PERFORMANCE OF AN ORGANIC RANKINE CYCLE WITH MULTICOMPONENT MIXTURES

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Abstract

There is a renewed interest in organic Rankine cycle (ORC) systems for power generation using solar thermal energy. Many authors have studied the performance of ORC with different pure fluids as well as binary zeotropic mixtures in order to improve the thermal efficiency. It has not been well appreciated that zeotropic mixtures can also be used to reduce the size and cost of an ORC system. The main objective of this paper is to present mixtures that help reduce the cost while maintaining high thermal efficiency. The proposed method also allows us to design an optimum mixture for a given expander. This new approach is particularly beneficial for designing mixtures for small ORC systems operating with solar thermal energy. A number of examples are presented to demonstrate this concept.

Keywords: Organic Rankine cycle, mixtures, optimization, design of mixtures

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1 INTRODUCTION

There is a worldwide interest in the development of organic Rankine cycles (ORC) operating with solar thermal energy as well as low temperature waste heat. Figure 1 shows the difference between a Clausius-Rankine cycle operating with water and an organic Rankine cycle operating with pentane at a boiling temperature of 150^{o}C. A large degree of superheating is required at the entry of the expander in the case of a Clausius-Rankine cycle to avoid expansion into the two-phase region (the so called wet expansion). Organic fluids such as pentanes, hexanes etc. exhibit a positive slope of the saturated vapour line on a temperature-entropy diagram at normal working pressures instead of a negative slope exhibited by water. Therefore, a saturated vapour of *n*-pentane can be expanded to a low pressure completely outside the vapour dome. On the other hand, water needs to be superheated to over 600^{o}C in an ideal Clausius-Rankine cycle shown in Fig. 1 even if the phase change of water occurs at 150^{o}C. Reheat cycles are therefore employed to decrease the degree of superheat required with water. Reheat cycles are, however, not suitable for small applications since an increase in the number of expansion stages leads to high cost and complexity of the system. Water is therefore not a good working fluid for use with solar/waste heat available at temperatures lower than 200^{o}C. Organic Rankine cycles are ideal for power generation when flat plate or evacuated tube solar collectors are used because of the requirement of zero superheat[2]. ORCs derive their name from organic fluids such as *n*-pentane, *n*-hexane etc. that were initially used in these systems. However, it is also possible to use other fluids such as fluorinated alkanes (refrigerants), siloxanes etc. Practical ORC systems include an additional internal heat exchanger to improve the thermal efficiency of the system (Figure 2).

Both pure fluids and zeotropic mixtures can be used as working fluids in organic Rankine cycles (Fig. 3). A variety of pure fluids such as hydrocarbons, siloxanes, hydrofluorocarbons, hydrofluoroolefins etc. have been proposed as the working fluid for ORC systems. A number of authors have studied

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[2] In practical ORC systems, a small degree of superheat is normally useful to prevent liquid droplets carried over by entrainment from entering the expander.

the relative performance of an ORC with different pure working fluids [1–13]. Many studies have also been reported in the literature on the use of zeotropic mixtures, especially binary mixtures as working fluid of organic Rankine cycles. The entropy generation in the condenser and boiler is normally lower in the case of ORC working with zeotropic mixtures since the mean temperature difference between the working fluid (mixture) and the heat transfer fluid is much smaller than that between a pure fluid and the heat transfer fluid in the two-phase region of the working fluid. The least entropy generation or exergy loss in the condenser and boiler occurs when the temperature change of the heat transfer fluid is the same as that of the working fluid in the two-phase region. This is also known in refrigeration literature as "glide matching"[14]. A number of authors have studied the performance of ORC with a variety of binary zeotropic mixtures [15–24] that attempt to improve the performance of an ORC by glide matching. In all these studies the composition of the binary mixture is varied systematically and the performance of the system is studied over the entire composition space to arrive at the best mixture composition for particular heat addition and heat rejection temperatures.

Only a few authors studied the performance of ORC systems with multicomponent zeotropic mixtures. Angelino et al. [16] compared the performance of an ORC with a five component mixture of siloxanes. Chys et al. [15] studied the performance of an ORC with three-component mixtures at specified mixture composition. Sami et al. [25] patented a four component mixture of HFC134a/HCFC123/HCFC124/HFC125 (10/70/10/10 mass %). Zimron and Bronicki [26] patented a multicomponent mixture of hydrocarbons, a refrigerant and a fire retardant as working fluid of an ORC. Zhang et al. [27] claimed mixtures based on HFO 1234yf with different components. For example, they claimed a mixture of HFO1234yf/HFC236fa/HFC143 in the range of 3 to 91, 4 to 92 and 5 to 93 mass% respectively. Similar claims were made by Zhang et al. [27] for a variety of multicomponent mixtures. Recently Sami [28] claimed a quaternary mixture of HFC245ca/HFC236ea/HFC125/HFC152a of composition 1-97% each. Similar claims were made by Sami [28] with other combination of refrigerants. There is very little information in any of the above literature on how the above authors arrived at the concentration of the multicomponent mixtures they studied or claimed in their patents.

