TITLE

USE OF E-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE IN HEAT PUMPS

FIELD OF THE INVENTION

This invention relates to methods and systems having utility in numerous applications, and in particular, uses for the compound E 1,1,1,4,4,4-hexafluoro-2-butene (E-HFO-1336mzz) in heat pumps, including high temperature heat pumps.

BACKGROUND OF THE INVENTION

The compositions of the present invention are part of a continued search for the next generation of low global warming potential materials. Such materials must have low environmental impact, as measured by low global warming potential and zero or negligible ozone depletion potential. New heat pump working fluids are needed.

Heating in the range from about 40°C to about 135°C is required in a wide range of applications, including space heating, water heating for domestic or other service, food drying, process heating, etc. Presently this heating is mostly provided through heaters using fossil fuels (e.g. heavy oil, natural gas etc.). Thus working fluids that can provide heating in this temperature range or even higher are needed.

SUMMARY OF THE INVENTION

~~This disclosure~~Embodiments relates~~s~~ to heat pump systems and methods using E-HFO-1336mzz as the working fluid to produce heating at temperatures in the range from about 40°C to about 135°C with reduced energy costs and reduced greenhouse gas emissions relative to fossil fuel heaters. ~~This disclosure also~~Embodiments relates~~s~~ to heat pump systems and methods using E-HFO-1336mzz as the working fluid (e.g. transcritical cycles) to produce heating at temperatures higher than about 140°C with reduced energy costs and reduced greenhouse gas emissions relative to fossil fuel heaters.

In accordance with a first aspect of the present invention, a method for producing heating in a heat pump is provided. The method comprises extracting heat from a working fluid comprising E-HFO-1336mzz, in a heat exchanger, thereby producing a cooled working fluid, wherein the heat pump is a high temperature heat pump and the heat exchanger operates at a temperature above about 50°C.

Also in accordance with a second aspect of the present invention, a method for producing heating in a ~~cascade~~ heat pump wherein heat is exchanged between at least two ~~heating~~ stages arranged in a cascade configuration is provided. The method comprises absorbing heat at a selected lower temperature in a first working fluid in a first cascade heating stage and transferring this heat to a second working fluid of a second cascade heating stage that ~~rejects~~ supplies heat at a higher temperature; wherein the second working fluid comprises E-HFO-1336mzz.

Also in accordance with a third aspect of the present invention, a heat pump apparatus is provided. The apparatus comprises a working fluid heater (e.g. an evaporator), compressor, working fluid cooler (e.g. a condenser or a supercritical working fluid cooler) and expansion device and said apparatus contains a working fluid comprising E-HFO-1336mzz, wherein the heat pump is a high temperature heat pump and the heat exchanger operates at a temperature above about 50°C.

Also in accordance with a fourth aspect of the present invention, a method for replacing CFC-12, CFC-114, HCFC-22, HFC-245fa, HFC-236fa, HCFC-124, HFC-134a, hydrocarbons, HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze, HFO-1243zf or blends containing HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze or HFO-1243zf ~~or CFC-12~~ as the working fluid in a heat pump or chiller designed for said working fluid is provided. The method comprises providing a replacement working fluid comprising E-HFO-1336mzz, wherein said heat pump is a high temperature heat pump having a working fluid cooler or condenser operating temperature above about 50°C.

Also in accordance with a fifth aspect of the present invention, a method for replacing HCFC-22 working fluid in a heat pump or chiller designed for said working fluid is provided. The method comprises providing a replacement working fluid comprising E-HFO-1336mzz.

Also in accordance with a sixth aspect of the present invention a method for replacing ~~HFO-1234yf or E-HFO-1234ze or Z-HFO-1234ze or HFO-1243zf working fluid or~~ a working fluid containing HFO-1234yf or E-HFO-1234ze or Z-HFO-1234ze or HFO-1243zf and optionally one or more ~~HFCs or HCs~~saturated hydrofluorocarbons or hydrocarbons in a heat pump or chiller designed for said working fluid is provided. The

method comprises providing a replacement working fluid comprising E-HFO-1336mzz.

