Energy and exergy analysis of new refrigerant mixtures in an Organic Rankine Cycle for low temperature power generation

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SYNOPSIS
This paper presents and discusses the performance of environmentally-friendly refrigerant mixtures in an Organic Rankine Cycle (ORC) for power generation. The performance has been compared at low and medium waste heat temperatures to other organic and non-organic fluids.

The refrigerant mixtures boil at extremely low temperatures and are capable of efficiently capturing waste heat at temperatures less than 27°C (80°F). The quaternary mixtures are fully HFCs and their compositions can be varied to best recover heat at temperatures up to 482°C (900°F). In this paper, energy and exergy analysis have been presented for the behaviour of the quaternary refrigerant mixtures and compared to other commonly used fluids.

Results showed that at this range of heat source temperatures the refrigerant mixtures efficiently recover waste heat and produce power at efficiencies significantly higher than with other working fluids. The results also showed that other low temperature applications are possible and economically viable with the use of these quaternary refrigerant mixtures.

INTRODUCTION

Significant amounts of excess heat are discharged into the environment by industrial facilities in the form of hot exhaust gases, high-pressure steam and grey water. In the energy recovery process a vast amount of waste heat can be recovered and converted into usable thermal heat and/or electricity, significantly lowering dependence on fossil fuels and reducing energy costs. In addition, waste heat recovery systems capture harmful pollutants that would otherwise be released into the environment.

It is estimated that energy wasted by all U.S. industrial facilities could produce power equivalent to 20% of U.S. electricity generation capacity, without burning any additional fossil fuel, and could help many industries to meet recent global warming regulations. Furthermore, by using heat recovery and Organic Rankine Cycle (ORC) technologies and tapping into other renewable resources, such as solar energy and geothermal energy as well as Ocean Thermal Energy Conversion (OTEC), our dependence on fossil fuel could be significantly reduced.

Reviews of renewable technologies [1, 2, 6] may provide some assurance to long-term funding of renewable energy facilities and lead to a resurgence in new renewable energy facilities. In the short term, there will be increasing pressure to deploy renewable energy facilities to help add generating capacity, improve system reliability and stabilise electricity prices. However, the strategic installation of these renewable energy facilities will be hindered by a lack of understanding of how they integrate into the existing fossil-based generation systems.

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Recent problems in electricity production emphasise the urgent need for a renewable approach to support the current electricity system, increase its existing capacity and, equally important, benefit the environment by reducing the need to build more power plants and utilising environmentally-friendly chemicals and heat recovery technologies such as ORC.

The Organic Rankine Cycle, (ORC) is a Rankine Cycle that uses a heated chemical instead of steam as found in the conventional Rankine Cycle. Non-organic fluids used in the ORC include pure refrigerants and refrigerant mixtures [3, 7]. Organic compounds generally have a higher molecular mass. This gives relatively small volume streams and results in a compact ORC unit. It also enables high turbine efficiency, up to 80% [13 and 15]. Unlike steam, organic compounds do not form liquid droplets upon expansion in the turbine. An absence of steam prevents erosion of the turbine blades and enables design flexibility on the heat exchangers [13].

From an operational standpoint, the ORC requires little maintenance and increasing the evaporator temperature and/or decreasing the condenser temperatures results in higher efficiencies. The use of ORC in low temperature applications under 37°C (100°F) is very limited and depends upon the thermodynamic and thermo-physical properties of the working fluid. A cost-effective optimum design criterion for Organic Rankine power cycles utilising low-temperature geothermal heat sources has been presented by [22]. Evaporation and condensation temperatures, geothermal and cooling water velocities were varied in the optimisation method. The optimum cycle performance was evaluated and compared for working fluids that include ammonia, HCFC123, n-Pentane and PF5050. Exergy analysis shows that the efficiency of the ammonia cycle has been more greatly compromised in the optimisation process than that of other working fluids. The fluids HCFC 123 and n-Pentane show better performance than PF 5050.

Energy performance is usually evaluated by the first law of thermodynamics. However, comparing energy analysis to exergy analysis can better show areas of inefficiencies. The results of that analysis can also be used to optimise and enhance the performance of power cycles. Various energy and exergy analyses of power cycles [4, 7, 18–25] have been reported.

Theoretical performances as well as thermodynamic and environmental properties of some fluids have been comparatively assessed for use in low-temperature solar organic Rankine cycle systems [26]. Efficiencies, volume flow rate, mass flow rate, pressure ratio, toxicity, flammability, ozone depletion potential (ODP) and global warming potential (GWP) were used for comparison. Of 20 fluids investigated, R134a appears as the most suitable for small scale solar applications. R152a, R600a, R600 and R290 offer attractive performances but need safety precautions, owing to their flammability.

The most promising working fluids are CFCs however they were phased out by 1996. Other existing HCFCs as well as hydrocarbons are either not environmentally friendly and/or have lower heat recovery efficiency. Other refrigerant mixtures developed [3] contain HCFCs that are scheduled to be banned by 2010. Therefore, a new family of HFCs refrigerant mixtures have been developed [7] to overcome the deficiencies of the current working fluids. This research work has been undertaken to enhance understanding of the Organic Rankine Cycle using the HFC quaternary refrigerant mixtures that enhance typical ORC performance. Energy and exergy analyses were applied to better understand the benefits of using the said quaternary refrigerant mixtures in various applications.

