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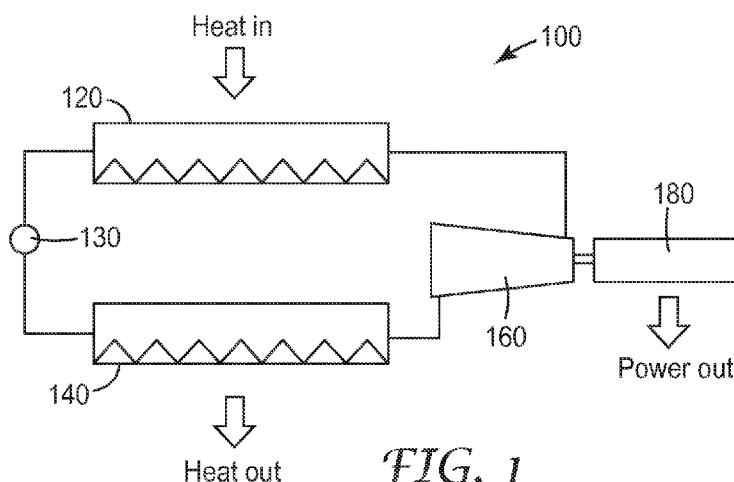
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[Continued on next page]

- (54) **Title:** FLUORINATED OXIRANES AS ORGANIC RANKINE CYCLE WORKING FLUIDS AND METHODS OF USING SAME

**FIG. 1**

- (57) **Abstract:** A process and an apparatus for converting thermal energy into mechanical energy in a Rankine cycle is provided. The process and apparatus include a working fluid that comprises a fluorinated oxirane. The fluorinated oxirane can contain substantially no hydrogen atoms bonded to carbon atoms and can have from about 4 to about 9 carbon atoms. The process can drive a turbine and, in some embodiments, generate electricity.



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**FLUORINATED OXIRANES AS ORGANIC RANKINE CYCLE WORKING FLUIDS
AND METHODS OF USING SAME**

5 **Field**

This disclosure relates to the use of fluorinated oxiranes as Rankine cycle working fluids.

Background

Rankine cycle systems are commonly used for generating electrical power that can then be
10 provided to a power distribution system, or grid for residential and commercial use. The electrical
power is generated by converting thermal energy into mechanical energy and then mechanical
energy into electrical energy. Closed Rankine systems are known that include a heat source such
as a boiler or evaporator of a motive fluid (working fluid), a turbine fed with the vapor from the
boiler to drive a generator or other load, a condenser for condensing the exhaust vapors from the
15 turbine, and a means to pump the recycled condensed fluid back to the heat source. U. S. Pat. No.
3,393,515 (Tabor et al.) describes a self-starting power generating unit which operates on a closed
Rankine cycle. The motive fluid that has been used in such systems has often been water. The
heat source has been any form of fossil fuel, e.g., oil, coal, or natural gas.

Organic working fluids can boil at temperatures up to the critical temperature above which
20 there is no boiling, fluids with higher critical temperatures result in higher Rankine cycle
efficiency. Typically, fluids such as 1,1,1,3,3-pentafluoropropane (R245fa Refrigerant, available
from Honeywell, Morristown, NJ under the trade designation GENETRON) has been used in
Rankine cycle system devices. More recently, other perfluorinated ketones having a higher
critical temperature than R245fa (critical temperature of 150°C) have been considered for use in
25 Rankine cycle devices since these materials have a higher critical temperature than R245fa. For
example, U. S. Pat. No. 7,100,380 (Brasz et al.) discloses organic Rankine cycle systems that use
other perfluorinated ketones with higher thermodynamic Rankine cycle efficiency than R245fa.
For example, Brasz et al. discloses the use of $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ and other related compounds
as Rankine working fluids.

30 The use of fluorinated oxiranes for fire extinguishing has been disclosed, for example, in
U.S.S.N. 61/431,119 entitled "Fluorinated Oxiranes as Fire Extinguishing Compositions and
Methods of Extinguishing Fires Therewith", filed January 10, 2011. The use of fluorinated
oxiranes as dielectric fluids has been disclosed, for example, in U.S.S.N. 61/435,867 entitled
"Fluorinated Oxiranes as Dielectric Fluids", filed January 25, 2011. Lubricants containing
35 fluorinated oxiranes has been disclosed, for example, in U.S.S.N. 61/448,826 entitled "Lubricant

Compositions Containing Fluorooxiranes", filed March 10, 2011. The use of fluorinated oxiranes as heat transfer fluids is disclosed in Applicants' copending application, U. S. Attorney Docket No., 67218US002, entitled "Fluorinated Oxiranes as Heat Transfer Fluids", which was filed on the same date herewith.

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Summary

There continues to be a need for organic Rankine cycle working fluids that have ever higher critical pressures and temperatures as well as good thermal stabilities. There is a need for working fluids that are less harmful to the environment and that have acceptable environmental properties and are nonflammable. There is also a need for working fluids that are more efficient in energy transfer and can still be used in systems that have simple equipment design.

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In one aspect, a process for converting thermal energy into mechanical energy in a Rankine cycle is provided that includes the steps of vaporizing a working fluid with a heat source to form a vaporized working fluid, expanding the vaporized working fluid through a turbine, cooling the vaporized working fluid using a cooling source to form a condensed working fluid, and pumping the condensed working fluid, wherein the working fluid comprises a fluorinated oxirane. The fluorinated oxirane can contain substantially no hydrogen atoms bonded to carbon atoms and can have a total of from about 4 to about 9 carbon atoms. In some embodiments, the fluorinated oxirane can contain 6 carbon atoms. The fluorinated oxirane can have a critical temperature of greater than about 150°C.

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In another aspect, a process for recovering waste heat is provided that includes passing a liquid working fluid through a heat exchanger in communication with a process that produces waste heat to produce a vaporized working fluid, removing the vaporized working fluid from the heat exchanger, passing the vaporized working fluid through an expander, wherein the waste heat is converted into mechanical energy, and cooling the vaporized working fluid after it has been passed through the expander, wherein the fluorinated oxirane compound contains substantially no hydrogen atoms bonded to carbon atoms.

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Finally, in another aspect, an apparatus for converting thermal energy into mechanical energy in a Rankine cycle is provided that includes a working fluid, a heat source to vaporize the working fluid and form a vaporized working fluid, a turbine through which the vaporized working fluid is passed thereby converting thermal energy into mechanical energy, a condenser to cool the vaporized working fluid after it is passed through the turbine, and a pump to recirculate the working fluid, wherein the working fluid comprises a fluorinated oxirane.

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In this disclosure:

"critical temperature and critical pressure" refers to the temperature and pressure at which the density of the vapor of a liquid in a sealed system is the same as that of the liquid.

"in-chain heteroatom" refers to an atom other than carbon (for example, oxygen and nitrogen) that is bonded to carbon atoms in a carbon chain so as to form a carbon-heteroatom-carbon chain;

"device" refers to an object or contrivance which is heated, cooled, or maintained at a predetermined temperature;

"inert" refers to chemical compositions that are generally not chemically reactive under normal conditions of use;

"fluorinated" refers to hydrocarbon compounds that have one or more C-H bonds replaced by C-F bonds;

"oxirane" refers to a substituted hydrocarbon that contains at least one epoxy group, and

"perfluoro-" (for example, in reference to a group or moiety, such as in the case of "perfluoroalkylene" or "perfluoroalkylcarbonyl" or "perfluorinated") means completely fluorinated such that, except as may be otherwise indicated, there are no carbon-bonded hydrogen atoms replaceable with fluorine.

