Energy 73 (2014) 204–213

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Selection and optimization of pure and mixed working fluids for low grade heat utilization using organic Rankine cycles

J.G. Andreasen*, U. Larsen, T. Knudsen, L. Pierobon, F. Haglind

Technical University of Denmark, Department of Mechanical Engineering, Building 403, Nils Koppels Allé, DK-2800 Kgs. Lyngby, Denmark

ARTICLE INFO

Article history:
Received 23 January 2014
Received in revised form
2 May 2014
Accepted 4 June 2014
Available online 10 July 2014

Keywords:
Organic Rankine cycle
Genetic algorithm
Fluid selection
Zeotropic mixtures
Low grade heat
Geothermal

ABSTRACT

We present a generic methodology for organic Rankine cycle optimization, where the working fluid is included as an optimization parameter, in order to maximize the net power output of the cycle. The method is applied on two optimization cases with hot fluid inlet temperatures at 120 °C and 90 °C. Pure fluids and mixtures are compared to see how mixed working fluids affect performance and important design parameters. The results indicate that mixed working fluids can increase the net power output of the cycle, while reducing the pressure levels. The maximum net power output is obtained by fluids with a critical temperature close to half of the hot fluid inlet temperature. For some mixtures we find the maximum net power when the temperature glide of condensation matches the temperature increase of the cooling water, while for other mixtures there are large differences between these two parameters. Ethane is a fluid that obtains a large net power increase when used in mixtures. Compared to pure ethane, an optimized ethane/propane mixture attains a 12.9% net power increase when the hot fluid inlet temperature is 120 °C and a 11.1% net power increase when the hot fluid inlet temperature is 90 °C.

1. Introduction

The ORC (organic Rankine cycle) is a technology, that can produce mechanical power from various heat sources. Compared to the traditional steam Rankine cycle the ORC has several advantages when considering utilization of low temperature heat [1]. This makes the ORC suited for environmentally-friendly power conversion from geothermal heat sources, concentrated solar energy, waste heat streams and as bottoming cycle for power plants.

An important part of the optimization and design of an ORC is the working fluid selection, since the properties of the working fluid affect both cycle performance and component design. The volume flow ratio, enthalpy drop and Mach number are some important parameters when considering expander design, while thermal conductivity and viscosity are key variables in heat exchanger design. Hazard levels, ODP (ozone depletion potential), GWP (global warming potential) and thermal stability must also be considered. When choosing a working fluid for an ORC, it is therefore necessary to consider many different parameters, in order to reach a feasible design. For example, it is possible that a thermodynamically beneficial working fluid requires infeasibly large heat exchanger areas or an overly expensive expander (e.g. a multistage axial turbine). The review on fluid selection studies recently provided by Bao and Zhao [2], gives an overview of the abundant literature which is available on fluid selection for pure fluids. Binary working fluids have been studied far less, despite the available literature suggesting possible performance benefits when zeotropic mixtures are used in ORCs.

The non-isothermal phase change of zeotropic mixtures, can be utilized to optimize the heat transfer processes in the evaporator and the condenser thus increasing the efficiency of the ORC [3]. Heberle et al. [4] optimized subcritical ORCs using the mixtures: isobutane/isopentane and R227ea/R245fa, as working fluids. The analysis showed that the second law efficiency of the best isobutane/isopentane mixture was 8% higher than that of pure isobutane. The best R227ea/R245fa mixture showed 0.8% higher second law efficiency than pure R227ea. For the isobutane/isopentane mixture, Heberle et al. [4] also showed that the condenser *UA*-value peaked with the second law efficiency, while the *UA*-values for the preheater and the evaporator remained close to constant over a range of mixture compositions.

Trapp and Colonna [5] maximized the net power output of an ORC for low grade waste heat recovery from a pre-combustion CO_2 capture process as part of an integrated gasification combined cycle power plant. The waste heat stream was a 140 °C syngas/water mixture which partly condensed as heat was transferred from the

---

* Corresponding author. Tel.: +45 45 25 41 23.
E-mail address: jgan@mek.dtu.dk (J.G. Andreasen).

http://dx.doi.org/10.1016/j.energy.2014.06.012
0360-5442/

waste heat stream to the ORC. For this unconventional heat source they showed that it was thermodynamically beneficial to have a supercritical boiler pressure and/or a binary zeotropic working fluid in the ORC. The results of an exergy analysis indicated that the exergetic efficiency of the condenser increased by 31% when a binary mixture was used instead of a pure fluid, and that the exergetic efficiency of the primary heat exchanger (boiler) was increased by 4–6% when an ORC with a supercritical boiler pressure was used instead of a subcritical ORC. An estimation of the required condenser heat transfer area indicated that a larger condenser is needed for mixtures than for pure working fluids.

Chys et al. [6] optimized a large number of working fluids (pure fluids, binary mixtures and three-component mixtures) in ORCs. For their low temperature heat source they optimized eight different binary mixtures of hydrocarbons and refrigerants to reach maximum thermal efficiency. For cyclohexane the thermal efficiency increased from 10.85% to 11.57% when isopentane was combined with cyclohexane to form a binary zeotropic working fluid, and a further increase to 11.74% was obtained when isohexane was added to form a three-component working fluid mixture.

