EXTENDED ABSTRACT: AN ASSESSMENT OF WORKING-FLUID MIXTURES IN ORGANIC RANKINE CYCLES FOR WASTE-HEAT RECOVERY USING SAFT-VR

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INTRODUCTION

Organic Rankine cycles (ORCs) generate power from low-grade heat using organic working fluids with low boiling points. They have intrinsically low thermal efficiencies due to the low temperature of the heat source (typically $< 300\,^{\circ}\mathrm{C}$). The goal is to maximize this efficiency, while driving the investment costs of ORC systems lower. In a typical ORC featuring a pure working fluid, the evaporator accounts for over 70% of its overall exergy destruction (Mago *et al.*, 2008). This is due to the irreversibilities associated with heat transfer from the heat source to the working fluid across a finite temperature difference. This loss is exacerbated in single-component working fluids due to the isothermal nature of phase-change heat addition at constant pressure (Fig. 1(a)).

On the other hand, phase changes in mixtures need not be isothermal; this circumvents the constant-temperature limitation (as illustrated in Fig. 1(b)). Their use can reduce the average temperature difference between the heat source and the cycle during the process of heat addition, thereby: (i) reducing the associated exergetic loss; (ii) improving the thermodynamic efficiency (due to heat addition at higher average temperatures); and (iii) increasing the net specific power output from the cycle (due to the larger area that the cycle occupies in a temperature-entropy (T-s) diagram). Garg *et al.* (2013) have shown that, as a consequence, the expansion irreversibility dominates the exergetic losses of the ORC when suitable fluid mixtures are used as working fluids.

Various other authors have also studied and suggested suitable fluid mixtures (*e.g.*, Wang *et al.* (2010); Heberle *et al.* (2012); Angelino and Colonna di Paliano (1998); Chen *et al.* (2011); Sami (2010); Van den Broeck *et al.* (2012)). These authors have illustrated the various benefits inherent in using carefully selected fluid mixtures/blends as working fluids in ORCs. When compared to pure fluids, suitable binary mixtures can increase power output by ∼30%, and thermal and exergetic efficiencies by over 15%, though the use of ternary mixtures provide only marginal further increases in these indices. Additionally, a variation in mixture composition can be used to adjust physical,

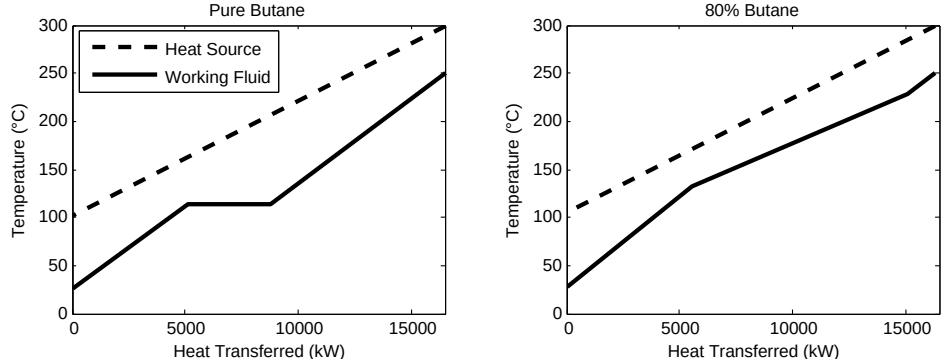


Figure 1: Temperature profiles of heat source (20 kg/s water) and working fluid (20 kg/s at 20 bar) in the evaporator for: (a) pure butane and (b) 80% butane mixture

environmental, safety and chemical properties of the working fluid; improve design parameters of cycle components; or reduce the size and cost of the system (Garg *et al.*, 2013).

Notwithstanding the aforementioned studies, most of which were limited to specific mole/mass ratios of the fluid components or particular heat-source temperatures, research into the deployment of suitable mixtures in ORC applications has not been particularly extensive. An obvious challenge lies in evaluating reliably the fluid properties (incl. phase behaviour, heat capacities, enthalpies, entropies, etc.) and other quantities of interest (*e.g.*, heat transfer coefficients) for such mixtures, since these properties are complex functions of the fluid mixtures and flow. An accurate knowledge of these parameters can greatly improve the accuracy of the overall results. In the present work we investigate the selection of working fluid mixtures and component mixing ratios for an ORC from a technological and economic point of view, focusing on thermodynamic property prediction with SAFT-VR. The effect of the working fluid mixture selection on the efficiency and power production is investigated, as is its effect on the sizes of the various components of the ORC. This is done in order to appreciate the role that the fluid mixtures would have on the investment/capital costs attributed to installing an ORC unit. Our investigations extend over a range heat source temperatures in order to ensure the robustness of the ORC model.