The main aim of this work is to present the performance of an ORC system with different multicomponent mixtures, along with a method for optimizing their composition.

2 THERMODYNAMIC MODEL FOR THE DESIGN OF ZEOTROPIC MIXTURES

Consider an organic Rankine cycle shown in Figure 2. The exergy efficiency (η_{ex}) of the system is given by the expression:

$$\eta_{ex} = \frac{\dot{W}_{net}}{\dot{W}_{rev}} = \frac{\dot{W}_{exp} - \dot{W}_{pump}}{\dot{m}(ex_7 - ex_8)} \tag{1}$$

In the above equation, $\dot{m}$ refers to the mass flow rate of the heat transfer fluid, *ex* to the specific exergy of the heat transfer fluid in the boiler and $\dot{W}_{exp}$ and $\dot{W}_{pump}$ the power output from the expander and the power input to the pump respectively. $\dot{W}_{rev}$ is the maximum possible work that can be obtained from the heat transfer fluid when it is cooled from state 7 to state 8.

Similarly, the volumetric expander work output (W_v) is the ratio of the expander power output to the volume flow rate of the working fluid at expander exit and is given by the expression:

$$W_v = \frac{\dot{W}_{exp}}{\dot{V}_4} = \rho_4(h_3 - h_4) \tag{2}$$

In the above expression, state points 3 and 4 correspond to expander inlet and outlet respectively (see Fig. 2).

It is possible to design a mixture that maximizes either the exergy efficiency (η_{ex}) or the volumetric expander work output (W_v). The relationship between the two is discussed in the following section. Exergy efficiency has been used as the objective function by a few authors [29–31] for identifying a pure working fluid. Other objective functions that have been considered for pure fluids are (a) heat exchanger area [32], combination of thermal efficiency, volume of the system, discounted payback period, and net present value [33], as well as combination of exergy efficiency and total product cost [34].

There is very little information in the literature on ORC on the use volumetric work as the objective function for the design of multicomponent mixtures for ORC. This approach, however, has been used in the design of cryogenic refrigeration and natural gas liquefaction systems [35]. The basic approach presented in Ref. [35] for cryogenic systems has been suitably modified and adopted for the design of multicomponent mixtures for ORC based power plants.

The design of the mixture can be mathematically posed as a constrained non-linear optimization problem as follows:

2.1 Objective function

Maximize η_{ex} or W_v

2.2 Subject to the following constraints

- Minimum temperature approach between the hot and cold streams is greater than or equal to the specified value in each heat exchanger (condenser, boiler and internal heat exchanger) (say greater than or equal to 5 K)
- Degree of superheat of the working fluid entering the expander is greater than or equal to that specified (say greater than 5 K)
- The expansion ratio of the expander (p_3/p_4) is the same as that specified (say 3 to 4)

The expansion ratio constraint needs to be specified only when designing mixtures around a given expander, for example a scroll compressor used as an expander. It is also useful when many local maxima exist in close vicinity.

2.3 Design variables

- Concentration of each component in the mixture (0 to 100%), but with a constraint that the sum of all concentrations is 100%
- Expander outlet pressure (1 to 7 bar)
- Pump outlet pressure (10 to 25 bar)
- Ratio of flow rate of the working fluid to that of the heat transfer fluid in the condenser (typical range depends on the temperature change of heat transfer fluid, say 5 to 50)
- Ratio of flow rate of the working fluid to that of the heat transfer fluid in the boiler (typical range depends on the temperature change of heat transfer fluid, say 5 to 50)
- Temperature change of the hot fluid in the internal heat exchanger (say greater than 5 K)

2.4 Design constants

- Isentropic efficiency of the expander (say 50 to 80%) and pump (say 30 to 70%)
- Temperature of the heat transfer fluids entering and leaving the condenser and boiler (say 5 to 20 K)
- Pressure drop of each stream in the condenser, boiler and internal heat exchanger (0 for an ideal case and typically about 0.1 to 0.5 bar for practical systems)

