in the condenser to form a second refrigerant liquid. The second refrigerant liquid exits the condenser through the outlet.

The cascade refrigeration system of the present invention also includes a second expansion device 28 having an inlet 28a and an outlet 28b. The second refrigerant liquid passes through the second expansion device, which reduces the pressure and temperature of the second refrigerant liquid exiting the condenser. This liquid may be partially vaporized during this expansion. The reduced pressure and temperature second refrigerant liquid circulates to the second inlet of the cascade heat exchanger system from the expansion device.

It should be noted that various modifications to the embodiment as shown in FIG. 1 may be made without departing from the spirit or scope of the present invention. For instance, it may be possible to include multiple cascade heat exchangers instead of a single cascade heat exchanger and multiple first compressors instead of a single first compressor, as shown in the cascade refrigeration system diagram in the publication titled "Price Chopper Remodel Features Hill Phoenix Next Generation Refrigeration System", May 5, 2008. In addition, a secondary heat transfer loop, as shown in this diagram, which uses a secondary heat transfer fluids such as glycol, may be used with the system of the present invention to transfer heat from bodies to be cooled (e.g., supermarket food display cases) to either the high or low refrigeration loops or both. In this instance the secondary heat transfer loop is used to transfer heat from a body to be cooled to the refrigeration loop, as opposed to a secondary heat transfer loop which is used to transfer heat between the refrigeration loops, as will be described below with respect to FIG. 3.

In accordance with the present invention, the second refrigerant in the cascade system of the embodiment of FIG. 1 comprises a fluoroolefin. That is, the second refrigerant, i.e., the refrigerant which circulates through the medium temperature loop, comprises a fluoroolefin. However, it is within the scope of the present invention for the first refrigerant, i.e., the refrigerant in the low temperature loop, to comprise CO_2. Additionally, in some embodiments, the second refrigerant may be any of the fluoroolefins or mixtures of fluoroolefins or mixtures of fluoroolefins with additional refrigerants as described herein.

Such fluoroolefins may be selected from the group consisting of:

(i) fluoroolefins of the formula *E*- or *Z*-$R^1CH{=}CHR^2$, wherein R^1 and R^2 are, independently, C_1 to C_6 perfluoroalkyl groups;

(ii) cyclic fluoroolefins of the formula cyclo-[$CX{=}CY(CZW)_n$-], wherein X, Y, Z, and W, independently, are H or F, and n is an integer from 2 to 5; and

(iii) fluoroolefins selected from the group consisting of: tetrafluoroethylene ($CF_2{=}CF_2$); hexafluoropropene ($CF_3CF{=}CF_2$);1,2,3,3,3-pentafluoro-1-propene ($CHF{=}CFCF_3$), 1,1,3,3,3-pentafluoro-1-propene ($CF_2{=}CHCF_3$), 1,1,2,3,3-pentafluoro-1-propene ($CF_2{=}CFCHF_2$), 1,2,3,3-tetrafluoro-1-propene ($CHF{=}CFCHF_2$), 2,3,3,3-tetrafluoro-1-propene

(CH_2=$CFCF_3$), 1,3,3,3-tetrafluoro-1-propene (CHF=$CHCF_3$), 1,1,2,3-tetrafluoro-1-propene (CF_2=$CFCH_2F$), 1,1,3,3-tetrafluoro-1-propene (CF_2=$CHCHF_2$), 1,2,3,3-tetrafluoro-1-propene (CHF=$CFCHF_2$), 3,3,3-trifluoro-1-propene (CH_2=$CHCF_3$), 2,3,3-trifluoro-1-propene (CHF_2CF=CH_2); 1,1,2-trifluoro-1-propene (CH_3CF=CF_2); 1,2,3-trifluoro-1-propene (CH_2FCF=CF_2); 1,1,3-trifluoro-1-propene (CH_2FCH=CF_2); 1,3,3-trifluoro-1-propene (CHF_2CH=CHF); 1,1,1,2,3,4,4,4-octafluoro-2-butene (CF_3CF=$CFCF_3$); 1,1,2,3,3,4,4,4-octafluoro-1-butene (CF_3CF_2CF=CF_2); 1,1,1,2,4,4,4-heptafluoro-2-butene (CF_3CF=$CHCF_3$); 1,2,3,3,4,4,4-heptafluoro-1-butene (CHF=$CFCF_2CF_3$); 1,1,1,2,3,4,4-heptafluoro-2-butene (CHF_2CF=$CFCF_3$); 1,3,3,3-tetrafluoro-2-(trifluoromethyl)-1-propene (($CF_3)_2C$=CHF); 1,1,3,3,4,4,4-heptafluoro-1-butene (CF_2=$CHCF_2CF_3$); 1,1,2,3,4,4,4-heptafluoro-1-butene (CF_2=$CFCHFCF_3$); 1,1,2,3,3,4,4-heptafluoro-1-butene (CF_2=$CFCF_2CHF_2$); 2,3,3,4,4,4-hexafluoro-1-butene (CF_3CF_2CF=CH_2); 1,3,3,4,4,4-hexafluoro-1-butene (CHF=$CHCF_2CF_3$); 1,2,3,4,4,4-hexafluoro-1-butene (CHF=$CFCHFCF_3$); 1,2,3,3,4,4-hexafluoro-1-butene (CHF=$CFCF_2CHF_2$); 1,1,2,3,4,4-hexafluoro-2-butene (CHF_2CF=$CFCHF_2$); 1,1,1,2,3,4-hexafluoro-2-butene (CH_2FCF=$CFCF_3$); 1,1,1,2,4,4-hexafluoro-2-butene (CHF_2CH=$CFCF_3$); 1,1,1,3,4,4-hexafluoro-2-butene (CF_3CH=$CFCHF_2$); 1,1,2,3,3,4-hexafluoro-1-butene (CF_2=$CFCF_2CH_2F$); 1,1,2,3,4,4-hexafluoro-1-butene (CF_2=$CFCHFCHF_2$); 3,3,3-trifluoro-2-(trifluoromethyl)-1-propene (CH_2=$C(CF_3)_2$); 1,1,1,2,4-pentafluoro-2-butene (CH_2FCH=$CFCF_3$); 1,1,1,3,4-pentafluoro-2-butene (CF_3CH=$CFCH_2F$); 3,3,4,4,4-pentafluoro-1-butene (CF_3CF_2CH=CH_2); 1,1,1,4,4-pentafluoro-2-butene (CHF_2CH=$CHCF_3$); 1,1,1,2,3-pentafluoro-2-butene (CH_3CF=$CFCF_3$); 2,3,3,4,4-pentafluoro-1-butene (CH_2=$CFCF_2CHF_2$); 1,1,2,4,4-pentafluoro-2-butene

($CHF_2CF=CHCHF_2$); 1,1,2,3,3-pentafluoro-1-butene ($CH_3CF_2CF=CF_2$); 1,1,2,3,4-pentafluoro-2-butene ($CH_2FCF=CFCHF_2$); 1,1,3,3,3-pentafluoro-2-methyl-1-propene ($CF_2=C(CF_3)(CH_3)$); 2-(difluoromethyl)-3,3,3-trifluoro-1-propene ($CH_2=C(CHF_2)(CF_3)$); 2,3,4,4,4-pentafluoro-1-butene ($CH_2=CFCHFCF_3$); 1,2,4,4,4-pentafluoro-1-butene ($CHF=CFCH_2CF_3$); 1,3,4,4,4-pentafluoro-1-butene ($CHF=CHCHFCF_3$); 1,3,3,4,4-pentafluoro-1-butene ($CHF=CHCF_2CHF_2$); 1,2,3,4,4-pentafluoro-1-butene ($CHF=CFCHFCHF_2$); 3,3,4,4-tetrafluoro-1-butene ($CH_2=CHCF_2CHF_2$); 1,1-difluoro-2-(difluoromethyl)-1-propene ($CF_2=C(CHF_2)(CH_3)$); 1,3,3,3-tetrafluoro-2-methyl-1-propene ($CHF=C(CF_3)(CH_3)$); 3,3-difluoro-2-(difluoromethyl)-1-propene ($CH_2=C(CHF_2)_2$); 1,1,1,2-tetrafluoro-2-butene ($CF_3CF=CHCH_3$); 1,1,1,3-tetrafluoro-2-butene ($CH_3CF=CHCF_3$); 1,1,1,2,3,4,4,5,5,5-decafluoro-2-pentene ($CF_3CF=CFCF_2CF_3$); 1,1,2,3,3,4,4,5,5,5-decafluoro-1-pentene ($CF_2=CFCF_2CF_2CF_3$); 1,1,1,4,4,4-hexafluoro-2-(trifluoromethyl)-2-butene ($(CF_3)_2C=CHCF_3$); 1,1,1,2,4,4,5,5,5-nonafluoro-2-pentene ($CF_3CF=CHCF_2CF_3$); 1,1,1,3,4,4,5,5,5-nonafluoro-2-pentene ($CF_3CH=CFCF_2CF_3$); 1,2,3,3,4,4,5,5,5-nonafluoro-1-pentene ($CHF=CFCF_2CF_2CF_3$); 1,1,3,3,4,4,5,5,5-nonafluoro-1-pentene ($CF_2=CHCF_2CF_2CF_3$); 1,1,2,3,3,4,4,5,5-nonafluoro-1-pentene ($CF_2=CFCF_2CF_2CHF_2$); 1,1,2,3,4,4,5,5,5-nonafluoro-2-pentene ($CHF_2CF=CFCF_2CF_3$); 1,1,1,2,3,4,4,5,5-nonafluoro-2-pentene ($CF_3CF=CFCF_2CHF_2$); 1,1,1,2,3,4,5,5,5-nonafluoro-2-pentene ($CF_3CF=CFCHFCF_3$); 1,2,3,4,4,4-hexafluoro-3-(trifluoromethyl)-1-butene ($CHF=CFCF(CF_3)_2$); 1,1,2,4,4,4-hexafluoro-3-(trifluoromethyl)-1-butene ($CF_2=CFCH(CF_3)_2$); 1,1,1,4,4,4-hexafluoro-2-(trifluoromethyl)-2-butene ($CF_3CH=C(CF_3)_2$); 1,1,3,4,4,4-hexafluoro-3-(trifluoromethyl)-1-butene ($CF_2=CHCF(CF_3)_2$); 2,3,3,4,4,5,5,5-octafluoro-1-pentene ($CH_2=CFCF_2CF_2CF_3$); 1,2,3,3,4,4,5,5-octafluoro-1-pentene ($CHF=CFCF_2CF_2CHF_2$);

3,3,4,4,4-pentafluoro-2-(trifluoromethyl)-1-butene ($CH_2=C(CF_3)CF_2CF_3$); 1,1,4,4,4-pentafluoro-3-(trifluoromethyl)-1-butene ($CF_2=CHCH(CF_3)_2$); 1,3,4,4,4-pentafluoro-3-(trifluoromethyl)-1-butene ($CHF=CHCF(CF_3)_2$); 1,1,4,4,4-pentafluoro-2-(trifluoromethyl)-1-butene ($CF_2=C(CF_3)CH_2CF_3$); 3,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene ($(CF_3)_2CFCH=CH_2$); 3,3,4,4,5,5,5-heptafluoro-1-pentene ($CF_3CF_2CF_2CH=CH_2$); 2,3,3,4,4,5,5-heptafluoro-1-pentene ($CH_2=CFCF_2CF_2CHF_2$); 1,1,3,3,5,5,5-heptafluoro-1-butene ($CF_2=CHCF_2CH_2CF_3$); 1,1,1,2,4,4,4-heptafluoro-3-methyl-2-butene ($CF_3CF=C(CF_3)(CH_3)$); 2,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene ($CH_2=CFCH(CF_3)_2$); 1,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene ($CHF=CHCH(CF_3)_2$); 1,1,1,4-tetrafluoro-2-(trifluoromethyl)-2-butene ($CH_2FCH=C(CF_3)_2$); 1,1,1,3-tetrafluoro-2-(trifluoromethyl)-2-butene ($CH_3CF=C(CF_3)_2$); 1,1,1-trifluoro-2-(trifluoromethyl)-2-butene ($(CF_3)_2C=CHCH_3$); 3,4,4,5,5,5-hexafluoro-2-pentene ($CF_3CF_2CF=CHCH_3$); 1,1,1,4,4,4-hexafluoro-2-methyl-2-butene ($CF_3C(CH_3)=CHCF_3$); 3,3,4,5,5,5-hexafluoro-1-pentene ($CH_2=CHCF_2CHFCF_3$); 4,4,4-trifluoro-2-(trifluoromethyl)-1-butene ($CH_2=C(CF_3)CH_2CF_3$); 1,1,2,3,3,4,4,5,5,6,6,6-dodecafluoro-1-hexene ($CF_3(CF_2)_3CF=CF_2$); 1,1,1,2,2,3,4,5,5,6,6,6-dodecafluoro-3-hexene ($CF_3CF_2CF=CFCF_2CF_3$); 1,1,1,4,4,4-hexafluoro-2,3-bis(trifluoromethyl)-2-butene ($(CF_3)_2C=C(CF_3)_2$); 1,1,1,2,3,4,5,5,5-nonafluoro-4-(trifluoromethyl)-2-pentene ($(CF_3)_2CFCF=CFCF_3$); 1,1,1,4,4,5,5,5-octafluoro-2-(trifluoromethyl)-2-pentene ($(CF_3)_2C=CHC_2F_5$); 1,1,1,3,4,5,5,5-octafluoro-4-(trifluoromethyl)-2-pentene ($(CF_3)_2CFCF=CHCF_3$); 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene ($CF_3CF_2CF_2CF_2CH=CH_2$); 4,4,4-trifluoro-3,3-bis(trifluoromethyl)-1-butene ($CH_2=CHC(CF_3)_3$); 1,1,1,4,4,4-hexafluoro-3-methyl-2-(trifluoromethyl)- 2-butene ($(CF_3)_2C=C(CH_3)(CF_3)$); 2,3,3,5,5,5-hexafluoro-4-

(trifluoromethyl)-1-pentene ($CH_2=CFCF_2CH(CF_3)_2$); 1,1,1,2,4,4,5,5,5-nonafluoro-3-methyl-2-pentene ($CF_3CF=C(CH_3)CF_2CF_3$); 1,1,1,5,5,5-hexafluoro-4-(trifluoromethyl)-2-pentene ($CF_3CH=CHCH(CF_3)_2$); 3,4,4,5,5,6,6,6-octafluoro-2-hexene ($CF_3CF_2CF_2CF=CHCH_3$); 3,3,4,4,5,5,6,6-octafluoro1-hexene ($CH_2=CHCF_2CF_2CF_2CHF_2$); 1,1,1,4,4-pentafluoro-2-(trifluoromethyl)-2-pentene ($(CF_3)_2C=CHCF_2CH_3$); 4,4,5,5,5-pentafluoro-2-(trifluoromethyl)-1-pentene ($CH_2=C(CF_3)CH_2C_2F_5$); 3,3,4,4,5,5,5-heptafluoro-2-methyl-1-pentene ($CF_3CF_2CF_2C(CH_3)=CH_2$); 4,4,5,5,6,6,6-heptafluoro-2-hexene ($CF_3CF_2CF_2CH=CHCH_3$); 4,4,5,5,6,6,6-heptafluoro-1-hexene ($CH_2=CHCH_2CF_2C_2F_5$); 1,1,1,2,2,3,4-heptafluoro-3-hexene ($CF_3CF_2CF=CFC_2H_5$); 4,5,5,5-tetrafluoro-4-(trifluoromethyl)-1-pentene ($CH_2=CHCH_2CF(CF_3)_2$); 1,1,1,2,5,5,5-heptafluoro-4-methyl-2-pentene ($CF_3CF=CHCH(CF_3)(CH_3)$); 1,1,1,3-tetrafluoro-2-(trifluoromethyl)-2-pentene ($(CF_3)_2C=CFC_2H_5$); 1,1,1,2,3,4,4,5,5,6,6,7,7,7-tetradecafluoro-2-heptene ($CF_3CF=CFCF_2CF_2C_2F_5$); 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoro-3-heptene ($CF_3CF_2CF=CFCF_2C_2F_5$); 1,1,1,3,4,4,5,5,6,6,7,7,7-tridecafluoro-2-heptene ($CF_3CH=CFCF_2CF_2C_2F_5$); 1,1,1,2,4,4,5,5,6,6,7,7,7-tridecafluoro-2-heptene ($CF_3CF=CHCF_2CF_2C_2F_5$); 1,1,1,2,2,4,5,5,6,6,7,7,7-tridecafluoro-3-heptene ($CF_3CF_2CH=CFCF_2C_2F_5$); and 1,1,1,2,2,3,5,5,6,6,7,7,7-tridecafluoro-3-heptene ($CF_3CF_2CF=CHCF_2C_2F_5$).