The provided processes and apparatuses that include fluorinated oxiranes as organic Rankine cycle working fluids can have ever lower boiling points, higher critical pressures and temperatures as well as good thermal stabilities compared to conventionally used fluorinated compositions with comparable numbers of carbon atoms. The provided Rankine cycle working fluids can be more efficient in energy transfer and can still be used in systems that have simple equipment design.

The above summary is not intended to describe each disclosed embodiment of every implementation of the present invention. The brief description of the drawings and the detailed description which follows more particularly exemplify illustrative embodiments.

Brief Description of the Drawings

Fig. 1 is a schematic illustration of an apparatus for converting thermal energy into mechanical energy in a Rankine cycle.

Fig. 2 is a schematic illustration of a Rankine cycle apparatus that includes a recuperator.

Fig. 3 is a graph (Temperature-Entropy Diagram) for an embodiment of the provided process.

Detailed Description

In the following description, reference is made to the accompanying set of drawings that form a part of the description hereof and in which are shown by way of illustration several specific embodiments. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present invention. The following detailed description, therefore, is not to be taken in a limiting sense.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein. The use of numerical ranges by endpoints includes all numbers within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

A process for converting thermal energy into mechanical energy in a Rankine cycle is provided that includes a working fluid comprising a fluorinated oxirane. Referring to Fig. 1, typical Rankine cycle system 100 is shown that includes evaporator/boiler 120 which receives heat from an external source. Evaporator/boiler 120 vaporizes an organic Rankine working fluid contained within closed system 100. Rankine cycle system 100 also includes turbine 160 which is driven by the vaporized working fluid in the system and is used to turn generator 180 thus producing electrical power. The vaporized working fluid is then channeled through condenser 140 removing excess heat and reliquifying the liquid working fluid. Power pump 130 increases the pressure of liquid leaving condenser 140 and also pumps it back into evaporator/boiler 120 for further use in the cycle. Heat released from condenser 140 can then be used for other purposes including driving a secondary Rankine system (not shown).

It is generally desirable to have fluids with saturated vapor curves that are either isentropic or have positive slope. In cases where the saturated vapor curve has a positive slope, Rankine cycle efficiency can be improved through the use of an extra heat exchanger (or recuperator) to recover heat from vapor exiting the expander and using the recovered heat to pre-heat liquid coming out of the pump. Fig. 2 is an illustration of Rankine cycle system that includes a recuperator.

Referring to Fig. 2, Rankine cycle system 200 is shown that includes evaporator/boiler 220 which receives heat from an external source. Evaporator/boiler 220 vaporizes an organic Rankine working fluid contained within closed system 200. Rankine cycle system 200 also includes

turbine 260 which is driven by the vaporized working fluid in the system and is used to turn generator 270 thus producing electrical power. The vaporized working fluid is then channeled through recuperator 280 removing some excess heat and from there to the condenser 250, where the working fluid condenses back to liquid. Power pump 240 increases the pressure of liquid leaving condenser 250 and also pumps it back into recuperator 280, where it is preheated before going back into the evaporator/boiler 220 for further use in the cycle. Heat released from condenser 250 can then be used for other purposes including driving a secondary Rankine system (not shown).

The provided apparatuses and processes include fluorinated oxiranes. Fluorinated oxiranes useful in the provided compositions and processes can be oxiranes that have a carbon backbone which is fully fluorinated (perfluorinated), i.e., substantially all of the hydrogen atoms in the carbon backbone have been replaced with fluorine or oxiranes that can have a carbon backbone which is fully or partially fluorinated having, in some embodiments, up to a maximum of three hydrogen atoms, or a combination thereof. The use of fluorinated oxiranes in an apparatus that includes a device and a mechanism for transferring heat to or from the device is disclosed in Applicants' copending application, U. S. Attorney Docket No. 67218US002, which has been filed on the same day herewith.

In addition to providing the required thermophysical properties for use in organic Rankine systems, the fluorinated oxiranes also demonstrate desirable environmental benefits. Many compounds that display high stability in use have also been found to be quite stable in the environment. Perfluorocarbons and perfluoropolyethers exhibit high stability but also have been shown to have long atmospheric lifetimes which result in high global warming potentials. The atmospheric lifetimes of C_6F_{14} and $CF_3OCF(CF_3)CF_2OCF_2OCF_3$ are reported as 3200 years and 800 years, respectively (see *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp, 2007.). The fluorinated oxiranes have been found to degrade in the environment on timescales that result in significantly reduced atmospheric lifetimes and lower global warming potentials compared to perfluorocarbons and perfluoropolyethers. Based on kinetic studies for reaction with hydroxyl radical, 2,3-difluoro-2-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-3-trifluoromethyl-oxirane has an estimated atmospheric lifetime of 20 years. In similar kinetic studies, 2-fluoro-2-pentafluoroethyl-3,3-bis-trifluoromethyl-oxirane demonstrates an estimated atmospheric lifetime of 77 years. As a result of their shorter atmospheric lifetimes, fluorinated

oxiranes have lower global warming potentials and would be expected to make significantly less contribution to global warming as compared to perfluorocarbons and perfluoropolyethers.

The provided fluorinated oxiranes can be derived from fluorinated olefins that have been oxidized with epoxidizing agents. In the provided fluorinated oxirane compositions the carbon backbone includes the whole carbon framework including the longest hydrocarbon chain (main chain) and any carbon chains branching off of the main chain. In addition, there can be one or more catenated heteroatoms interrupting the carbon backbone such as oxygen and nitrogen, for example ether or trivalent amine functionalities. The catenated heteroatoms are typically not directly bonded to the oxirane ring. In these cases the carbon backbone includes the heteroatoms and the carbon framework attached to the heteroatom.

Typically, the majority of halogen atoms attached to the carbon backbone are fluorine; most typically, substantially all of the halogen atoms are fluorine so that the oxirane is a perfluorinated oxirane. The provided fluorinated oxiranes can have a total of 4 to 12 carbon atoms. Representative examples of fluorinated oxirane compounds suitable for use in the provided processes and compositions include 2,3-difluoro-2,3-bis-trifluoromethyl-oxirane, 2,2,3-trifluoro-3-pentafluoroethyl-oxirane, 2,3-difluoro-2-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-3-trifluoromethyl-oxirane, 2-fluoro-2-pentafluoroethyl-3,3-bis-trifluoromethyl-oxirane, 1,2,2,3,3,4,4,5,5,6-decafluoro-7-oxa-bicyclo[4.1.0]heptane, 2,3-difluoro-2-trifluoromethyl-3-pentafluoroethyl-oxirane, 2,3-difluoro-2-nonafluorobutyl-3-trifluoromethyl-oxirane, 2,3-difluoro-2-heptafluoropropyl-3-pentafluoroethyl-oxirane, 2-fluoro-3-pentafluoroethyl-2,3-bis-trifluoromethyl-oxirane, 2,3-bis-pentafluoroethyl-2,3-bis-trifluoromethyl-oxirane, 2,3-bis-trifluoromethyl-oxirane, 2-pentafluoroethyl-3-trifluoromethyl-oxirane, 2-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-3-trifluoromethyl-oxirane, 2-nonafluorobutyl-3-pentafluoroethyl-oxirane, 2-fluoro-2-trifluoromethyl-oxirane, 2,2-bis-trifluoromethyl-oxirane, 2-fluoro-3-trifluoromethyl-oxirane, 2-heptafluoroisopropylloxirane, 2-heptafluoropropylloxirane,

2-nonafluorobutylloxirane, 2-tridecafluorohexylloxirane, and oxiranes of HFP trimer including 2-pentafluoroethyl-2-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-3,3-bis-trifluoromethyl-oxirane, 2-fluoro-3,3-bis-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-2-trifluoromethyl-oxirane, 2-fluoro-3-heptafluoropropyl-2-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-3-trifluoromethyl-oxirane, 2-(1,2,2,3,3,3-hexafluoro-1-trifluoromethyl-propyl)-2,3,3-tris-trifluoromethyl-oxirane and 2-[1,1,2,3,3,3-hexafluoro-2-(trifluoromethyl)propyl]-2-(trifluoromethyl)oxirane.