It is also possible to specify the log mean temperature difference instead of specifying the minimum temperature approach. Internal pinch points can occur in the condenser and boiler since the enthalpy of multicomponent mixtures can vary non-linearly in the two-phase region [36,37]. Log mean temperature or heat exchanger effectiveness cannot be easily defined when internal pinch points occur. It is therefore customary to specify the minimum temperature difference between the streams in heat exchangers used in mixed refrigerant processes [35]. The minimum temperature approach can be estimated by dividing the heat exchanger into many parts such that either the temperature change of the minimum heat capacity fluid is the same, or the heat transferred in each part is the same. The unknown temperature of any part is determined by energy balance, starting from the warm end of the heat exchanger. After estimating the temperature profile with a finite number of parts (say 10 or 20), mathematical methods such as Brent's method are usually employed to determine the exact location of the pinch and its value.

At least three components need to be used in a zeotropic mixture to avoid internal pinches. Alternately, a binary mixture with nearly equimolar concentration needs to be used [36,37]. Therefore at least three components are normally chosen for the mixture. Since the concentration of components that are not required becomes zero on convergence, more than three components are normally specified at the start. However, a reasonable guess of the composition is required to start the optimization calculations from a feasible region where all the constraints are satisfied. The Sequential Quadratic Programming (SQP) method has been used in this work for solving the non-linear maximization problem. The properties of the mixtures were determined using the Peng-Robinson equation of state. The sequential modular approach [35] was used for the simulation of the ORC cycle. The optimization was carried out using Aspen Plus Software.

3 RESULTS AND DISCUSSION

Table 1 shows the list of pure fluids studied and Table 2 shows the components and composition of the mixtures optimized in this work. Different combinations of pure fluids were used to arrive at different mixtures presented in Table 2. The method presented in the previous section was used for both pure fluids and mixtures. In the case of pure fluids, only one fluid is chosen, and its concentration is limited to 100%. The other design variables listed in Sec. 2.3 are varied to determine the optimum configuration. The calculations were carried out for the following design constants: (a) isentropic efficiency of the expander and pump is 70%. Temperature of the heat transfer fluid entering and leaving the condenser is taken as 35 and 43^{o}C. The temperature of the heat transfer fluid entering the boiler was assumed to be 100^{o}C. The temperature change of the heat transfer fluid in the boiler was assumed to be 10 K. Though studies were carried out at values other than 10 K, the same have not been presented here. The pressure drop has been assumed zero in all the pipelines and heat exchangers.

The following specifications were used for the constraint: (a) the minimum temperature approach between the streams is ≥ 5 K, and (b) the degree of superheat is zero.

Figures 4 and 5 show the temperature profiles in the boiler and the condenser with mixture M1 (Table 2) respectively. It can be observed that the temperature change of the heat transfer fluid and the working fluid are very close in both the condenser and evaporator in the two-phase region of the working fluid. In other words, there is good glide matching in the condenser and the boiler with the optimized mixture. Good glide matching is an outcome of the thermodynamic method used in this work, as against some authors who have recommended glide matching itself as the objective function [38].

Glide matching also depends on the specified temperature change of the heat transfer fluid. Good glide matching may not be possible if the temperature change of the heat transfer fluids is very large or very small. Even in such cases, the mixture composition is so chosen as to reduce the overall exergy loss in the system. Hence, the best possible glide matching is an automatic consequence of the thermodynamic method presented.

It can also be observed from Figs. 4 and 5 that the temperature profiles are nearly linear in the condenser in the case of mixture M1. The enthalpy of zeotropic mixtures can vary non-linearly with temperature in the two-phase region [36]. Since glide matching requires the enthalpy-temperature variation of the heat transfer fluid to be the same as that of the working fluid (mixture), the method presented in this work also results in nearly linear variation of enthalpy with temperature in the two-phase region for most optimum mixtures. Large internal temperature pinches are therefore automatically avoided with the present method.

It is customary to compare the exergy efficiency with different pure fluids or mixtures to determine the most appropriate working fluid for an ORC system. What is not well recognized is that higher the exergy efficiency that can be obtained with a particular fluid, lower is the volumetric work that can be derived from the expander (see Fig. 6). Higher the difference between the critical and the ambient temperature, higher is the efficiency of an ORC. Fluids with higher critical temperature therefore offer higher efficiency. However, the ratio of normal boiling point temperature to critical temperature varies from about 0.6 to 0.65 for most pure fluids used in ORC (see Table 1). Fluids with higher critical temperature therefore have higher normal boiling point temperature. If the normal boiling point is higher than ambient temperature, the condensing pressure at ambient temperature would be sub-atmospheric. Since the density at expander exit is directly proportional to the condensing pressure, fluids whose normal boiling point temperature is lower than the ambient offer higher volumetric expander work, but at lower thermal efficiency.

