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Heat Recovery and Conversion Technologies with Organic Fluid Cycles: Optimal Working Fluid and System Design

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Statement of Originality

I hereby certify that, to the best of my knowledge, the content of this thesis is original and the result of my own work. All of the assistance I received and the sources I used have been properly acknowledged.

Oyeniya Alabi Oyewunmi,

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The Family. Again.

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Abstract

Heat recovery and conversion technologies have become increasingly important for a variety of reasons relating to growing global concerns on energy security, rising electricity costs, CO₂ emissions and global warming. Although many energy intensive industries could benefit significantly from the integration of these technologies, the current adoption rate is limited due to the high investment costs involved and the difficulty of prospective investors and end-users to recognise and, ultimately, realise the potential energy savings from such deployment. Thus, the wider adoption of these technologies can be facilitated by improved performance and reduced investment costs. In this context, integrated thermoeconomic optimisation of such power systems through the optimal design of working fluids and operating parameters is invaluable in improving economic viability.

The performance of single-component working fluids is limited by the large exergy destruction associated with evaporation and condensation. Thus, working-fluid mixtures promise reduced exergy losses due to their non-isothermal phase-change behaviour, and improved cycle efficiencies and power outputs over their constituent pure fluids. The optimisation of organic Rankine cycle (ORC) systems revealed that mixtures do indeed show a thermodynamic improvement (in terms of the system power output and efficiency) over the pure-fluids. Although systems with fluid mixtures could see up to a 30% increase in power output over those with pure ones, they require larger expansion devices and heat exchangers (evaporators and condensers) due to their deterioration in heat transfer during the phase-change processes; thus, the resulting ORC systems are also associated with higher costs. Hence, ORC systems with pure working fluids have lower plant costs per unit power output, up to 14% lower than those with mixtures, highlighting the importance of considering system cost minimisation in designing ORC plants.

The Up-THERM heat converter is a two-phase unsteady heat engine; it contains fewer moving parts than conventional ones and represents an attractive alternative for remote or off-grid power generation. With the aid of a validated first-order lumped dynamic model, its performance with respect to working-fluid selection for its prospective applications is investigated. With the engine's power output and efficiency being conflicting objectives, fluids with low critical temperatures (and high critical pressures, reduced pressures and temperatures) resulted in designs with high power outputs and correspondingly low effi-

ciencies. For a nominal Up-THERM design corresponding to a target application with a heat-source temperature of 360 °C, R113 was identified as the optimal fluid, followed by *i*-hexane in maximising the power output. The Up-THERM heat converter was also seen to be effective over a range of heat-source temperatures delivering in excess of 10 kW (about four times higher than with water as working fluid in the nominal design) when utilising thermal energy at temperatures above 200 °C. Of all the working fluids considered, ammonia, R245ca, R32, propene and butane feature prominently as optimal and versatile fluids on the developed optimal working-fluid selection maps, delivering high power over a wide range of heat-source temperatures.

To facilitate simultaneous optimal working fluid and process design of waste-heat recovery systems, a mixed-integer non-linear programming (MINLP) optimisation framework for the computer aided molecular and process design of heat engines was developed. The components of the framework, consisting of thermodynamic process models, heat-exchanger sizing models, component cost correlations, economic evaluation models, transport property group-contribution correlations and the SAFT- γ Mie group-contribution equation of state are individually and collectively validated to acceptable degrees of accuracy against experimental and available commercial data. Following validation, the framework is used to identify optimal working-fluids for ORC systems with three different industrial waste-heat sources (150, 250 and 350 °C), with different objective functions.

