Energy 67 (2014) 106–116

Contents lists available at ScienceDirect

Energy

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

Investigation of hydrofluoroolefins as potential working fluids in organic Rankine cycle for geothermal power generation

Wei Liu [a,*], Dominik Meinel [a], Christoph Wieland [a], Hartmut Spliethoff [a,b]

[a] Institute of Energy Systems, Faculty of Mechanical Engineering, Technische Universität München, Boltzmannstrasse 15, 85748 Garching, Germany
[b] The Bavarian Center for Applied Energy Research (ZAE Bayern), Division 1, Technology for Energy Systems and Renewable Energy, Walther-Meissner-Str. 6, 85748 Garching, Germany

ARTICLE INFO

Article history:
Received 1 August 2013
Received in revised form
3 November 2013
Accepted 29 November 2013
Available online 9 January 2014

Keywords:
Hydrofluoroolefins
Geothermal ORC power generation
System efficiency
Optimal heat source temperature
Global warming potential

ABSTRACT

Recently, HFOs (hydrofluoroolefins) are presented as a group of the fourth generation refrigerants with zero ODP (Ozone Depletion Potential) and a very low GWP (Global Warming Potential). This paper presents a study on eight different HFOs and their potential applications in ORC (Organic Rankine Cycle) for geothermal power generation. The thermodynamic properties are calculated based on Peng–Robinson equation of state, and are used for simulating a standard ORC for geothermal heat sources with different temperatures. System efficiency, which involves both heat transfer efficiency and thermal efficiency, is considered to be the main criterion to evaluate the ORC system performance. An innovative term, i.e. the optimal heat source temperature is proposed for the determination of thermodynamic performances of each investigated working fluid in combination with the pinch point analysis. Based on the system efficiencies of all HFOs, some of them are selected in a series of case studies for comparison with other relevant ORC fluids. As a conclusion, some of the presented HFOs show promising performances in terms of system efficiency especially for low-to medium temperature geothermal ORC power generation ($120\ ^\circ\mathrm{C} \le t_{\mathrm{hs}} \le 150\ ^\circ\mathrm{C}$).

1. Introduction

For the last hundred years Clausius–Rankine-Process has been considered as the main method to convert high temperature heat into electricity. However, low-to-medium heat sources such as geothermal energy or industrial waste heat which possess even larger amount of heat are less concerned because of the technical difficulties for exploitation. ORC (Organic Rankine Cycle), as one of the most promising methods to utilize low-to-medium heat sources, has attracted great attention since the 1980s [1]. Up to date, an increasing number of power plants and micro-power generators based on ORC technology have been brought into operation [2].

What makes organic Rankine cycle different from the conventional Clausius–Rankine-Cycle is the organic working medium which enables phase change at low-to-medium temperatures. However, most of the existing ORC fluids are listed in the family of refrigerants, and have harmful effects on the environment, e.g. depletion of the ozone layer or global warming. Looking back upon the progressive evolution of refrigerants from CFCs (chlorofluorocarbons), HCFCs (hydrochlorofluorocarbons) to HFCs (hydrofluorocarbons), tremendous efforts have been put into developing a group of compounds which not only have similar thermodynamic properties as the traditional ones but also have less impact on the environment. Today, the use of the first two generation refrigerants has been either banned or restricted due to their high ODP (Ozone Depletion Potential) values. The so-called third generation refrigerants HFCs, which are currently dominating the refrigerants market, have no effect on the ozone layer but extremely high GWP (Global Warming Potential) values. In fact, they have been considered as one of the six main greenhouse gases according to Kyoto Protocol [3]. For instance, the widely used ORC fluid R245fa, which belongs to the family of HFC, has a very high GWP value of 1030 [4].

From this background, HFOs (hydrofluoroolefins) have been developed as the fourth generation refrigerants in order to overcome the environmental drawbacks of the current refrigerants. Unlike HFCs, which are derivatives of alkanes, HFOs are derived from alkenes containing at least one double bond. For this reason, their atmospheric lifetimes can be greatly shortened to only few days compared to years for most of the other fluorinated compounds. Another very promising aspect for HFO is the low GWP value (<10) [5]. The encouraging aspects of HFOs have attracted an increasing number of development studies and two of them, i.e. R1234yf and R1234zeE,

---

* Corresponding author. Tel.: +49 89 289 16284; fax: +49 89 289 16271.
E-mail addresses: wliu2_05@hotmail.com, wei.liu@tum.de (W. Liu).