Most authors in the past have tried to find the best mixture composition that maximizes the exergy efficiency or thermal efficiency. To the best of our knowledge, there has been no attempt in the past to mix pure fluids to achieve both high efficiency as well as high volumetric expander work. A high volumetric expander work results in a smaller expander size, and thereby lowers the capital cost. Since the total cost is largely controlled by the expander cost, the use of mixtures is therefore particularly advantageous for small ORC systems.

It is evident from Fig. 6 that the optimum mixtures presented in Table 2 offer both higher exergy efficiency as well as higher volumetric expander work. For example, for nearly the same exergy efficiency, the volumetric expander work with mixture M10 is about an order of magnitude more than that with pure fluids P5 and P6. Similarly, if the mixture M8 is chosen instead of mixture M1, the exergy efficiency decreases from 51% to 47% but the volumetric work output increases by a factor of nearly six. It is thus evident from the above discussion and Fig. 6 that mixtures can be designed both for higher exergy efficiency and/or high volumetric expander work compared to pure fluids.

Figure 7 shows the expansion ratio (p3/p4 in Fig. 2) with different pure fluids and mixtures. It can be observed that for the same expansion ratio, the volumetric expander work is much higher with mixtures than with pure fluids. For example, for an expansion ratio of about 3, the volumetric work output with mixture M8 is about four times that with pure fluid P4. Thus the expander volume and cost would be much smaller with mixtures for the same expansion ratio.

If pure fluid P4 (pentane) were to be used, the working pressures would be 4.8 and 1.5 bar respectively, and a turbo expander custom designed for pentane may need to be used. It can be observed from Figs. 8 and 9 that the working pressures with mixture M8 would be about 12 bar and 4 bar respectively. These pressures are close to those observed in traditional refrigeration applications. Therefore, positive displacement refrigeration compressors such (e.g., Scroll, Screw) can be used as expanders with appropriate zeotropic mixtures.

Optimum mixtures can be easily designed for a given expansion ratio at which the overall exergy efficiency of the expander and generator is the highest using the present method by using an additional constraint as explained in Sec. 2.4.

4 CONCLUSIONS

A thermodynamic method has been presented for the design of multicomponent mixtures for ORC. The results presented show that the size of the expander with a mixture can be much smaller than that with a pure fluid for the same exergy efficiency. In many cases, both higher exergy efficiency and larger volumetric expander work (or smaller expander size) can be obtained with optimized mixtures. Mixtures should therefore be viewed not as a means of improving efficiency alone, but as a means of reducing the size of the expander as well.

The current practice is to design an expander for a given pure fluid or a binary mixture. With the method presented in this work, it becomes possible to design a mixture to work with a particular offthe-shelf expander. This new approach should help reduce the overall system cost and should prove to be particularly beneficial for small systems operating with solar thermal energy.

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7 NOMENCLATURE

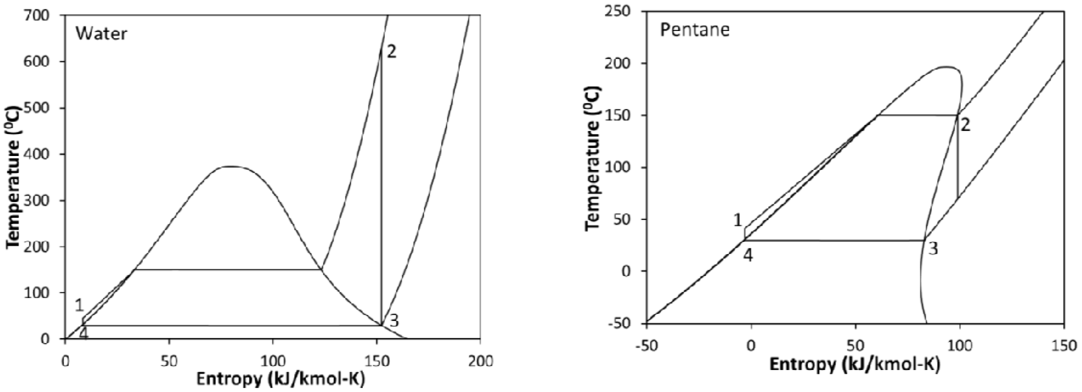
ex	Specific exergy of flow = $h - T_{amb}\, s$ (kJ/kg)
h	Specific enthalpy (kJ/kg)
HC	Hydrocarbon
HFC	Hydrofluorocarbon
HFO	Hydrofluorooelfin (unsaturated HFC)
$\dot{m}$	Mass flow rate (kg/s)
p	Pressure (bar)
s	Specific entropy (kJ/kg.K)
T	Temperature (K)
T_{amb}	Ambient temperature (K)
W_v	Volumetric expander work (see Eq. 2)
$\dot{W}_{exp}$	Expander power output (W)
$\dot{W}_{net}$	Net power output (W)
$\dot{W}_{pump}$	Pump input power (W)
η_{ex}	Exergy efficiency (see Eq. 1)
$\Delta T_{htf,b}$	Temperature change of the heat transfer fluid in the boiler (K)
$\Delta T_{htf,c}$	Temperature change of the heat transfer fluid in the condenser (K)
ρ	Density (kg/m^3)