The provided fluorinated oxirane compounds can be prepared by epoxidation of the corresponding fluorinated olefin using an oxidizing agent such as sodium hypochlorite, hydrogen peroxide or other well known epoxidizing agent such as peroxycarboxylic acids such as meta-chloroperoxybenzoic acid or peracetic acid. The fluorinated olefinic precursors can be directly available as, for example, in the cases of 1,1,1,2,3,4,4,4-octafluoro-but-2-ene (for making 2,3-difluoro-2,3-bis-trifluoromethyl oxirane), 1,1,1,2,3,4,4,5,5,5-decafluoro-pent-2-ene or 1,2,3,3,4,4,5,5,6,6 decafluoro-cyclohexene (for making 1,2,2,3,3,4,4,5,5,6-decafluoro-7-oxa-bicyclo[4.1.0]heptane). Other useful fluorinated olefinic precursors can include oligomers of hexafluoropropene (HFP) and tetrafluoroethylene (TFE) such as dimers and trimers. The HFP oligomers can be prepared by contacting 1,1,2,3,3,3-hexafluoro-1-propene (hexafluoropropene) with a catalyst or mixture of catalysts selected from the group consisting of cyanide, cyanate, and thiocyanate salts of alkali metals, quaternary ammonium, and quaternary phosphonium in the presence of polar, aprotic solvents such as, for example, acetonitrile. The preparation of these HFP oligomers is disclosed, for example, in U. S. Pat. No. 5,254,774 (Prokop). Useful oligomers include HFP trimers or HFP dimers. HFP dimers include a mixture of cis- and trans- isomers of perfluoro-4-methyl-2-pentene as indicated in Table 1 in the Example section below. HFP trimers include a mixture of isomers of C₉F₁₈. This mixture has six main components that are also listed in Table 1 in the Example section.

The provided fluorinated oxirane compounds can have a boiling point in a range of from about -10°C to about 150°C. In some embodiments, the fluorinated oxirane compounds can have a boiling point in the range of from about 0°C to about 55°C. Some exemplary materials and their boiling point ranges are disclosed in the Examples section below.

The provided process for converting thermal energy into mechanical energy in a Rankine cycle includes using a heat source to vaporize a working fluid comprising fluorinated oxiranes to form a vaporized working fluid. In some embodiments, the heat is transferred from the heat source to the working fluid in an evaporator or boiler. The vaporized working fluid is pressurized and can be used to do work by expansion. The heat source can be of any form such as from fossil fuels, e.g., oil, coal, or natural gas. Additionally, in some embodiments, the heat source can come from nuclear power, solar power, or fuel cells. In other embodiments, the heat can be "waste heat" from other heat transfer systems that would otherwise be lost to the atmosphere. The "waste heat", in some embodiments, can be heat that is recovered from a second Rankine cycle system from the condenser or other cooling device in the second Rankine cycle.

An additional source of "waste heat" can be found at landfills where methane gas is flared off. In order to prevent methane gas from entering the environment and thus contributing to global

warming, the methane gas generated by the landfills can be burned by way of "flares" producing carbon dioxide and water which are both less harmful to the environment in terms of global warming potential than methane. Other sources of "waste heat" that can be useful in the provided processes are geothermal sources and heat from other types of engines such as gas turbine engines that give off significant heat in their exhaust gases and to cooling liquids such as water and lubricants.

In the provided process, the vaporized working fluid is expanded through a device that can convert the pressurized working fluid into mechanical energy. In some embodiments, the vaporized working fluid is expanded through a turbine which can cause a shaft to rotate from the pressure of the vaporized working fluid expanding. The turbine can then be used to do mechanical work such as, in some embodiments, operate a generator, thus generating electricity. In other embodiments, the turbine can be used to drive belts, wheels, gears, or other devices that can transfer mechanical work or energy for use in attached or linked devices.

After the vaporized working fluid has been converted to mechanical energy the vaporized (and now expanded) working fluid can be condensed using a cooling source to liquefy for reuse. The heat released by the condenser can be used for other purposes including being recycled into the same or another Rankine cycle system, thus saving energy. Finally, the condensed working fluid can be pumped by way of a pump back into the boiler or evaporator for reuse in a closed system.

The desired thermodynamic characteristics of organic Rankine cycle working fluids are well known to those of ordinary skill and are discussed, for example, in U. S. Pat. Appl. Publ. No. 2010/0139274 (Zyhowski et al.). The greater the difference between the temperature of the heat source and the temperature of the condensed liquid or a provided heat sink after condensation, the higher the Rankine cycle thermodynamic efficiency. The thermodynamic efficiency is influenced by matching the working fluid to the heat source temperature. The closer the evaporating temperature of the working fluid to the source temperature, the higher the efficiency of the system. Toluene can be used, for example, in the temperature range of 79°C (boiling point of toluene) to about 260°C, however toluene has toxicological and flammability concerns. Fluids such as 1,1-dichloro-2,2,2-trifluoroethane and 1,1,1,3,3-pentafluoropropane can be used in this temperature range as an alternative. But 1,1-dichloro-2,2,2-trifluoroethane can form toxic compounds below 300°C and need to be limited to an evaporating temperature of about 93°C to about 121°C. Thus, there is a desire for other environmentally-friendly Rankine cycle working fluids with higher critical temperatures so that source temperatures such as gas turbine and internal combustion engine exhaust can be better matched to the working fluid. Additionally, fluids with higher heat

capacities contribute to higher Rankine cycle efficiencies due to increases thermal energy utilization—greater energy recovery from expansion.