In some embodiments, fluoroolefins are compounds, which comprise carbon atoms, fluorine atoms and optionally hydrogen or chlorine atoms. In one embodiment, the fluoroolefins used in the compositions of the present invention comprise compounds with 2 to 12 carbon atoms. In another embodiment the fluoroolefins comprise compounds with 3 to 10 carbon atoms, and in yet another embodiment the fluoroolefins comprise compounds with 3 to 7 carbon atoms. Representative fluoroolefins include but are not limited to all compounds as listed in Table 1, Table 2, and Table 3.

In one embodiment of the present invention the first refrigerant is selected from fluoroolefins having the formula *E*- or *Z*-$R^1CH=CHR^2$ (Formula (i)), wherein R^1 and R^2 are, independently, C_1 to C_6 perfluoroalkyl groups. Examples of R^1 and R^2 groups include, but are not limited to, CF_3, C_2F_5, $CF_2CF_2CF_3$, $CF(CF_3)_2$, $CF_2CF_2CF_2CF_3$, $CF(CF_3)CF_2CF_3$, $CF_2CF(CF_3)_2$, $C(CF_3)_3$, $CF_2CF_2CF_2CF_2CF_3$, $CF_2CF_2CF(CF_3)_2$, $C(CF_3)_2C_2F_5$, $CF_2CF_2CF_2CF_2CF_2CF_3$, $CF(CF_3)CF_2CF_2C_2F_5$, and $C(CF_3)_2CF_2C_2F_5$. In one embodiment the fluoroolefins of Formula (i) have at least 4 carbon atoms in the molecule. In another embodiment, the first refrigerant is selected from fluoroolefins of Formula (i) having at least 5 carbon atoms in the molecule. In yet another embodiment, the first refrigerant is selected from fluoroolefins of Formula (i) having at least 6 carbon atoms in the molecule. Exemplary, non-limiting Formula (i) compounds are presented in Table 1.

TABLE 1

Code	Structure	Chemical Name
F11E	$CF_3CH=CHCF_3$	1,1,1,4,4,4-hexafluorobut-2-ene
F12E	$CF_3CH=CHC_2F_5$	1,1,1,4,4,5,5,5-octafluoropent-2-ene
F13E	$CF_3CH=CHCF_2C_2F_5$	1,1,1,4,4,5,5,6,6,6-decafluorohex-2-ene
F13iE	$CF_3CH=CHCF(CF_3)_2$	1,1,1,4,5,5,5-heptafluoro-4-(trifluoromethyl)pent-2-ene
F22E	$C_2F_5CH=CHC_2F_5$	1,1,1,2,2,5,5,6,6,6-decafluorohex-3-ene
F14E	$CF_3CH=CH(CF_2)_3CF_3$	1,1,1,4,4,5,5,6,6,7,7,7-dodecafluorohept-2-ene
F14iE	$CF_3CH=CHCF_2CF\text{-}(CF_3)_2$	1,1,1,4,4,5,6,6,6-nonafluoro-5-(trifluoromethyl)hex-2-ene
F14sE	$CF_3CH=CHCF(CF_3)\text{-}C_2F_5$	1,1,1,4,5,5,6,6,6-nonfluoro-4-(trifluoromethyl)hex-2-ene
F14tE	$CF_3CH=CHC(CF_3)_3$	1,1,1,5,5,5-hexafluoro-4,4-bis(trifluoromethyl)pent-2-ene
F23E	$C_2F_5CH=CHCF_2C_2F_5$	1,1,1,2,2,5,5,6,6,7,7,7-dodecafluorohept-3-ene
F23iE	$C_2F_5CH=CHCF(CF_3)_2$	1,1,1,2,2,5,6,6,6-nonafluoro-5-(trifluoromethyl)hex-3-ene
F15E	$CF_3CH=CH(CF_2)_4CF_3$	1,1,1,4,4,5,5,6,6,7,7,8,8,8-tetradecafluorooct-2-ene
F15iE	$CF_3CH=CH\text{-}CF_2CF_2CF(CF_3)_2$	1,1,1,4,4,5,5,6,7,7,7-undecafluoro-6-(trifluoromethyl)hept-2-ene
F15tE	$CF_3CH=CH\text{-}C(CF_3)_2C_2F_5$	1,1,1,5,5,6,6,6-octafluoro-4,4-bis(trifluoromethyl)hex-2-ene
F24E	$C_2F_5CH=CH(CF_2)_3CF_3$	1,1,1,2,2,5,5,6,6,7,7,8,8,8-tetradecafluorooct-3-ene
F24iE	$C_2F_5CH=CHCF_2CF\text{-}(CF_3)_2$	1,1,1,2,2,5,5,6,7,7,7-undecafluoro-6-(trifluoromethyl)hept-3-ene
F24sE	$C_2F_5CH=CHCF(CF_3)\text{-}C_2F_5$	1,1,1,2,2,5,6,6,7,7,7-undecafluoro-5-(trifluoromethyl)hept-3-ene
F24tE	$C_2F_5CH=CHC(CF_3)_3$	1,1,1,2,2,6,6,6-octafluoro-5,5-bis(trifluoromethyl)hex-3-ene
F33E	$C_2F_5CF_2CH=CH\text{-}CF_2C_2F_5$	1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluorooct-4-ene
F3i3iE	$(CF_3)_2CFCH=CH\text{-}CF(CF_3)_2$	1,1,1,2,5,6,6,6-octafluoro-2,5-bis(trifluoromethyl)hex-3-ene
F33iE	$C_2F_5CF_2CH=CH\text{-}CF(CF_3)_2$	1,1,1,2,5,5,6,6,7,7,7-undecafluoro-2-(trifluoromethyl)hept-3-ene

Code	Structure	Chemical Name
F16E	$CF_3CH=CH(CF_2)_5CF_3$	1,1,1,4,4,5,5,6,6,7,7,8,8,9,9,9-hexadecafluoronon-2-ene
F16sE	$CF_3CH=CHCF(CF_3)(CF_2)_2C_2F_5$	1,1,1,4,5,5,6,6,7,7,8,8,8-tridecafluoro-4-(trifluoromethyl)hept-2-ene
F16tE	$CF_3CH=CHC(CF_3)_2CF_2C_2F_5$	1,1,1,6,6,6-octafluoro-4,4-bis(trifluoromethyl)hept-2-ene
F25E	$C_2F_5CH=CH(CF_2)_4CF_3$	1,1,1,2,2,5,5,6,6,7,7,8,8,9,9,9-hexadecafluoronon-3-ene
F25iE	$C_2F_5CH=CH-CF_2CF_2CF(CF_3)_2$	1,1,1,2,2,5,5,6,6,7,8,8,8-tridecafluoro-7-(trifluoromethyl)oct-3-ene
F25tE	$C_2F_5CH=CH-C(CF_3)_2C_2F_5$	1,1,1,2,2,6,6,7,7,7-decafluoro-5,5-bis(trifluoromethyl)hept-3-ene
F34E	$C_2F_5CF_2CH=CH-(CF_2)_3CF_3$	1,1,1,2,2,3,3,6,6,7,7,8,8,9,9,9-hexadecafluoronon-4-ene
F34iE	$C_2F_5CF_2CH=CH-CF_2CF(CF_3)_2$	1,1,1,2,2,3,3,6,6,7,8,8,8-tridecafluoro-7-(trifluoromethyl)oct-4-ene
F34sE	$C_2F_5CF_2CH=CH-CF(CF_3)C_2F_5$	1,1,1,2,2,3,3,6,7,7,8,8,8-tridecafluoro-6-(trifluoromethyl)oct-4-ene
F34tE	$C_2F_5CF_2CH=CH-C(CF_3)_3$	1,1,1,5,5,6,6,7,7,7-decafluoro-2,2-bis(trifluoromethyl)hept-3-ene
F3i4E	$(CF_3)_2CFCH=CH-(CF_2)_3CF_3$	1,1,1,2,5,5,6,6,7,7,8,8,8-tridecafluoro-2(trifluoromethyl)oct-3-ene
F3i4iE	$(CF_3)_2CFCH=CH-CF_2CF(CF_3)_2$	1,1,1,2,5,5,6,7,7,7-decafluoro-2,6-bis(trifluoromethyl)hept-3-ene
F3i4sE	$(CF_3)_2CFCH=CH-CF(CF_3)C_2F_5$	1,1,1,2,5,6,6,7,7,7-decafluoro-2,5-bis(trifluoromethyl)hept-3-ene
F3i4tE	$(CF_3)_2CFCH=CH-C(CF_3)_3$	1,1,1,2,6,6,6-heptafluoro-2,5,5-tris(trifluoromethyl)hex-3-ene
F26E	$C_2F_5CH=CH(CF_2)_5CF_3$	1,1,1,2,2,5,5,6,6,7,7,8,8,9,9,10,10,10-octadecafluorodec-3-ene
F26sE	$C_2F_5CH=CHCF(CF_3)(CF_2)_2C_2F_5$	1,1,1,2,2,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-5-(trifluoromethyl)non-3-ene
F26tE	$C_2F_5CH=CHC(CF_3)_2CF_2C_2F_5$	1,1,1,2,2,6,6,7,7,8,8,8-dodecafluoro-5,5-bis(trifluoromethyl)oct-3-ene
F35E	$C_2F_5CF_2CH=CH-(CF_2)_4CF_3$	1,1,1,2,2,3,3,6,6,7,7,8,8,9,9,10,10,10-octadecafluorodec-4-ene
F35iE	$C_2F_5CF_2CH=CH-$	1,1,1,2,2,3,3,6,6,7,7,8,9,9,9-pentadecafluoro-8-

Code	Structure	Chemical Name
	$CF_2CF_2CF(CF_3)_2$	(trifluoromethyl)non-4-ene
F35tE	$C_2F_5CF_2CH=CH-C(CF_3)_2C_2F_5$	1,1,1,2,2,3,3,7,7,8,8,8-dodecafluoro-6,6-bis(trifluoromethyl)oct-4-ene
F3i5E	$(CF_3)_2CFCH=CH-(CF_2)_4CF_3$	1,1,1,2,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-2-(trifluoromethyl)non-3-ene
F3i5iE	$(CF_3)_2CFCH=CH-CF_2CF_2CF(CF_3)_2$	1,1,1,2,5,5,6,6,7,8,8,8-dodecafluoro-2,7-bis(trifluoromethyl)oct-3-ene
F3i5tE	$(CF_3)_2CFCH=CH-C(CF_3)_2C_2F_5$	1,1,1,2,6,6,7,7,7-nonafluoro-2,5,5-tris(trifluoromethyl)hept-3-ene
F44E	$CF_3(CF_2)_3CH=CH-(CF_2)_3CF_3$	1,1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10,10-octadecafluorodec-5-ene
F44iE	$CF_3(CF_2)_3CH=CH-CF_2CF(CF_3)_2$	1,1,1,2,3,3,6,6,7,7,8,8,9,9,9-pentadecafluoro-2-(trifluoromethyl)non-4-ene
F44sE	$CF_3(CF_2)_3CH=CH-CF(CF_3)C_2F_5$	1,1,1,2,2,3,6,6,7,7,8,8,9,9,9-pentadecafluoro-3-(trifluoromethyl)non-4-ene
F44tE	$CF_3(CF_2)_3CH=CH-C(CF_3)_3$	1,1,1,5,5,6,6,7,7,8,8,8-dodecafluoro-2,2,-bis(trifluoromethyl)oct-3-ene
F4i4iE	$(CF_3)_2CFCF_2CH=CH-CF_2CF(CF_3)_2$	1,1,1,2,3,3,6,6,7,8,8,8-dodecafluoro-2,7-bis(trifluoromethyl)oct-4-ene
F4i4sE	$(CF_3)_2CFCF_2CH=CH-CF(CF_3)C_2F_5$	1,1,1,2,3,3,6,7,7,8,8,8-dodecafluoro-2,6-bis(trifluoromethyl)oct-4-ene
F4i4tE	$(CF_3)_2CFCF_2CH=CH- C(CF_3)_3$	1,1,1,5,5,6,7,7,7-nonafluoro-2,2,6-tris(trifluoromethyl)hept-3-ene
F4s4sE	$C_2F_5CF(CF_3)CH=CH-CF(CF_3)C_2F_5$	1,1,1,2,2,3,6,7,7,8,8,8-dodecafluoro-3,6-bis(trifluoromethyl)oct-4-ene
F4s4tE	$C_2F_5CF(CF_3)CH=CH- C(CF_3)_3$	1,1,1,5,6,6,7,7,7-nonafluoro-2,2,5-tris(trifluoromethyl)hept-3-ene
F4t4tE	$(CF_3)_3CCH=CH-C(CF_3)_3$	1,1,1,6,6,6-hexafluoro-2,2,5,5-tetrakis(trifluoromethyl)hex-3-ene

Compounds of Formula (i) may be prepared by contacting a perfluoroalkyl iodide of the formula R^1I with a perfluoroalkyltrihydroolefin of the formula $R^2CH=CH_2$ to form a trihydroiodoperfluoroalkane of the formula $R^1CH_2CHIR^2$. This trihydroiodoperfluoroalkane can then be dehydroiodinated to form $R^1CH=CHR^2$. Alternatively, the olefin

$R^1CH{=}CHR^2$ may be prepared by dehydroiodination of a trihydroiodoperfluoroalkane of the formula $R^1CHICH_2R^2$ formed in turn by reacting a perfluoroalkyl iodide of the formula R^2I with a perfluoroalkyltrihydroolefin of the formula $R^1CH{=}CH_2$.

The contacting of a perfluoroalkyl iodide with a perfluoroalkyltrihydroolefin may take place in batch mode by combining the reactants in a suitable reaction vessel capable of operating under the autogenous pressure of the reactants and products at reaction temperature. Suitable reaction vessels include fabricated from stainless steels, in particular of the austenitic type, and the well-known high nickel alloys such as Monel® nickel-copper alloys, Hastelloy® nickel based alloys and Inconel® nickel-chromium alloys.

Alternatively, the reaction may be conducted in semi-batch mode in which the perfluoroalkyltrihydroolefin reactant is added to the perfluoroalkyl iodide reactant by means of a suitable addition apparatus such as a pump at the reaction temperature.

The ratio of perfluoroalkyl iodide to perfluoroalkyltrihydroolefin should be between about 1:1 to about 4:1, preferably from about 1.5:1 to 2.5:1. Ratios less than 1.5:1 tend to result in large amounts of the 2:1 adduct as reported by Jeanneaux, et. al. in Journal of Fluorine Chemistry, Vol. 4, pages 261-270 (1974).

Preferred temperatures for contacting of said perfluoroalkyl iodide with said perfluoroalkyltrihydroolefin are preferably within the range of about 150°C to 300°C, preferably from about 170°C to about 250°C, and most preferably from about 180°C to about 230°C.

Suitable contact times for the reaction of the perfluoroalkyl iodide with the perfluoroalkyltrihydroolefin are from about 0.5 hour to 18 hours, preferably from about 4 to about 12 hours.

The trihydroiodoperfluoroalkane prepared by reaction of the perfluoroalkyl iodide with the perfluoroalkyltrihydroolefin may be used directly in the dehydroiodination step or may preferably be recovered and purified by distillation prior to the dehydroiodination step.