~~Also in accordance with the present invention is provided a method for supplying simultaneous heating and cooling in a cascade heat pump system. The method comprises providing a low temperature cascade stage containing a working fluid selected from the group consisting of CO_2, N_2O, HFC-32, HFC-125, HFC-143a, HFC-227ea, HFO-1234yf, E-HFO-1234ze, HFO-1243zf, HFC-134a, HFC-134, HFC-161, HFC-152a, and mixtures thereof; and providing a high temperature cascade stage containing a working fluid comprising E-HFO-1336mzz; wherein said low temperature cascade stage and said high temperature cascade stage are in thermal contact.~~

Also in accordance with a seventh aspect of the present invention, there is provided a method for supplying simultaneous heating and cooling in a cascade heat pump system. The method comprises providing a low temperature cascade stage (or cycle) containing a working fluid selected from the group consisting of NH_3, CO_2, N_2O, HFC-32, HFC-125, HFC-143a, HFC-227ea, HFC-227ca, HFC-245cb, HFC-236fa, HFC-236ea, HFO-1234yf, E-HFO-1234ze, HFO-1243zf, E-HFO-1234ye, HFO-1336yf, HFO-1243yf, Z-HFO-1234ze, HCFO-1233xf, HFC-134a, HFC-134, HFC-161, HFC-152a, hydrocarbons, and mixtures thereof; and providing a high temperature cascade stage containing a working fluid comprising E-HFO-1336mzz; wherein said low temperature cascade stage and said high temperature cascade stage are in thermal contact.

Also in accordance with a eighth aspect of the present invention, a composition for use in a heat pump is provided. The composition comprises: (i) a working fluid consisting essentially of E-HFO-1336mzz; and (ii) a stabilizer to prevent degradation at temperatures of 50°C or above, or (iii) a lubricant suitable for use at 50°C or above, or both (ii) and (iii).

CLAIMS

What is claimed is:

1. A method for producing heating in a heat pump comprising: extracting heat from a working fluid comprising E-HFO-1336mzz, in a heat exchanger, thereby producing a cooled working fluid; wherein the heat pump is a high temperature heat pump and the heat exchanger operates at a temperature above about 50°C.

2. The method of claim 1 wherein the heat exchanger is selected from the group consisting of a supercritical working fluid cooler and a condenser.

3. The method of claim 1 further comprising passing a first heat transfer medium through the heat exchanger, whereby said extraction of heat heats the first heat transfer medium, and passing the heated first heat transfer medium from the heat exchanger to a body to be heated.

4. The method of claim 1 further comprising expanding the working fluid and then heating the working fluid in a second heat exchanger to produce a heated working fluid.

5. A method for producing heating in a heat pump wherein heat is exchanged between at least two stages arranged in a cascade configuration, comprising:

   absorbing heat at a selected lower temperature in a first working fluid in a first cascade stage and transferring this heat to a second working fluid of a second cascade stage that supplies heat at a higher temperature; wherein the second working fluid comprises E-HFO-1336mzz.

6. A heat pump apparatus comprising a working fluid heater, compressor, working fluid cooler and expansion device, wherein said apparatus contains a working fluid comprising E-HFO-1336mzz; wherein the heat pump is a high temperature heat pump and the heat exchanger operates at a temperature above about 50°C.

7. The heat pump apparatus of claim 6 having at least two stages arranged as a cascade system, each stage circulating a working fluid therethrough, wherein heat is transferred to a final cascade stage from the preceding cascade stage and wherein the working fluid of the final stage comprises E-HFO-1336mzz.

8. The heat pump apparatus of claim 7 having at least two stages arranged as a cascade system, each stage circulating a working fluid therethrough comprising:

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

(b) a working fluid heater having an inlet and an outlet, wherein the first working fluid from the first expansion device enters the working fluid heater through the working fluid heater inlet and is heated in the working fluid heater to form a heated first working fluid, and circulates to the outlet of the working fluid heater;

(c) a first compressor having an inlet and an outlet, wherein the heated first working fluid vapor from the working fluid heater circulates to the inlet of the first compressor and is compressed, thereby increasing the pressure and the temperature of the heated first working fluid producing compressed heated first working fluid, and the compressed heated first working fluid 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 heated first working fluid circulates from the first inlet to the first outlet and is cooled in the heat exchanger system to form a cooled first working fluid, thereby rejecting heat, and

(ii) a second inlet and a second outlet, wherein a second working fluid circulates from the second inlet to the second outlet and absorbs the heat rejected by the first working fluid and forms a heated second working fluid;

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

(f) a working fluid cooler having an inlet and an outlet for circulating the heated second working fluid therethrough and for cooling the heated second working fluid from the second compressor to form a cooled second working fluid, thereby supplying heat, wherein the cooled second working fluid exits the working fluid cooler through the outlet; and

(g) a second expansion device for reducing the pressure and temperature of the cooled second working fluid exiting the working fluid cooler and entering the second inlet of the cascade heat exchanger system;

wherein the second working fluid comprises E-HFO-1336mzz.