Subscripts

1-6	State points

c	Critical point
NBP	Normal boiling point
rev	Reversible

8 List of Figures



(a) (b)

Figure 1.(a) Ideal Clausius-Rankine cycle operating with water and (b) Ideal organic Rankine cycle operating with pentane as the working fluid

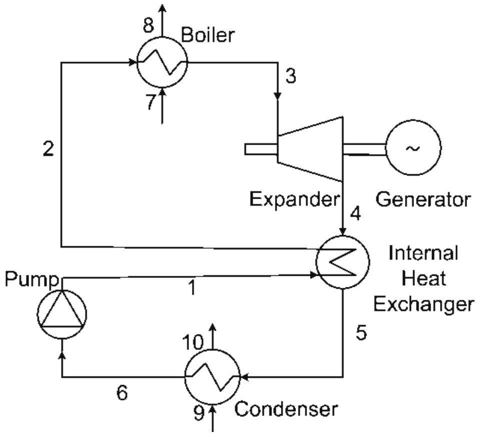
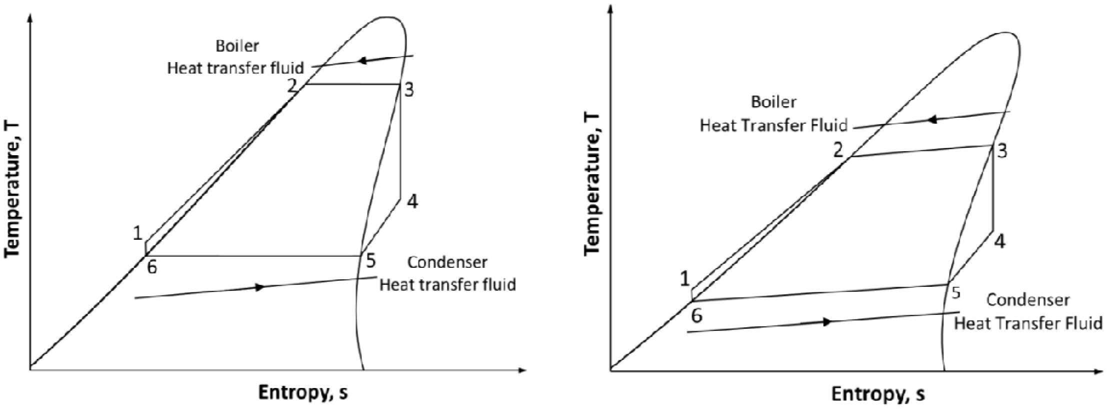


Figure 2. Organic Rankine cycle with an internal heat exchanger



(a) (b)

Figure 3. Ideal organic Rankine cycle operating with (a) pure fluid and (b) zeotropic mixture