The dehydroiodination step is carried out by contacting the trihydroiodoperfluoroalkane with a basic substance. Suitable basic substances include alkali metal hydroxides (e.g., sodium hydroxide or potassium hydroxide), alkali metal oxide (for example, sodium oxide), alkaline earth metal hydroxides (e.g., calcium hydroxide), alkaline earth metal oxides (e.g., calcium oxide), alkali metal alkoxides (e.g., sodium methoxide or sodium ethoxide), aqueous ammonia, sodium amide, or mixtures of basic substances such as soda lime. Preferred basic substances are sodium hydroxide and potassium hydroxide.

Said contacting of the trihydroiodoperfluoroalkane with a basic substance may take place in the liquid phase preferably in the presence of a solvent capable of dissolving at least a portion of both reactants. Solvents suitable for the dehydroiodination step include one or more polar organic solvents such as alcohols (e.g., methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, and tertiary butanol), nitriles (e.g., acetonitrile, propionitrile, butyronitrile, benzonitrile, or adiponitrile), dimethyl sulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, or sulfolane. The choice of solvent may depend on the boiling point product and the ease of separation of traces of the solvent from the product during purification. Typically, ethanol or isopropanol are good solvents for the reaction.

Typically, the dehydroiodination reaction may be carried out by addition of one of the reactants (either the basic substance or the trihydroiodoperfluoroalkane) to the other reactant in a suitable reaction vessel. Said reaction may be fabricated from glass, ceramic, or metal and is preferably agitated with an impeller or stirring mechanism.

Temperatures suitable for the dehydroiodination reaction are from about 10ºC to about 100ºC, preferably from about 20ºC to about 70ºC. The dehydroiodination reaction may be carried out at ambient pressure or at reduced or elevated pressure. Of note are dehydroiodination reactions in which the compound of Formula (i) is distilled out of the reaction vessel as it is formed.

Alternatively, the dehydroiodination reaction may be conducted by contacting an aqueous solution of said basic substance with a solution of the trihydroiodoperfluoroalkane in one or more organic solvents of lower polarity such as an alkane (e.g., hexane, heptane, or octane), aromatic hydrocarbon (e.g., toluene), halogenated hydrocarbon (e.g., methylene chloride, chloroform, carbon tetrachloride, or perchloroethylene), or ether (e.g., diethyl ether, methyl tert-butyl ether, tetrahydrofuran, 2-methyl tetrahydrofuran, dioxane, dimethoxyethane, diglyme, or tetraglyme) in the presence of a phase transfer catalyst. Suitable phase transfer catalysts include quaternary ammonium halides (e.g., tetrabutylammonium bromide, tetrabutylammonium hydrosulfate, triethylbenzylammonium chloride, dodecyltrimethylammonium chloride, and tricaprylylmethylammonium chloride), quaternary phosphonium halides (e.g., triphenylmethylphosphonium bromide and tetraphenylphosphonium chloride), or cyclic polyether compounds known in the art as crown ethers (e.g., 18-crown-6 and 15-crown-5).

Alternatively, the dehydroiodination reaction may be conducted in the absence of solvent by adding the trihydroiodoperfluoroalkane to a solid or liquid basic substance.

Suitable reaction times for the dehydroiodination reactions are from about 15 minutes to about six hours or more depending on the solubility of the reactants. Typically the dehydroiodination reaction is rapid and requires about 30 minutes to about three hours for completion. The compound of Formula (i) may be recovered from the dehydroiodination reaction mixture by phase separation after addition of water, by distillation, or by a combination thereof.

In another embodiment of the present invention, the refrigerant is selected from fluoroolefins comprising cyclic fluoroolefins (cyclo-

[CX=CY(CZW)$_n$-] (Formula (ii)), wherein X, Y, Z, and W are independently selected from H and F, and n is an integer from 2 to 5). In one embodiment the fluoroolefins of Formula (ii), have at least about 3 carbon atoms in the molecule. In another embodiment, the fluoroolefins of Formula (ii) have at least about 4 carbon atoms in the molecule. In another embodiment, the fluoroolefins of Formula (ii) have at least about 5 carbon atoms in the molecule. In yet another embodiment, the fluoroolefins of Formula (ii) have at least about 6 carbon atoms in the molecule. Representative cyclic fluoroolefins of Formula (ii) are listed in Table 2.

TABLE 2

Cyclic fluoroolefins	Structure	Chemical name
HFO-C1316cc	cyclo-CF_2CF_2CF=CF-	1,2,3,3,4,4-hexafluorocyclobutene
HFO-C1334cc	cyclo-CF_2CF_2CH=CH-	3,3,4,4-tetrafluorocyclobutene
HFO-C1436	Cyclo-$CF_2CF_2CF_2CH$=CH-	3,3,4,4,5,5,-hexafluorocyclopentene
HFO-C1418y	Cyclo-CF_2CF=$CFCF_2CF_2$-	1,2,3,3,4,4,5,5-octafluorocyclopentene
HFO-C151-10y	Cyclo-CF_2CF=$CFCF_2CF_2CF_2$-	1,2,3,3,4,4,5,5,6,6-decafluorocyclohexene

The first refrigerant of the present invention may comprise a single compound of Formula (i) or Formula (ii), for example, one of the compounds in Table 1 or Table 2, or may comprise a combination of compounds of Formula (i) or Formula (ii).

In another embodiment, the first refrigerant is selected from fluoroolefins comprising those compounds listed in Table 3.

TABLE 3

Name	Structure	Chemical name
HFO-1225ye	CF_3CF=CHF	1,2,3,3,3-pentafluoro-1-propene
HFO-1225zc	CF_3CH=CF_2	1,1,3,3,3-pentafluoro-1-propene
HFO-1225yc	CHF_2CF=CF_2	1,1,2,3,3-pentafluoro-1-propene

Name	Structure	Chemical name
HFO-1234ye	$CHF_2CF=CHF$	1,2,3,3-tetrafluoro-1-propene
HFO-1234yf	$CF_3CF=CH_2$	2,3,3,3-tetrafluoro-1-propene
HFO-1234ze	$CF_3CH=CHF$	1,3,3,3-tetrafluoro-1-propene
HFO-1234yc	$CH_2FCF=CF_2$	1,1,2,3-tetrafluoro-1-propene
HFO-1234zc	$CHF_2CH=CF_2$	1,1,3,3-tetrafluoro-1-propene
HFO-1243yf	$CHF_2CF=CH_2$	2,3,3-trifluoro-1-propene
HFO-1243zf	$CF_3CH=CH_2$	3,3,3-trifluoro-1-propene
HFO-1243yc	$CH_3CF=CF_2$	1,1,2-trifluoro-1-propene
HFO-1243zc	$CH_2FCH=CF_2$	1,1,3-trifluoro-1-propene
HFO-1243ye	$CH_2FCF=CHF$	1,2,3-trifluoro-1-propene
HFO-1243ze	$CHF_2CH=CHF$	1,3,3-trifluoro-1-propene
HCFO-1233xf	$CF_3CCl=CH_2$	2-chloro-3,3,3-trifluoro-1-propene
HCFO-1233zd	$CF_3CH=CHCl$	1-chloro-3,3,3-trifluoro-1-propene
HFO-1318my	$CF_3CF=CFCF_3$	1,1,1,2,3,4,4,4-octafluoro-2-butene
HFO-1318cy	$CF_3CF_2CF=CF_2$	1,1,2,3,3,4,4,4-octafluoro-1-butene
HFO-1327my	$CF_3CF=CHCF_3$	1,1,1,2,4,4,4-heptafluoro-2-butene
HFO-1327ye	$CHF=CFCF_2CF_3$	1,2,3,3,4,4,4-heptafluoro-1-butene
HFO-1327py	$CHF_2CF=CFCF_3$	1,1,1,2,3,4,4-heptafluoro-2-butene
HFO-1327et	$(CF_3)_2C=CHF$	1,3,3,3-tetrafluoro-2-(trifluoromethyl)-1-propene
HFO-1327cz	$CF_2=CHCF_2CF_3$	1,1,3,3,4,4,4-heptafluoro-1-butene
HFO-1327cye	$CF_2=CFCHFCF_3$	1,1,2,3,4,4,4-heptafluoro-1-butene
HFO-1327cyc	$CF_2=CFCF_2CHF_2$	1,1,2,3,3,4,4-heptafluoro-1-butene
HFO-1336yf	$CF_3CF_2CF=CH_2$	2,3,3,4,4,4-hexafluoro-1-butene
HFO-1336ze	$CHF=CHCF_2CF_3$	1,3,3,4,4,4-hexafluoro-1-butene
HFO-1336eye	$CHF=CFCHFCF_3$	1,2,3,4,4,4-hexafluoro-1-butene

Name	Structure	Chemical name
HFO-1336eyc	$CHF=CFCF_2CHF_2$	1,2,3,3,4,4-hexafluoro-1-butene
HFO-1336pyy	$CHF_2CF=CFCHF_2$	1,1,2,3,4,4-hexafluoro-2-butene
HFO-1336qy	$CH_2FCF=CFCF_3$	1,1,1,2,3,4-hexafluoro-2-butene
HFO-1336pz	$CHF_2CH=CFCF_3$	1,1,1,2,4,4-hexafluoro-2-butene
HFO-1336mzy	$CF_3CH=CFCHF_2$	1,1,1,3,4,4-hexafluoro-2-butene
HFO-1336qc	$CF_2=CFCF_2CH_2F$	1,1,2,3,3,4-hexafluoro-1-butene
HFO-1336pe	$CF_2=CFCHFCHF_2$	1,1,2,3,4,4-hexafluoro-1-butene
HFO-1336ft	$CH_2=C(CF_3)_2$	3,3,3-trifluoro-2-(trifluoromethyl)-1-propene
HFO-1345qz	$CH_2FCH=CFCF_3$	1,1,1,2,4-pentafluoro-2-butene
HFO-1345mzy	$CF_3CH=CFCH_2F$	1,1,1,3,4-pentafluoro-2-butene
HFO-1345fz	$CF_3CF_2CH=CH_2$	3,3,4,4,4-pentafluoro-1-butene
HFO-1345mzz	$CHF_2CH=CHCF_3$	1,1,1,4,4-pentafluoro-2-butene
HFO-1345sy	$CH_3CF=CFCF_3$	1,1,1,2,3-pentafluoro-2-butene
HFO-1345fyc	$CH_2=CFCF_2CHF_2$	2,3,3,4,4-pentafluoro-1-butene
HFO-1345pyz	$CHF_2CF=CHCHF_2$	1,1,2,4,4-pentafluoro-2-butene
HFO-1345cyc	$CH_3CF_2CF=CF_2$	1,1,2,3,3-pentafluoro-1-butene
HFO-1345pyy	$CH_2FCF=CFCHF_2$	1,1,2,3,4-pentafluoro-2-butene
HFO-1345eyc	$CH_2FCF_2CF=CHF$	1,2,3,3,4-pentafluoro-1-butene
HFO-1345ctm	$CF_2=C(CF_3)(CH_3)$	1,1,3,3,3-pentafluoro-2-methyl-1-propene
HFO-1345ftp	$CH_2=C(CHF_2)(CF_3)$	2-(difluoromethyl)-3,3,3-trifluoro-1-propene
HFO-1345fye	$CH_2=CFCHFCF_3$	2,3,4,4,4-pentafluoro-1-butene
HFO-1345eyf	$CHF=CFCH_2CF_3$	1,2,4,4,4-pentafluoro-1-butene
HFO-1345eze	$CHF=CHCHFCF_3$	1,3,4,4,4-pentafluoro-1-butene
HFO-1345ezc	$CHF=CHCF_2CHF_2$	1,3,3,4,4-pentafluoro-1-butene

Name	Structure	Chemical name
HFO-1345eye	$CHF=CFCHFCHF_2$	1,2,3,4,4-pentafluoro-1-butene
HFO-1354fzc	$CH_2=CHCF_2CHF_2$	3,3,4,4-tetrafluoro-1-butene
HFO-1354ctp	$CF_2=C(CHF_2)(CH_3)$	1,1,3,3-tetrafluoro-2-methyl-1-propene
HFO-1354etm	$CHF=C(CF_3)(CH_3)$	1,3,3,3-tetrafluoro-2-methyl-1-propene
HFO-1354tfp	$CH_2=C(CHF_2)_2$	2-(difluoromethyl)-3,3-difluoro-1-propene
HFO-1354my	$CF_3CF=CHCH_3$	1,1,1,2-tetrafluoro-2-butene
HFO-1354mzy	$CH_3CF=CHCF_3$	1,1,1,3-tetrafluoro-2-butene
HFO-141-10myy	$CF_3CF=CFCF_2CF_3$	1,1,1,2,3,4,4,5,5,5-decafluoro-2-pentene
HFO-141-10cy	$CF_2=CFCF_2CF_2CF_3$	1,1,2,3,3,4,4,5,5,5-decafluoro-1-pentene
HFO-1429mzt	$(CF_3)_2C=CHCF_3$	1,1,1,4,4,4-hexafluoro-2-(trifluoromethyl)-2-butene
HFO-1429myz	$CF_3CF=CHCF_2CF_3$	1,1,1,2,4,4,5,5,5-nonafluoro-2-pentene
HFO-1429mzy	$CF_3CH=CFCF_2CF_3$	1,1,1,3,4,4,5,5,5-nonafluoro-2-pentene
HFO-1429eyc	$CHF=CFCF_2CF_2CF_3$	1,2,3,3,4,4,5,5,5-nonafluoro-1-pentene
HFO-1429czc	$CF_2=CHCF_2CF_2CF_3$	1,1,3,3,4,4,5,5,5-nonafluoro-1-pentene
HFO-1429cycc	$CF_2=CFCF_2CF_2CHF_2$	1,1,2,3,3,4,4,5,5-nonafluoro-1-pentene
HFO-1429pyy	$CHF_2CF=CFCF_2CF_3$	1,1,2,3,4,4,5,5,5-nonafluoro-2-pentene
HFO-1429myyc	$CF_3CF=CFCF_2CHF_2$	1,1,1,2,3,4,4,5,5-nonafluoro-2-pentene
HFO-1429myye	$CF_3CF=CFCHFCF_3$	1,1,1,2,3,4,5,5,5-nonafluoro-2-pentene
HFO-1429eyym	$CHF=CFCF(CF_3)_2$	1,2,3,4,4,4-hexafluoro-3-

Name	Structure	Chemical name
		(trifluoromethyl)-1-butene
HFO-1429cyzm	CF_2=CFCH$(CF_3)_2$	1,1,2,4,4,4-hexafluoro-3-(trifluoromethyl)-1-butene
HFO-1429mzt	CF_3CH= C$(CF_3)_2$	1,1,1,4,4,4-hexafluoro-2-(trifluoromethyl)-2-butene
HFO-1429czym	CF_2=CHCF$(CF_3)_2$	1,1,3,4,4,4-hexafluoro-3-(trifluoromethyl)-1-butene
HFO-1438fy	CH_2=CFCF_2CF_2CF_3	2,3,3,4,4,5,5,5-octafluoro-1-pentene
HFO-1438eycc	CHF=CFCF_2CF_2CHF_2	1,2,3,3,4,4,5,5-octafluoro-1-pentene
HFO-1438ftmc	CH_2=C(CF_3)CF_2CF_3	3,3,4,4,4-pentafluoro-2-(trifluoromethyl)-1-butene
HFO-1438czzm	CF_2=CHCH$(CF_3)_2$	1,1,4,4,4-pentafluoro-3-(trifluoromethyl)-1-butene
HFO-1438ezym	CHF=CHCF$(CF_3)_2$	1,3,4,4,4-pentafluoro-3-(trifluoromethyl)-1-butene
HFO-1438ctmf	CF_2=C(CF_3)CH_2CF_3	1,1,4,4,4-pentafluoro-2-(trifluoromethyl)-1-butene
HFO-1447fzy	$(CF_3)_2$CFCH=CH_2	3,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene
HFO-1447fz	CF_3CF_2CF_2CH=CH_2	3,3,4,4,5,5,5-heptafluoro-1-pentene
HFO-1447fycc	CH_2=CFCF_2CF_2CHF_2	2,3,3,4,4,5,5-heptafluoro-1-pentene
HFO-1447czcf	CF_2=CHCF_2CH_2CF_3	1,1,3,3,5,5,5-heptafluoro-1-pentene
HFO-1447mytm	CF_3CF=C$(CF_3)(CH_3)$	1,1,1,2,4,4,4-heptafluoro-3-methyl-2-butene
HFO-1447fyz	CH_2=CFCH$(CF_3)_2$	2,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene
HFO-1447ezz	CHF=CHCH$(CF_3)_2$	1,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene
HFO-1447qzt	CH_2FCH=C$(CF_3)_2$	1,4,4,4-tetrafluoro-2-(trifluoromethyl)-2-butene
HFO-1447syt	CH_3CF=C$(CF_3)_2$	2,4,4,4-tetrafluoro-2-(trifluoromethyl)-2-butene