9. The heat pump apparatus of claim 8, wherein the first working fluid comprises at least one fluoroolefin selected from the group consisting of HFO-1234yf, E-HFO-1234ze, E-HFO-1234ye, HFO-1336yf, HFO-1243yf, Z-HFO-1234ze, HCFO-1233xf, and HFC-1243zf; or at least one fluoroalkane selected from the group consisting of HFC-32, HFC-125, HFC-134a, HFC-134, HFC-143a, HFC-152a, HFC-161, HFC-227ca, HFC-245cb, HFC-236fa, HFC-236ea and HFC-227ea; or at least one working fluid selected from hydrocarbons, NH_3, CO_2 or N_2O.

10. A method for replacing CFC-12, CFC-114, HCFC-124, HCFC-22, HFC-134a, HFC-236fa, HFC-245fa, hydrocarbons, HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze, HFO-1243zf or blends containing HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze or HFO-1243zf as the working fluid in a heat pump or chiller designed for said working fluid comprising providing a replacement working fluid comprising E-HFO-1336mzz; wherein said heat pump is a high temperature heat pump

having a working fluid cooler or condenser operating temperature above about 50°C.

11. The method of claim 10 wherein the working fluid being replaced is HFC-236fa, HCFC-124, HFC-134a or CFC-12, HCFC-22, HFO-1234yf, E-HFO-1234ze, HFO-1243zf or blends containing HFO-1234yf or E-HFO-1234ze or HFO-1243zf and wherein the maximum feasible condensing temperature is increased above that achievable with said replaced working fluid.

12. The method of claim 11, wherein the maximum feasible condensing temperature is increase to about 118°C.

13. The method of claim 11 wherein the chiller designed for said working fluid is converted to a heat pump.

14. A method for supplying simultaneous heating and cooling in a cascade heat pump system comprising providing a low temperature cascade stage containing a working fluid selected from the group consisting of NH_3, CO_2, N_2O, HFC-32, HFC-125, HFC-143a, HFC-227ea, HFC-227ca, HFC-245cb, HFC-236fa, HFC-236ea, HFO-1234yf, E-HFO-1234ze, HFO-1243zf, E-HFO-1234ye, HFO-1336yf, HFO-1243yf, Z-HFO-1234ze, HCFO-1233xf, HFC-134a, HFC-134, HFC-161, HFC-152a, hydrocarbons and mixtures thereof; and providing a high temperature cascade stage containing a working fluid comprising E-HFO-1336mzz; wherein said low temperature cascade stage and said high temperature cascade stage are in thermal contact.

15. A composition comprising: (i) a working fluid consisting essentially of E-HFO-1336mzz; and (ii) a stabilizer to prevent degradation at temperatures of 50°C or above, or (iii) a lubricant suitable for use at 50°C or above, or both (ii) and (iii).

16. A method for replacing HCFC-22 working fluid in a heat pump or chiller designed for HCFC-22 working fluid comprising providing a replacement working fluid comprising E-HFO-1336mzz.

17. A method for replacing a working fluid comprising HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze or HFO-1243zf and optionally one or more saturated hydrofluorocarbons or hydrocarbons in a heat pump or chiller designed for said working fluid comprising providing a replacement working fluid comprising E-HFO-1336mzz.

CLAIMS

What is claimed is:

1. A method for producing heating in a heat pump comprising: extracting heat from a working fluid comprising E-HFO-1336mzz, in a heat exchanger, thereby producing a cooled working fluid.

2. The method of claim 1 wherein the heat exchanger is selected from the group consisting of a supercritical working fluid cooler and a condenser.

3. The method of claim 1 wherein the heat pump is a high temperature heat pump and the heat exchanger operates at a temperature above about 50°C.

4. The method of claim 1 further comprising passing a first heat transfer medium through the heat exchanger, whereby said extraction of heat heats the first heat transfer medium, and passing the heated first heat transfer medium from the heat exchanger to a body to be heated.

5. The method of claim 4, wherein the first heat transfer medium is water and the body to be heated is water.

6. The method of claim 4, wherein the first heat transfer medium is water and the body to be heated is air for space heating.