0360-5442/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.11.081

Nomenclature

C_{mol}	molar heat capacity, J/mol K
d_i	ideal gas heat capacity constant, J/mol K
e	specific exergy, kJ/kg
E	exergy flow, kW
h	specific enthalpy, kJ/kg
m	mass flow rate, kg/s
p	pressure, bar, Pascal
Q	heat flow, kW
HE	heat exchanger
IHE	internal heat exchanger
s	specific entropy, kJ/kg K
T	temperature, K
t	temperature, °C
V_m	molar volume, m^3/mol
W	work, kW
Z	compressibility factor

Greek letters

ω	acentric factor
η	efficiency, %

Superscripts

lower	lower limit
ideal	ideal state
is	isentropic parameter
upper	upper limit

Subscripts

0	ambient state
1, 2,…,10	working states
destruction	exergy destruction
evp	evaporator
hs	geothermal heat source
HEx	heat exchange
in	input heat
loss	exergy loss
p	pump
pre	preheater
sys	system
t	turbine
total	total
th	thermal
out	output heat
opt	optimal
cal	calculated values
r	reduced parameter
wf	working fluid
sat	saturated states
dev	deviated values
REFPROP	data in REFPROP

have been commercially available as of the year 2013. Specifically, theoretical studies regarding the thermodynamic properties of R1234yf were carried out in combination with a number of experimental studies [6,7]. More recently, both fluids have been added into some commercial software such as REFPROP 9.0 [8], which allows realistic process simulations for various applications. For its application in refrigeration system, R1234yf has been considered to be an excellent replacement for the conventional refrigerant HFC-134a [9]. In fact, some large automotive manufacturers in Europe are planning to gradually adopt R1234yf as one of the main refrigerants for the automotive refrigeration system. On the contrary, for its application in ORC system, simulation study suggests that R1234yf is not very preferable in terms of thermal efficiency at least for low-to-medium temperature heat sources [10]. The drawbacks for the application of R1234yf in ORCs can be summarized as: 1) low critical temperature, which limits the evaporation temperature; 2) low heat of evaporation; 3) low normal boiling point.

On the structural basis of R1234yf, more than 30 different HFOs can be obtained when taking into account the isomers as well as the stereoisomers. However, due to the lack of thermodynamic properties, few of them can be found in open literature, let alone their applications in ORC systems.

In the present work, eight of the potential HFOs are selected from Brown's work [11] in which their critical parameters have been particularly discussed. The state parameters are described using Peng–Robinson equation of state in combination with the group contribution methods. For further calculation of system performance, the caloric properties such as enthalpy and entropy are calculated with the help of departure functions and ideal gas heat capacity constants. The comparison with the database benchmark follows for validation of the used calculation methods. Afterwards, a standard ORC system is chosen, along with a detailed specification of its working conditions. The heat source is represented by the geothermal brine and its temperature, along with the system operating pressure are considered to be the main variables for the ORC system. The system performances of each given HFO are compared at different system operating pressures for a given set of geothermal heat source temperatures in order to determine an optimal heat source temperature region. Subsequently, the system performances of the investigated HFOs are compared. The influence of system operating pressure on system performance is also investigated in combination with pinch point analysis. Based on the thermodynamic performances of all investigated HFOs, some of them are selected for further comparisons with some of commercially available ORC fluids. Simulations are carried out in Matlab, in which the self-developed calling function, namely the OFluid function (see equation (1)) are added for calculation of thermodynamic properties and system performances. During cycle simulations, the desired parameters, such as the specific enthalpy at a specified state, are "called" by using the OFluid function with required inputs.

$$\text{Desired Parameter} = \text{OFluid}(\text{Fluid},\ \text{function},\ \text{Input1},\ \text{Input2}) \tag{1}$$

2. Estimation of thermodynamic properties

EOS (Equation Of State) enables the determination of the thermodynamic properties required in cycle simulations. These EOSs include the cubic PR EOS (Peng–Robinson EOS) [12], the PT EOS (Patel–Teja EOS) [13], the MH EOS (Martin–Hou EOS) [14], as well as a family of physically based EOS, i.e. BACKONE [15,16]. The aforementioned equations of state show that more experimental data are required in order to obtain sufficient high accuracies for the thermodynamic predictions. For example, in construction of BACKONE, it is necessary to fit relevant equations to a large number of experimental parameters. Akasaka has used the Patel–Teja EOS and ECS (Extended Corresponding State) model for predicting the