Name	Structure	Chemical name
HFO-1456szt	$(CF_3)_2C{=}CHCH_3$	3-(trifluoromethyl)-4,4,4-trifluoro-2-butene
HFO-1456szy	$CF_3CF_2CF{=}CHCH_3$	3,4,4,5,5,5-hexafluoro-2-pentene
HFO-1456mstz	$CF_3C(CH_3){=}CHCF_3$	1,1,1,4,4,4-hexafluoro-2-methyl-2-butene
HFO-1456fzce	$CH_2{=}CHCF_2CHFCF_3$	3,3,4,5,5,5-hexafluoro-1-pentene
HFO-1456ftmf	$CH_2{=}C(CF_3)CH_2CF_3$	4,4,4-trifluoro-2-(trifluoromethyl)-1-butene
HFO-151-12c	$CF_3(CF_2)_3CF{=}CF_2$	1,1,2,3,3,4,4,5,5,6,6,6-dodecafluoro-1-hexene (or perfluoro-1-hexene)
HFO-151-12mcy	$CF_3CF_2CF{=}CFCF_2CF_3$	1,1,1,2,2,3,4,5,5,6,6,6-dodecafluoro-3-hexene (or perfluoro-3-hexene)
HFO-151-12mmtt	$(CF_3)_2C{=}C(CF_3)_2$	1,1,1,4,4,4-hexafluoro-2,3-bis(trifluoromethyl)-2-butene
HFO-151-12mmzz	$(CF_3)_2CFCF{=}CFCF_3$	1,1,1,2,3,4,5,5,5-nonafluoro-4-(trifluoromethyl)-2-pentene
HFO-152-11mmtz	$(CF_3)_2C{=}CHC_2F_5$	1,1,1,4,4,5,5,5-octafluoro-2-(trifluoromethyl)-2-pentene
HFO-152-11mmyyz	$(CF_3)_2CFCF{=}CHCF_3$	1,1,1,3,4,5,5,5-octafluoro-4-(trifluoromethyl)-2-pentene
PFBE (or HFO-1549fz)	$CF_3CF_2CF_2CF_2CH{=}CH_2$	3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (or perfluorobutylethylene)
HFO-1549fztmm	$CH_2{=}CHC(CF_3)_3$	4,4,4-trifluoro-3,3-bis(trifluoromethyl)-1-butene
HFO-1549mmtts	$(CF_3)_2C{=}C(CH_3)(CF_3)$	1,1,1,4,4,4-hexafluoro-3-methyl-2-(trifluoromethyl)-2-butene
HFO-1549fycz	$CH_2{=}CFCF_2CH(CF_3)_2$	2,3,3,5,5,5-hexafluoro-4-(trifluoromethyl)-1-pentene
HFO-1549myts	$CF_3CF{=}C(CH_3)CF_2CF_3$	1,1,1,2,4,4,5,5,5-nonafluoro-3-methyl-2-pentene
HFO-1549mzzz	$CF_3CH{=}CHCH(CF_3)_2$	1,1,1,5,5,5-hexafluoro-4-(trifluoromethyl)-2-pentene
HFO-1558szy	$CF_3CF_2CF_2CF{=}CHCH_3$	3,4,4,5,5,6,6,6-octafluoro-2-hexene

Name	Structure	Chemical name
HFO-1558fzccc	CH_2=$CHCF_2CF_2CF_2CHF_2$	3,3,4,4,5,5,6,6-octafluoro-2-hexene
HFO-1558mmtzc	$(CF_3)_2C$=$CHCF_2CH_3$	1,1,1,4,4-pentafluoro-2-(trifluoromethyl)-2-pentene
HFO-1558ftmf	CH_2=$C(CF_3)CH_2C_2F_5$	4,4,5,5,5-pentafluoro-2-(trifluoromethyl)-1-pentene
HFO-1567fts	$CF_3CF_2CF_2C(CH_3)$=CH_2	3,3,4,4,5,5,5-heptafluoro-2-methyl-1-pentene
HFO-1567szz	$CF_3CF_2CF_2CH$=$CHCH_3$	4,4,5,5,6,6,6-heptafluoro-2-hexene
HFO-1567fzfc	CH_2=$CHCH_2CF_2C_2F_5$	4,4,5,5,6,6,6-heptafluoro-1-hexene
HFO-1567sfyy	CF_3CF_2CF=CFC_2H_5	1,1,1,2,2,3,4-heptafluoro-3-hexene
HFO-1567fzfy	CH_2=$CHCH_2CF(CF_3)_2$	4,5,5,5-tetrafluoro-4-(trifluoromethyl)-1-pentene
HFO-1567myzzm	CF_3CF=$CHCH(CF_3)(CH_3)$	1,1,1,2,5,5,5-heptafluoro-4-methyl-2-pentene
HFO-1567mmtyf	$(CF_3)_2C$=CFC_2H_5	1,1,1,3-tetrafluoro-2-(trifluoromethyl)-2-pentene
HFO-161-14myy	CF_3CF=$CFCF_2CF_2C_2F_5$	1,1,1,2,3,4,4,5,5,6,6,7,7,7-tetradecafluoro-2-heptene
HFO-161-14mcyy	CF_3CF_2CF=$CFCF_2C_2F_5$	1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoro-2-heptene
HFO-162-13mzy	CF_3CH=$CFCF_2CF_2C_2F_5$	1,1,1,3,4,4,5,5,6,6,7,7,7-tridecafluoro-2-heptene
HFC162-13myz	CF_3CF=$CHCF_2CF_2C_2F_5$	1,1,1,2,4,4,5,5,6,6,7,7,7-tridecafluoro-2-heptene
HFO-162-13mczy	CF_3CF_2CH=$CFCF_2C_2F_5$	1,1,1,2,2,4,5,5,6,6,7,7,7-tridecafluoro-3-heptene
HFO-162-13mcyz	CF_3CF_2CF=$CHCF_2C_2F_5$	1,1,1,2,2,3,5,5,6,6,7,7,7-tridecafluoro-3-heptene
PEVE	CF_2=$CFOCF_2CF_3$	pentafluoroethyl trifluorovinyl ether
PMVE	CF_2=$CFOCF_3$	trifluoromethyl trifluorovinyl ether

The compounds listed in Table 2 and Table 3 are available commercially or may be prepared by processes known in the art or as described herein.

1,1,1,4,4-pentafluoro-2-butene may be prepared from 1,1,1,2,4,4-hexafluorobutane ($CHF_2CH_2CHFCF_3$) by dehydrofluorination over solid KOH in the vapor phase at room temperature. The synthesis of 1,1,1,2,4,4-hexafluorobutane is described in US 6,066,768. 1,1,1,4,4,4-hexafluoro-2-butene may be prepared from 1,1,1,4,4,4-hexafluoro-2-iodobutane ($CF_3CHICH_2CF_3$) by reaction with KOH using a phase transfer catalyst at about 60°C. The synthesis of 1,1,1,4,4,4-hexafluoro-2-iodobutane may be carried out by reaction of perfluoromethyl iodide (CF_3I) and 3,3,3-trifluoropropene ($CF_3CH=CH_2$) at about 200°C under autogenous pressure for about 8 hours.

3,4,4,5,5,5-hexafluoro-2-pentene may be prepared by dehydrofluorination of 1,1,1,2,2,3,3-heptafluoropentane ($CF_3CF_2CF_2CH_2CH_3$) using solid KOH or over a carbon catalyst at 200-300°C. 1,1,1,2,2,3,3-heptafluoropentane may be prepared by hydrogenation of 3,3,4,4,5,5,5-heptafluoro-1-pentene ($CF_3CF_2CF_2CH=CH_2$).

1,1,1,2,3,4-hexafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,2,3,3,4-heptafluorobutane ($CH_2FCF_2CHFCF_3$) using solid KOH.

1,1,1,2,4,4-hexafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,2,2,4,4-heptafluorobutane ($CHF_2CH_2CF_2CF_3$) using solid KOH.

1,1,1,3,4,4-hexafluoro2-butene may be prepared by dehydrofluorination of 1,1,1,3,3,4,4-heptafluorobutane ($CF_3CH_2CF_2CHF_2$) using solid KOH.

1,1,1,2,4-pentafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,2,2,3-hexafluorobutane ($CH_2FCH_2CF_2CF_3$) using solid KOH.

1,1,1,3,4-pentafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,3,3,4-hexafluorobutane ($CF_3CH_2CF_2CH_2F$) using solid KOH.

1,1,1,3-tetrafluoro-2-butene may be prepared by reacting 1,1,1,3,3-pentafluorobutane ($CF_3CH_2CF_2CH_3$) with aqueous KOH at 120 °C.

1,1,1,4,4,5,5,5-octafluoro-2-pentene may be prepared from ($CF_3CHICH_2CF_2CF_3$) by reaction with KOH using a phase transfer catalyst at about 60°C. The synthesis of 4-iodo-1,1,1,2,2,5,5,5-octafluoropentane may be carried out by reaction of perfluoroethyliodide (CF_3CF_2I) and 3,3,3-trifluoropropene at about 200°C under autogenous pressure for about 8 hours.

1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene may be prepared from 1,1,1,2,2,5,5,6,6,6-decafluoro-3-iodohexane ($CF_3CF_2CHICH_2CF_2CF_3$) by reaction with KOH using a phase transfer catalyst at about 60°C. The synthesis of 1,1,1,2,2,5,5,6,6,6-decafluoro-3-iodohexane may be carried out by reaction of perfluoroethyliodide (CF_3CF_2I) and 3,3,4,4,4-pentafluoro-1-butene ($CF_3CF_2CH=CH_2$) at about 200°C under autogenous pressure for about 8 hours.

1,1,1,4,5,5,5-heptafluoro-4-(trifluoromethyl)-2-pentene may be prepared by the dehydrofluorination of 1,1,1,2,5,5,5-heptafluoro-4-iodo-2-(trifluoromethyl)-pentane ($CF_3CHICH_2CF(CF_3)_2$) with KOH in isopropanol. $CF_3CHICH_2CF(CF_3)_2$ is made from reaction of $(CF_3)_2CFI$ with $CF_3CH=CH_2$ at high temperature, such as about 200°C.

1,1,1,4,4,5,5,6,6,6-decafluoro-2-hexene may be prepared by the reaction of 1,1,1,4,4,4-hexafluoro-2-butene ($CF_3CH=CHCF_3$) with tetrafluoroethylene ($CF_2=CF_2$) and antimony pentafluoride (SbF_5).

2,3,3,4,4-pentafluoro-1-butene may be prepared by dehydrofluorination of 1,1,2,2,3,3-hexafluorobutane over fluorided alumina at elevated temperature.

2,3,3,4,4,5,5,5-ocatafluoro-1-pentene may be prepared by dehydrofluorination of 2,2,3,3,4,4,5,5,5-nonafluoropentane over solid KOH.

1,2,3,3,4,4,5,5-octafluoro-1-pentene may be prepared by dehydrofluorination of 2,2,3,3,4,4,5,5,5-nonafluoropentane over fluorided alumina at elevated temperature.

Many of the compounds of Formula 1, Formula 2, Table 1, Table 2 and Table 3 exist as different configurational isomers or stereoisomers. When the specific isomer is not designated, the present invention is intended to include all single configurational isomers, single stereoisomers, or any combination thereof. For instance, F11E is meant to represent the *E*-isomer, *Z*-isomer, or any combination or mixture of both isomers in any ratio. As another example, HFO-1225ye is meant to represent the *E*-isomer, *Z*-isomer, or any combination or mixture of both isomers in any ratio.

Additionally, the refrigerant may be any of the single fluoroolefins of Formula (i), Formula (ii), Table 1, Table 2 and Table 3, or may be any combination of the different fluoroolefins from Formula (i), Formula (ii), Table 1, Table 2 and Table 3.

In some embodiments, the refrigerant may be any combination of a single fluoroolefin or multiple fluoroolefins selected from Formula (i), Formula (ii), Table 1, Table 2 and Table 3 with at least one additional refrigerant selected from hydrofluorocarbons, fluoroethers, hydrocarbons, CF_3I, ammonia (NH_3), carbon dioxide (CO_2), nitrous oxide (N_2O), and mixtures thereof, meaning mixtures of any of the foregoing compounds.

In some embodiments, the refrigerant may contain hydrofluorocarbons comprising at least one saturated compound containing carbon, hydrogen, and fluorine. Of particular utility are hydrofluorocarbons having 1-7 carbon atoms and having a normal boiling point of from about -90°C to about 80°C. Hydrofluorocarbons are commercial products available from a number of sources or may be prepared by methods known in the art. Representative hydrofluorocarbon compounds include but are not limited to fluoromethane (CH_3F, HFC-41), difluoromethane (CH_2F_2, HFC-32), trifluoromethane (CHF_3, HFC-23), pentafluoroethane (CF_3CHF_2, HFC-125), 1,1,2,2-tetrafluoroethane (CHF_2CHF_2, HFC-134), 1,1,1,2-tetrafluoroethane (CF_3CH_2F, HFC-134a), 1,1,1-trifluoroethane (CF_3CH_3, HFC-143a), 1,1-difluoroethane (CHF_2CH_3, HFC-152a), fluoroethane (CH_3CH_2F, HFC-161), 1,1,1,2,2,3,3-heptafluoropropane ($CF_3CF_2CHF_2$, HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3, HFC-227ea), 1,1,2,2,3,3,-hexafluoropropane ($CHF_2CF_2CHF_2$, HFC-236ca), 1,1,1,2,2,3-hexafluoropropane ($CF_3CF_3CH_2F$, HFC-236cb), 1,1,1,2,3,3-hexafluoropropane ($CF_3CHFCHF_2$, HFC-236ea), 1,1,1,3,3,3-hexafluoropropane ($CF_3CH_2CF_3$, HFC-236fa), 1,1,2,2,3-pentafluoropropane ($CHF_2CF_2CH_2F$, HFC-245ca), 1,1,1,2,2-pentafluoropropane ($CF_3CF_2CH_3$, HFC-245cb), 1,1,2,3,3-pentafluoropropane ($CHF_2CHFCHF_2$, HFC-245ea), 1,1,1,2,3-pentafluoropropane (CF_3CHFCH_2F, HFC-245eb), 1,1,1,3,3-pentafluoropropane ($CF_3CH_2CHF_2$, HFC-245fa), 1,2,2,3-tetrafluoropropane ($CH_2FCF_2CH_2F$, HFC-254ca), 1,1,2,2-tetrafluoropropane ($CHF_2CF_2CH_3$, HFC-254cb), 1,1,2,3-tetrafluoropropane (CHF_2CHFCH_2F, HFC-254ea), 1,1,1,2-tetrafluoropropane (CF_3CHFCH_3, HFC-254eb), 1,1,3,3-tetrafluoropropane ($CHF_2CH_2CHF_2$, HFC-254fa), 1,1,1,3-tetrafluoropropane ($CF_3CH_2CH_2F$, HFC-254fb), 1,1,1-trifluoropropane ($CF_3CH_2CH_3$, HFC-263fb), 2,2-difluoropropane ($CH_3CF_2CH_3$, HFC-272ca), 1,2-difluoropropane ($CH_2FCHFCH_3$, HFC-272ea), 1,3-difluoropropane ($CH_2FCH_2CH_2F$, HFC-272fa), 1,1-difluoropropane ($CHF_2CH_2CH_3$, HFC-272fb), 2-fluoropropane (CH_3CHFCH_3, HFC-281ea), 1-fluoropropane ($CH_2FCH_2CH_3$, HFC-281fa), 1,1,2,2,3,3,4,4-octafluorobutane ($CHF_2CF_2CF_2CHF_2$, HFC-338pcc), 1,1,1,2,2,4,4,4-octafluorobutane ($CF_3CH_2CF_2CF_3$, HFC-338mf), 1,1,1,3,3-

pentafluorobutane ($CF_3CH_2CHF_2$, HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-decafluoropentane ($CF_3CHFCHFCF_2CF_3$, HFC-43-10mee), and 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoroheptane ($CF_3CF_2CHFCHFCF_2CF_2CF_3$, HFC-63-14mee).