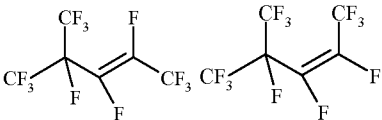
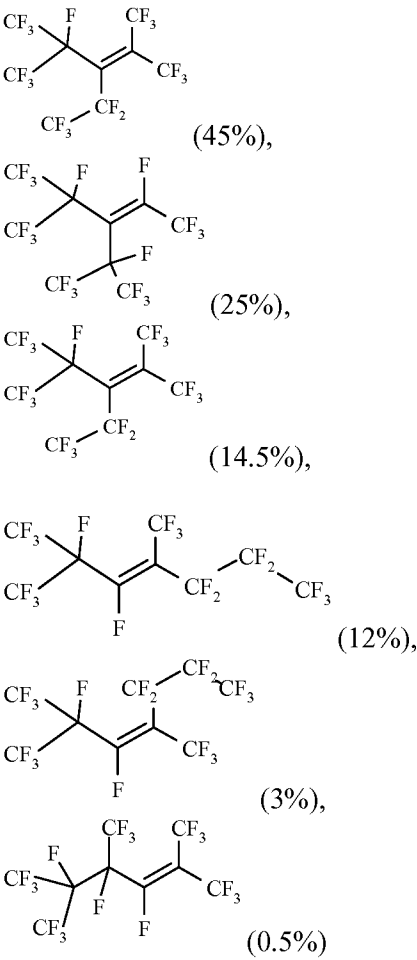
Also provided is an apparatus for converting thermal energy into mechanical energy in a Rankine cycle that includes a working fluid that includes a fluorinated oxirane, a heat source to vaporize the working fluid and form a vaporized working fluid, a turbine to convert the thermal energy (and pressure) of the vaporized working fluid into mechanical energy, a condenser to cool the vaporized working fluid after it has transferred energy to the turbine and a pump to recirculate the working fluid and to build pressure. The recirculated working fluid can then be reheated in an evaporator boiler in the provided method and as described above.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. The apparatus is typically a closed loop

Examples

Table 1

Materials

Chemical	Description	Source
1,1,1,2,3,4,5,5,5-nonafluoro-4-trifluoromethyl-pent-2-ene	HFP Dimer 2 isomers; 	3M Foam Additive FA-188, 3M, St. Paul, MN.
1,2,3,3,4,4,5,5,6,6-decafluoro-cyclohexene		Available from Sigma-Aldrich, St. Louis, MO.
HFP Trimer	HFP Trimer 6 Isomers; 	US Pat No 5,254,774
Dodecafluoro-2-methylpentan-3-one	$C_2F_5C(O)CF(CF_3)_2$	3M NOVEC 649: 3M Company, St Paul, MN
Sodium Hydroxide	NaOH	GFS Chemicals, Inc., Powell, OH
Sodium Hypochlorite	$Na^+[ClO]^-$	Alfa Aesar, Ward Hill, MA

Potassium Hydroxide	KOH	Sigma Aldrich, Milwaukee, WI
Hydrogen Peroxide	H ₂ O ₂	GFS Chemicals, Inc., Powell, OH
Acetonitrile	CH ₃ CN	Honeywell Burdick & Jackson, Morristown, NJ

Materials

Example 1 - Synthesis of 2,3-difluoro-2-(1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-3-trifluoromethyl-oxirane. (C₆F₁₂O)

In a 1.5 liter glass reactor fitted with a mixer and a cooling jacket, 400 grams of acetonitrile, 200 grams of 1,1,1,2,3,4,5,5,5-nonafluoro-4-trifluoromethyl-pent-2-ene and 150 grams of 50% potassium hydroxide were added. The reactor temperature was controlled at 0°C using the reactor cooling jacket. Then 100 grams of 50% hydrogen peroxide was slowly added to the reactor under strong mixing while controlling the reactor temperature at 0°C. After all the hydrogen peroxide was added within about 2 hours, the mixer was turned off to allow the product crude to phase split from solvent and aqueous phases. 155 grams of the product crude was collected from the bottom product phase. The product crude was then washed with 200 grams of water to remove solvent acetonitrile and then purified in a 40-tray Oldershaw fractionation column with condenser being cooled to 15°C. The fractionation column was operated in such a way so that the reflux ratio (the distillate flow rate going back to the fractionation column to the distillate flow rate going to the product collection cylinder) was at 10:1. The final product was collected as the condensate when the head temperature in the fractionation column was between 52°C and 53°C.

The 90 grams of the final product collected from the method above was analyzed by 376.3 MHz ¹⁹F-NMR spectra and identified as a mixture of 2,3-difluoro-2-(1,2,2,2-tetrafluoro-1-trifluoro-methyl-ethyl)-3-trifluoromethyl-oxirane, 95.8% and 2.2% of 2-fluoro-2-pentafluoroethyl-3,3-bis-trifluoromethyl-oxirane.

Example 2 - Oxirane Synthesis and Purification of 1,2,2,3,3,4,4,5,5,6-decafluoro-7-oxa-bicyclo[4.1.0]heptane. c(C₆F₁₂O)

In a 1.5 liter glass reactor fitted with a mixer and a cooling jacket, 400 grams of acetonitrile, 200 grams of 1,2,3,3,4,4,5,5,6,6-decafluoro-cyclohexene (89.3% purity) and 150 grams of 50% potassium hydroxide were added. The reactor temperature was controlled at 0°C using the reactor cooling jacket. Then 100 grams of 50% hydrogen peroxide was slowly added to the reactor under strong mixing while controlling the reactor temperature at 0°C. After all the hydrogen peroxide was added within about 2 hours, the mixer was turned off to allow the product

crude to phase split from solvent and aqueous phases. 100 grams of the product crude was collected from the bottom product phase. The product crude was then washed with 100 grams of water to remove solvent acetonitrile and then purified in a 40-tray Oldershaw fractionation column with condenser being cooled to 15°C. The fractionation column was operated in such a way that the reflux ratio (the distillate flow rate going back to the fractionation column to the distillate flow rate going to the product collection cylinder) was at 10:1. The final product was collected as the condensate when the head temperature in the fractionation column was between 47°C and 55°C.

The 70 grams of the final product collected from the method above was analyzed by 376.3 MHz ¹⁹F-NMR spectra and identified as 1,2,2,3,3,4,4,5,5,6-decafluoro-7-oxa-bicyclo[4.1.0]heptane with a purity of 94.1% with an additional 2.6% isomers.

Example 3 - C₉ Oxirane Synthesis and purification of HFP Trimer-oxirane (C₉F₁₈O).

In a 1.5 liter glass reactor fitted with a mixer and a cooling jacket, 400 grams of acetonitrile, 200 grams of HFP Trimer (C₉F₁₈), and 150 grams of 50% potassium hydroxide were added. The reactor temperature was controlled at 0°C using the reactor cooling jacket. Then 100 grams of 50% hydrogen peroxide was slowly added to the reactor under strong mixing while controlling the reactor temperature between 0°C and 20°C. After all the hydrogen peroxide was added within about 2 hours, the mixer was turned off to allow the product crude to phase split from solvent and aqueous phases. 180 grams of the product crude was collected from the bottom product phase. The product crude was then washed with 200 grams of water to remove solvent acetonitrile and then purified in a 40-tray Oldershaw fractionation column with condenser being cooled to 15°C. The fractionation column was operated in such a way so that the reflux ratio (the distillate flow rate going back to the fractionation column to the distillate flow rate going to the product collection cylinder) was at 10:1. The final product was collected as the condensate when the head temperature in the fractionation column was between 120°C and 122°C.

The 150 grams of the final product collected from the method above was analyzed by 376.3 MHz ¹⁹F-NMR spectra and identified as oxiranes of HFP trimer (C₉F₁₈O) with 5 isomeric forms. The sum of all 5 isomers had a purity of 99.4%.

Table II shows some thermophysical properties of exemplary fluorinated oxiranes and a comparative material (docecafluoro-2-methylpentan-3-one).

Example 4 – Synthesis of 2-nonafluorobutyloxirane (C₄F₉CH(O)CH₂).