Although slightly related, maximising the power output and minimising the specific investment costs (SIC) are not equivalent objectives. From NLP optimisations, *n*-propane, 2-pentene and 2-hexene were the optimal working fluids when maximising power output, while *n*-propane, 2-butane and 2-heptene were optimal when SIC is minimised. With MINLP optimisations minimising the SIC, 1,3-butadiene and 4-methyl-2-pentene were the best performing working fluids for the 150 °C and 250 °C heat sources respectively; these novel working fluids do not belong to the common hydrocarbon families assessed in the NLP optimisations. Similarly, with multi-objective cost-power optimisation, the same molecules are identified, striking a delicate balance between investment costs and system performance. Ultimately, the results demonstrate the potential of this framework to drive the search for the next generation of organic Rankine cycle and waste-heat recovery systems, and to provide meaningful insights into identifying the working fluids that represent the optimal choices for targeted applications.

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Nomenclature

Abbreviations

BDC	Bottom dead centre
CAM(P)D	Computer-aided molecular (and process) design
CEPCI	Chemical engineering plant cost index
CFC	Chlorofluorocarbon
CHP	Combined heat and power
CHX	Cold heat exchanger
Cn	Condenser
DSh	Desuperheater
EoS	Equation of state
EU	European Union
Ev	Evaporator
f/F	A function of
GC	Group contribution
H	Heaviside step function
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HHX	Hot heat exchanger
HTA	Heat transfer area
HTC	Heat transfer coefficient
MINLP	Mixed integer nonlinear programming
NIFTE	Non-inertive-feedback thermofluidic engine
NLP	Nonlinear programming

NSGA-II Non-dominated sorting genetic algorithm-II

ODE Ordinary differential equation

ORC Organic Rankine cycle

PH Preheater

SAFT Statistical associating fluid theory

SIC Specific investment cost

SPEC Specific purchased equipment cost

TDC Top dead centre

TFO Two-phase thermofluidic oscillator

TIC Total investment cost

VLI Vapour-liquid interface

WHR Waste-heat recovery

Dimensionless Numbers

Nu Nusselt number

Pr Prandtl number

Re Reynolds number

Greek Symbols

α Temperature amplitude [K]

β Heat exchanger temperature profile parameter [1/m]

δ Gap between piston and cylinder [m]

ϵ Depth of Mie-potential well [J]

ϵ Gap between shaft and motor [m]

η Efficiency [%]

η_L Liquid dynamic viscosity [Pa·s]

η_V Vapour dynamic viscosity [Pa·s]

γ Heat capacity ratio [–]

λ Thermal conductivity [W/(m·K)]

λ_a, λ_r	Attractive and repulsive exponents in Mie potential [-]
λ_L	Liquid thermal conductivity [W/(m·K)]
λ_V	Vapour thermal conductivity [W/(m·K)]
μ	Dynamic viscosity [Pa·s, kg/(s·m)]
ω	Acentric factor [-]
ρ	Density [kg/m ³]
σ	Segment size in SAFT model [Å]
σ	Surface tension [N/m]
θ_{SH}	Degree of superheat [-]

Roman Symbols

Δh	Latent heat of vaporisation [J/kg]
ΔP	Pressure drop [bar, Pa]
$\dot{m}$	Mass flowrate [kg/s]
$\dot{Q}$	Heat flowrate [W]
$\dot{q}$	Heat flux [W/m ²]
$\dot{Q}_{in}$	Rate of heat addition [W]
$\dot{Q}_{out}$	Rate of heat rejection [W]
$\dot{S}$	Entropy flowrate [W/K]
$\dot{V}$	Volumetric flowrate [m ³ /s]
$\dot{W}$	Power [W]
$\dot{W}_n$	Net power output [W]
dx	Heat exchanger tube thickness [m]
PR	Expander pressure ratio [-]
VR	Expander volume ratio [-]
A	Heat transfer area [m ²]
a	Helmholtz free energy [J]