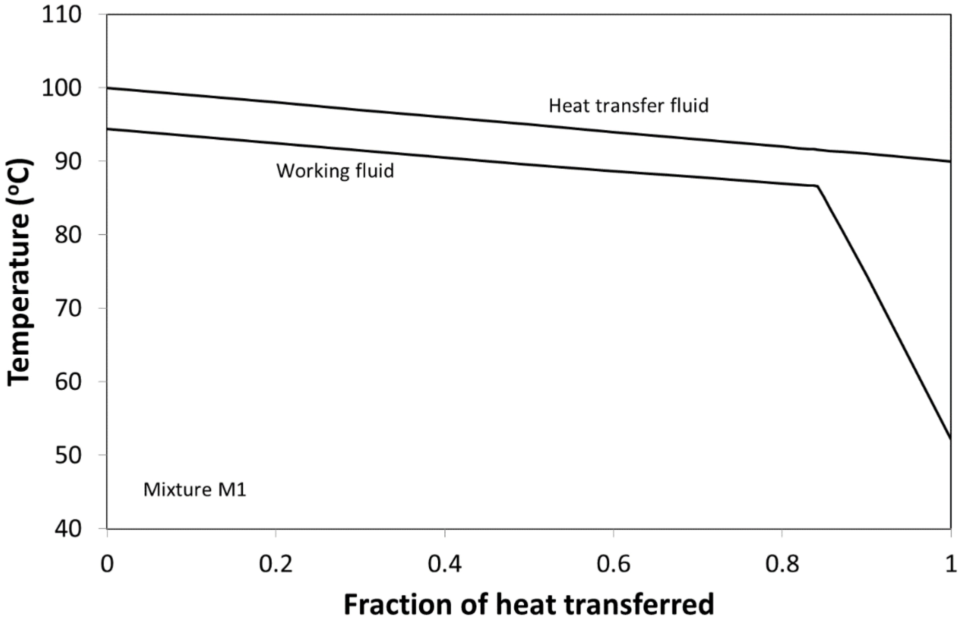


Figure 4. Temperature profiles in the boiler with mixture M1

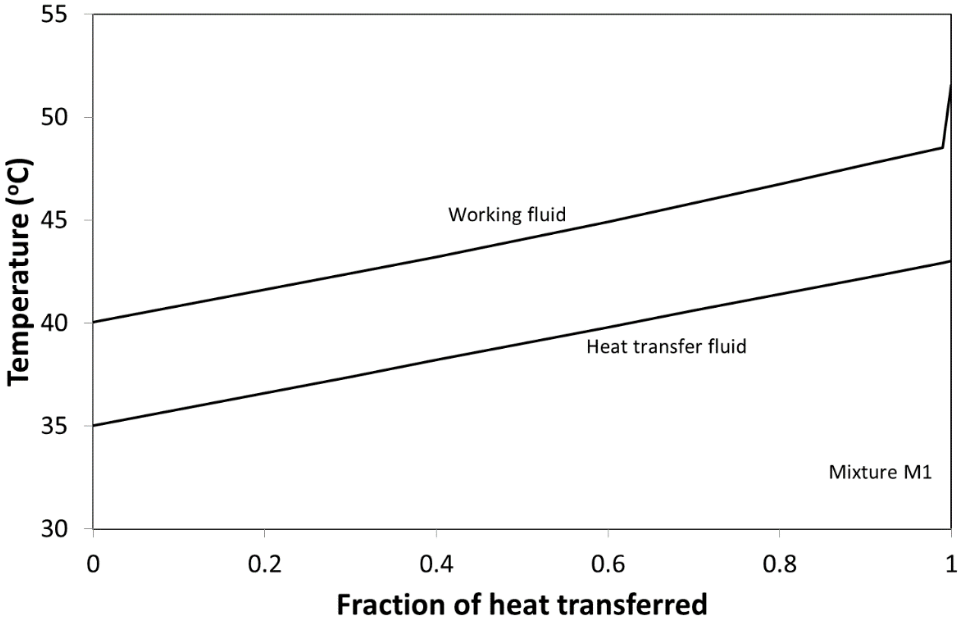


Figure 5. Temperature profiles in the condenser with mixture M1

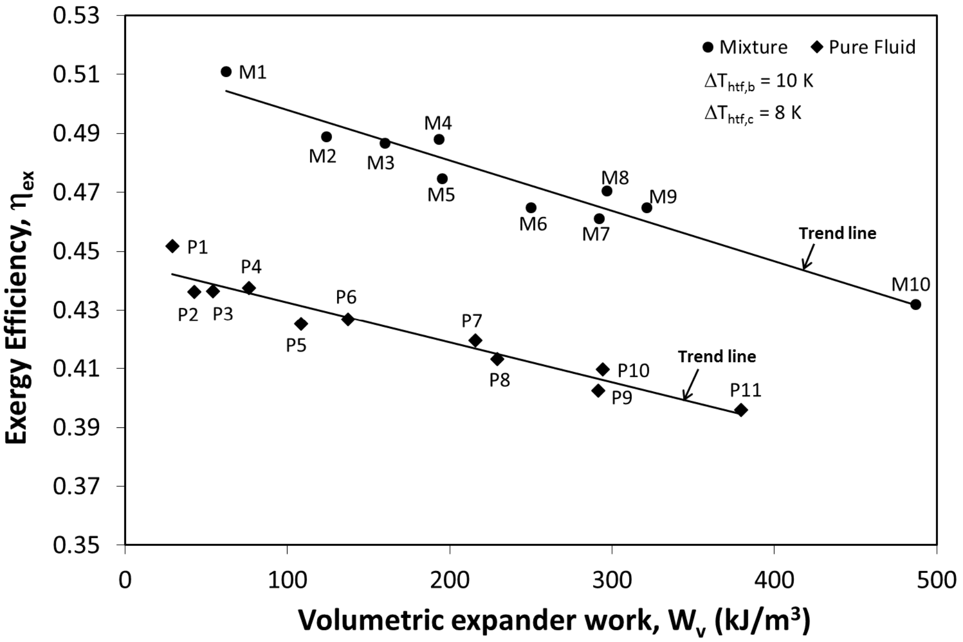


Figure 6. Variation of exergy efficiency with volumetric expander work for a boiler heat transfer fluid inlet temperature of 100^{o}C

