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Industrial waste-heat recovery through integrated computer-aided working-fluid and ORC system optimisation using SAFT-γ Mie

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ABSTRACT

A mixed-integer non-linear programming optimisation framework is formulated and developed that combines a molecular-based, group-contribution equation of state, SAFT-γ Mie, with a thermodynamic description of an organic Rankine cycle (ORC) power system. In this framework, a set of working fluids is described by its constituent functional groups (*e.g.*, since we are focussing here on hydrocarbons: $-CH_3$, $-CH_2-$, *etc.*), and integer optimisation variables are introduced in the description the working-fluid structure. Molecular feasibility constraints are then defined to ensure all feasible working-fluid candidates can be found. This optimisation framework facilitates combining the computer-aided molecular design of the working fluid with the power-system optimisation into a single framework, thus removing subjective and pre-emptive screening criteria, and simultaneously moving towards the next generation of tailored working fluids and optimised systems for waste-heat recovery applications. SAFT-γ Mie has not been previously employed in such a framework. The optimisation framework, which is based here on hydrocarbon functional groups, is first validated against an alternative formulation that uses (pseudo-experimental) thermodynamic property predictions from REFPROP, and against an optimisation study taken from the literature. The framework is then applied to three industrial waste-heat recovery applications. It is found that simple molecules, such as propane and propene, are the optimal ORC working fluids for a low-grade (150 °C) heat source, whilst molecules with increasing molecular complexity are favoured at higher temperatures. Specifically, 2-alkenes emerge as the optimal working fluids for medium- and higher-grade heat-sources in the 250–350 °C temperature range. Ultimately, the results demonstrate the potential of this framework to drive the search for the next generation of ORC systems, and to provide meaningful insights into identifying the working fluids that represent the optimal choices for targeted applications. Finally, the effects of the working-fluid structure on the expander and pump are investigated, and the suitability of group-contribution methods for evaluating the transport properties of hydrocarbon working-fluids are considered, in the context of performing complete thermoeconomic evaluations of these systems.

1. Introduction

Increasing concerns over depleting fossil-fuel reserves and the detrimental effects on human health and the environment linked to the release of their combustion products have led to a surge of interest in renewable and sustainable energy systems in recent years. Within this remit fall a number of technologies which aim to recover waste heat from a variety of industrial processes, and which are of particular interest given their significant potential to improve resource utilisation efficiency and to reduce simultaneously industrial primary energy use and emissions. One such technology is the organic Rankine cycle (ORC), which is highly suitable for the conversion of lower-temperature (or, lower-grade) heat to useful electrical power, either for on-site use or export to the grid [1]. This ability to utilise effectively heat sources at lower temperatures is facilitated by the lower critical temperatures of organic working-fluids, compared to using conventional Rankine cycles, for example. Typically, for heat sources with temperatures between 100 and 400 °C and at scales (in the power range) of a few kW up to tens of MW, the ORC can be considered a suitable technology for the conversion of heat to power with thermal efficiencies in excess of 25% reported at the higher temperatures and larger scales. Although ORC technology has achieved some maturity, with units available commercially from manufacturers and aimed at the aforementioned ranges of temperatures and sizes,

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Nomenclature

Abbreviations

BWR	Back work ratio
CAMD	Computer-aided molecular design
MINLP	Mixed-integer non-linear programming
ORC	Organic Rankine cycle
SAFT	Statistical associating fluid theory
WHR	Waste heat recovery

Greek symbols

η	efficiency
η_L	liquid dynamic viscosity, Pa s
η_V	vapour dynamic viscosity, Pa s
λ_L	liquid thermal conductivity, W/(m K)
λ_V	vapour thermal conductivity, W/(m K)
ω	acentric factor
σ	surface tension, N/m

Roman symbols

ΔT_{sh}	degree of superheating, K
$\dot{m}$	mass flow rate, kg/s
$\dot{W}$	power, W
Ma	mach number
PP	pinch point, K
c_p	specific heat capacity at constant pressure, J/(kg K)
c_v	specific heat capacity at constant volume, J/(kg K)
h	specific enthalpy, J/kg
P	pressure, Pa
P_r	reduced pressure
T	temperature, K
T_r	reduced temperature
V_m	specific (molar) volume, m^3/mol
w	specific work, J/kg

Subscripts

1–4	ORC state points
b	boiling
c	heat sink
cr	critical point
e	expander
h	heat source
i	inlet
n	net
o	outlet
p	pinch, pump
th	thermal

a number of important challenges remain that limit the true potential of this technology, both from technical and economic perspectives [2].