b	Effusivity [W·s ^{1/2} /(m ² ·K)]
C	Analogous electrical capacitance [m ⁴ ·s ² /kg]
C	Cost factor [£/(W/K)]
C_n	Number of carbon atoms
c_p	Isobaric (constant pressure) specific heat capacity [J/(kg·K)]
C_p^0	Component base-cost in cost correlations [£, \$]
c_v	Isochoric (constant volume) specific heat capacity [J/(kg·K)]
D	Tube diameter [m]
d	Diameter [m]
F	Material factor in cost correlations
f	Frequency [1/s]
f_0	Friction factor [-]
F_i	Dimensionless function in heat transfer coefficient calculation [-]
G	Mass flux [kg/(m ² ·s)]
g	Gravitational acceleration [m/s ²]
H	Pump head [m]
h	Heat transfer coefficient [W/(m ² ·K)]
h	Height [m]
h	Specific enthalpy [J/kg]
k	Spring constant [N/m]
k	Thermal conductivity [W/(m·K)]
L	Analogous electrical inductance [kg/m ⁴]
L	Heat exchanger length [m]
l	Length [m]
m	Mass [kg]
n	Exponent in heat flux calculation [-]

P	Pressure [bar, Pa]	b	Boiling
P_{cr}	Critical pressure [bar, Pa]	b	Slide bearing
P_{r}	Reduced pressure [-]	bub	Bubble point
q	Vapour quality on mass basis [-]	c	Connection tube
R	Analogous electrical resistance [kg/(m ⁴ ·s)]	c, cr	Critical
r	Radius [m]	C,d	Liquid column in displacer cylinder
R_{a}	Surface roughness [m]	C,v	Gas spring at top of displacer cylinder
s	Specific entropy [J/(kg·K)]	Cn	Condenser
T	Temperature [°C, K]	cond	Condensation/condenser
t	Time [s]	cs	Cooling stream
T_{cr}	Critical temperature [°C, K]	cv	Check valve
T_{r}	Reduced temperature [-]	d	Displacer cylinder
U	Overall heat transfer coefficient [W/(m ² ·K)]	dew	Dew point
U	Volumetric flowrate [m ³ /s]	DSH	Desuperheater
u	Fluid velocity [m/s]	eq	Equilibrium
V	Volume [m ³]	Ev	Evaporator
V_{cr}	Critical volume [cm ³ /mol]	evap	Evaporation/evaporator
X	Sizing attribute in cost correlations	ex	Exergy
x	Working-fluid composition [-]	exp	Expander
X_{tt}	Martinelli parameter [-]	f	Frictional
Z_{1-4}	Cost coefficients in cost correlations	fg	Phase change
x	Mass fraction [-]	g	Gas phase
x, y, z	Spatial coordinates [-]	gen	Power generating
Subscripts and Superscripts		hm	Hydraulic motor
0	Equilibrium	hs	Heat-source stream
a	Acceleration	hx	Heat exchanger
acc	Accumulator	in	Inlet
		is	Isentropic
		l	Leakage flow

l	Liquid
lm	Logarithmic-mean
lub	Lubricant
max	Maximum/maximise
min	Minimum/minimise
ms	Mechanical spring
n	Normalised
nl	Non-linear
out	Outlet
p	Piston
PH	Preheater
pist	Piston in displacer cylinder
pp	Pinch point
pv	Piston valve
r	Reduced variable (temperature or pressure)
sat	Saturation
sh	Shaft
sh	Shell-side
tb	Tube-side
th	Thermal (domain)
v	Vapour (volume)
w	Wall
wf	Working fluid
wfl	Working-fluid liquid
wm	Wall material
wr	Surface roughness

Chapter 1

Introduction

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1.1 Background and motivation

Recent trends in world energy usage have shown that energy demand and energy consumption have been on the increase especially amongst developing countries. With the exception of the very recent drop in the price of oil, energy prices have also been increasing steadily over the past few decades due to a combination of a growing demand for energy and the possibility of exhaustion of reserves of easily accessible fossil fuels. The desire for secure, reliable and affordable energy provision in the light of the continual increases in energy costs that have been experienced worldwide, along with concerns related to the adverse effects on human health and the environment caused by the release of gases from the combustion of fossil fuels into the atmosphere, have led to an acceleration of research efforts towards the realisation and deployment of alternative, renewable energy sources, including sources of renewable thermal energy such as solar, geothermal, and (arguably) biomass/biogas.