The oxirane was prepared according to a modification of the procedure of WO2009/096265 (Daikin Industries Ltd.). A 500 mL, magnetically stirred, three-necked round

bottom flask was equipped with a water condensor, thermocouple and an addition funnel. The flask was cooled in a water bath. Into the flask were placed $\text{C}_4\text{F}_9\text{CH}=\text{CH}_2$ (50 g, 0.2 mol, Alfa Aesar), N-bromosuccinimide (40 g, 0.22 mol, Aldrich Chemical Company) and dichloromethane as the solvent (250 mL). Chlorosulfonic acid (50 g, 0.43 mol, Alfa Aesar) was placed in the addition funnel and added slowly to the stirred reaction mixture while keeping the reaction temperature below 30 °C. After the addition was completed the reaction mixture was held at ambient temperature for 16 hours. The entire reaction mixture was then poured carefully onto ice, the lower dichloromethane phase separated and washed once more with an equal volume of water and the solvent removed by rotary evaporation yielding 82 g of the chlorosulfite $\text{C}_4\text{F}_9\text{CHBrCH}_2\text{OSO}_2\text{Cl}$ in about 65% purity by glc and which contained some $\text{C}_4\text{F}_9\text{CHBrCH}_2\text{Br}$. The chlorosulfite mixture was used without further purification in the next step.

The chlorosulfite, benzyltrimethylammonium chloride (0.6 g, 0.003 mol, Alfa Aesar) and water (350 mL) were placed in a 1 L, magnetically stirred, three-necked round bottom flask which was equipped with a water condensor, thermocouple and an addition funnel. A solution of potassium iodide (66.3 g, 0.4 mol, EMD Chemicals Inc.) dissolved in water (66 mL) was placed in the separatory funnel and added to the chlorosulfite solution dropwise over about 1.5 hours and the mixture stirred for 16 hours at ambient temperature. Dichloromethane (300 mL) was then added, the mixture filtered and the filter cake washed with an additional 100 mL of dichloromethane. The dichloromethane layer was separated and the remaining aqueous layer extracted with an additional 200 mL of dichloromethane. The dichloromethane solvent was then removed by rotary evaporation. The residue, combined with material from another preparation, was distilled bp = 66-70 °C/20 torr and the distillate once again dissolved in dichloromethane and washed one time with 5% aqueous sodium bisulfite to remove iodine and the solvent removed by rotary evaporation. At this stage the desired product bromohydrin (82 g) $\text{C}_4\text{F}_9\text{CHBrCH}_2\text{OH}$ had a purity of 87% and contained about 5% $\text{C}_4\text{F}_9\text{CHBrCH}_2\text{Br}$ and 8% $\text{C}_4\text{F}_9\text{CHClCH}_2\text{Br}$.

The bromohydrin (82 g), diethyl ether solvent (200 mL) and tetrabutylammonium bromide (3.0 g, 0.009 mol, Aldrich) were placed in a 500 mL, magnetically stirred, round bottom flask equipped with a condensor and thermocouple. To this mixture was added all at once a solution of sodium hydroxide (24 g, 0.6 mol) in water (33 g). The mixture was stirred vigorously for four hours. The ether solution was then washed once with saturated sodium chloride solution and once with 5% HCl solution and subsequently dried over magnesium sulfate and the residue fractionally distilled through a concentric tube column with the fraction boiling at 101°C collected to give a product (40.9 g) which was 88.5% the desired oxirane $\text{C}_4\text{F}_9\text{CH}(\text{O})\text{CH}_2$ and 7.3% bromoolefin $\text{C}_4\text{F}_9\text{CBr}=\text{CH}_2$. Final purification of the epoxide by removal of most of the bromoolefin was

carried out by reaction of the oxirane/bromoolefin mixture, which was degassed three times under nitrogen using a Firestone valve connected to a source of dry nitrogen and mineral oil bubbler, with 2,2'-azobis(2-methylpropionitrile) [0.5 g, 0.003 mol, Aldrich] and bromine [4.0 g, 0.025 mol, Aldrich] at 65 °C for eight hours. The reaction mixture was treated with an aqueous solution of 5% by weight sodium bisulfite to remove the excess bromine, the phases were separated and the lower phase fractionally distilled through a concentric tube column to afford the final oxirane (25 g) in 97.9% purity (b.p. = 102°C). The product identity was confirmed by GCMS, H-1 and F-19 NMR spectroscopy.

Example 5 – Synthesis of 2-tridecafluorohexyloxirane ($C_6F_{13}CH(O)CH_2$).

A 1L, magnetically stirred, three-necked round bottom flask was equipped with a water condensor, thermocouple and an addition funnel. The flask was cooled in a water bath. Into the flask were placed fuming sulfuric acid (20% SO_3 content) (345 g, 0.86 mol SO_3 , Aldrich) and bromine (34.6 g, 0.216 mol, Aldrich). Into the addition funnel was placed $C_6F_{13}CH=CH_2$ (150 g, 0.433 mol, Alfa Aesar) which was added to the acid solution over a two hour period. There was no noticeable exotherm. The reaction mixture was stirred at ambient temperature for 16 hours. Water (125 g) was placed in the separatory funnel and added very cautiously over about a two hour period. The initial 5-10 g addition was extremely exothermic. Once the addition was complete, more water (50 g) was added all at once and the reaction mixture heated to 90°C for 16 hours. Diethyl ether (300 mL) was added to the reaction mixture and the two phases separated with the lower phase containing the product. The remaining aqueous phase was extracted once more with ether (150 mL), the upper ether phase separated and combined with the previous lower phase. The ether layer was washed with 5% by weight aqueous potassium hydroxide solution and the solvent removed by rotary evaporation to give 112 g of a white crystalline solid which was about 72% $C_6F_{13}CHBrCH_2OH$, 8% $C_6F_{13}CHBrCH_2Br$ and 19% $(C_6F_{13}CHBrCH_2O)SO_2$. This solid was distilled and the fraction collected (36 g) of boiling range = 68-74 °C/6 torr which was found to be 90.7% the desired bromohydrin and 9.3% the dibromide.

The bromohydrin mixture was then placed in a 250 mL, magnetically stirred, round bottom flask equipped with a water condensor and thermocouple along with tetrabutylammonium bromide (1.5 g, 0.005 mol, Aldrich) dissolved in 5 g water and a solution of 8.2 g of sodium hydroxide (0.2 mol) dissolved in 15 g water. After one hour of vigorous stirring the reaction mixture was analyzed by glc which showed about a 40% conversion of the bromohydrin to the oxirane. The reaction was stirred for an additional 5 hours. The lower aqueous phase was separated and the remaining ether phase washed once with dilute aqueous hydrochloric acid,

prepared by adding a few drops of 2N aqueous HCl to 50 mL water, dried over magnesium sulfate and distilled to afford the product oxirane (12 g) $C_6F_{13}CH(O)CH_2$ in 98.3% purity (b.p. = 144 °C) and 1.5% bromoolefin $C_6F_{13}CBr=CH_2$. The product structure was confirmed by GCMS, H-1 and F-19 NMR.