In some embodiments, the refrigerant may further comprise fluoroethers. Fluoroethers comprise at least one compound having carbon, fluorine, oxygen and optionally hydrogen, chlorine, bromine or iodine. Fluoroethers are commercially available or may be produced by methods known in the art. Representative fluoroethers include but are not limited to nonafluoromethoxybutane ($C_4F_9OCH_3$, any or all possible isomers or mixtures thereof); nonafluoroethoxybutane ($C_4F_9OC_2H_5$, any or all possible isomers or mixtures thereof); 2-difluoromethoxy-1,1,1,2-tetrafluoroethane (HFOC-236eaEβγ, or $CHF_2OCHFCF_3$); 1,1-difluoro-2-methoxyethane (HFOC-272fbEβγ,□$CH_3OCH_2CHF_2$); 1,1,1,3,3,3-hexafluoro-2-(fluoromethoxy)propane (HFOC-347mmzEβγ, or $CH_2FOCH(CF_3)_2$); 1,1,1,3,3,3-hexafluoro-2-methoxypropane (HFOC-356mmzEβγ, or $CH_3OCH(CH_3)_2$); 1,1,1,2,2-pentafluoro-3-methoxypropane (HFOC-365mcEγδ, or $CF_3CF_2CH_2OCH_3$); 2-ethoxy-1,1,1,2,3,3,3-heptafluoropropane (HFOC-467mmyEβγ, or $CH_3CH_2OCF(CF_3)_2$ □; and mixtures thereof.

In some embodiments, the refrigerant may further comprise at least one hydrocarbon. Hydrocarbons are compounds having only carbon and hydrogen. Of particular utility are compounds having 3-7 carbon atoms. Hydrocarbons are commercially available through numerous chemical suppliers. Representative hydrocarbons include but are not-limited to propane, n-butane, isobutane, cyclobutane, n-pentane, 2-methylbutane, 2,2-dimethylpropane, cyclopentane, n-hexane, 2-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 3-methylpentane, cyclohexane, n-heptane, cycloheptane, and mixtures thereof. In some embodiments, the disclosed compositions may comprise hydrocarbons containing heteroatoms, such as dimethylether (DME, CH_3OCH_3). DME is commercially available.

The first refrigerant is carbon dioxide (CO_2). Carbon dioxide is commercially available from various sources or may be prepared by methods known in the art.

In particular embodiments, the first and the second refrigerants may be as shown in the Table 4 below.

TABLE 4

	First Refrigerant for Low Temp Circuit	Second Refrigerant for Medium Temp Circuit
1	CO_2	HFO-1234yf
2	CO_2	HFO-1234yf/HFC-134a
3	CO_2	HFO-1234yf/ HFC-32
4	CO_2	trans HFO-1234ze/HFC-32
5	CO_2	trans HFO-1234ze/HFC-134a
6	CO_2	trans HFO-1234ze/HFC-125

In certain embodiments, the second refrigerant may consist essentially of HFO-1234yf. In other embodiments, the second refrigerant may comprise HFO-1234yf and R134a. In yet other embodiments, the second refrigerant may comprise HFO-1234yf and R32, or it may comprise trans HFO-1234ze and HFC-32, or trans HFO-1234ze and HFC-134a or trans HFO-1234ze and HFC-125.

In the embodiment where the second refrigerant consists essentially of HFO-1234yf, the first refrigerant is carbon dioxide (CO_2).

In the embodiment where the second refrigerant comprises HFO-1234yf and HFC-134a, or when the second refrigerant comprises HFO-1234yf and HFC-32, the first refrigerant is carbon dioxide.

In the particular embodiment where the second refrigerant comprises HFO-1234yf and R134a, the second refrigerant may comprise 1 – 99% HFO-1234yf and 99 - 1% HFC-134a. In one embodiment, the second refrigerant comprises 1 – 53.1% HFO-1234yf and 46.9 – 99% HFC-134a. In particular, the second refrigerant comprises 53% HFO-1234yf and 47% HFC-134a. In one embodiment, the second refrigerant comprises 1 – 59% HFO-1234yf and 41 – 99% HFC-134a. In this embodiment, the second refrigerant is non-flammable at 100° C or 60° C. This composition is non-flammable and has maximum capacity in the range of 40 - 59% 1234yf and 41 – 60% 134a. In particular, the second refrigerant may comprise 53% HFO-1234yf and 47% HFC-134a.

In the particular embodiment where the second refrigerant comprises HFO-1234yf and HFC-32, the ranges for these components may be 1 – 99% HFO-1234yf and 99 - 1% HFC-32. In a particular embodiment, the second refrigerant may comprise 20 – 99% HFO-1234yf and 80 – 99% HFC-32. More particularly, the second refrigerant may comprise 50 – 99% HFO-1234yf and 50 – 99% HFC-32, and even more particularly, the second refrigerant may comprise 63% HFO-1234yf and 37% HFC-32. In this embodiment, the second refrigerant may be used as a replacement for R404A. In another embodiment, the second refrigerant may comprise 27.5% HFO-1234yf and 72.5% HFC-32. In this embodiment, the second refrigerant may be used as a replacement for R410A. In any of the embodiments of the foregoing embodiments where the second refrigerant comprises a particular range of HFO-1234yf and HFC-32, the first refrigerant is CO_2.

In the embodiment where the second refrigerant comprises trans HFO-1234ze and HFC-32, the first refrigerant is carbon dioxide.

In the particular embodiment where the second refrigerant comprises trans HFO-1234ze and HFC-32, the second refrigerant comprises 1 – 99% HFO-1234ze and 99 - 1% HFC-32. The 1234ze may be either trans-1234ze or cis-1234ze. In any of the embodiments of the foregoing embodiments where the second refrigerant comprises a particular range of trans HFO-1234ze and HFC-32, the first refrigerant is CO_2.

In the embodiment where the second refrigerant comprises trans HFO-1234ze and HFC-134a, the first refrigerant is CO_2.

In the embodiment where the second refrigerant comprises trans HFO-1234ze and HFC-125, the first refrigerant is carbon dioxide.

Various configurations of cascade systems also come within the scope of the present invention. For instance, reference is made to FIG. 2, which shows a cascade system according to the present invention, where elements which correspond to the elements shown in FIG. 1 are indicated with a like reference numeral and a prime ('). The elements in FIG. 2 which correspond to the elements shown in FIG. 1 all operate as described above with respect to FIG. 1. In addition, the cascade system of FIG. 2 includes a secondary heat transfer loop, which includes a secondary fluid chiller 30 and a secondary fluid heat exchanger 32. The secondary fluid heat exchanger is located near a body to be cooled, such as food in a medium temperature display case. The secondary chiller cools a secondary heat transfer fluid. The use of a secondary heat transfer loop in the embodiment of FIG. 2 is advantageous because it limits the amount of refrigerant that must be used and the length of piping through which refrigerant must circulate, while at the same time transferring heat between locations that have to be remote from each other (e.g., remote locations in a large supermarket). Minimization of the amount of refrigerant and length of refrigerant piping reduces refrigerant cost, leakage rates and mitigates risks associated with using refrigerants which are flammable and/or toxic. In addition, or alternatively to the configuration as shown in FIG. 2, a secondary loop could be used to transfer heat form low temp display cases to the LOW temp loop in a configuration similar to that shown in Fig. 2 for the high or mid temp loop. However, the choice of secondary heat transfer fluids would be quit limited because the viscosity of liquids and associated pumping costs increase at low temperatures.

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The cascade refrigeration system of FIG. 2 also includes a cascade heat exchanger system disposed between the low temperature refrigeration loop and the medium temperature refrigeration loop. As in the above embodiments, the cascade heat exchanger system has a first inlet 22a' and a first outlet 22b', wherein the first refrigerant vapor circulates from the first inlet to the first outlet and is condensed in the heat exchanger system to form a first refrigerant liquid, thereby rejecting heat. The cascade heat exchanger system also includes a second inlet 22c' and a second outlet 22d', wherein a second refrigerant liquid circulates from the second inlet to the second outlet and absorbs the heat rejected by the first refrigerant and forms a second refrigerant vapor, as will be explained below. Thus, in the embodiment of FIG. 2, the heat rejected by the first refrigerant is directly absorbed by the second refrigerant.

Referring specifically to FIG. 2, a secondary heat transfer fluid enters the secondary chiller at a first inlet 30a and exits the secondary chiller at a first outlet 30b. The secondary heat transfer fluid may comprise ethylene glycol, propylene glycol, carbon dioxide, water brine or any of several other fluids or slurries known to the art. In some embodiments, the secondary heat transfer fluid may undergo a phase change. In addition the secondary chiller includes a second inlet 30c and a second outlet 30d. The second refrigerant enters the secondary fluid chiller through second inlet 30c and evaporates, thus causing the heat transfer fluid in the chiller to be cooled. The cooled heat transfer fluid exits the chiller 30 through first outlet 30b and circulates to a secondary fluid heat exchanger 32 located near a body to be cooled. This body to be cooled may be food items inside a refrigerated display case in a supermarket. The heat transfer fluid is warmed by this body and returns to the secondary fluid chiller to be cooled again by the evaporation of the second refrigerant, which also circulates through the secondary fluid chiller. A liquid pump (not shown) pumps the heat transfer fluid from the secondary fluid heat exchanger back to the secondary fluid chiller. This warmed heat transfer fluid causes the second refrigerant to evaporate in the secondary fluid chiller. A separate expansion device (not shown) may be disposed in the inlet line entering cascade heat exchanger 22' and the inlet line entering secondary fluid chiller 30 in order to control the pressure and flow rate through the cascade heat exchanger and the secondary fluid chiller, respectively. Although cascade heat exchanger 22' and secondary fluid chiller 30 are shown connected in parallel, they may alternatively be connected in series without departing from the scope of the present invention.

A portion of the reduced pressure and temperature second refrigerant liquid which exits condenser 26' enters the cascade heat exchanger 22' at inlet 22c'. In cascade heat exchanger 22', as in the first embodiment of FIG. 1, the first refrigerant is condensed, and the second refrigerant evaporates and exits from the heat exchanger 22' at outlet 22d'. The second refrigerant which exits secondary fluid chiller 30 at second outlet 30d merges with the second refrigerant from outlet 22d' of the cascade heat exchanger and circulates to second compressor 24'. The cycle through medium temperature loop 14' and low temperature loop 12' are otherwise the same as discussed above with respect to FIG. 1.

Another embodiment of the cascade refrigeration system of the present invention is shown in FIG. 3. In the embodiment of FIG. 3, elements which correspond to the elements shown in FIG. 1 are indicated with a like reference numeral and a double prime ("). The elements in FIG. 3 which correspond to the elements shown in FIG. 1 all operate as described above with respect to FIG. 1. The system of FIG. 3 includes a secondary heat transfer loop, shown generally at 40, which includes two cascade heat exchangers instead of one cascade heat exchanger as shown in the embodiments of FIGS. 1 and 2. As in the embodiment of FIG. 2, the use of a secondary heat transfer loop in the embodiment of FIG. 3 is advantageous because it limits the amount of refrigerant that must be used and the length of piping through which refrigerant must circulate, while at the same time transferring heat between locations that have to be remote from each other.

The embodiment of FIG. 3 includes a cascade heat exchanger system which includes two cascade heat exchangers connected to each other through a secondary heat transfer loop. The cascade heat exchanger system in FIG. 3 has a first inlet 42a and a first outlet 42b, wherein the first refrigerant vapor circulates from the first inlet to the first outlet and is condensed in the cascade heat exchanger system to form a first refrigerant liquid, thereby rejecting heat. The cascade heat exchanger system also includes a second inlet 44c and a second outlet 44d, wherein a second refrigerant liquid circulates from the second inlet to the second outlet and indirectly absorbs the heat rejected by the first refrigerant and forms a second refrigerant vapor. In the embodiment of FIG. 3, the second refrigerant liquid indirectly absorbs the heat rejected by the first refrigerant through the secondary heat transfer fluid, that is to say, the first refrigerant rejects heat to the heat transfer fluid, and the heat transfer fluid circulates to the second cascade heat exchanger 44 where it transfers the heat from the first refrigerant to the second refrigerant, as will be described below. This heat is rejected to ambient.

Referring to FIG. 3, cascade refrigeration system 10" includes a first cascade heat exchanger 42 in low temperature loop 12", having a first inlet 42a and a first outlet 42b, and a second inlet 42c and a second outlet 42d. The medium temperature loop 14" includes a second cascade heat exchanger 44, having a first inlet 44a and a first outlet 44b, and a second inlet 44c and a second outlet 44d. Compressed first refrigerant vapor circulates from the outlet of the first compressor 20b" as shown in FIG. 3 to the first inlet 42a of the first heat exchanger 42. As in the embodiment shown in FIG. 1, this compressed refrigerant vapor is condensed in the first cascade heat exchanger to form a first refrigerant liquid, thereby rejecting heat. The first refrigerant liquid then circulates to the first outlet 42b of the first cascade heat exchanger. A heat transfer fluid circulates in the secondary heat transfer loop between the first cascade heat exchanger and a second cascade heat exchanger 44, which is also part of the medium temperature loop 14". Specifically, the heat transfer fluid enters first heat exchanger 42 through a second inlet 42c and exits the first heat exchanger through a second outlet 42d. This heat transfer fluid absorbs the heat rejected by the condensing first refrigerant that enters that heat exchanger through inlet 42a, and is warmed. The warmed heat transfer fluid exits the first heat exchanger through second outlet 42d and circulates to second heat exchanger 44. The heat transfer fluid is cooled in the second heat exchanger by rejecting heat to the second refrigerant, which enters the second heat exchanger at a second inlet 44c, and exits the second heat exchanger at a second outlet 44d. The second refrigerant evaporates in the second cascade heat exchanger since it is warmed by the heat transfer fluid, and forms a second refrigerant vapor. Cooled heat transfer fluid exits the first outlet 44b of the second heat exchanger. The cycle through the low temperature loop 12" and the medium temperature loop 14" are otherwise the same as discussed above with respect to FIG. 1, except that in this embodiment, the first and/or second refrigerant may be, but need not necessarily be, a fluoroolefin.

A further embodiment of the cascade refrigeration system of the present invention is shown in FIG. 4. In the embodiment of FIG. 4, elements which correspond to the elements shown in FIG. 1 are indicated with a like reference numeral and a triple prime ("'). The elements in FIG. 4 which correspond to the elements shown in FIG. 1 all operate as described above with respect to FIG. 1. The system of FIG. 4 includes two low temperature loops, Loop 12 A, which is similar to the low temperature loop 12 of FIG. 1, and Loop 12B. One of the two low temperature loops, e.g., loop 12B, provides refrigeration at a temperature which is different from, for example, intermediate to, the temperature at which refrigeration is provided by the other low temperature loop and by the medium temperature loop. The advantage of such a system is that the refrigerant in the low temperature loop can be used to cool two different bodies, such as two separate freezer display cases, at two different temperatures.

In the embodiment of FIG. 4, a cascade heat exchanger system is disposed between the two loops. The cascade heat exchanger system has a first inlet 22a'" and a second inlet 22b'", and a first outlet 52 wherein the first refrigerant vapor circulates from the first and second inlets to the first outlet and is condensed in the heat exchanger system to form a first refrigerant liquid, thereby rejecting heat. The cascade heat exchanger system also includes a third inlet 22c''' and a second outlet 22d''', wherein a second refrigerant liquid circulates from the third inlet to the second outlet and absorbs the heat rejected by the first refrigerant and forms a second refrigerant vapor. Thus, in the embodiment of FIG. 4, the heat rejected by the first refrigerant is directly absorbed by the second refrigerant and this is rejected to ambient.