ORGANIC RANKINE CYCLE (ORC)

An Organic Rankine Cycle (ORC) engine is a standard steam engine that utilises heated vapour to drive a turbine. However, the vapour is a heated organic chemical instead of superheated steam. Figure 1 illustrates the basic components of an ORC. The organic chemicals used by an ORC have included CFCs (known as Freon) and most of the other traditional refrigerants, iso-pentane, CFCs, HFCs, butane, propane, and ammonia. These traditional refrigerants require a high temperature heat source.

What differentiates the quaternary refrigerant mixtures in the current study [7] from the traditional refrigerants is that the quaternary refrigerant mixtures boil at extremely low temperatures and are capable of capturing heat at temperatures lower than 26°C (80°F), thus generating power from low and medium waste heat. Figure 2 shows a Pressure-Enthalpy curve for a typical quaternary refrigerant mixture where the saturation temperature varies at constant pressure. The degree of variation or gliding temperature depends upon the mixture components and their boiling points as well as thermodynamic and physical properties.

The composition of refrigerant mixture can be adjusted to boil the mixture and generate power at a wide range of temperatures. However, several refrigerant mixtures have been developed to match the heat transfer profile of the heat source at various temperatures and in particular the low temperature application range to reduce losses and enhance heat recovery [7]. Using the quaternary refrigerant mixtures, power can be produced from captured low and medium heat in applications such as process industries, solar energy and geothermal energy, grey water and warm ocean waters. The use of quaternary

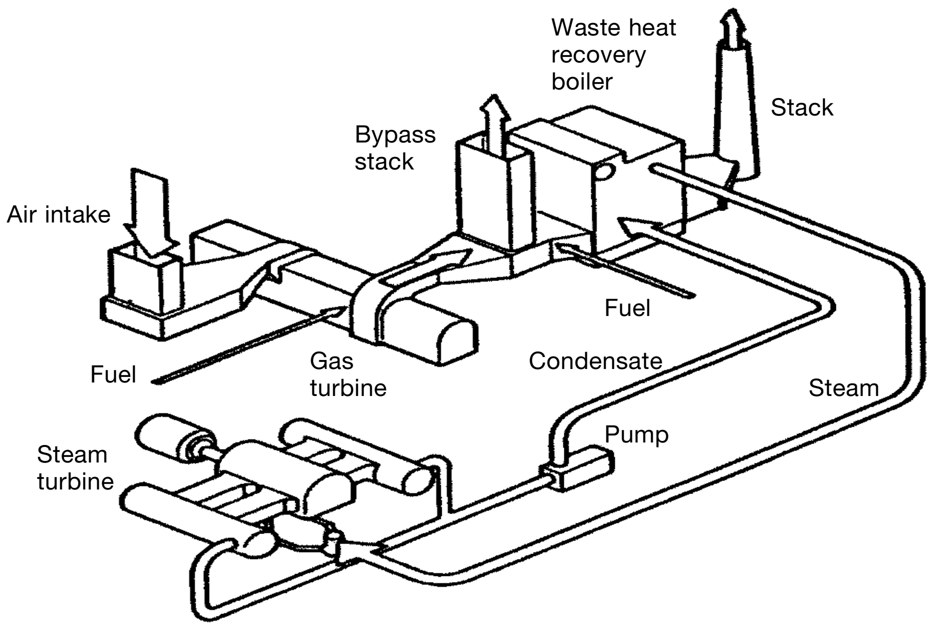

Figure 1
Typical Rankine Cycle [3].