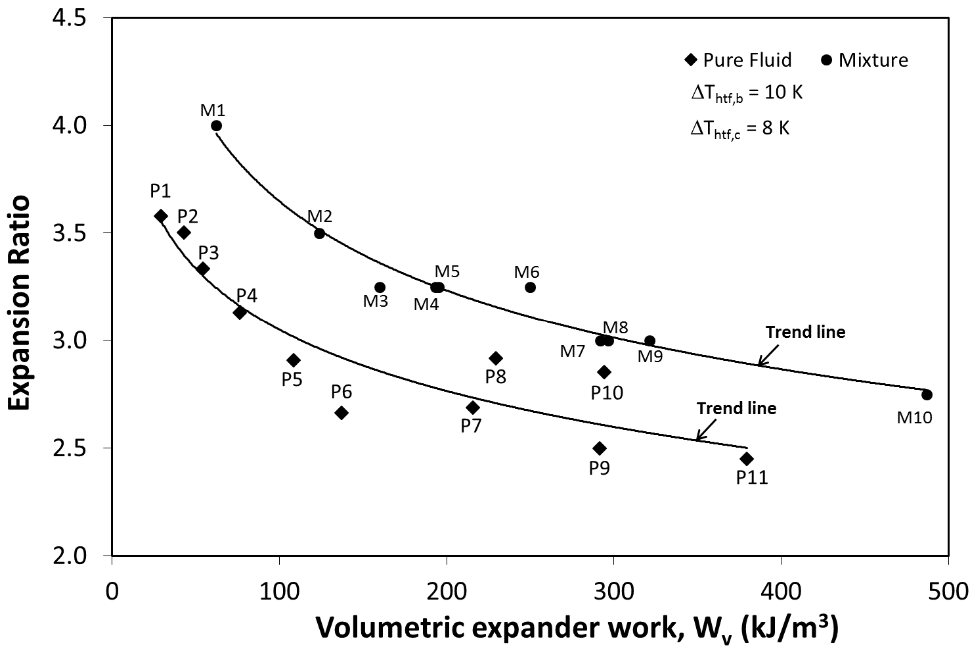


Figure 7. Variation of expansion ratio(p_3/p_4 in Fig. 2) with volumetric expander work for a boiler heat transfer fluid inlet temperature of 100^{o}C

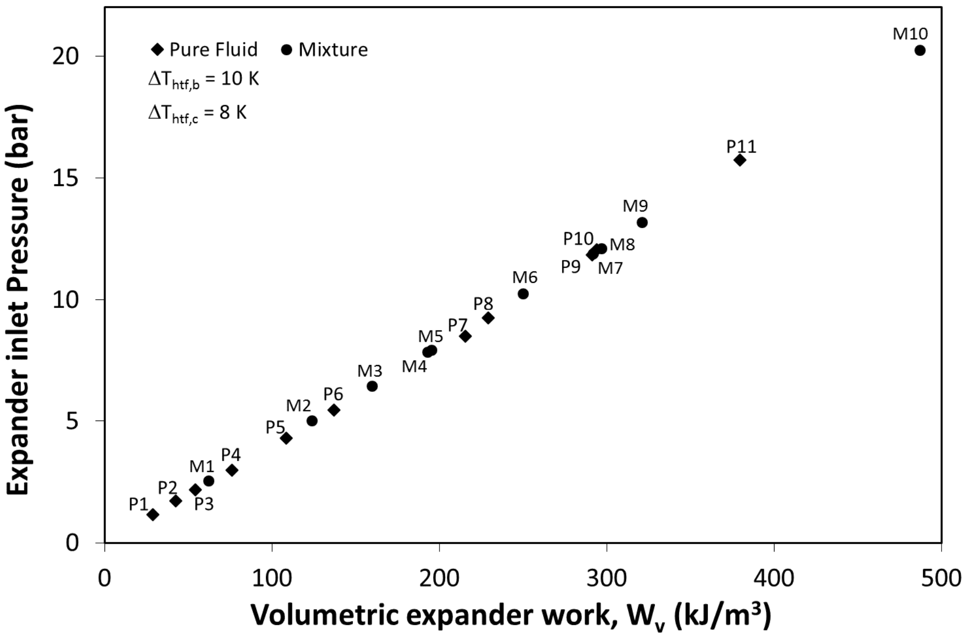


Figure 8. Variation of expander inlet pressure with volumetric expander work for a boiler heat transfer fluid inlet temperature of 100°C

