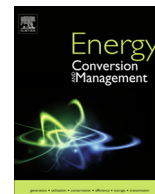




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Exergy analysis of zeotropic mixtures as working fluids in Organic Rankine Cycles

S. Lecompte^{a,b,*}, B. Ameel^a, D. Ziviani^{a,b}, M. van den Broek^{b,a}, M. De Paepe^a

^a Department of Flow, Heat and Combustion Mechanics, Ghent University – UGent, Sint-Pietersnieuwstraat 41, 9000 Gent, Belgium

^b Department of Industrial System and Product Design, Ghent University – UGent, Graaf Karel de Goedelaan 5, 8500 Kortrijk, Belgium

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ABSTRACT

The thermodynamic performance of non-superheated subcritical Organic Rankine Cycles (ORCs) with zeotropic mixtures as working fluids is examined based on a second law analysis. In a previous study, a mixture selection method based on a first law analysis was proposed. However, to assess the performance potential of zeotropic mixtures as working fluids the irreversibility distributions under different mixtures compositions are calculated. The zeotropic mixtures under study are: R245fa–pentane, R245fa–R365mfc, isopentane–isohehexane, isopentane–cyclohexane, isopentane–isohehexane, isobutane–isopentane and pentane–hexane. The second law efficiency, defined as the ratio of shaft power output and input heat carrier exergy, is used as optimization criterion. The results show that the evaporator accounts for the highest exergy loss. Still, the best performance is achieved when the condenser heat profiles are matched. An increase in second law efficiency in the range of 7.1% and 14.2% is obtained compared to pure working fluids. For a heat source of 150 °C, the second law efficiency of the pure fluids is in the range of 26.7% and 29.1%. The second law efficiency in function of the heat carrier temperature between 120 °C and 160 °C shows an almost linear behavior for all investigated mixtures. Furthermore, between optimized ORCs with zeotropic mixtures as working fluid the difference in second law efficiency varies less than 3 percentage points.

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1. Introduction

The worldwide electricity demand is still growing. Future projections assume an increase with 33% by 2020 and 84% by 2035 [1]. Besides growing demand, electricity prices have risen in the last decade with 12%, both in Europe [2] and in the USA [3]. Furthermore, environmental aspects, such as global warming, ozone layer depletion and high-levels of pollution represent a large concern and heavily influence the global energy policy. Therefore, in order to reduce the dependency on fossil fuels, it is necessary to emphasize the use of emerging and well-known renewable energy approaches. ORCs have the ability to convert low temperature heat (<300 °C) to electricity. In particular, studies show that low grade waste heat accounts for more than 50% of the total heat generated in the industry [4]. Besides waste heat, geothermal and solar sources are available to provide a clean alternative to fossil fuel combustion.

Because of the simplicity of the technology and the availability of components, the ORC has the potential to become an established technology in the near future. The basic ORC is already well known in literature and in industry. However, in order to improve the cycle performance, several modifications to the basic ORC are proposed [5]. One of these modifications is the use of zeotropic mixtures as working fluid. Zeotropic mixtures have a non-isothermal phase shift. As such, they have the ability to decrease the irreversibility associated with heat transfer over a finite temperature difference across the working fluid and the thermal heat source or heat sink reservoir. Zeotropic mixtures as working fluids have been investigated for heat pumps [6–8] and vapor compression cycles [8–10]. The use of zeotropic mixtures as working fluids for the ORC has gained interest recently. Still, only a few studies on this subject have been published. Several studies focus solely on the first law efficiency with a limited selection of mixtures: Wang et al. [11] (R245fa–R152a), Garg et al. [12] (R245fa–isopentane) and Borsukiewiczgozdur and Nowak [13] (propane–ethane). A systematic and comparative study of zeotropic mixtures as working fluids based on a first law analysis is given by the authors in a previous study [14].

* Corresponding author at: Department of Flow, Heat, and Combustion Mechanics, Ghent University – UGent, Sint-Pietersnieuwstraat 41, 9000 Gent, Belgium. Tel.: +32 470045524; fax: +32 92643289.

E-mail address: steven.lecompte@ugent.be (S. Lecompte).