5

Example 6 - Preparation of 2-[1,1,2,3,3,3-hexafluoro-2-(trifluoromethyl)propyl]-2-(trifluoromethyl)oxirane $((CF_3)_2CFCF_2C(CF_3)OCH_2)$

In a 600mL Parr reactor, hexafluoropropene dimer (300 g, 1.0 mol 3M Company), methanol (100 g, 3.12 mol, Aldrich) and TAPEH (t-amylperoxy-2-ethylhexanoate) (4 g, 0.017 mol) were charged. The reactor was sealed and the temperature was set to 75 deg. C. After stirring for 16 hours at temperature the reactor contents were emptied and washed with water to remove excess methanol. The fluorochemical phase that was recovered was dried over anhydrous magnesium sulfate and then filtered. This reaction was repeated two additional times to generate a total of 500g of product (2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl)pentan-1-ol). The crude reaction product was then purified by fractional distillation using a 15-tray Oldershaw column. The fluorinated alcohol product, 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl)pentan-1-ol (257 g, 0.77 mol) was charged to a 1L round bottom flask equipped with magnetic stirring, cold water condenser, thermocouple (J-Kem controller) and an addition funnel. Thionyl chloride (202.25 g, 1.7 mol, Aldrich) was charged via the addition funnel to the fluorinated alcohol at room temperature. Once the addition was complete the temperature was increased to 85 deg. C until no more offgas was observed. The water condenser was removed and a 1-plate distillation apparatus was put in place. The excess thionyl chloride was then distilled from the reaction mixture. 300g of the product was collected. This product was charged to a flask containing 150 g of potassium fluoride in 500 mL of N-methyl-pyrrolidinone solvent. The reaction mixture was then stirred overnight at 35 deg. C. The following day the reaction flask was set up for distillation and the product 3,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl)pent-1-ene was distilled from the reaction flask. A total of 140 g was collected.

In a 500mL jacketed reaction flask equipped with overhead stirring, cold water condenser, N2 bubbler and thermocouple, sodium hydroxide (2.5 g, 0.0636 mol, Aldrich), sodium hypochlorite (12% concentration 80 g, 0.127 mol), Aliquat 336 (1 g, Alfa-Aesar) were charged. The flask was cooled to 4 deg. C. The olefin, 3,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl)pent-1-ene (20 g, 0.0636 mol) was charged to the mixture which was then stirred for 2 hours. After 2 hours, stirring was stopped and a lower FC phase was separated from the mixture. A total of 20g of FC was collected. A sample of this was analyzed by ^{19}F , 1H and ^{13}C NMR which confirmed the

product structure for 2-[1,1,2,3,3,3-hexafluoro-2-(trifluoromethyl)propyl]-2-(trifluoromethyl)oxirane.

5

Table II

Thermophysical Properties of Fluorinated Oxiranes and Comparative Materials

Example	Material	Normal Boiling Point (°C)	Pour Point (°C)	Viscosity @ 25°C (x10 ⁻⁷ m ² /s)	Heat of Vaporization @ 25°C (kJ/kg)	Specific Heat Capacity (J/kg-K)	Critical Temperature (°C)	Critical Pressure (kPa)	Critical Density (kg/m ³)
Comparative 1	C ₂ F ₅ C(O)CF(CF ₃) ₂	49.3	-108	4.0	94.3	1103	168.7	1865	594.2
Example 1	C ₆ F ₁₂ O	51.7	-145	3.7	99.2	1145	180.0	2386	611.9
Example 2	cC ₆ F ₁₂ O	56.1	-88	6.6	109.8	1083	200.3	2615	601.2
Example 3	C ₉ F ₁₈ O	121.9	-103	12.5	96.9	869	236.9	1421	613.6

The critical temperature and pressure of the fluorinated oxiranes in Table II were determined from their molecular structures using the method of Wilson-Jasperson given in Reid, Prausnitz and Poling, *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, 2000. The critical densities were calculated using the method of Joback given in Reid, Prausnitz and Poling, *The Properties of Gases and Liquids*, 5th edition, McGraw-Hill, 2000. Exemplary fluorinated oxirane thermodynamic properties were derived using the Peng-Robinson equation of state (Peng, D.Y., and Robinson, D.B., *Ind. & Eng. Chem. Fund.* **15**: 59–64., 1976), with an applied volume shift for liquid densities. Inputs required for the equation of state were critical temperature, critical density, critical pressure, acentric factor, molecular weight and ideal gas heat capacity. Ideal gas heat capacity was calculated using a group contribution method (Rihani, D., Doraiswamy, L., *Ind. & Eng. Chem. Fund.*, 4, 17, 1965). For Comparative Example 1, thermophysical property data were fitted to a Helmholtz equation of state, with the functional form described in Lemmon E.W., McLinden M.O., and Wagner W., *J. Chem. & Eng. Data*, **54**: 3141-3180., 2009.

Fig. 3 shows temperature-entropy diagrams for Examples 1, 2 and 3 (Ex. 1, Ex. 2, and Ex. 3), along with Comparative Example 1 (Comp. 1). Each plot was generated using the equations of state described above for each fluid. Though all the fluids have saturated vapor lines with a positive slope, Examples 1, 2 and 3 have greater positive slopes, thereby requiring less

desuperheating (or recuperation) after expansion, which could be advantageous when sizing recuperator heat exchangers for the Rankine cycle configuration of fig. 2.

A Rankine cycle based on the configuration of fig. 1, and operating between 50°C and 140°C, was used to assess the performance of the exemplary fluorinated oxiranes and the comparative example. The Rankine cycle was modeled using the calculated thermodynamic properties from the equations of state and the procedure described in Cengel Y.A. and Boles M.A., *Thermodynamics: An Engineering Approach, 5th Edition*; McGraw Hill, 2006. The heat input for the cycle was 1000 kW, with working fluid pump and expander efficiencies taken to be 60% and 80% respectively. Results are shown in Table III. Thermal efficiencies of the exemplary fluorinated oxiranes are greater than that of the comparative example.

Table III
Calculated Rankine Cycle Performance

	Example 1 C₆F₁₂O	Example 2 cC₆F₁₂O	Example 3 C₉F₁₈O	Comparative Example 1 C₂F₅C(O)CF(CF₃)₂
Condenser Temperature [°C]	50.0	50.0	50.0	50.0
Condenser Pressure [kPa]	97.0	82.2	6.4	103.9
Boiler Temperature [°C]	140	140	140	140
Boiler Pressure [kPa]	1114.8	893.2	177.0	1069.9
Fluid Flow [kg/s]	6.0	6.0	5.8	6.2
Pump Work [kJ/kg]	1.10	0.84	0.16	1.05
Q, Boiler [kJ/kg]	168.0	166.4	173.5	161.4
Expander Work [kJ/kg]	18.14	20.30	18.32	16.71
Net Work [kJ/kg]	17.0	19.5	18.2	15.7
Net Work [kW]	101.4	117.0	104.6	97.0
Thermal Efficiency	0.101	0.117	0.105	0.097

As discussed above, for a given heat source, thermodynamic efficiency in a Rankine cycle can be improved when the boiling point of the working fluid is close to that of the temperature of the heat source. Higher critical temperatures therefore lead to greater thermodynamic efficiencies. Exemplary fluorinated oxiranes can have critical temperatures of greater than 175°C, greater than 200°C, or even greater than 230°C as shown in Table II.

Following are exemplary embodiments of fluorinated oxiranes as organic rankine cycle working fluids and methods of using same according to aspects of the present invention.

Embodiment 1 is a process for converting thermal energy into mechanical energy in a Rankine cycle comprising: vaporizing a working fluid with a heat source to form a vaporized working fluid; expanding the vaporized working fluid through a turbine; cooling the vaporized working fluid using a cooling source to form a condensed working fluid; and pumping the condensed working fluid; wherein the working fluid comprises a fluorinated oxirane.

Embodiment 2 is a process for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 1, wherein the fluorinated oxirane compound includes up to a maximum of three hydrogen atoms.

Embodiment 3 is a process for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 1, wherein the fluorinated oxirane compound contains substantially no hydrogen atoms bonded to carbon atoms.

