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([Fig. 2\)](#page-1-0).

Performance of an organic Rankine cycle with multicomponent mixtures

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ABSTRACT

There is a renewed interest in ORC (organic Rankine cycle) 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.

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1. Introduction

There is a worldwide interest in the development of ORC (organic Rankine cycles) operating with solar thermal energy as well as low temperature waste heat. [Fig. 1](#page-1-0) 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 \degree 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 temperatureentropy 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 $600 °C$ in an ideal Clausius–Rankine cycle shown in [Fig. 1](#page-1-0) even if the phase change of water occurs at 150 \degree 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

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

with solar/waste heat available at temperatures lower than 200 \degree 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 superheat¹. 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

Both pure fluids and zeotropic mixtures can be used as working fluids in organic Rankine cycles ([Fig. 3\)](#page-1-0). 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 the relative performance of an ORC with different pure working fluids $[1-13]$ $[1-13]$ $[1-13]$. 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

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

Fig. 2. Organic Rankine cycle with an internal heat exchanger.

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" [\[14\]](#page--1-0). A number of authors have studied the performance of ORC with a variety of binary zeotropic mixtures $[15-24]$ $[15-24]$ $[15-24]$ 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. [\[16\]](#page--1-0) compared the performance of an ORC with a five component mixture of siloxanes. Chys et al. [\[15\]](#page--1-0) studied the performance of an ORC with three-component mixtures at specified mixture composition. Sami et al. [\[25\]](#page--1-0) patented a four component mixture of HFC134a/HCFC123/HCFC124/HFC125 (10/70/10/10 mass %). Zimron and Bronicki [\[26\]](#page--1-0) patented a multicomponent mixture of hydrocarbons, a refrigerant and a fire retardant as working fluid of an ORC. Zhang et al. [\[27\]](#page--1-0) claimed mixtures based on HFO 1234yf with different components. For example, they claimed a mixture of HFO1234yf/HFC236fa/HFC143 in the range of 3-91, 4 to 92 and 5 to 93 mass% respectively. Similar claims were made by Zhang et al. [\[27\]](#page--1-0) for a variety of multicomponent mixtures. Recently Sami [\[28\]](#page--1-0) claimed a quaternary mixture of HFC245ca/HFC236ea/HFC125/ HFC152a of composition 1–97% each. Similar claims were made by Sami [\[28\]](#page--1-0) 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.

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

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