METHODOLOGY

A mathematical model of a sub-critical ORC was constructed in MATLAB. It contains sub-models for the evaporator, condenser, pump and expander used in a basic non-regenerative ORC. Further input parameters for the cycle include the working fluid mass flow rate ($\dot{m}_{\mathrm{wf}}$), the isobaric fluid pressures in the evaporator and condenser, and the isentropic efficiencies of the pump and expander. Additional parameters required for the evaporator and condenser heat exchanger calculations are the mass flow rates, specific heat capacities and inlet temperatures of the heat source and cold sink fluid streams, and the limiting pinch temperature difference between the fluids.

The working fluid leaves the evaporator as a saturated or superheated vapour. The expander power can thus be evaluated from knowledge of its isentropic efficiency. The cycle efficiency is the net power output over the heat transferred to the working fluid in the evaporator. Costs for the evaporator and condenser heat exchangers are calculated as a function of the heat load and logarithmic mean temperature difference, using the C-value method. Cost data for ORC turbomachine expanders and positive-displacement expanders were collected by market survey. A three-dimensional interpolation was used to return an individual cost from this data using the ORC system parameters in the MATLAB model. The same approach was used for the working fluid pump.

An important part of our modelling approach is the accurate prediction of the thermodynamic state properties and phase behaviour of the fluid mixtures. We employ the SAFT-VR Mie equation of state (Lafitte *et al.* (2013)), a state-of-the-art version of the molecular-based statistical associating fluid theory (SAFT) (Chapman *et al.* (1989, 1990)) to generate thermodynamic data; these are provided in tabulated form and interpolated as necessary during the simulation. By the adoption of the Mie (or generalised Lennard-Jones) intermolecular potential, together with recent developments in the underlying theory, SAFT-VR Mie is able to provide simultaneously (*i.e.*, using the same fluid model) an excellent description not only of fluid phase behaviour, but also of thermodynamic properties, including second-derivative properties such as heat capacities. In our current work, attention is restricted to mixtures comprising compo-

nents from the same chemical family (such as the alkanes) to minimize complex fluid interactions; thereby unlike molecular interactions are well described using the simple Lorentz-Berthelot combining rules (without need for a binary-interaction parameter).

DISCUSSION OF RESULTS

We have investigated the optimal selection of fluid mixtures and mixing ratios of components to maximize power production from an ORC, and to minimize the associated economic costs. We focus here on ORC simulations using binary mixtures of decane and butane as the working fluid. Simulations were carried out starting with pure decane as a reference fluid, successively increasing the butane mole fraction at intervals of 0.1 while all other input parameters were held constant. Key performance indicators of the cycle (work output, cycle efficiency and capital cost of equipment) were noted.

The variations of the specific power output (power per unit $\dot{m}_{\mathrm{wf}}$) and unit cost (£/kW) with the mixture composition in non-superheated cycles are depicted in Fig. 2(a) and Fig. 2(b) respectively. In most of the considered cases, using an appropriate fluid mixture gives a better performance (in terms of power and cost) than using pure butane or decane. A mixture with 90% butane gives the maximum power output and the minimum unit cost.