Embodiment 4 is a process for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 1, wherein the fluorinated oxirane has a total of from about 4 to about 9 carbon atoms.

Embodiment 5 is a process for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 4, wherein the fluorinated oxirane contains 6 carbon atoms.

Embodiment 6 is a process for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 1, wherein the fluorinated oxirane has a critical temperature greater than about 150°C.

Embodiment 7 is a process for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 1, wherein the turbine generates electrical energy.

Embodiment 8 is a process for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 1, wherein the vaporized working fluid is at a pressure greater than ambient pressure.

Embodiment 9 is a process for recovering waste heat comprising: passing a liquid working fluid through a heat exchanger in communication with a process that produces waste heat to produce a vaporized working fluid; removing the vaporized working fluid from the heat exchanger; passing the vaporized working fluid through an expander, wherein the waste heat is converted into mechanical energy; and cooling the vaporized working fluid after it has been passed through the expander, wherein the fluorinated oxirane compound contains substantially no hydrogen atoms bonded to carbon atoms.

Embodiment 10 is a process for recovering waste heat comprising according to embodiment 9, wherein the fluorinated oxirane has a total of from about 4 to about 9 carbon atoms.

Embodiment 11 is a process for recovering waste heat comprising according to embodiment 10, wherein the fluorinated oxirane contains 6 carbon atoms.

Embodiment 12 is a process for recovering waste heat comprising according to embodiment 10, wherein the fluorinated oxirane has a critical temperature of greater than about 150°C.

Embodiment 13 is an apparatus for converting thermal energy into mechanical energy in a Rankine cycle comprising: a working fluid; a heat source to vaporize the working fluid and form a vaporized working fluid; a turbine through which the vaporized working fluid is passed thereby converting thermal energy into mechanical energy; a condenser to cool the vaporized working fluid after it is passed through the turbine; and a pump to recirculate the working fluid, wherein the working fluid comprises a fluorinated oxirane.

Embodiment 14 is an apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 13, wherein the working fluid is in a closed loop.

Embodiment 15 is an apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 13, wherein the fluorinated oxirane contains substantially no hydrogen atoms bonded to carbon atoms.

Embodiment 16 is an apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 15, wherein the fluorinated oxirane has a total of from about 4 to about 9 carbon atoms.

5 Embodiment 17 is an apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 16, wherein the fluorinated oxirane contains 6 carbon atoms.

10 Embodiment 18 is an apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to embodiment 13, wherein the fluorinated oxirane has a critical temperature greater than about 150°C.

15 Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows. All references cited in this disclosure are herein incorporated by reference in their entirety.

20

What is claimed is:

1. A process for converting thermal energy into mechanical energy in a Rankine cycle comprising:

5 vaporizing a working fluid with a heat source to form a vaporized working fluid;
expanding the vaporized working fluid through a turbine;
cooling the vaporized working fluid using a cooling source to form a condensed working fluid; and

pumping the condensed working fluid;
wherein the working fluid comprises a fluorinated oxirane.

10 2. A process for converting thermal energy into mechanical energy in a Rankine cycle according to claim 1, wherein the fluorinated oxirane compound includes up to a maximum of three hydrogen atoms.

15 3. A process for converting thermal energy into mechanical energy in a Rankine cycle according to claim 1, wherein the fluorinated oxirane compound contains substantially no hydrogen atoms bonded to carbon atoms.

20 4. A process for converting thermal energy into mechanical energy in a Rankine cycle according to claim 1, wherein the fluorinated oxirane has a total of from about 4 to about 9 carbon atoms.

25 5. A process for converting thermal energy into mechanical energy in a Rankine cycle according to claim 4, wherein the fluorinated oxirane contains 6 carbon atoms.

6. A process for converting thermal energy into mechanical energy in a Rankine cycle according to claim 1, wherein the fluorinated oxirane has a critical temperature greater than about 150°C.

30 7. A process for converting thermal energy into mechanical energy in a Rankine cycle according to claim 1, wherein the turbine generates electrical energy.

8. A process for converting thermal energy into mechanical energy in a Rankine cycle according to claim 1, wherein the vaporized working fluid is at a pressure greater than ambient pressure.

5 9. A process for recovering waste heat comprising:
passing a liquid working fluid through a heat exchanger in communication with a process that produces waste heat to produce a vaporized working fluid;
removing the vaporized working fluid from the heat exchanger;
10 passing the vaporized working fluid through an expander, wherein the waste heat is converted into mechanical energy; and
cooling the vaporized working fluid after it has been passed through the expander, wherein the fluorinated oxirane compound contains substantially no hydrogen atoms bonded to carbon atoms.

15 10. A process for recovering waste heat comprising according to claim 9, wherein the fluorinated oxirane has a total of from about 4 to about 9 carbon atoms.

11. A process for recovering waste heat comprising according to claim 10, wherein the fluorinated oxirane contains 6 carbon atoms.

20 12. A process for recovering waste heat comprising according to claim 10, wherein the fluorinated oxirane has a critical temperature of greater than about 150°C.

25 13. An apparatus for converting thermal energy into mechanical energy in a Rankine cycle comprising:
a working fluid;
a heat source to vaporize the working fluid and form a vaporized working fluid;
a turbine through which the vaporized working fluid is passed thereby converting thermal energy into mechanical energy;
30 a condenser to cool the vaporized working fluid after it is passed through the turbine; and
a pump to recirculate the working fluid,
wherein the working fluid comprises a fluorinated oxirane.

14. An apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to claim 13, wherein the working fluid is in a closed loop.