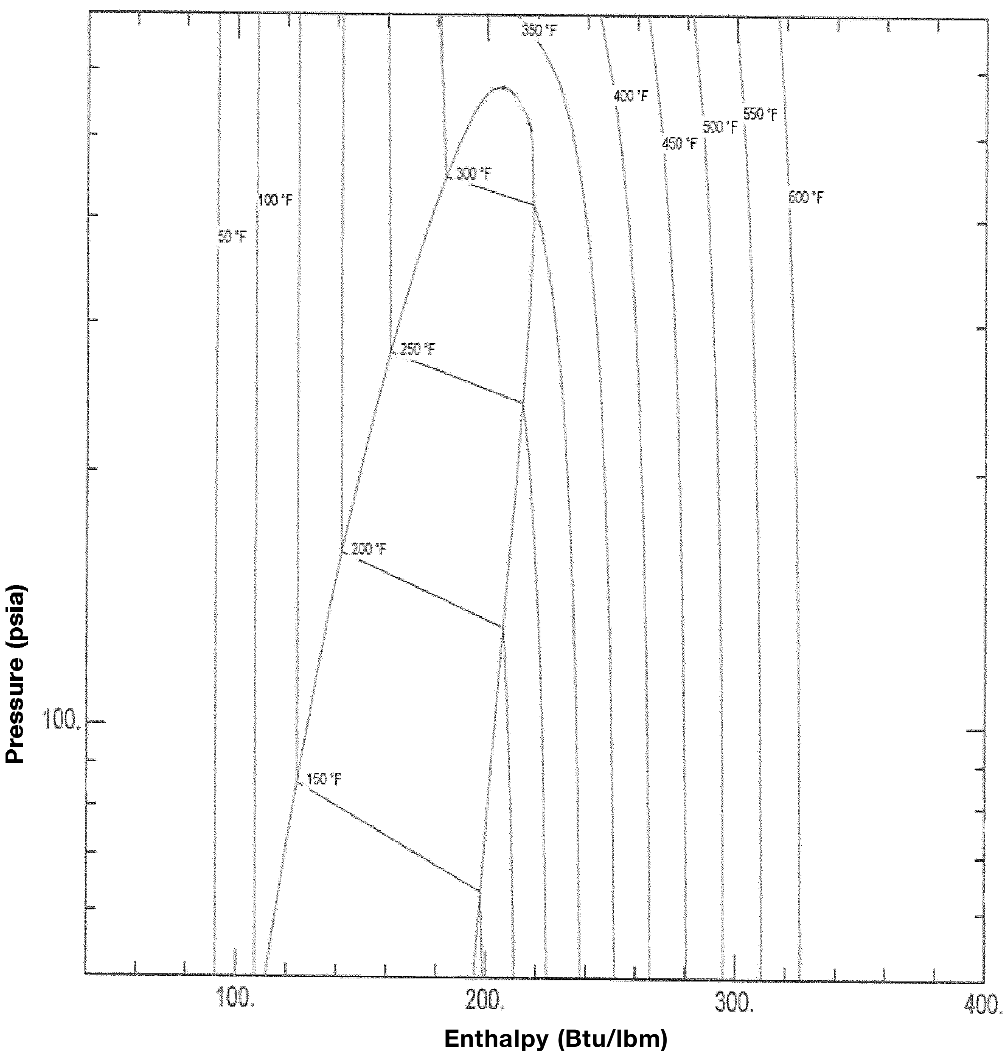

Figure 2
Typical Pressure-Enthalpy diagram of the refrigerant mixture [7].

refrigerant mixtures in the ORC reduces emissions and global warming. Compared to typical fossil fuels, using the new HFC refrigerant mixtures significantly reduces Oxides of Nitrogen (NOx) (by over 4 tons per year) and CO_2 emission. Furthermore, the family of quaternary refrigerant mixtures has a long life-cycle and requires reduced maintenance and repair costs that results in a relatively short payback period compared to other existing ORC systems [5].

As well as from utilising, for environmentally sound power regeneration, what is typically an unrecoverable waste heat source – from hot flue gases wasted at smoke stacks at various temperatures, solar energy using different collector geometries, and geothermal energy as well as grey water, a byproduct in process industries – it is possible to produce cheaper, more ecologically-friendly power, due to the lower boiling temperature of the patented quaternary refrigerant mixture and its higher latent heat of evaporation.

Thermodynamic and thermophysical properties are determined using the well-known NIST REFPROP.8 program [12]. In addition to these properties, the finite difference convergence technique was used to obtain the thermal behaviour for each component, represented by a finite control volume.

THEORTICAL CONSIDERATIONS

There are four processes in the Organic Rankine Cycle similar to the steam cycle, each changing the state of the working fluid. These states are identified by a number in the diagram (see Figure 3). Firstly the working fluid is pumped from low to high pressure by a pump. Pumping requires a power input, (for example mechanical or electrical). Secondly the high pressure liquid enters a boiler where it is heated at a constant pressure by an external heat source to become a superheated vapour. Common heat sources for power plant systems are coal, natural gas, or nuclear power. Thirdly the superheated vapour expands through a turbine to generate power output. Ideally, this expansion is isentropic. This decreases the temperature and pressure of the vapour. Fourthly the vapour then enters a condenser where it is cooled to become a saturated liquid. This liquid then re-enters the pump and the cycle repeats.

SYSTEM EQUATIONS

Energy analysis. Each of the first four equations is easily derived from the energy and mass balance for a control volume. The fifth equation defines the thermodynamic efficiency of the cycle as the ratio of net power output to heat input.

$$\frac{\dot{Q}_{in}}{\dot{m}} = h_3 - h_2 \qquad (1)$$

$$\frac{\dot{Q}_{out}}{\dot{m}} = h_4 - h_1 \qquad (2)$$

$$\frac{\dot{W}_{turbine}}{\dot{m}} = h_3 - h_4 = (h_3 - h_{4s}) \times \eta_{turb} \qquad (3)$$