Due to the large number of potential ORC working-fluids, working-fluid selection has remained a particular focus of research. First and foremost, thermodynamic performance remains one of the most important drivers, and there have been many studies concerning the thermodynamic analysis of ORC systems. Chen et al. [3] categorised working fluids based on critical temperature and the slopes of their saturation curves, with the aim of providing general selection criteria based on the heat-source temperature and cycle architecture. Alternatively, many parametric studies have been completed in which a number of working-fluids are optimised for the same heat-source conditions and an optimal working-fluid is selected based on thermodynamic performance, for example in Refs. [4–6]. More recently, Li et al. [7] identified optimal working-fluids for heat-source temperatures between 200 and 500 °C, whilst Song et al. [8] incorporated component modelling into the working-fluid selection procedure.

Alongside using pure working-fluids, it is also possible to consider using fluid mixtures. Lecompte et al. [9] report possible improvements in the second law efficiency between 7.1 and 14.2%, and similar improvements in thermodynamic performance have been reported in Refs. [10–12]. Furthermore, Zhou et al. [13] investigated working-fluid mixtures operating within partially evaporated ORC systems. Whilst many of these studies report higher power outputs and higher exergy efficiencies, they also report larger heat exchanger costs.

In addition to thermodynamic performance, more general working-fluid selection criteria are also available in the literature, and these consider aspects such as component performance, material compatibility, safety, environmental properties and cost. In an early study, Badr et al. [14] listed the desirable properties of a working fluid, and more recently, Rahbar et al. [15] reported similar selection criteria. Specific research into the thermal stability of working-fluids for high temperature waste heat recovery (WHR) has also been conducted [16]. In general, working-fluid selection criteria are introduced during a fluid-selection study in which a group of known fluids, taken from a database such as NIST [17], are screened based on predefined criteria. For example, Drescher and Brüggemann [18] evaluated 1,800 substances, from which five were identified as suitable working-fluids for a biomass application. Similiarly, Tchanche et al. [19] evaluated 20 fluids for a 90 °C heat source, and whilst no fluid met all selection criteria, optimal working-fluids were identified after a qualitative comparison was conducted. More recently, Schwöbel et al. [20] devised a screening process in which 3,174 fluids were considered for a particular application. However, after identifying an optimal working fluid from a thermodynamic perspective, it was necessary to reject this fluid due to safety concerns, highlighting the difficulty in identifying a fluid which meets all predefined criteria.

Alternatively, computer-aided molecular design (CAMD) could be used to identify optimal working-fluids. In CAMD several molecular groups are defined (*e.g.*, $-CH_3$, $-CH_2-$, $>CH-$, $>C<$, $=CH_2$, $=CH-$) which can be combined according to a series of rules in order to form different molecules. Initially, CAMD was applied to solvent design and used to identify molecules with specific solvent properties [21]. More recently, this has developed further and involves coupling CAMD methods with process models, facilitating the integrated design and optimisation of the solvent and the separation process [22–25]. Such problems require molecular feasibility constraints, a group-contribution equation of state, and a mixed-integer non-linear programming (MINLP) optimiser. Molecular feasibility constraints ensure a generated set of molecular groups is a genuine molecule [26–28], whilst a group-contribution equation of state determines the fluid properties of a molecule based on the molecular groups from which it is composed. Early examples are the empirical Joback and Reid group-contribution method [29] and the UNIFAC method [30]. However, an alternative to these empirical methods is the use of molecular-based equations of state based on statistical associating fluid theory (SAFT) [31,32], for which group-contribution methods have recently become available [33–44].

The application of CAMD to ORC problems allows the working fluid and thermodynamic system to be simultaneously optimised in a single CAMD-ORC optimisation framework. This framework

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