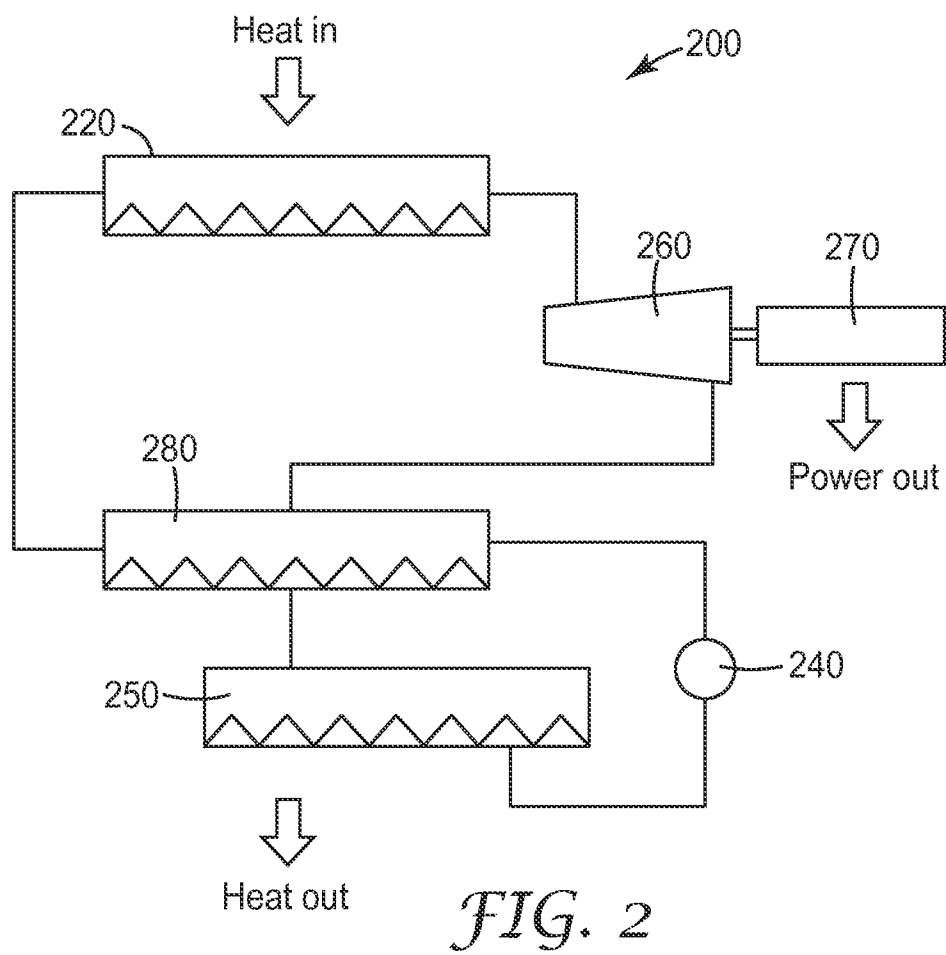
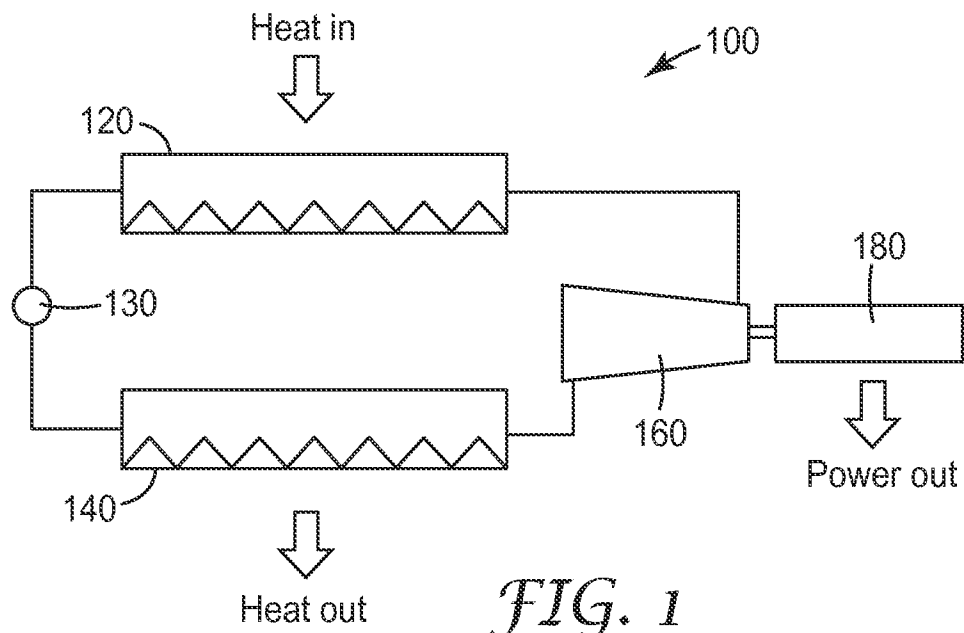
15. An apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to claim 13, wherein the fluorinated oxirane contains substantially no hydrogen atoms bonded to carbon atoms.

16. An apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to claim 15, wherein the fluorinated oxirane has a total of from about 4 to about 9 carbon atoms.

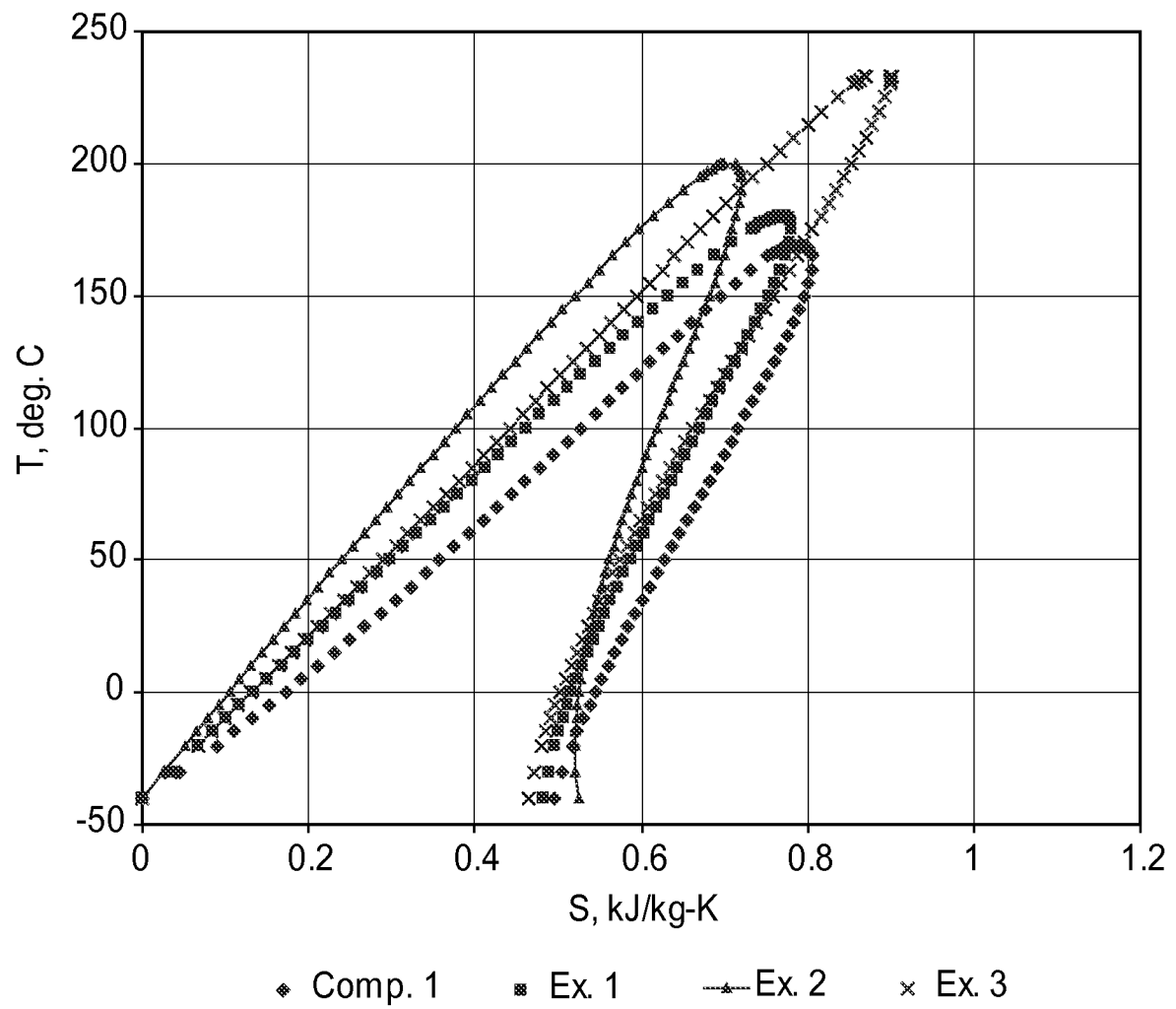
17. An apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to claim 16, wherein the fluorinated oxirane contains 6 carbon atoms.

18. An apparatus for converting thermal energy into mechanical energy in a Rankine cycle according to claim 13, wherein the fluorinated oxirane has a critical temperature greater than about 150°C.

1/2



2/2

*FIG. 3*