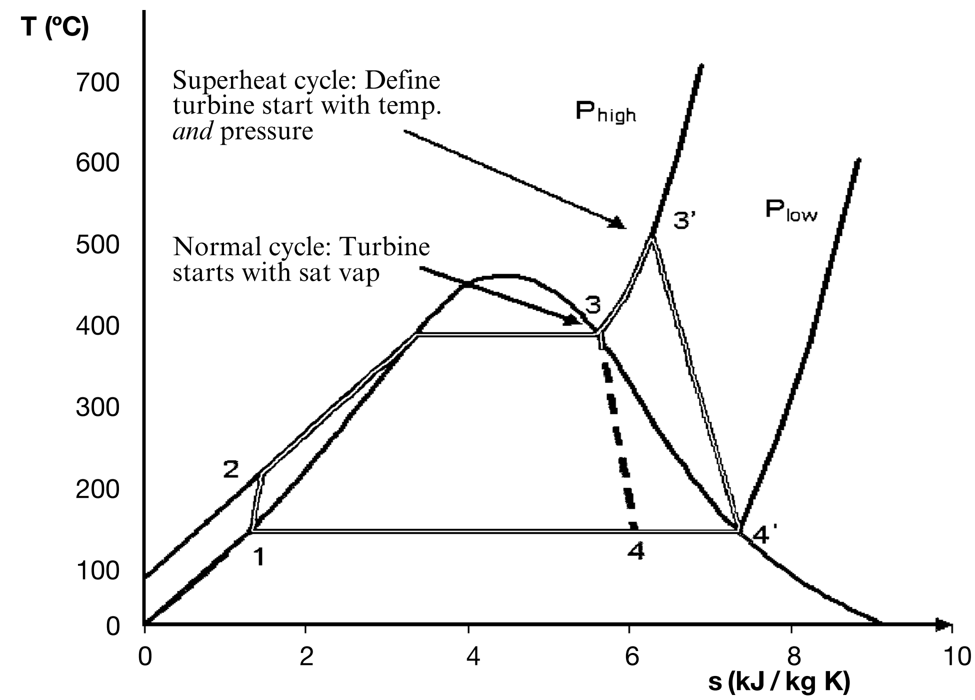

Figure 3a
Typical Rankine Cycle:
T–S diagram for steam [3].

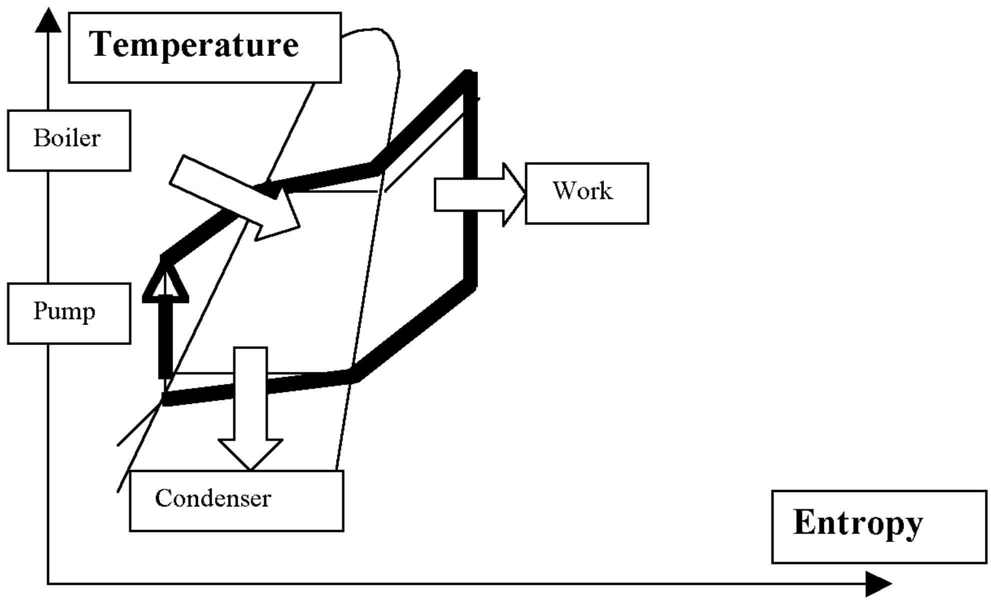

Figure 3b
Typical Rankine Cycle: T–S diagram with refrigerant mixtures (Thick lines – Refrigerant mixture; Thin lines – Pure refrigerant) [3].

$$\frac{\dot{W}_{pump}}{\dot{m}} = h_2 - h_1 \approx \frac{\upsilon_1 \Delta p}{\eta_{pump}} \approx \frac{\upsilon_1 (p_2 - p_1)}{\eta_{pump}} \quad (4)$$

$$\eta_{therm} = \frac{\dot{W}_{turbine} - \dot{W}_{pump}}{\dot{Q}_{in}} \approx \frac{\dot{W}_{turbine}}{\dot{Q}_{in}} \quad (5)$$

$$NHR = Q_{in} / W_{turbine} \quad (6)$$

In a real Organic Rankine Cycle, the pumping and expansion processes are non-reversible and entropy is increased during the two processes. Modern practices are implemented such as reheat and regenerative cycles. In the regenerative Organic Rankine Cycle the working fluid is heated by steam tapped from the hot portion of the cycle. This increases the average temperature of heat addition, which in turn increases the cycle efficiency. Both the reheat and regenerative options will be implemented in the proposed system.

Exergy and energy efficiency. The use of exergy in assessing power cycles such as the ORC is highly beneficial. The efficiency of the ORC based upon exergy, as the ratio of total exergy output to exergy input, is given by:

$$\eta_{ex} = Ex_{out} / Ex_{input} = (W_{net} + Ex_{heat}) / Ex_{input} \quad (7)$$

and can be equated to:

$$= 1 - Ex_{dest} / Ex_{input} \quad (8)$$

where Ex_{heat} represents the rate of exergy transfer associated with transfer of heat, Ex_{dest} is the rate of exergy destruction and W_{net} represents the net work.

In this analysis the thermal exergy rate is expressed in terms of the decrease of the hot fluid:

$$Ex_{heat} = -\Delta Ex_{heat\text{-}hot}$$

$$= \dot{m}\,[h_i - h_e - T_o (s_e - s_i)] \quad (9)$$

The subscripts, i, and e, refer to the inlet and exit states of the fluid in the heat exchanger and $\dot{m}$ is the mass flow rate of the fluid circulating in the ORC.