It should be noted that it is within the scope of the present invention that the embodiment of FIG. 4 encompasses all cascade heat exchanger systems that transfer heat in the above described manner.

In the system of the embodiment of FIG. 4, the flow of the first refrigerant liquid is split as or after it exits the cascade heat exchanger 22''' at 52. One portion circulates through one low temperature loop 12A, and another portion circulates through the other low temperature loop 12B. The portion of the first refrigerant that circulates through loop 12B enters an additional expansion device 54 at inlet 54a, and the pressure and temperature of this portion of the first refrigerant liquid is reduced. This reduced pressure and temperature liquid refrigerant then circulates through outlet 54b of the additional expansion device, and circulates to an additional evaporator 56. It should be noted that this liquid may be partially vaporized during this expansion. The additional evaporator 56 includes an inlet 56a and an outlet 56b. The refrigerant liquid from the additional expansion device enters the evaporator through evaporator inlet 56a and is evaporated in the evaporator to form a refrigerant vapor, thereby producing cooling, and circulates to outlet 56b. Low temperature loop 12B also includes an additional compressor 58 having an inlet 58a and an outlet 58b. The first refrigerant vapor from additional evaporator 56 circulates to inlet 58a of the additional compressor 58 and is compressed, thereby increasing the pressure and the temperature of the first refrigerant vapor, and the compressed first refrigerant vapor circulates to outlet 58b of the additional compressor and to the inlet 22b''' of the cascade heat exchanger 22'''. The cycle through the other low temperature loop 12A and the medium temperature loop 14''' are otherwise the same as discussed above with respect to FIG. 1. In particular, low temperature loop 12A also includes an evaporator 18''', which could be housed inside a freezer display case, and additional evaporator 56 could be housed inside a freezer display case. This system thereby could provide cooling to two separate freezer display cases.

Further in accordance with the present invention, there is provided a method of exchanging heat between at least two refrigeration loops, comprising: (a) absorbing heat from a body to be cooled in a first refrigeration loop and rejecting this heat to a second refrigeration loop; and (b) absorbing the heat from the first refrigeration loop in the second refrigeration loop and rejecting this heat to ambient. The refrigerant in either loop, i.e., the loop in which heat is absorbed or the loop in which heat is rejected, or both, may comprise a fluoroolefin. The heat from the first refrigeration loop may be absorbed directly in the second refrigeration loop, such as in the embodiments of FIGS. 1, 2 and 4, or it may be directly absorbed in the second refrigeration loop, such as in the embodiment of FIG. 3.

EXAMPLES

EXAMPLE 1

Cooling Performance for Upper Temperature Circuit of a Cascade System

Table 5 shows the performance of some exemplary compositions as compared to HFC-134a. In Table 5, Evap Pres is evaporator pressure, Cond Pres is condenser pressure, Comp Disch T is compressor discharge temperature, COP is coefficient of performance (analogous to energy efficiency), CAP is capacity, Avg. Temp. glide is the average of the temperature glide in the evaporator and condenser, and GWP is global warming potential. The data are based on the following conditions.

Evaporator temperature	-10°C
Condenser temperature	40.0°C
Subcool amount	6°C
Return gas temperature	10°C
Compressor efficiency is	70%

Note that the evaporator superheat enthalpy is not included in cooling capacity and energy efficiency determinations.

TABLE 5

Composition	Evap Press (kPa)	Cond Press (kPa)	Compr Disch Temp (°C)	CAP (Kw)	CAP relative to 134a (%)	COP	COP relative to 134a (%)	Avg. Temp. Glide, °C	GWP*
HFC-134a	200.6	1016.5	81.4	2.231		2.742		0	1430
HFO-1234yf	220.5	1015.6	68.3	2.113	94.7	2.580	94.1	0	4
HFO-1234yf/HFC-134a (20/80 wt %)	224.8	1097.0	78.1	2.371	106.3	2.685	97.9	0.05	1145
HFO-1234yf/HFC-134a (40/60 wt %)	245.3	1149.3	74.7	2.470	110.7	2.653	96.8	0.25	848
HFO-1234yf/HFC-134a (53/47 wt %)	252.1	1160.2	72.8	2.487	111.5	2.640	96.3	0.10	674
HFO-1234yf/HFC-134a (60/40 wt %)	252.7	1156.7	72.0	2.475	110.9	2.635	96.1	0.11	574
HFO-1234yf/HFC-134a (80/20 wt %)	243.4	1112.0	70.0	2.357	105.6	2.618	95.5	0.80	138
HFO-1234ze/HFC-134a (20/80 wt%)	193.9	981.3	80.2	2.150	96	2.741	100	0.17	1145
HFO-1234ze/HFC-134a (40/60 wt%)	184.6	937.6	79.1	2.052	92	2.744	100	0.40	860
HFO-1234ze/HFC-134a (50/50 wt%)	189.3	912.9	78.6	1.996	89	2.746	100	0.51	718
HFO-1234ze/HFC-134a (60/40 wt%)	173.4	886.4	78.1	1.937	87	2.749	100	0.59	576
HFO-1234ze/HFC-134a (80/20 wt%)	160.7	828.6	77.2	1.808	81	2.756	101	0.53	293
HFO-1234ze/HFC-125 (95/5 wt%)	156.7	814.4	76.3	1.769	79	2.756	101	1.61	184
HFO-1234ze/HFC-125 (90/10 wt%)	166.6	864.4	76.4	1.869	84	2.746	100	2.96	355
HFO-1234ze/HFC-125 (85/15 wt%)	176.9	915.0	76.4	1.968	88	2.735	100	4.08	530
HFO-1234ze/HFC-125 (80/20 wt%)	187.7	966.1	76.4	2.067	93	2.718	99	4.99	705

*The GWP value for HFC-134a is taken from the "Climate Change 2007 – IPCC (Intergovernmental Panel on Climate Change) Fourth Assessment Report on Climate Change", from the section entitled "Working Group 1 Report: "The Physical Science Basis", Chapter 2, pp. 212-213, Table 2.14. The value for HFO-1234yf was published in Papadimitriou et al., *Physical Chemistry Chemical Physics*, 2007, vol. 9, pp. 1-13. Specifically, the 100 year time horizon GWP values are used. The GWP values for the compositions containing HFC-134a and HFO-1234yf are calculated as weighted averages of the individual component GWP values.

The data in Table 5 indicate that the 1234yf/134a compositions are a close match to 134a, in terms of COP, capacity, pressures and temperatures in the system, with lower GWP values. In addition, all the compositions have low temperature glide and a specific composition could be selected based on regulatory requirements for GWP, which have not at this time been determined. The composition containing 53 wt% HFO-1234yf and 47 wt% HFC-134a has the particular benefit of providing a low GWP and a peak in the cooling capacity. This is shown graphically in FIG. 5.

EXAMPLE 2

Flammability of HFO-1234yf/HFC-134a Mixtures

Flammable compositions may be identified by testing under ASTM (American Society of Testing and Materials) E681-2004, with an electronic ignition source. Such tests of flammability were conducted on compositions containing HFO-1234yf and HFC-134a at 101 kPa (14.7 psia), 50 percent relative humidity, and about 23 °C (room temperature), 60 °C and 100 °C at various concentrations in air in order to determine if flammable and if so, to find the lower flammability limit (LFL) and the upper flammability limit (UFL). The results are given in Table 6.

TABLE 6

% HFO-1234yf	% HFC-134a	Room Temp.		60 °C		100 °C	
		LFL	UFL	LFL	UFL	LFL	UFL
50.00	50.00	non-flammable		non-flammable		non-flammable	
52.50	47.50	non-flammable		non-flammable		non-flammable	
53.10	46.9	non-flammable		non-flammable		non-flammable	
53.75	46.25	non-flammable		non-flammable		**10.0% (single point)**	
55.00	45.00	non-flammable		non-flammable		**9.0%**	**10.5%**
57.50	42.50	non-flammable		non-flammable		**8.0%**	**12.0%**
59.00	41.0	non-flammable		non-flammable		not tested	
60.00	40.00	non-flammable		**10.0% (single point)**		not tested	
60.63	39.37	non-flammable		**10.0%**	**11.0%**	not tested	
61.25	38.75	non-flammable		**10.0%**	**11.0%**	not tested	
62.50	37.50	non-flammable		**8.75%**	**10.75%**	not tested	
65.00	35.00	non-flammable		**8.0%**	**12.0%**	not tested	
66.25	33.75	non-flammable		not tested		not tested	
67.50	32.50	**10.0% (single point)**		not tested		not tested	
70.00	30.00	**9.0%**	**11.0%**	not tested		not tested	

At room temperature conditions (about 23°C), compositions with 66.25 weight percent or less HFO-1234yf in HFC-134a would be considered non-flammable. At 60°C, compositions with 60.00 weight percent or less HFO-1234yf in HFC-134a would be considered non-flammable. At 100°C, compositions containing 53.10 weight percent or less HFO-1234yf in HFC-134a would be considered non-flammable.

EXAMPLE 3

Cooling Performance for Low Temperature Circuit of a Cascade System

Table 7 shows the performance of certain compositions as compared to CO_2, R404A (ASHRAE designation for a mixture containing HFC-125, HFC-134a, and HFC-143a), R410A (ASHRAE designation for a mixture containing HFC-32 and HFC-125) and HFC-32. In Table 7, Evap Pres is evaporator pressure, Cond Pres is condenser pressure, Comp Disch T is compressor discharge temperature, COP is coefficient of performance (analogous to energy efficiency), CAP is capacity, Avg. Temp. glide is the average of the temperature glide in the evaporator and condenser, and GWP is global warming potential. The data are based on the following conditions.

Evaporator temperature	-35°C
Condenser temperature	-6°C
Subcool amount	0°C
Return gas temperature	-25°C
Compressor efficiency is	70%

Note that the evaporator superheat enthalpy is not included in cooling capacity and energy efficiency determinations.

TABLE 7

Composition	Evap Press (kPa)	Cond Press (kPa)	Compr Disch Temp (°C)	CAP (kW)	COP	Avg. Temp. Glide, °C	GWP*
CO_2	1204.7	2960.8	57.3	12.132	4.229	0	1
R404A	168.3	449.4	20.0	2.175	4.791	0.5	3922
HFO-1234yf/HFC-32 (63/37 wt%)	163.6	503.5	31.5	2.271	4.875	6.7	252
R410A	220.1	654.1	38.3	2.966	4.836	0.1	2088
HFO-1234yf/HFC-32 (27.5/72.5 wt%)	213.6	635.4	46.4	2.934	4.865	0.8	490
HFO-1234yf/HFC-32	185.6	561.8	36.9	2.547	4.853	4.3	340

Composition	Evap Press (kPa)	Cond Press (kPa)	Compr Disch Temp (ºC)	CAP (kW)	COP	Avg. Temp. Glide, ºC	GWP*
(50/50 wt%)							
HFO-1234yf/HFC-32 (40/60 wt%)	200.2	599.6	41.0	2.739	4.851	2.5	407
HFO-1234yf/HFC-32 (20/80 wt%)	218.2	649.8	50.2	3.015	4.852	0.3	541
HFC-32	221.0	666.3	60.8	3.126	4.833	0	675
HFO-1234ze/HFC-32 (90/10 wt%)	60.8	220.1	28.6	0.982	4.947	4.7	73
HFO-1234ze/HFC-32 (80/20 wt%)	74.7	266.2	33.2	1.201	4.958	7.5	140
HFO-1234ze/HFC-32 (70/30 wt%)	89.1	311.4	37.4	1.419	4.968	9.1	207
HFO-1234ze/HFC-32 (60/40 wt%)	104.1	356.1	41.4	1.637	4.958	9.8	274
HFO-1234ze/HFC-32 (50/50 wt%)	119.6	400.9	45.2	1.855	4.944	9.8	341
HFO-1234ze/HFC-32 (40/60 wt%)	135.9	446.6	48.8	2.074	4.927	9.2	407
HFO-1234ze/HFC-32 (35/65 wt%)	144.1	469.9	50.6	2.185	4.907	8.6	441
HFO-1234ze/HFC-32 (30/70 wt%)	153.0	493.8	52.4	2.298	4.892	8.0	474
HFO-1234ze/HFC-32 (25/75 wt%)	162.1	518.4	54.1	2.413	4.875	7.2	508
HFO-1234ze/HFC-32 (20/80 wt%)	171.7	543.9	55.7	2.532	4.858	6.2	541
HFO-1234ze/HFC-32 (10/90 wt%)	193.1	599.4	58.7	2.793	4.830	3.7	608

*The GWP value for HFCs are taken from the “Climate Change 2007 – IPCC (Intergovernmental Panel on Climate Change) Fourth Assessment Report on Climate Change”, from the section entitled “Working Group 1 Report: “The Physical Science Basis”, Chapter 2, pp. 212-213, Table 2.14. The value for HFO-1234yf was published in Papadimitriou et al., *Physical Chemistry Chemical Physics*, 2007, vol. 9, pp. 1-13. Specifically, the 100 year time horizon GWP values are used. The GWP values for the compositions containing more than one component are calculated as weighted averages of the individual component GWP values.

The composition containing 63 wt% HFO-1234yf and 37 wt% HFC-32 actually shows improved COP and capacity relative to R404A and also has significantly lower GWP. The composition containing 27.5 wt% HFO-1234yf and 72.5 wt% HFC-32 matches the COP and capacity of R410A, has very low temperature glide indicating azeotrope-like behavior and also has significantly lower GWP.

Note that all compositions comprising mixtures of HFO-1234yf and HFC-32 have improved COP (energy efficiency) as compared to CO_2.

EXAMPLE 4

Total Equivalent Warming Impact

The total equivalent warming impact (TEWI) is determined for systems as disclosed herein in comparison to conventional uncoupled supermarket refrigeration systems as well as conventional cascade systems. The TEWI takes into consideration the effects of the energy efficiency of the system, the contribution due to the energy source used to provide the electrical power to the equipment, and the amount of refrigerant charged to the system as well as the rate of leakage to quantify a more complete environmental impact of use of different refrigerants.

This Example uses a conventional European direct expansion (DX) supermarket refrigeration system, traditionally using R404A in both medium temperature (MT) and low temperature (LT) refrigeration systems, as the base case for comparison. Certain assumptions were made based on a typical European supermarket system are shown in Table 8. Additionally, the expected equipment life was assumed to be 15 years and the CO_2 emitted from electricity generation was estimated to be 0.616 kg CO_2/kw-hr.

2010315264 02 Nov 2015

TABLE 8

Variable	MT cycle	LT cycle
Operating power (kw)	75	20
Fractional run time (%)	55	85
Refrigerant charge (kg)	200	100
Average refrigerant emission rate* (% of charge per year)	15	15
End-of-life recovery of refrigerant (%)	80	80

*Includes fugitive and accidental releases, independent of refrigerant choice.

Table 9 provides the conditions for which the system performance (COP, or coefficient of performance, a measure of energy efficiency) was estimated. In Table 9, temp is temperature, evap is evaporator, cond is condenser, and comp is compressor.

TABLE 9

Cycle	Uncoupled	Cascade
MT	evap temp = -10 ºC cond temp = 40 ºC return gas temp = +10 ºC subcool temp = 6 ºC comp efficiency = 0.70	evap temp = -10 ºC cond temp = 40 ºC return gas temp = +10 ºC subcool temp = 6 ºC comp efficiency = 0.70
LT	evap temp = -35 ºC cond temp = 40 ºC return gas temp = -15 ºC subcool temp = 6 ºC comp efficiency = 0.70	evap temp = -35 ºC cond temp = -6 ºC return gas temp = -15 ºC subcool temp = 0 ºC comp efficiency = 0.70

Table 10 lists several different embodiments of the present invention (system designation 3, 4 and 6 to 11) as compared to conventional uncoupled (system designation 0 and 1) and cascade systems (system designation 1a, 2, 5a and 5b). Determinations of TEWI are made, as well as the estimated COP values as calculated based on the conditions listed above in Table 9.