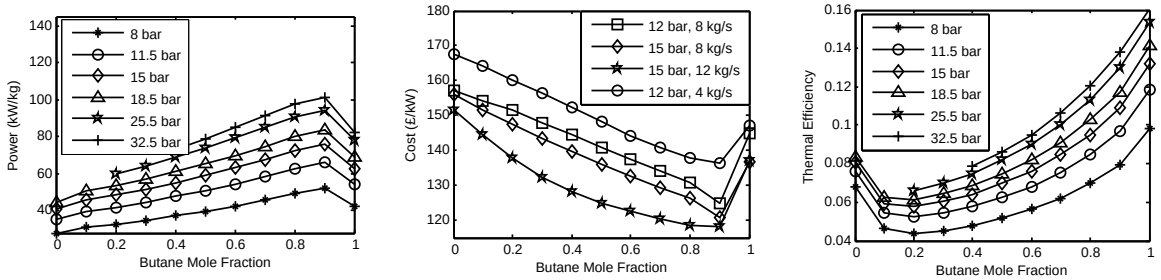


Figure 2: Variation of (a) power output, (b) capital cost and (c) efficiency with butane mole fraction

Fluid mixtures allow an increase in the heat extracted from the hot stream (not shown here), and hence a larger amount of heat is available for conversion to power. Nevertheless, the thermal efficiency of the cycle does not always increase; therefore, neither does the conversion of this heat to power. The variation in cycle efficiency with working-fluid mixing is presented in Fig. 2(c). At low butane concentrations, the cycles are less efficient than using pure decane even though more heat is extracted from the heat source. It is only at higher butane concentrations that the extra heat translates to improved power and hence higher efficiencies.

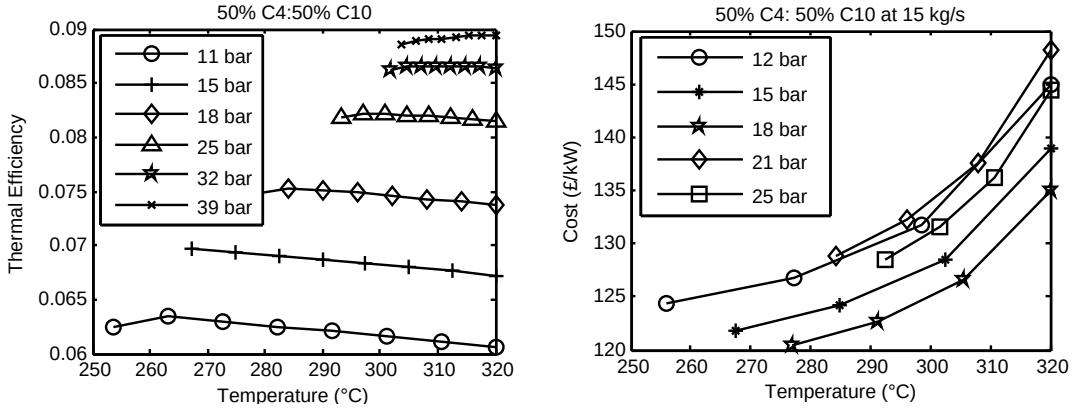


Figure 3: Variation of (a) efficiency and (b) unit cost with degree of superheating

Decane is a dry fluid, whereas butane is almost isentropic. Their mixtures vary in degree of dryness; only those comprising over 90% butane appear isentropic. Thus, the efficiencies of the investigated mixtures decrease with superheat – as illustrated in Fig. 3(a) for an equimolar mixture – although at high evaporating pressures (close to the critical points) the variation becomes insignificant. As expected, superheating the working-fluid mixture results in increased power production – but at extra costs. For the same mixture the unit costs (£/kW) at $\dot{m}_{\mathrm{wf}} = 15$ kg/s are presented in Fig. 3(b); superheating results in an increase of 20% in some cases.

CONCLUSIONS

Mathematical simulations of sub-critical ORCs using binary mixtures of decane and butane – whose properties have been calculated using SAFT-VR Mie – as the working fluid have demonstrated a significant improvement in work output and thermal efficiency compared to pure decane. Fluid mixtures can increase the average temperature of heat addition, therefore, the cycle is able to extract up to 42% more heat from the heat source. Furthermore, power production from the cycle can be increased by using appropriate mixtures (up to 60% compared to pure decane).

Compared with those of pure decane, the thermodynamic properties of decane-butane mixtures are favourable. Butane has higher specific enthalpies than decane at the specified pressures; thereby a working fluid comprising such a mixture provides improved cycle performance compared with one of decane alone. However, pure butane may yield higher efficiency than any of the mixtures, particularly if superheating is considered. Thus, adding decane to a butane-based working fluid may not be beneficial. This implies that some preliminary screening should be undertaken when selecting fluids for mixing. Only fluids that would improve the base working fluid should be selected.

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