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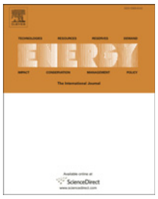

Working fluids for high-temperature organic Rankine cycles

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ABSTRACT

Alkanes, aromates and linear siloxanes are considered as working fluids for high-temperature organic Rankine cycles (ORCs). Case studies are performed using the molecular based equations of state BACKONE and PC-SAFT. First, "isolated" ORC processes with maximum temperatures of 250 °C and 300 °C are studied at sub- or supercritical maximum pressures. With internal heat recovery, the thermal efficiencies η_{th} averaged over all substances amount to about 70% of the Carnot efficiency and increase with the critical temperature. Second, we include a pinch analysis for the heat transfer from the heat carrier to the ORC working fluid by an external heat exchanger (EHE). The question is for the least heat capacity flow rates of the heat carrier required for 1 MW net power output. For the heat carrier inlet temperatures of 280 °C and 350 °C are considered. Rankings based on the thermal efficiency of the ORC and on the heat capacity flow rates of the heat carrier as well as on the volume and the heat flow rates show cyclopentane to be the best working fluid for all cases studied.

1. Introduction

Organic Rankine cycles (ORC) can be used for conversion of heat to power. Heat at different temperature levels may be available as geothermal heat, as biogenic heat from biomass and biogas combustion, as solar or as waste heat. Whilst ORC processes are known already for some time [1–3] they gain presently a rapidly increasing interest. An actual overview was given in [4]. A crucial problem in designing an ORC process is the selection of the working fluid where thermodynamic, stability, safety and environmental aspects have to be considered. A classification of the cycles can be done according to their maximum working fluid temperature T_{max}. Here we consider working fluids for cycles with T_{max} between 180 °C and 300 °C to which we refer as high-temperature cycles. Earlier studies of high-temperature cycles which concentrate mainly on the thermodynamic aspects are given, e.g. in [5–9]. For low temperature cycles an extensive investigation of working fluids at subcritical and supercritical pressures with T_{max} up to 100 °C was given in [10]. Other interesting work on low temperature cycles is reported in [8,9,11–17].

Regarding the modeling of high-temperature ORC processes, Angelino and Colonna considered first alkanes, aromates and perfluorinated benzene [5] and then siloxanes [6] as working fluids. Actually, existing high-temperature ORC plants use mainly siloxanes [18–20] and some few also toluene [21,22]. Recently, Drescher and Brüggemann [7] considered about 700 working fluids for the high-temperature range and concluded that the highest thermal efficiencies are found for the alkylbenzenes. A certain problem with the thermodynamic studies in [5–7] is that they are based on cubic equations of state. This was already realized by Colonna et al. [23] who consequently developed multi-parameter equations of state for the siloxanes. As these equations contain 12 substance parameters which are fitted to rather limited experimental datasets, there remains again some uncertainty. In this situation a promising alternative is to use molecular based equations of state like BACKONE [24] or PC-SAFT [25] which need only 3–5 substance-specific parameters. For alkanes BACKONE parameters are available from a previous study on natural gas [26]. In addition, we determined recently also BACKONE parameters for the cycloalkanes cyclopentane and cyclohexane, for the aromates benezene, toluene, ethylbenzene, butylbenze, *m*-xylene, *o*-xylene and *p*-xylene [27] and PC-SAFT parameters for the first five linear siloxanes [28]. Instead of the full chemical names of the siloxanes we use the abbreviations MM for hexamethyldisiloxane ($C_6H_{18}OSi_2$), MDM for octamethyltrisiloxane ($C_8H_{24}O_2Si_3$), MD2M for decamethyltetrasiloxane, ($C_{10}H_{30}O_3Si_4$), and MD3M for dodecamethylpentasiloxane ($C_{12}H_{36}O_4Si_5$).

In the present paper we consider as working fluids (1) the alkanes *n*-butane, *n*-pentane, and cyclopentane, (2) the aromates toluene, ethylbenzene, butylbenze, *m*-xylene, *o*-xylene and *p*-xylene, and (3) the linear siloxanes MM, MDM, MD2M, and MD3M. We first perform thermodynamic case studies of ORC