TABLE 10

System designation	MT refrigerant	Composition (wt%)	GWP	MT COP	LT refrigerant (GWP)	LT COP	Cascade/ uncoupled
0	R-404A	100	3922	2.62	R-404A (3922)	1.36	Uncoupled
1	134a	100	1430	2.88	R-404A (3922)	1.36	Uncoupled
1a	134a	100	1430	2.88	R-404A (3922)	4.75	Cascade
2	R-404A	100	3922	2.62	CO_2 (1)	4.20	Cascade
3	1234yf/134a	53/47	674	2.89	CO_2 (1)	4.20	Cascade
4	1234yf	100	4	2.80	CO_2 (1)	4.20	Cascade
5a (northern EU)	Supercritical CO_2	100	1	2.31*	CO_2 (1)	4.20	Cascade
5b (southern EU)	Supercritical CO_2	100	1	2.04*	CO_2 (1)	4.20	Cascade
6	trans-1234ze	100	6	2.90	CO_2 (1)	4.20	Cascade
7	32/1234yf	21.5/78.5	148	2.73	CO_2 (1)	4.20	Cascade
8	32/1234yf	35/65	239	2.69	CO_2 (1)	4.20	Cascade
9	33/1234yf	68.9/31.1	466	2.65	CO_2 (1)	4.20	Cascade
10	32/125/1234yf	67/7/26	698	2.64	CO_2 (1)	4.20	Cascade
11	32/125/1234yf/134a	24.3/24.7/25.3/25.7	1397	2.86	CO_2 (1)	4.20	Cascade
12	trans-1234ze/134a	58/42	604	2.88	CO_2 (1)	4.20	Cascade
13	trans-1234ze/134a	60/40	576	2.86	CO_2 (1)	4.20	Cascade
14	trans-1234ze/125	96/4	146	2.89	CO_2 (1)	4.20	Cascade
15	trans-1234ze/125	86/14	495	2.85	CO_2 (1)	4.20	Cascade
16	trans-1234ze/32	32/68	461	2.69	CO_2 (1)	4.20	Cascade
17	trans-1234ze/32	78.6/21.4	149	2.83	CO_2 (1)	4.20	Cascade
18	trans-1234ze/32	65/35	240	2.79	CO_2 (1)	4.20	Cascade

*These values for COP were estimated to match published data on energy consumption relative to a system using R404A in both MT and LT loops. (Sienel, T.; Finckh, O., "CO_2-DX Systems for Medium- and Low-Temperature Refrigeration in Supermarket Applications", International Congress of Refrigeration, 2007, Beijing, China).

The TEWI value includes an indirect contribution, which incorporates energy source and usage, and a direct contribution due to the emissions of refrigerant with a given GWP from a system. Table 11 lists the indirect and direct contributions and the TEWI value calculated for the different

2010315264 24 Feb 2016

systems described above, in terms of equivalent CO_2 emissions over equipment life (in million kg) in order from greatest to least environmental impact.

TABLE 11

System designation	From energy consumption, MT loop	From energy consumption, LT loop	Indirect contribution	From refrigerant emissions, MT loop	From refrigerant emissions, LT loop	Direct contribution	TEWI
0	3.34	1.38	4.72	1.92	0.96	2.88	7.60
1	3.04	1.38	4.42	0.70	0.96	1.66	6.08
2	3.34	0.45	3.79	1.92	0	1.92	5.71
1a	3.04	0.39	3.43	0.70	0.96	1.66	5.09
5b	4.27	0.45	4.72	0	0	0	4.72
5a	3.81	0.45	4.26	0	0	0	4.26
3	3.04	0.45	3.57	0.33	0	0.33	3.81
4	3.12	0.45	3.57	0	0	0	3.57
6	3.02	0.45	3.47	0	0	0	3.47
7	3.21	0.45	3.66	0.07	0	0.07	3.73
8	3.26	0.45	3.71	0.12	0	0.12	3.83
9	3.31	0.45	3.76	0.23	0	0.23	3.99
10	3.32	0.45	3.77	0.34	0	0.34	4.11
11	3.04	0.45	3.49	0.68	0	0.68	4.17
12	3.04	0.45	3.49	0.30	0	0.3	3.79
13	3.04	0.45	3.49	0.28	0	0.28	3.77
14	3.03	0.45	3.48	0.07	0	0.07	3.55
15	3.07	0.45	3.52	0.24	0	0.24	3.76
16	3.26	0.45	3.71	0.23	0	0.23	3.94
17	3.09	0.45	3.54	0.07	0	0.07	3.61
18	3.14	0.45	3.59	0.12	0	0.12	3.71

The results in Table 11 demonstrate that the use of HFO-based refrigerants (e.g. in the medium temperature loop of cascade refrigeration systems 3, 4, 6 to 11) can lead to lower TEWI values than those for

2010315264 02 Nov 2015

uncoupled or cascade refrigeration systems using refrigerants known to the prior art.

Any prior art citation or statement provided in the specification is not to be taken as an admission that such art constitutes, or is to be understood as constituting, part of the common general knowledge in Australia.

2010315264 24 Feb 2016

The Claims defining the invention are as follows:

1. A cascade refrigeration system having at least two refrigeration loops, each circulating a refrigerant therethrough, comprising:

   (a) a first expansion device for reducing the pressure and temperature of a first refrigerant liquid;

   (b) an evaporator having an inlet and an outlet, wherein th e first refrigerant liquid from the first expansion device enters the evaporator through the evaporator inlet and is evaporated in the evaporator to form a first refrigerant vapor, thereby producing cooling, and circulates to the outlet;

   (c) a first compressor having an inlet and an outlet, wherein the first refrigerant vapor from the evaporator circulates to the inlet of the first compressor and is compressed, thereby increasing the pressure and the temperature of the first refrigerant vapor, and the compressed first refrigerant vapor circulates to the outlet of the first compressor;

   (d) a cascade heat exchanger system having:

      (i) a first inlet and a first outlet, wherein the first refrigerant vapor circulates from the first inlet to the first outlet and is condensed in the cascade heat exchanger system to form a first refrigerant liquid, thereby rejecting heat, and

      (ii) a second inlet and a second outlet, wherein a second refrigerant liquid circulates from the second inlet to the second outlet and absorbs the heat rejected by the first refrigerant and forms a second refrigerant vapor;

   (e) a second compressor having an inlet and an outlet, wherein the second refrigerant vapor from the cascade heat exchanger system is drawn into the second compressor and is compressed, thereby increasing the pressure and temperature of the second refrigerant vapor;

   (f) a condenser having an inlet and an outlet for circulating the second refrigerant vapor therethrough and for condensing the second refrigerant vapor from the second compressor to form a second refrigerant liquid, wherein the second refrigerant liquid exits the condenser through the outlet; and

(g) a second expansion device for reducing the pressure and temperature of the second refrigerant liquid exiting the condenser and entering the second inlet of the cascade heat exchanger system;

wherein the first refrigerant is CO_2 and the second refrigerant comprises at least one fluoroolefin selected from the group consisting of HFO-1234yf, trans-HFO-1234ze, and mixtures thereof.

2. The system of claim 1, wherein the second refrigerant consists essentially of HFO-1234yf.

3. The system of claim 1, wherein the second refrigerant also comprises R134a.

4. The system of claim 1, wherein the second refrigerant also comprises HFC-32.

5. The system of claim 4, wherein the second refrigerant comprises HFO-1234yf.

6. The system of claim 1, wherein the second refrigerant consists essentially of trans-HFO-1234ze.

7. A cascade refrigeration system having at least two refrigeration loops, each circulating a refrigerant therethrough, comprising:

(a) a first expansion device for reducing the pressure and temperature of a first refrigerant liquid;

(b) an evaporator having an inlet and an outlet, wherein the first refrigerant liquid from the first expansion device enters the evaporator through the evaporator inlet and is evaporated in the evaporator to form a first refrigerant vapor, thereby producing cooling, and circulates to the outlet;

(c) a first compressor having an inlet and an outlet, wherein the first refrigerant vapor from the evaporator circulates to the inlet of the first compressor and is compressed, thereby increasing the pressure and the temperature of the first refrigerant vapor, and the compressed first refrigerant vapor circulates to the outlet of the first compressor;

(d) a cascade heat exchanger system comprising:

(i) a first cascade heat exchanger having:

(A) a first inlet and a first outlet, wherein the first refrigerant vapor from the evaporator circulates from the first inlet to the first outlet and is condensed in the first cascade heat exchanger to form a first refrigerant liquid, thereby rejecting heat, and

(B) a second inlet and a second outlet, wherein a heat transfer fluid circulates from the second inlet to the second outlet, wherein the heat rejected by the first refrigerant vapor as it is condensed is absorbed by the heat transfer fluid,

(ii) a second cascade heat exchanger having:

(A) a first inlet and a first outlet, wherein the heat transfer fluid from the first cascade heat exchanger circulates from the first inlet to the first outlet and rejects the heat absorbed in the first cascade heat exchanger, and

(B) a second inlet and a second outlet, wherein a second refrigerant liquid circulates from the second inlet to the second outlet and absorbs the heat rejected by the heat transfer fluid and forms a second refrigerant vapor;

(e) a second compressor having an inlet and an outlet, wherein the second refrigerant vapor from the second cascade heat exchanger is drawn into the second compressor and is compressed, thereby increasing the pressure and temperature of the second refrigerant vapor;

(f) a condenser having an inlet and an outlet for circulating the second refrigerant vapor therethrough and for condensing the second refrigerant vapor from the second compressor to form a second refrigerant liquid, wherein the second refrigerant liquid exits the condenser through the outlet; and

(g) a second expansion device for reducing the pressure and temperature of the second refrigerant liquid exiting the condenser and entering the second inlet of the second cascade heat exchanger;

wherein the first refrigerant is CO_2 and the second refrigerant comprises at least one fluoroolefin selected from the group consisting of HFI-1234yf, trans-HFO-1234ze, and mixtures thereof.

8. A method of exchanging heat between at least two refrigeration loops, comprising:

(a) absorbing heat from a body to be cooled in a first refrigeration loop and rejecting this heat to a second refrigeration loop; and

(b) absorbing the heat from the first refrigeration loop in the second refrigeration loop and rejecting this heat to ambient, wherein the first refrigerant is CO_2 and the second refrigerant comprises at lease one fluoroolefin selected from the group consisting of HFO-1234yf, trans-HFO-1234ze, and mixtures thereof.

9. The method of claim 8, wherein the second refrigerant also comprises R134a.

10. The method of claim 8, wherein the second refrigerant also comprises HFC-32.

11. The system of any one of claims 1 to 7, wherein the total equivalent warming impact of the system is a value lower than that for a system with CO_2 as the first refrigerant and CO_2 as the second refrigerant.

12. The system of any one of claims 1 to 7 or claim 11 substantially as hereinbefore described with reference to the accompanying Examples.

13. The method of any one of claims 8 to 10 substantially as hereinbefore described with reference to the accompanying Examples.

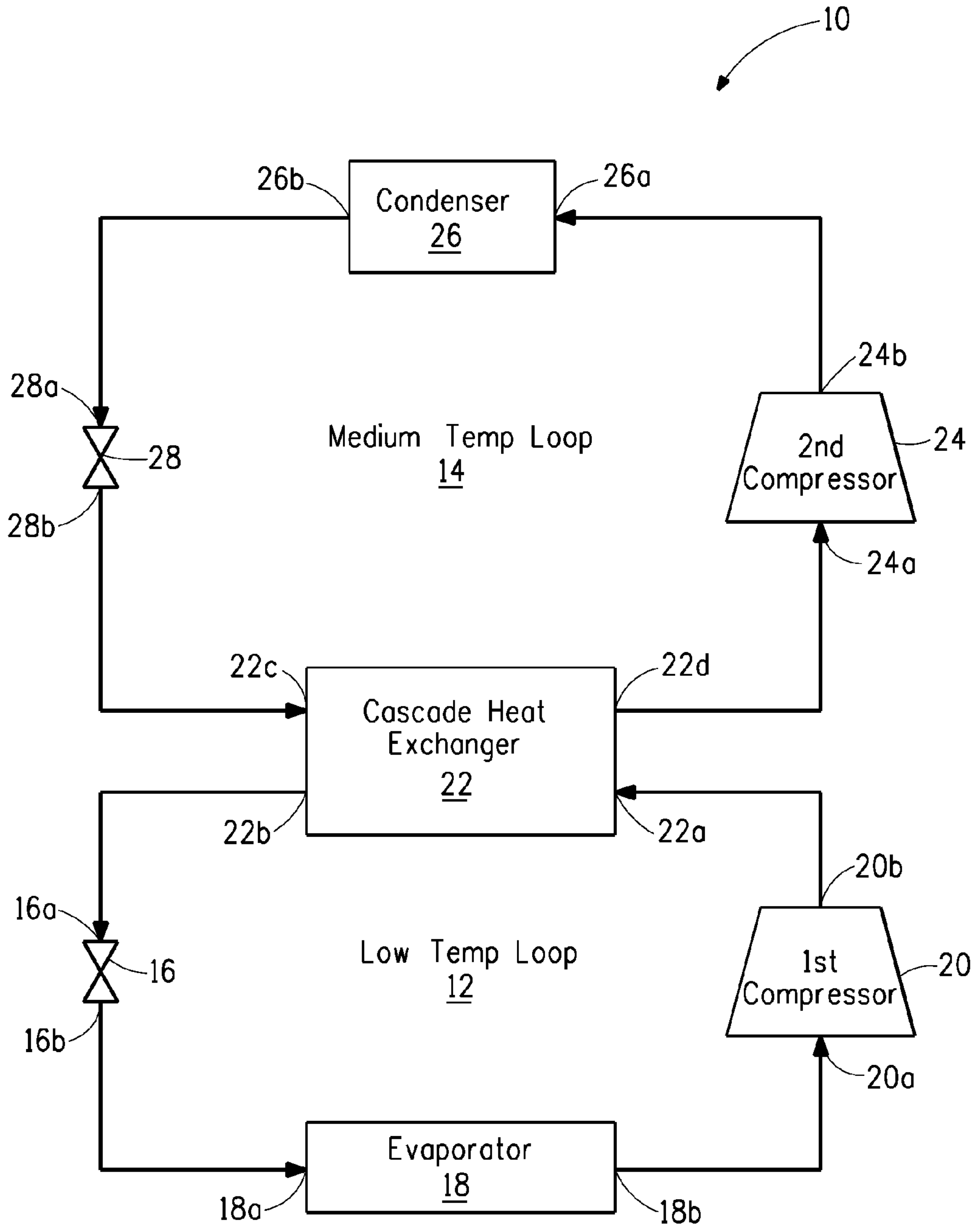
10
Condenser
26
26b
26a
28a
28
28b
Medium Temp Loop
14
24b
2nd
Compressor
24
24a
22c
22d
Cascade Heat
Exchanger
22
22b
22a
16a
16
16b
Low Temp Loop
12
20b
1st
Compressor
20
20a
Evaporator
18
18a
18b