Nomenclature

C	mole fraction (–)
C_p	heat capacity (kJ/(kg K))
e	specific exergy (kJ/kg)
\dot{E}	exergy flow rate (kW)
h	specific enthalpy (kJ/kg)
\dot{I}	irreversibility rate (kW)
M	molar mass (g/mol)
\dot{m}	mass flow rate (kg/s)
P	pressure (bar)
PP	pinch point temperature difference (°C)
\dot{Q}	heat transfer rate (kW)
s	specific entropy (kJ/kg K)
T	temperature (°C)
ΔT_{hs}	temperature glide cooling fluid (°C)
T_{pp}	pinch point temperature heat carrier (°C)
\dot{W}	work (kW)

Abbreviations

HTC	heat transfer coefficient (–)
ORC	Organic Rankine Cycle (–)

WF	working fluid (–)
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Greek symbols

η	efficiency (–)
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Subscripts

I	first law (–)
II	second law (–)
<i>cond</i>	condenser (–)
<i>evap</i>	evaporator (–)
<i>ext</i>	external (–)
<i>hc</i>	heat carrier (–)
<i>in</i>	input stream (–)
<i>int</i>	internal (–)
N	number of discretizations (–)
o	dead state (–)
<i>wf</i>	working fluid (–)

Systematic studies which investigate the thermodynamic influence of varying mixture composition on the Organic Rankine Cycle components are valuable but scarce. Second law analysis provides the tools for this research. The use of second law analysis on Organic Rankine Cycles is well-known in open literature. Mago et al. [15] examined the exergy destruction in Organic Rankine Cycles. Visual representations using an exergy wheel clearly show the exergy accounting for each thermodynamic process. The results show that the evaporator has by far the highest exergy destruction rate, followed by the turbine. Therefore, it seems that cycle modifications, of which the aim is to reduce exergy destruction in the evaporator, have a major potential to increase the power output of the ORC. Roy et al. [16] studied the output power, the second and first law efficiency and irreversibilities of an ORC using R12, R123 and R134a as working fluids. The ORC was driven by flue gas waste heat at 140 °C. Their results show that the point of maximum thermal efficiency and maximum power output do not coincide. Furthermore the second law efficiency is strongly affected by the pinch point temperature difference in the evaporator. The optimal evaporation temperature for a subcritical ORC based on maximization of the second law efficiency was investigated by Liu et al. [17].

Only a few studies investigate the ORC with zeotropic mixtures from a second law perspective. Furthermore, only a limited selection of working fluids are considered. Heberle et al. [18] investigated the second law efficiency of an ORC with zeotropic mixtures of isobutane–isopentane and R227ea–R245fa as working fluids. The results show that for temperatures below 120 °C the second law efficiencies increased in the range of 4.3–15%. The optimal second law efficiency was achieved when the temperature glide of condensation and cooling water matched. Ho et al. [5] compared the Organic Flash Cycle (OFC) to an optimized basic ORC cycle, a zeotropic rankine cycle with a binary ammonia–water mixture and a transcritical CO₂ cycle. A distinction is made between utilization efficiency and second law internal efficiency. The former definition assumes that the exergy which is left in the waste heat stream is discarded or unused, while the latter discards exergy destruction due to heat transfer in the evaporator. The definition of second law efficiency is therefore not unique; it is

based on a carefully selected set of chosen input and output streams. Therefore, a clear understanding of the purpose of the system is needed before defining the second law efficiency [19].

The objective of this study is to analyze the performance of zeotropic working fluids based on a second law analysis. The work focusses on non-superheated subcritical cycles. Comparisons are made among a selection of zeotropic working fluids. Special care is taken to quantify the distribution of irreversibilities within the system. The ORC is optimized and the cause of the optimization potential is analyzed.

2. Cycle**2.1. Description of the ORC**

The schematic diagram of the ORC analyzed in this study is given in Fig. 1. Fig. 1a shows the basic cycle while Fig. 1b represents the cycle with recuperator. The basic ORC consists of a pump which pressurizes the working fluid and transports it to the evaporator. In the evaporator the working fluid is heated to the point of saturated vapor. Next, the working fluid expands through the turbine and produces work. This shaft power is then converted to electric power by the generator. The superheated working fluid at the outlet of the turbine is condensed to saturated liquid in the condenser. The liquid working fluid is again pressurized by the pump, completing the cycle. A recuperator (Fig. 1b) cools down the superheated vapor at the exit of the expander and heats up the working fluid after the pump. As a result, the load on the condenser is decreased.

2.2. Working fluid selection

The selected pure working fluids are all hydrocarbons and can be found in Table 1. The selection corresponds with that of a previous study by the authors [14]. Guidelines for mixture component selection in cryogenic applications are adopted [20,21]. The first component is volatile at 1–1.5 bar and therefore, low temperatures after expansion can be obtained without the need to reach vacuum. The

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