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Nomenclature

A, B, C, D, E	ideal gas heat capacity fit coefficients
CHP	combined heat power
$\dot{C}$	heat capacity flow rate [kW/K]
c_p	heat capacity of the heat carrier [kJ/kgK]
c_p^0	ideal gas heat capacity [J/molK]
e_5	Specific exergy of heat carrier at inlet of the EHE [kJ/kg]
$\dot{E}_c$	exergy flow rate of heat carrier [kW]
EHE	external heat exchanger
F	Helmholtz energy
F_A, F_{A1}, F_{A2}	attractive dispersion force contributions to F
F_H	hard-body contribution to F
F_Q	quadrupolar contribution to F
h	specific enthalpy [kJ/kg]
$\dot{H}$	enthalpy flow rate
k	Boltzmann constant
IHE	internal heat exchanger
$\dot{m}$	mass flow rate [kg/s]
m	number of segments in PC-SAFT
MD_2M	decamethyltetrasiloxane, $C_{10}H_{30}O_3Si_4$
MD_3M	dodecamethylpentasiloxane, $C_{12}H_{36}O_4Si_5$
MDM	octamethyltrisiloxane, $C_8H_{24}O_2Si_3$
MM	hexamethyldisiloxane, $C_6H_{18}OSi_2$
o2	cycle at subcritical p_{max} without superheating
o3	cycle at subcritical p_{max} with superheating
ORC	organic Rankine cycle
p	pressure [MPa]
$\dot{Q}$	heat flow rate [kW]
Q^{*2}	reduced squared quadrupole moment
R	ideal gas constant [J/molK]
s	specific entropy [kJ/kgK] or [J/molK]
s2	cycle at supercritical p_{max}
T	temperature [K]
v	specific volume [l/kg], 1 l = 1×10^{-3} m^3
$\dot{V}$	volume flow rate [l/s], 1 l = 1×10^{-3} m^3
w	specific work [kJ/kg]
$\|\dot{W}\|$	net power output of a cycle [kW]

Greek symbols

α	anisotropy parameter in BACKONE
Δ	difference of quantities
ε	energy parameter in PC-SAFT (ε/k in [K])
η_{IHE}	efficiency of the internal heat exchanger
$\eta_{s,P}$	isentropic pump efficiency
$\eta_{s,T}$	isentropic turbine efficiency
η_{th}	thermal efficiency of the cycle
$\eta_{th,Carnot}$	thermal efficiency of the Carnot cycle
η_{th-}	thermal efficiency of cycle without IHE
η_{th+}	thermal efficiency of cycle with IHE
ξ_P	exergy efficiency for power production
ρ	density [mol/l]
σ	segment diameter in PC-SAFT [nm]

Subscripts

0	characteristic quantity in BACKONE
1, 2, 2a, 3, 4, 4a	state points of ORC working fluid
5,6	state points of heat carrier
AI	auto-ignition
c	critical point; heat carrier
i	state point
IHE	internal heat exchanger
in	ingoing flows; Inlet temperature of heat carrier
max	maximum quantities of working fluid (state point 3)
min	minimum quantities of working fluid (state point 1)
out	outgoing flows
P	pump, power
p	pinch (hot stream)
r	reduced with respect to critical quantity
s	isentropic; saturation state
T	turbine
u	environment state of heat carrier

processes for given maximum and minimum temperatures and pressures. The maximum ORC temperatures are assumed to be 250 °C and 300 °C. As we do not include in these systems a pinch analysis of external heat exchangers (EHEs) for the heat transfer to and from the cycle, we call them "isolated" ORC processes. The importance of including such pinch analyses in modeling ORC systems depends on the specific heat source [10] or the plant design [7]. In many cases, however, e.g. if waste heat is used, the pinch point problem in the EHE where the heat is transferred from a heat carrier to the working fluid (EHE) plays a crucial role for the power output of the system. Hence, we consider in a second step systems consisting of an ORC plus an EHE. For these studies heat carrier inlet temperatures T_{in} of 280 °C and 350 °C are assumed. As it is known [10,29,30] that supercritical pressures of the working fluid may improve the heat transfer in the EHE considerably, we will study processes with sub- and supercritical maximum pressures.

In Section 2 we describe ORC processes in general, consider different cycle types and address the heat transfer from the heat carrier to the working fluid. In Section 3 we select potential working fluids for the temperature ranges considered. For the selected working fluids the parameters for BACKONE and PC-SAFT equations are given together with equations for the isobaric ideal gas heat capacities. Moreover, we show the reliability of these equations of state. In Section 4 we give minimum temperatures T_{min} and maximum temperatures T_{max} and other boundary conditions and discuss the selection of the maximum pressures p_{max}. In Section 5 the results for the thermal efficiencies and other thermodynamic properties of "isolated" ORC processes with different working fluids are shown for three pairs of (T_{min}, T_{max}). In Section 6 systems including the heat transfer by a single stage EHE to the ORC will be considered. Heat capacity flow rates for production of 1 MW net power output are studied for different cycles and working fluids and results of optimized EHE + ORC systems are presented.

2. Description of ORC processes

2.1. Plant configurations and fluid flows

The Clausius–Rankine cycle is known from the standard textbooks of thermodynamics as, e.g. [1]. The plant configuration of an ORC with internal heat exchanger (IHE) is shown in Fig. 1. The IHE transfers heat from (4,4a) to (2,2a) and is not contained in the most simple configuration.

Let us first describe the plant and the process without IHE. The plant consists of a pump, a heater, a turbine and a cooler-condenser. The mass flow rate of the working fluid is denoted by $\dot{m}$. In state 1 the working fluid is a saturated liquid with temperature T_1 at the pressure p_1, where $T_1 = T_{min}$ is the minimum temperature and $p_1 = p_{min}$ is the minimum pressure in the cycle. Then the pressure of the liquid is increased by the pump with isentropic pump efficiency η_{sP} to $p_2 = p_{max}$, which is the maximum pressure in the cycle. Thereafter, the fluid is heated in an isobaric process to the