FIG. 1

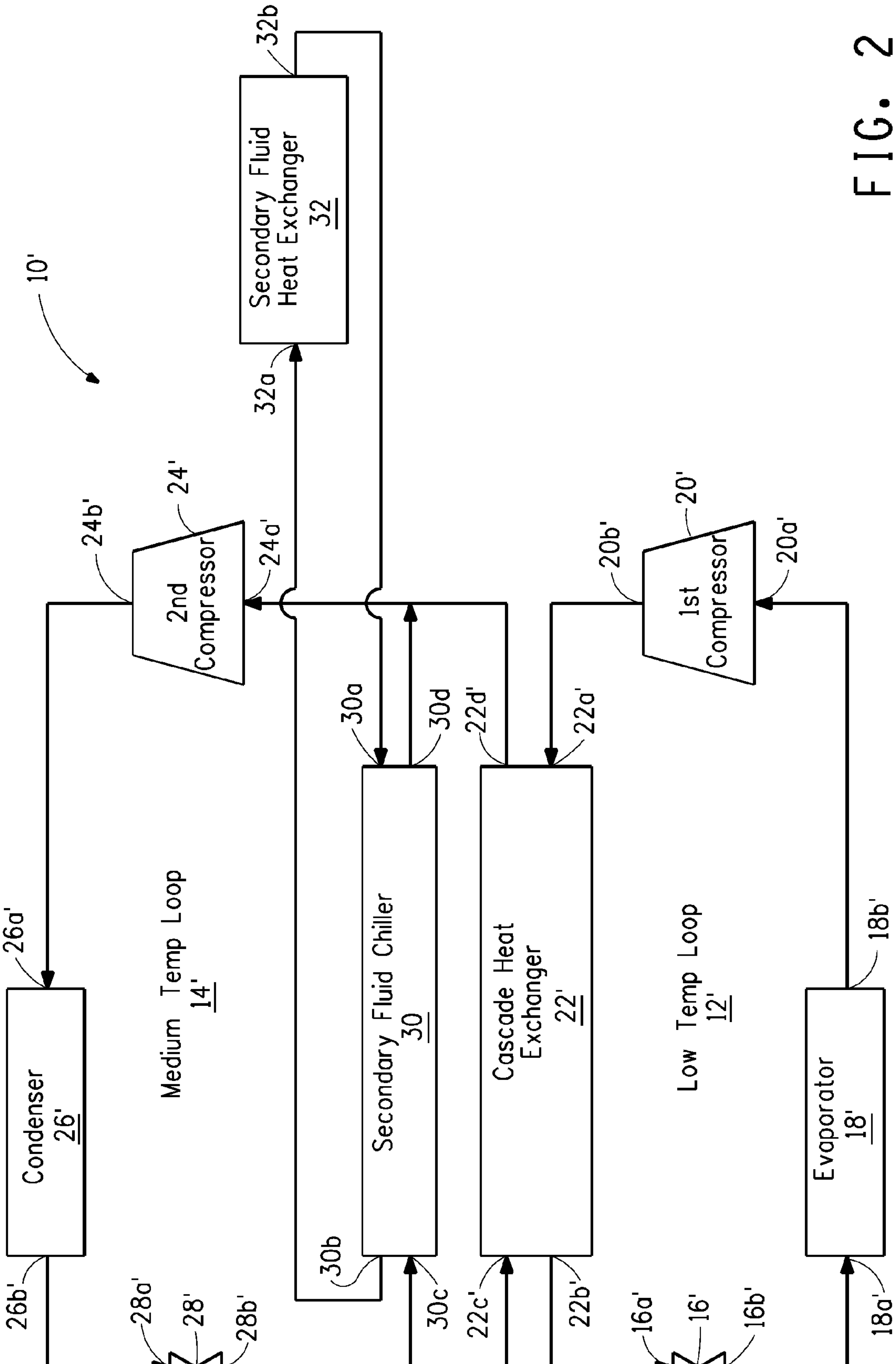
10'
Secondary Fluid Heat Exchanger 32
32a
32b
2nd Compressor
24'
24a'
24b'
1st Compressor
20'
20a'
20b'
Condenser 26'
26a'
26b'
Medium Temp Loop 14'
Secondary Fluid Chiller 30
30a
30b
30c
30d
Cascade Heat Exchanger 22'
22a'
22b'
22c'
22d'
Low Temp Loop 12'
Evaporator 18'
18a'
18b'
28'
28a'
28b'
16'
16a'
16b'

FIG. 2

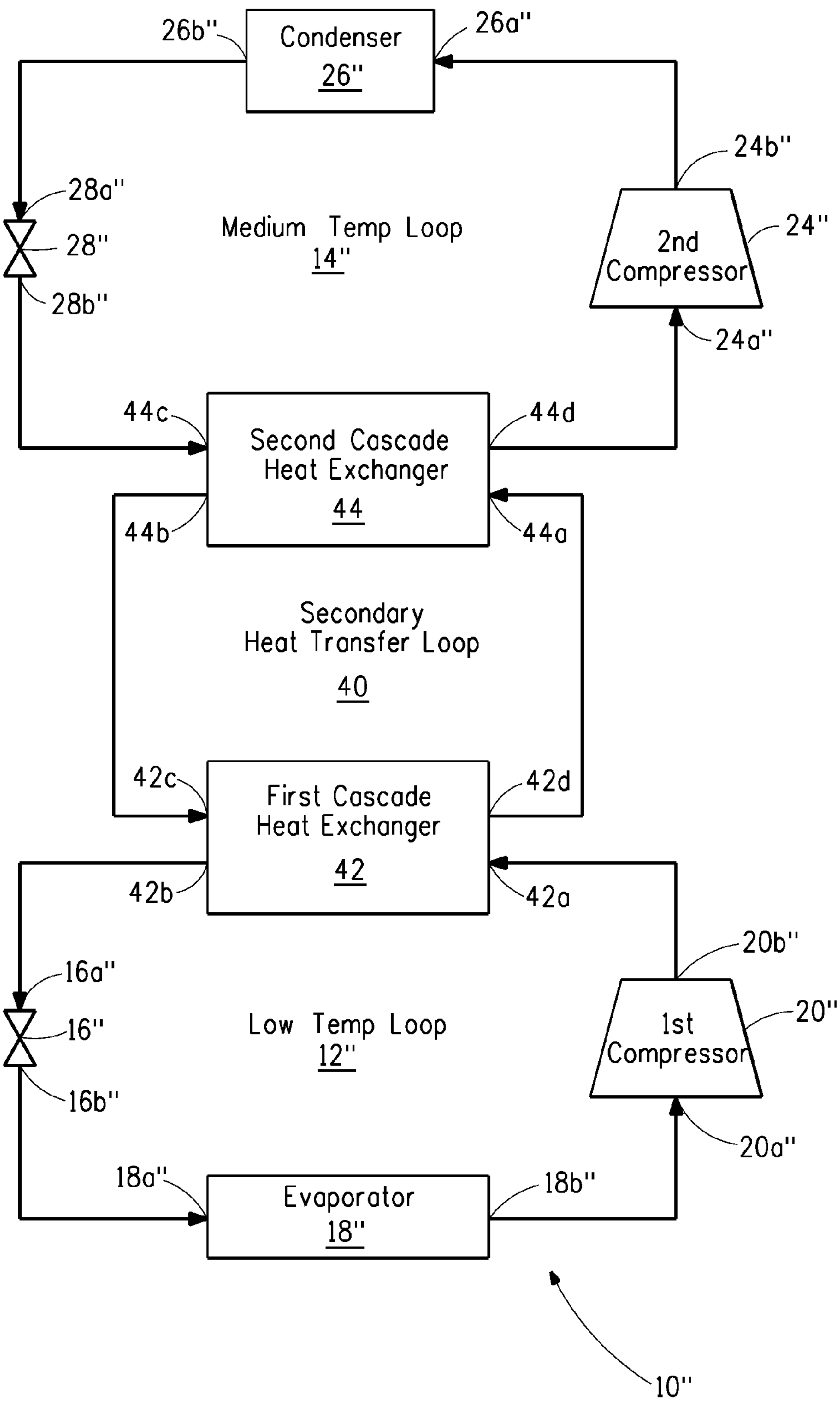
Condenser
26''
26b''
26a''
24b''
28a''
28''
28b''
Medium Temp Loop
14''
2nd
Compressor
24''
24a''
44c
44d
Second Cascade
Heat Exchanger
44
44b
44a
Secondary
Heat Transfer Loop
40
42c
42d
First Cascade
Heat Exchanger
42
42b
42a
16a''
16''
16b''
Low Temp Loop
12''
20b''
1st
Compressor
20''
20a''
18a''
Evaporator
18''
18b''
10''

FIG. 3

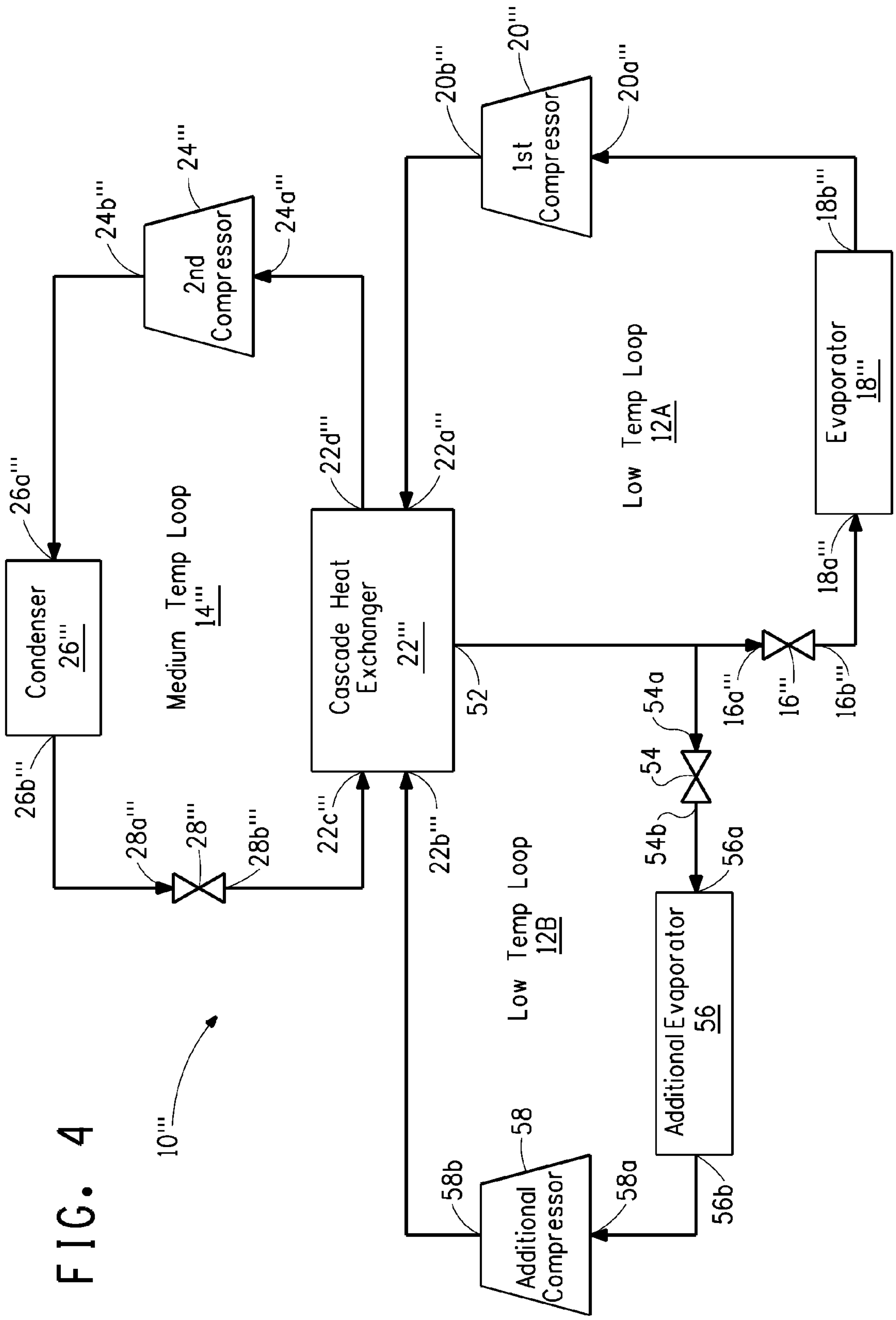
1st Compressor
20'''
20b'''
20a'''
2nd Compressor
24'''
24b'''
24a'''
Low Temp Loop
12A
Evaporator
18'''
18b'''
18a'''
26a'''
22d'''
22a'''
Condenser
26'''
Medium Temp Loop
14'''
Cascade Heat Exchanger
22'''
52
54a
16a'''
16'''
16b'''
54
26b'''
28a'''
28'''
28b'''
22c'''
22b'''
54b
56a
Low Temp Loop
12B
Additional Evaporator
56
10'''
58
58b
58a
56b
Additional Compressor

FIG. 4

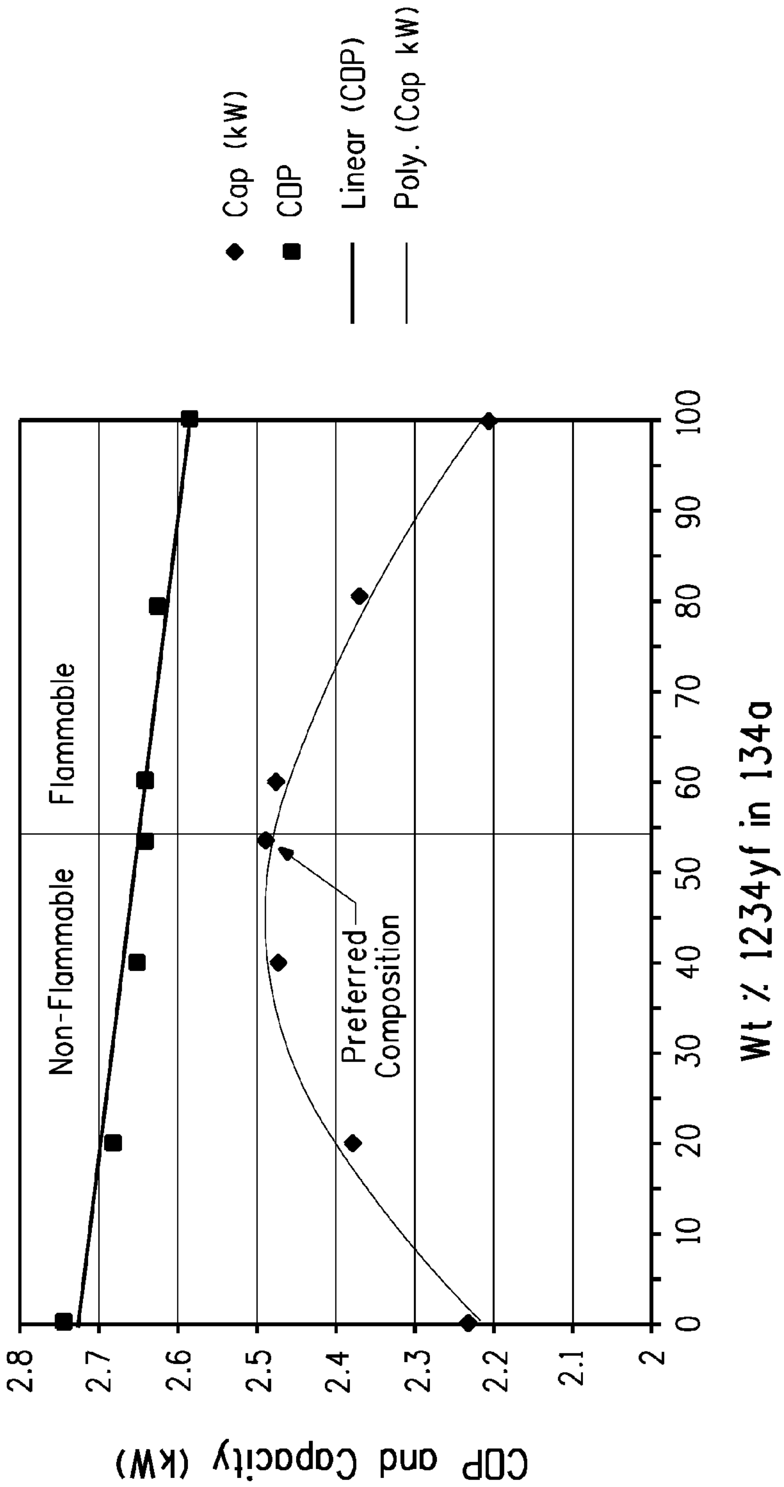
Cap (kW)
COP
Linear (COP)
Poly. (Cap kW)
Non-Flammable
Flammable
Preferred Composition
COP and Capacity (kW)
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
0
10
20
30
40
50
60
70
80
90
100
Wt % 1234yf in 134a

FIG. 5