7. The method of claim 4, wherein the first heat transfer medium is an industrial heat transfer liquid and the body to be heated is a chemical process stream.

8. The method of claim 1 further comprising expanding the working fluid and then heating the working fluid in a second heat exchanger to produce a heated working fluid.

9. The method of claim 8 wherein said second heat exchanger is an evaporator and the heated working fluid is a vapor.

10. The method of claim 8 further comprising compressing the working fluid in a dynamic or a positive displacement compressor.

11. The method of claim 4, wherein the first heat transfer medium is air and is passed from the heat exchanger to a space to be heated.

12. The method of claim 4, wherein the first heat transfer fluid is a portion of a process stream and is passed from the heat exchanger back to the process.

13. A method for producing heating in a heat pump wherein heat is exchanged between at least two stages arranged in a cascade configuration, comprising:

absorbing heat at a selected lower temperature in a first working fluid in a first cascade stage and transferring this heat to a second working fluid of a second cascade stage that supplies heat at a higher temperature; wherein the second working fluid comprises E-HFO-1336mzz.

14. A heat pump apparatus comprising a working fluid heater, compressor, working fluid cooler and expansion device, wherein said apparatus contains a working fluid comprising E-HFO-1336mzz.

15. The heat pump apparatus of claim 14 wherein said heat pump is a high temperature heat pump having a working fluid cooler operating temperature above about 50°C.

16. The heat pump apparatus of claim 14 comprising a dynamic or a positive displacement compressor.

17. The heat pump apparatus of claim 14 having at least two stages arranged as a cascade system, each stage circulating a working fluid therethrough, wherein heat is transferred to a final cascade stage from the preceding cascade stage and wherein the working fluid of the final stage comprises E-HFO-1336mzz.

18. The heat pump apparatus of claim 17 having at least two stages arranged as a cascade system, each stage circulating a working fluid therethrough comprising:

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

(b) a working fluid heater having an inlet and an outlet, wherein the first working fluid from the first expansion device enters the working fluid heater through the working fluid heater inlet and is heated in the working fluid heater to form a heated first working fluid, and circulates to the outlet of the working fluid heater;

(c) a first compressor having an inlet and an outlet, wherein the heated first working fluid vapor from the working fluid heater circulates to the inlet of the first compressor and is compressed, thereby increasing the pressure and the temperature of the heated first working fluid producing compressed heated first working fluid, and the compressed heated first working fluid 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 heated first working fluid circulates from the first inlet to the first outlet and is cooled in the heat exchanger system to form a cooled first working fluid, thereby rejecting heat, and

(ii) a second inlet and a second outlet, wherein a second working fluid circulates from the second inlet to the second outlet and absorbs the heat rejected by the first working fluid and forms a heated second working fluid;

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

(f) a working fluid cooler having an inlet and an outlet for circulating the heated second working fluid therethrough and for cooling the heated second working fluid from the second compressor to form a cooled second working fluid, thereby supplying heat, wherein the cooled second working fluid exits the working fluid cooler through the outlet; and

(g) a second expansion device for reducing the pressure and temperature of the cooled second working fluid exiting the working fluid cooler and entering the second inlet of the cascade heat exchanger system;

wherein the second working fluid comprises E-HFO-1336mzz.

19. The heat pump apparatus of claim 18, wherein the first working fluid comprises at least one fluoroolefin selected from the group consisting of HFO-1234yf, E-HFO-1234ze, E-HFO-1234ye, HFO-1336yf, HFO-1243yf, Z-HFO-1234ze, HCFO-1233xf, and HFC-1243zf.

20. The heat pump apparatus of claim 18 wherein the first working fluid comprises at least one fluoroalkane selected from the group consisting of HFC-32, HFC-125, HFC-134a, HFC-134, HFC-143a, HFC-152a, HFC-161, HFC-227ca, HFC-245cb, HFC-236fa, HFC-236ea and HFC-227ea.

21. The heat pump apparatus of claim 18 wherein the first working fluid comprises at least one working fluid selected from hydrocarbons, NH_3, CO_2 or N_2O.

22. The heat pump apparatus of claim 18, wherein the working fluid of the cascade stage preceding the final cascade stage comprises at least one fluoroolefin selected from the group consisting of HFO-1234yf, E-HFO-1234ze, E-HFO-1234ye, HFO-1336yf, HFO-1243yf, Z-HFO-1234ze, HCFO-1233xf, and HFC-1243zf.