Finally, the ORC efficiency based upon the rate of exergy destruction is:

$$\eta_{ex} = (W_{net,out} + \dot{m}\,[h_i - h_e - T_o (s_i - s_e)\,] / Ex_{input} \quad (10)$$

and the rate of exergy input is:

$$Ex_{input} = \dot{m}\,[h_e - h_i - T_o (s_e - s_i)] \quad (11)$$

In the particular case of heat recovery across a waste heat boiler:

$$Ex_{input} = \dot{m}\,[C_p (T_e - T_i - T_o (s_e - s_i)] \quad (12)$$

and the entropy change of flue gases is:

$$(s_e - s_i) = C_p \,Ln\, (T_e / T_i) \quad (13)$$

Furthermore, the second law efficiency can be given as follows:

$$\eta_{II} = Ex_{output} / Ex_{input} \quad (14)$$

$$Ex_{output} = (\Delta h - T_o (\Delta s)\,)_{turbine,\ net} \quad (15)$$

DISCUSSION AND ANALYSIS

To analyse the thermodynamic behaviour of the ORC cycle using the quaternary refrigerant mixtures the aforementioned equations are integrated with the REFPROP program [12], which calculates the thermodynamic and thermophysical properties of the mixtures in question. The resultant equations are solved using the finite difference control volumes approach. The quaternary refrigerant mixtures in question include the following components; HFC 125, HFC 134a, HFC 245fa, HFC 152a, HFC 236ea and HFC 245ca where these components are mixed in different combinations at various concentrations [7] to maximise heat recovery. The use of the quaternary refrigerant mixtures results in the following benefits: operate at boiling pressure under 2000 kPa (300 psi) and condensing temperatures under 12°C (55°F), environmentally sound, non toxic, non flammable, low maintenance and repair costs, scalable utilising mass-produced off-the-shelf components and high efficiency (up to 30%) depending upon the heat source and sink temperatures (see Table 1).

A comparative study has been made between the behaviour of this mixture [7] and other refrigerants reported in the literature of similar applications, comprising the system simulation of the various refrigerants: R-11, R-114, R-245fa as well as [3] and proposed mixtures under operating conditions [4]; 112°C (235°F) and 1585 kPa (230 psi) at the waste heat boiler exit and 29°C (85°F) and 68 kPa (10 psi) at the condenser inlet. System capacity is 125 kW. The ORC system is retrofitted to a CHP system, comprising a gas turbine system with a steam generator. Typically, the temperature of the flue gases at the gas turbine exit varies between 426°C (800°F) to 537°C (1000°F). In addition, the flue gas temperature after the steam generator is around 148°C (300°F) to 204°C (400°F). At this temperature range it is possible to recover heat and produce power at significantly higher efficiency using the proposed mixture compared to other fluids. The results of the comparative study have been plotted in Figure 4. It is evident from this figure that using the refrigerant mixture results in lower values of Net Heat Rate (NHR) and more power production at the same heat input at the waste heat boiler. This is mainly due to the lower boiling temperature of the mixture and higher latent heat of evaporation compared to the refrigerants under investigation.

Table 1 Heat Source temperature applications.

Heat source temperature °C	Applications
426–537	Gas turbine – ICE
95–115	Solar collectors
149–200	Geothermal
25–30	OTEC

Figure 4 displays the system efficiency using the proposed refrigerant mixture [7] compared to the other refrigerants under investigation. It is apparent that the refrigerant mixture has superior cycle efficiency. This is due to the increase in work produced at the same heat source. This comparison is significant since it compares the refrigerant mixture efficiency to that of R-245fa which is currently used and considered as an alternative to the CFCs R-11 and R-114 in chillers and ORC applications. The higher efficiency is also due to the high heat transfer ratio between the thermal energy and kinetic energy at the turbine side as well as the pressure ratio.

The impact of using the refrigerant mixtures [7] on the ORC efficiency at various heat source temperatures is shown in Figure 5, where a water cooled condenser is used at a condensing temperature of 12°C (55°F). The data clearly show that the higher the flue gas temperature the more power produced at the turbine side. This result is expected, since increasing the flue

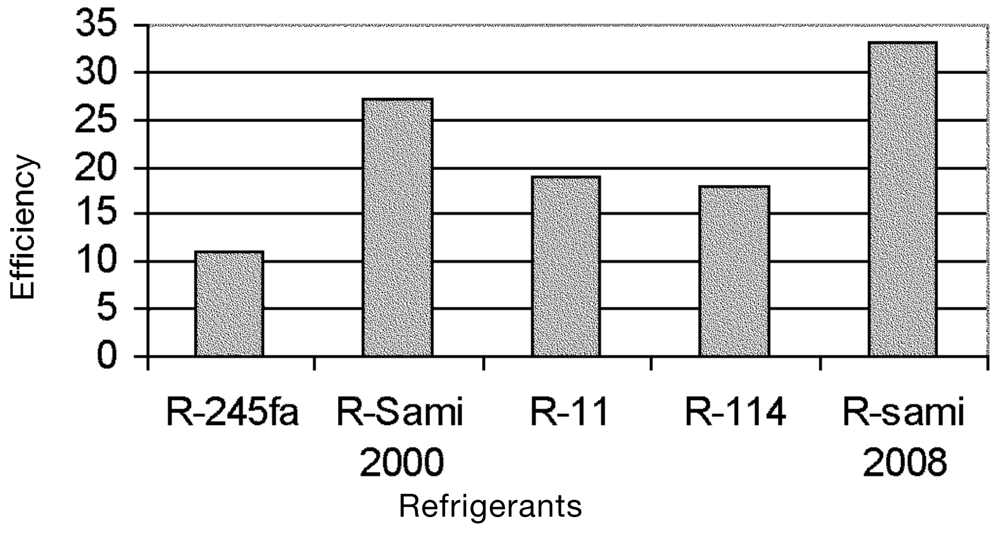

Figure 4
Efficiency for different refigerants.