Papadopoulos et al. [7] recently presented a fluid selection method where the Computer Aided Molecular Design approach was used to find optimal molecular structures for fluids used in binary working fluid mixtures. The method was applied to maximize the exergetic efficiency of an ORC utilizing a heat stream with an inlet temperature at 95 °C and yielded 10 potentially optimal fluid mixtures containing neopentane and/or fluorinated hydrocarbons.

A fluid selection and optimization study of ORCs, considering a large group of binary mixtures as possible working fluids, combined with an evaluation of parameters which affect the design of components, for a non-condensing (temperature independent c_p) heat source, has not yet been published in the scientific literature. Previous studies on binary mixtures in ORCs concerned optimization and preliminary component design for specific fluid mixtures, while other studies have considered many different binary mixtures with a primary focus on efficiency maximization.

This paper provides an ORC optimization analysis where both pure fluids and mixtures are considered as possible working fluids. Two liquid water streams with inlet temperatures at 120 °C and 90 °C representing geothermal heat sources or industrial waste heat streams are chosen as the basis of the analysis. These low temperatures are chosen, since mixtures have shown beneficial performance compared to pure fluids when the hot fluid inlet temperature is low [3–7]. A systematic methodology using a genetic algorithm optimizer is developed to find promising pure fluids and mixtures for the maximization of the net ORC power output. Both subcritical-saturated, subcritical-superheated and transcritical ORCs are considered as possible solutions. The best candidates are evaluated based on: thermodynamic performance, pressure levels, volume flow ratio over the expander, a turbine size parameter, $\overline{UA}$-values, fluid hazard levels and GWP, which are the critical parameters for the expander design, heat exchanger design, safety and the environment. Furthermore, the critical temperature and the temperature glide of condensation are evaluated in order to investigate if the working fluids yielding maximum net power have common characteristics.

The paper begins with a description of the used methodology in Section 2. Then the results are presented in Section 3. Section 4 provides a discussion of the results and a comparison with the existing literature. Finally conclusions are given in Section 5.

2. Methodology

The ORC is optimized in its simplest configuration. In this configuration it consists of four components: a pump, a boiler, an expander and a condenser. For subcritical cycles the boiler contains a preheater, an evaporator and a superheater (optional). A sketch of the simple cycle can be seen in Fig. 1 (a), while Fig. 1 (b) shows a subcritical and a transcritical ORC with a zeotropic working fluid in a *Ts*-diagram.

The assumptions used in the numerical simulations are listed in Table 1. Additional assumptions are the following: no pressure loss in piping or heat exchangers, no heat loss from the system, steady state condition and homogeneous flow in terms of thermodynamic properties.

The net power, $\dot{W}_{\mathrm{NET}}$, given as the difference between the expander power and the pump power, is chosen as the objective function in the optimization

$$\dot{W}_{\mathrm{NET}} = \dot{m}_{\mathrm{wf}}[h_3 - h_4 - (h_2 - h_1)] \tag{1}$$

where $\dot{m}_{\mathrm{wf}}$ is the mass flow of the working fluid and h is the specific enthalpy.

The net power is chosen as the objective function, since the purpose of the ORC is to produce maximum net power using the available heat. The corresponding optimization variables can be expressed in an array as

$$Y = \left[T_3, P_3, T_{\mathrm{hf},o}, \text{fluid } 1, \text{fluid } 2, X_{\mathrm{wf}}\right] \tag{2}$$

where T is the temperature, P is the pressure, and X_{wf} is the composition of the working fluid (for mixtures).

Table 2 shows the optimization parameters, and the range in which they are allowed to vary. For the expander inlet temperature and the hot fluid outlet temperature, the upper limit is dependent on the hot fluid inlet temperature.

The parameters listed in Tables 1 and 2 are used to determine all state points and mass flows in the ORC. The condenser pinch point is used to determine the condensation pressure, and the boiler pinch point is used to check if the minimum limit on the boiler pinch point is violated for the given hot fluid outlet temperature $T_{\mathrm{hf},o}$ and boiler pressure P_3. The thermal energy input and the net power output of the ORC vary depending on the outcome of the optimizations. For the hot fluid characteristics chosen in this paper, the thermal energy input to the cycle varies in the ranges 12.0–17.4 MW and 7.4–10.9 MW, while the net power output varies in the ranges 1.0–1.5 MW and 0.4–0.6 MW for the 120 °C and 90 °C hot fluid inlet temperature cases, respectively.

The thermodynamic simulation models were created using Matlab language, and the database provided by Lemmon et al. [8] was used to obtain thermodynamic property data. All pure fluids and predefined mixtures (e.g. R507A and R404A), with ODP = 0, within the database are included as potential fluid candidates. The group of predefined mixtures consists of mixtures including up to five fluids, and these mixtures are treated as pure fluids in the optimizations. The property database also provides the possibility of combining pure fluids to form mixtures of arbitrary composition. In this study we only consider the possibility of combining pure fluids in binary mixtures. In order to ensure reliable property data for these mixtures, we only consider mixtures, for which accurate and validated property data is available. Accurate property data models for mixtures (relevant as ORC working fluids) are provided by: Lemmon and Jacobsen [9] (R32, R125, R134a, R143a, R152a) and Kunz and Wagner [10] (natural gas components, primarily hydrocarbons). For the pure fluids reported in this paper the highest estimated uncertainties are the following: 1% in density, 2% in speed of sound and 5% in heat capacities, within the temperature and pressure ranges encountered in the optimizations. For the refrigerant mixtures in the model of Lemmon and Jacobsen [9] the