23. The heat pump apparatus of claim 18 wherein the working fluid of the cascade stage preceding the final cascade stage comprises at least one fluoroalkane selected from the group consisting of HFC-32, HFC-

125, HFC-134a, HFC-134, HFC-143a, HFC-152a, HFC-161, HFC-227ca, HFC-245cb, HFC-236fa, HFC-236ea and HFC-227ea.

24. The heat pump apparatus of claim 18 wherein the working fluid of the cascade stage preceding the final cascade stage comprises at least one working fluid selected from hydrocarbons, NH_3, CO_2 or N_2O.

25. The method of claim 11 or the apparatus of claim 17 wherein said dynamic compressor is selected from the group consisting of axial and centrifugal.

26. The method of claim 11 or the apparatus of claim 17 wherein said positive displacement compressor is selected from the group consisting of reciprocating, screw and scroll.

27. The method of claim 18 wherein the working fluid heater is an evaporator.

28. A method for replacing CFC-12, CFC-114, HCFC-124, HCFC-22, HFC-134a, HFC-236fa, HFC-245fa, hydrocarbons, HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze, HFO-1243zf or blends containing HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze or HFO-1243zf as the working fluid in a heat pump or chiller designed for said working fluid comprising providing a replacement working fluid comprising E-HFO-1336mzz.

29. The method of claim 28 wherein said heat pump is a high temperature heat pump having a working fluid cooler or condenser operating temperature above about 50°C.

30. The method of claim 28 wherein the working fluid being replaced is HFC-236fa, HCFC-124, HFC-134a or CFC-12, HCFC-22, HFO-1234yf, E-HFO-1234ze, HFO-1243zf or blends containing HFO-1234yf or E-HFO-1234ze or HFO-1243zf and wherein the maximum feasible condensing temperature is increased above that achievable with said replaced working fluid.

31. The method of claim 30, wherein the maximum feasible condensing temperature is increase to about 118°C.

32. The method of claim 28 wherein the chiller designed for said working fluid is converted to a heat pump.

33. A method for supplying simultaneous heating and cooling in a cascade heat pump system comprising providing a low temperature cascade stage containing a working fluid selected from the group consisting of NH_3, CO_2, N_2O, HFC-32, HFC-125, HFC-143a, HFC-227ea, HFC-227ca, HFC-245cb, HFC-236fa, HFC-236ea, HFO-1234yf, E-HFO-1234ze, HFO-1243zf, E-HFO-1234ye, HFO-1336yf, HFO-1243yf, Z-HFO-1234ze, HCFO-1233xf, HFC-134a, HFC-134, HFC-161, HFC-152a, hydrocarbons and mixtures thereof; and providing a high temperature cascade stage containing a working fluid comprising E-HFO-1336mzz; wherein said low temperature cascade stage and said high temperature cascade stage are in thermal contact.

34. A composition comprising: (i) a working fluid consisting essentially of E-HFO-1336mzz; and (ii) a stabilizer to prevent degradation at temperatures of 50°C or above, or (iii) a lubricant suitable for use at 50°C or above, or both (ii) and (iii).

35. A method for replacing HCFC-22 working fluid in a heat pump or chiller designed for HCFC-22 working fluid comprising providing a replacement working fluid comprising E-HFO-1336mzz.

36. A method for replacing a working fluid comprising HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze or HFO-1243zf and optionally one or more saturated hydrofluorocarbons or hydrocarbons in a heat pump or chiller designed for said working fluid comprising providing a replacement working fluid comprising E-HFO-1336mzz.

37. A method for supplying simultaneous heating and cooling in a cascade heat pump system comprising providing a low temperature cascade stage containing a working fluid selected from the group consisting of NH_3, CO_2, N_2O, HFC-32, HFC-125, HFC-143a, HFC-227ea, HFC-227ca, HFC-245cb, HFC-236fa, HFC-236ea, HFO-1234yf, E-HFO-1234ze, HFO-1243zf, E-HFO-1234ye, HFO-1336yf,

HFO-1243yf, Z-HFO-1234ze, HCFO-1233xf, HFC-134a, HFC-134, HFC-161, HFC-152a, hydrocarbons, and mixtures thereof; and providing a high temperature cascade stage containing a working fluid comprising E-HFO-1336mzz; wherein said low temperature cascade stage and said high temperature cascade stage are in thermal contact.