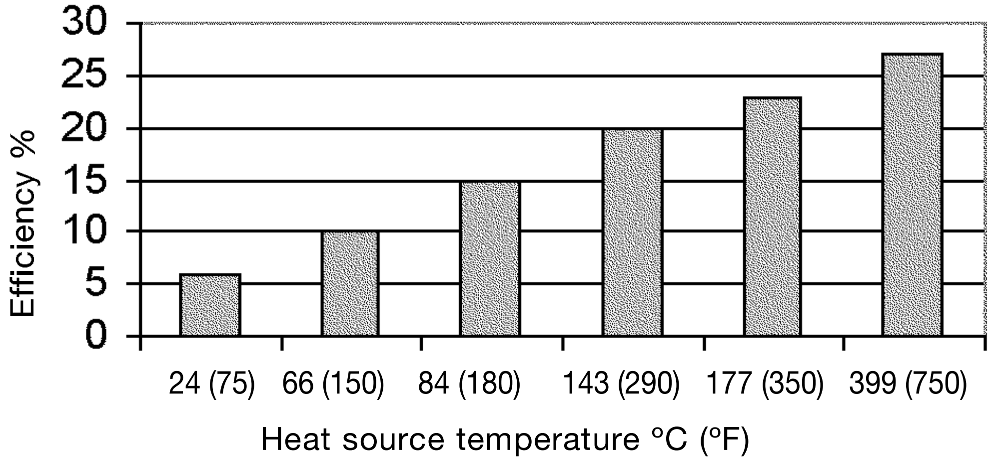

Figure 5
Cycle efficiency using Sami [4] refrigerant mixtures. Heat source temperature curve for a water cooled condenser condensing at 12°C (55°F).

gas temperature increases the thermal energy dissipated at the turbine and converted to kinetic energy. The data displayed in Figure 5 clearly show that retrofitting the proposed ORC will significantly enhance the efficiency and reduce the Net Heat Rate (NHR) and will also have a positive impact on the environment by cooling down the flue gases and reduce emissions and global warming.

The data presented in Figure 5 demonstrates that the proposed quaternary refrigerant mixture can be effectively used in ORCs at applications such as Ocean Thermal Energy Conversion (OTEC) where the surface water of the ocean is used to drive the ORC boiler and deep shallow water to cool down the ORC condenser. In this application, with heat source temperature of 29°C (85°F) at the ocean surface and a sink temperature of 4°C (40°F) the heat recovery efficiency using the proposed refrigerant mixture is between 6–9% depending upon the saline water concentration compared to 1–3% reported on such applications [24–26] using Isobutene which is a flammable refrigerant.

Another application in the same temperature range, of great significance to the process and HVAC industries, is to use the ORC system as an alternative to cooling towers, thus eliminating the associated maintenance issues and high cost of operation. The heat source and heat sink temperatures are 25°C (78°F) and 7°C (45°F) respectively. Comparative data are presented in Figure 6 between the proposed quaternary refrigerant mixture and other working fluids such as isobutene in the temperature range for both OTEC and cooling tower applications. The data clearly show the added value in using the proposed refrigerant mixtures and the significant potential in using the ORC system with proposed refrigerant mixtures as a renewable energy source.

In most solar applications, heat transfer fluids circulating in flat plate or evacuated collectors are at temperatures between 95°C (203°F) and 115°C (234°F). ORCs coupled with solar collectors for solar thermal power production mostly use Isobutene and or R-245fa and yield low heat recovery efficiency under 7% depending upon the heat transfer fluid temperature [27]. Data displayed in Figure 6 demonstrate the added value of using the refrigerant mixture under investigation,

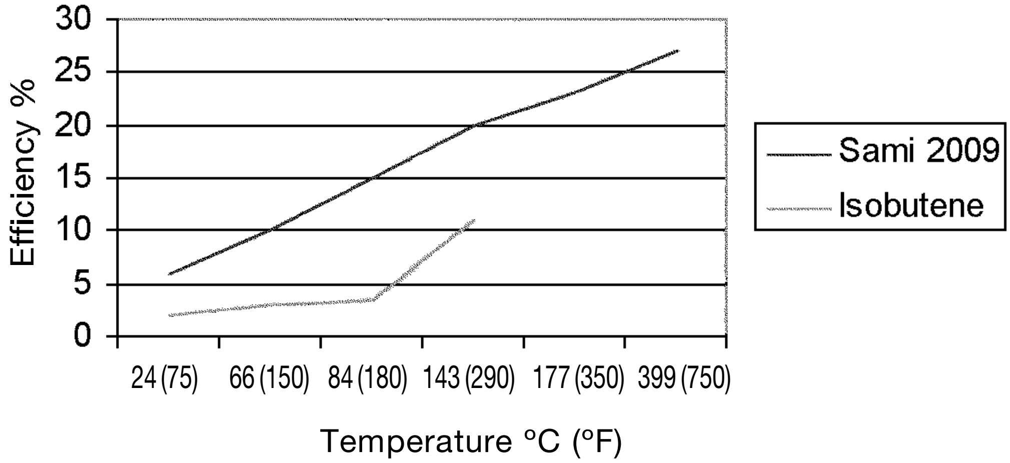

Figure 6
Low temperature efficiency curves show the advantages of the proposed refrigerant mixture in low temperature applications.