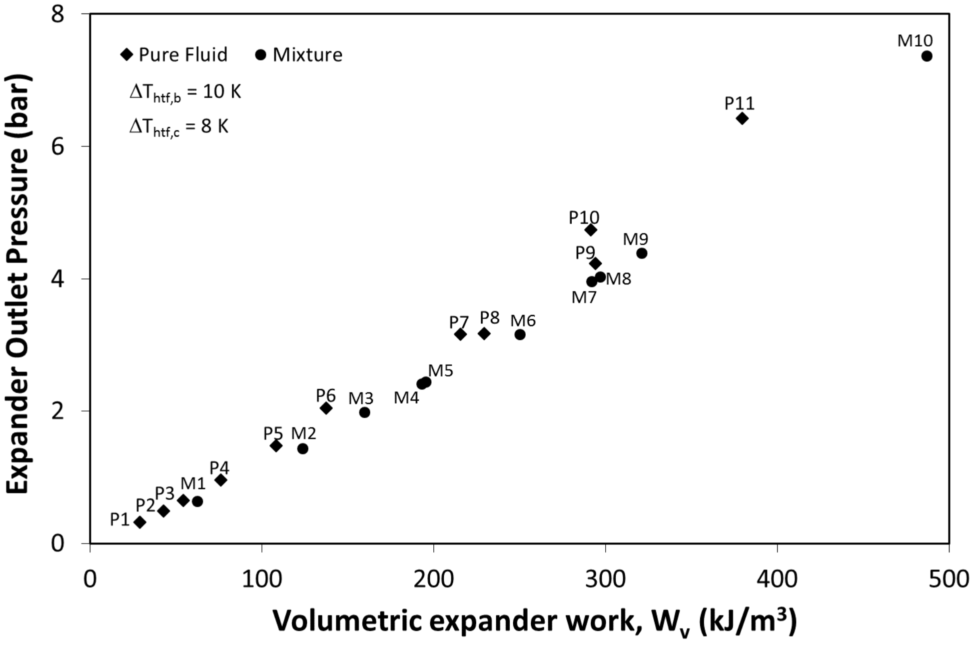


Figure 9. Variation of expander outlet pressure with volumetric expander work for a boiler heat transfer fluid inlet temperature of 100^{o}C

Table 1. Pure fluids studied in this work

Pure fluid No.	Name	T_{NBP} (K)	T_c (K)	T_{NBP}/T_c (K/K)
P1	Cyclohexane	353.87	553.60	0.64
P2	Hexane	341.86	507.82	0.67
P3	Isohexane	333.36	497.70	0.67
P4	Cyclopentane	322.41	511.72	0.63
P5	Pentane	309.21	469.70	0.66
P6	Isopentane	300.98	460.35	0.65
P7	Cyclobutane	285.65	460.15	0.62
P8	R245fa	288.29	427.16	0.67
P9	R236ea	279.32	412.44	0.68
P10	Butane	272.66	425.13	0.64
P11	Isobutane	261.40	407.81	0.64

Table 2. Mixtures optimized in this work

Mixture	Components	Mole percent
M1	Isopentane/Cyclopentane/Cyclohexane	4.6/64.7/30.7
M2	Isobutane/Pentane/Isopentane/Cyclohexane	3.7/48.1/40.3/6.9
M3	Isobutane/Cyclobutane/Isopentane/Cyclohexane	10.3/3.9/83.7/2.1
M4	Butane/Isobutane/Pentane/Isopentane	36.1/3.2/18.0/42.7
M5	Butane/Isobutane/Pentane/Isopentane	38.1/2.7/18.2/41.0
M6	Isobutane/R236ea/Isopentane/Cyclohexane	24.0/39.6/36.1/0.3
M7	Propane/Butane/Isobutane/Pentane/Isopentane /Cyclohexane	5.5/26.9/21.6/25.4/19.5/2.1
M8	Butane/Isobutane/Pentane/Isopentane	29.4/50.3/15.8/4.5
M9	Isobutane/R236ea/Isopentane/Cyclohexane	56.6/33.1/8.4/1.9
M10	Propane/Butane/Isobutane	35.1/37.7/27.2