particularly at temperatures lower than the 82.2ºC (180ºF). Other solar panels used focus the sun's rays to generate greater heat with conical designs and parabolic configuration. Heat transfer fluids circulating in these panels have temperatures higher than 150ºC (290ºF) and existing ORCs can not operate at these temperatures since they exceed the critical temperatures of their working fluids.

Geothermal resources can supply the minimum 149ºC (300ºF) heat energy necessary for conversion to mechanical energy mostly through steam turbines [28]. However, electrical production from liquid-dominated sources is technically more complex, expensive and has low thermal conversion efficiencies because of the steam's low temperature and significant losses. Current geo-thermal power plants inject steam into the rocks to heat up the rock beds in order to increase the water temperature to meet the requirements of steam turbines. In addition, current ORCs fail to generate electricity with economically viable solutions because of the thermodynamic characteristics of the working fluids used. The use of the proposed refrigerant mixtures enables electricity to be produced in the aforementioned temperature range efficiently, more simply and less expensively since the ORC is connected directly to the well water. Figure 6 shows the possible power production efficiencies at the geothermal resources temperature range.

Figures 7 and 8 have been constructed to present the energy and the second law thermal efficiencies as well as exergy performance results of the various fluids used in this study; namely; R-245fa, R-114, R-11, Sami 2000 [3] and the

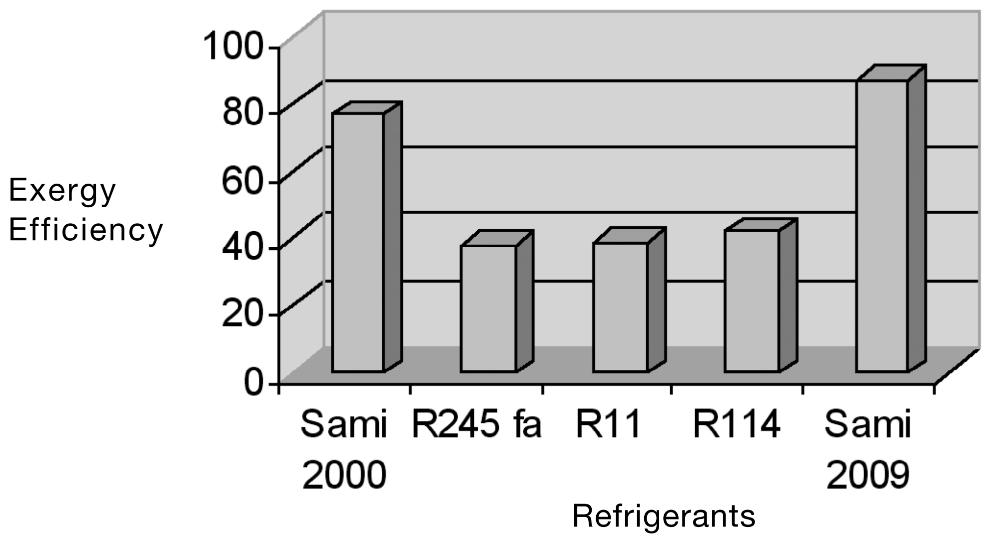

Figure 7
Exergy comparison of refrigerants.

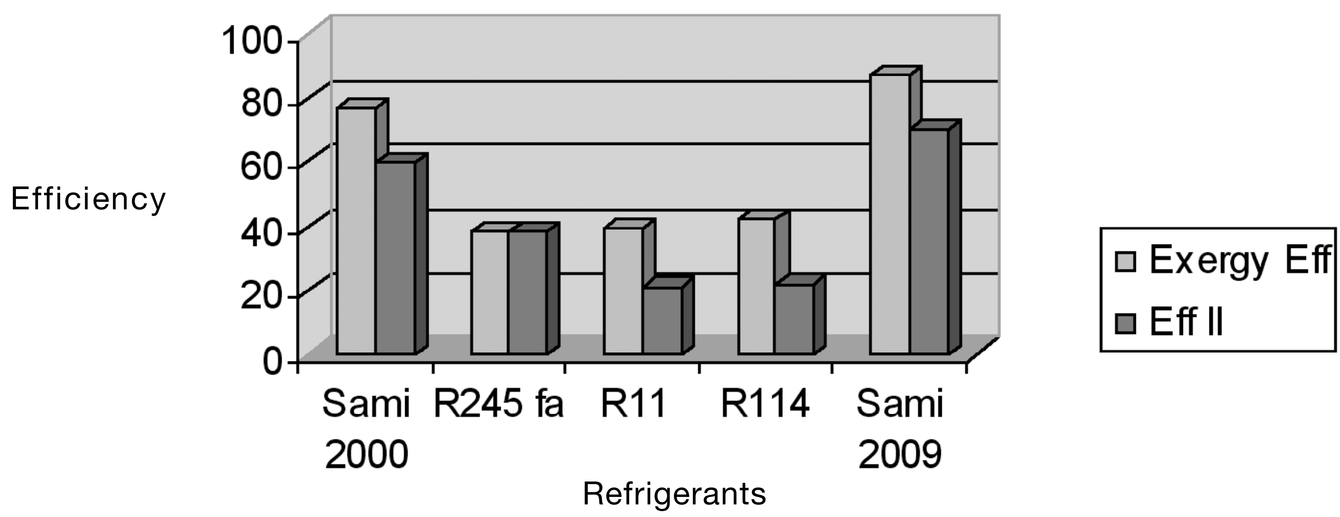

Figure 8 Comparisons between Exergy and Second Law efficiencies.

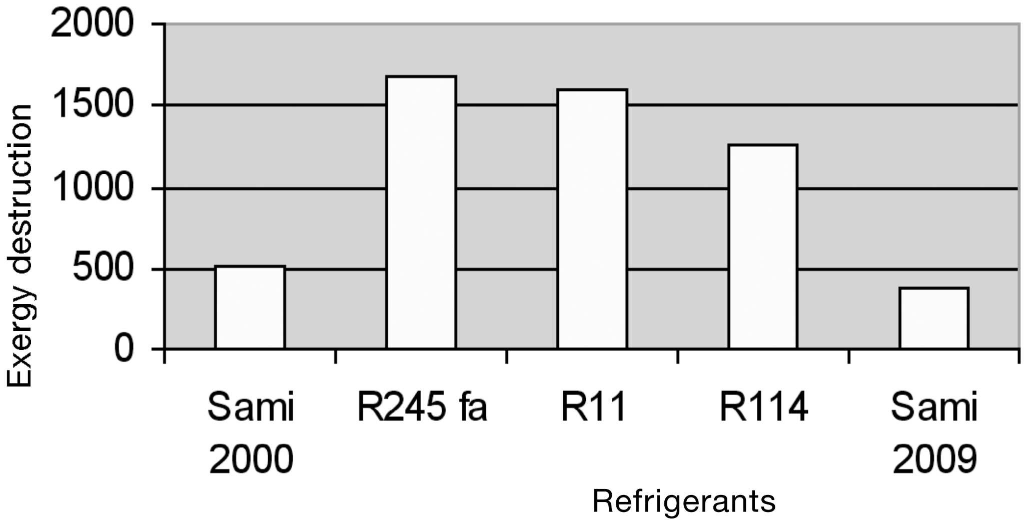

Figure 9
Exergy destruction.

quaternary refrigerant mixture [7]. To facilitate the comparison of the refrigerants, the same heat source and sink conditions were used; 4.5 MW, 112°C (235°F) and 29°C (85°F) respectively. Operating parameters were selected to yield the same flow rate in each case.

Clearly the ORC operating with the quaternary refrigerant mixture has the highest energy efficiency compared to the others. Examining the exergy efficiencies displayed in Figures 7 and 8 shows that the quaternary refrigerant mixture has a higher thermal efficiency compared to the other refrigerants under study. R-245fa has the lowest thermal efficiency because of its low boiling point compared to the quaternary refrigerant mixture as well as the others.

Similar results can be observed from Figure 8 when examining the second law efficiencies. Furthermore, the results presented in Figure 9 clearly show that the exergy destruction is much lower in conditions where the quaternary refrigerant mixture [6] is used compared to other refrigerants. In addition, the results displayed in this figure also show that R-245fa has the highest exergy destruction among the refrigerants under investigation in this study, because of its low boiling point.

CONCLUSIONS

In this analytical study the performance of an Organic Rankine Cycle (ORC) has been analysed and discussed. The proposed ORC uses a new quaternary refrigerant mixture that is environmentally sound and thermodynamically very efficient when using low and medium waste heat. The mixture composition can be formulated to effectively capture heat at a wider range of temperatures than is currently available.

Various comparative studies have been presented using energy and exergy analysis to demonstrate the superior performance of the proposed refrigerant mixture compared to alternative fluids. The data presented clearly show that the proposed quaternary refrigerant mixture has the capability to produce power from low and medium waste heat with significant thermodynamic efficiency and less exergy destruction.

NOMENCLATURE

C_p Specific heat (kJ/kg K)
Ex Exergy rate (kJ/kg/s)
η_{ex} Exergy efficiency
η_{pump} Pump efficiency
η_{turb} Turbine efficiency
η Cycle efficiency
$\dot{Q}_{in}$ Heat input rate (kJ/s)
Q Heat transfer (kJ/kg)
$\dot{m}$ mass flow rate (kg/s)
$\dot{W}$ Mechanical power used by or provided to the system (kJ/s)
NHR Thermodynamic efficiency of the process (power used for turbine per heat input, Net Heat Rate (kWh))
h_1,h_2,h_3,h_4 These are the specific enthalpies at indicated points on the T-S diagram (kJ/kg)
ΔP Pressure drop (kPa)
S Entropy (kJ/kg K)
T Temperature (K)
v Specific volume (m^3/kg)
W Work (kJ/kg)

Subscripts

3 Turbine inlet and saturated vapour
3’ Turbine inlet superheated vapour
4 Turbine outlet and wet vapour
4’ Condenser inlet and saturated vapour
2 Waste heat boiler inlet
1 Inlet to the pump
in Input to waste heat boiler
i input
e output
des destruction
o ambient

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