1.1.1 Perspectives and opportunities for heat recovery

These challenges will continue to act as important drivers behind the interest in the recovery of low- and medium-grade heat and subsequent conversion to electricity and/or shaft power. The main characteristic of such waste heat is that it has a low-temperature, generally less than and up to 300 °C. Additionally, the recovery and (re-)utilisation of low- and medium-grade waste heat has been identified as a major pathway towards a high-efficiency, low-carbon and sustainable energy future [1–3]. The research into appropriate technologies for such heat recovery schemes thus naturally follows from this interest.

Presently, vast amounts of thermal energy at ‘low’ temperatures (in the form of furnace and boiler flue-gas exhausts, cooling streams in energy intensive industries, vehicle exhausts, *etc.*) are disposed off to the biosphere from a diverse range of sources in the domestic, commercial, industrial and transport sectors. Recent estimates show that over 60% of the energy generated from various renewable and non-renewable sources is rejected into the atmosphere. Specifically, 59.0 Quads ($\sim 62 \times 10^{18}$ J) worth of energy was ‘rejected’ to the atmosphere in the U.S. in the year 2013 [4]. This amount of energy is in excess of the actual energy consumed (38.4 Quads) by over 50%. Similar figures were reported for Europe, Asia and the world in general [5].

A typical energy pathway diagram for the world, showing the average energy production from both renewable and non-renewable energy sources and showing the energy consumption by sectors, is presented in Figure 1.1. From this diagram, it is clear that, on

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average, the non-renewable energy sources (petroleum, natural gas and coal) still account for over 85% of the the world's energy supply. This implies that these sources account for almost the total energy supply for countries in Asia and Africa as they have lower renewable energy footprint than Europe and North America, and are more heavily reliant on coal and petroleum. Also, the largest contributors to the wasted energy happen to be from electricity power plants, transportation and oil refining. These three sources, lumped together, contribute about 220 EJ ($1 \text{ EJ} = 10^{18} \text{ J}$) to the energy rejected to the environment, representing over 75% of the total energy rejected for the year, and demonstrating the inherent inefficiencies in their associated processes.

Therefore, important opportunities exist for heat recovery and integration, re-use and, where suitable, conversion to useful work (*e.g.*, mechanical, hydraulic, or electrical), thus allowing improvements to overall process efficiency, minimisation of primary-fuel consumption, and consequently, emission abatement. At the same time, renewable sources of low- and medium-grade heat, such as solar or geothermal heat, can play a key role in displacing the consumption of primary energy (fossil fuels) [6]. Low- and medium-grade waste or renewable heat can be converted into useful power such as electricity, or recovered to provide heating directly to buildings (for hot water or space heating), or a combination of the two in cogeneration schemes.

Although these streams are rejected at varying temperatures, usually below 100 °C and up to 300 °C, which may seem relatively low with respect to the primary energy source such as coal or natural gas, it is quite high when the temperature of the receiving environment (the atmosphere and/or the hydrosphere) is taken into account. For most parts of Europe, the daily temperature averages between −5 °C and 20 °C [7, 8], thus, introducing these streams at such temperatures to the environment would severely disturb the local ecosystems that are accustomed to the ambient temperatures. The recovery and re-use of such waste heat streams would ultimately reduce their final rejection temperatures (to less than 50 °C) and make them less damaging to their local ecosystems.

Due to the low temperature of the rejected streams, typical heat engines utilising these streams as heat sources would inherently have low thermal efficiencies. The Chambadal-Novikov efficiency¹ ($\eta_{\text{C-N}} = 1 - \sqrt{T_{\text{sink}}/T_{\text{source}}}$) [9, 10] for such heat engines utilising heat sources with temperatures below 300 °C is less than 30% and drops further to 10% at heat-source temperatures of 100 °C. Despite the seeming low efficiencies, the development and utilisation of such engines represents an interesting economic proposition since these

¹This represents the expected thermal efficiency of real heat engines as opposed to the idealized maximum efficiency derived from the Carnot engine.

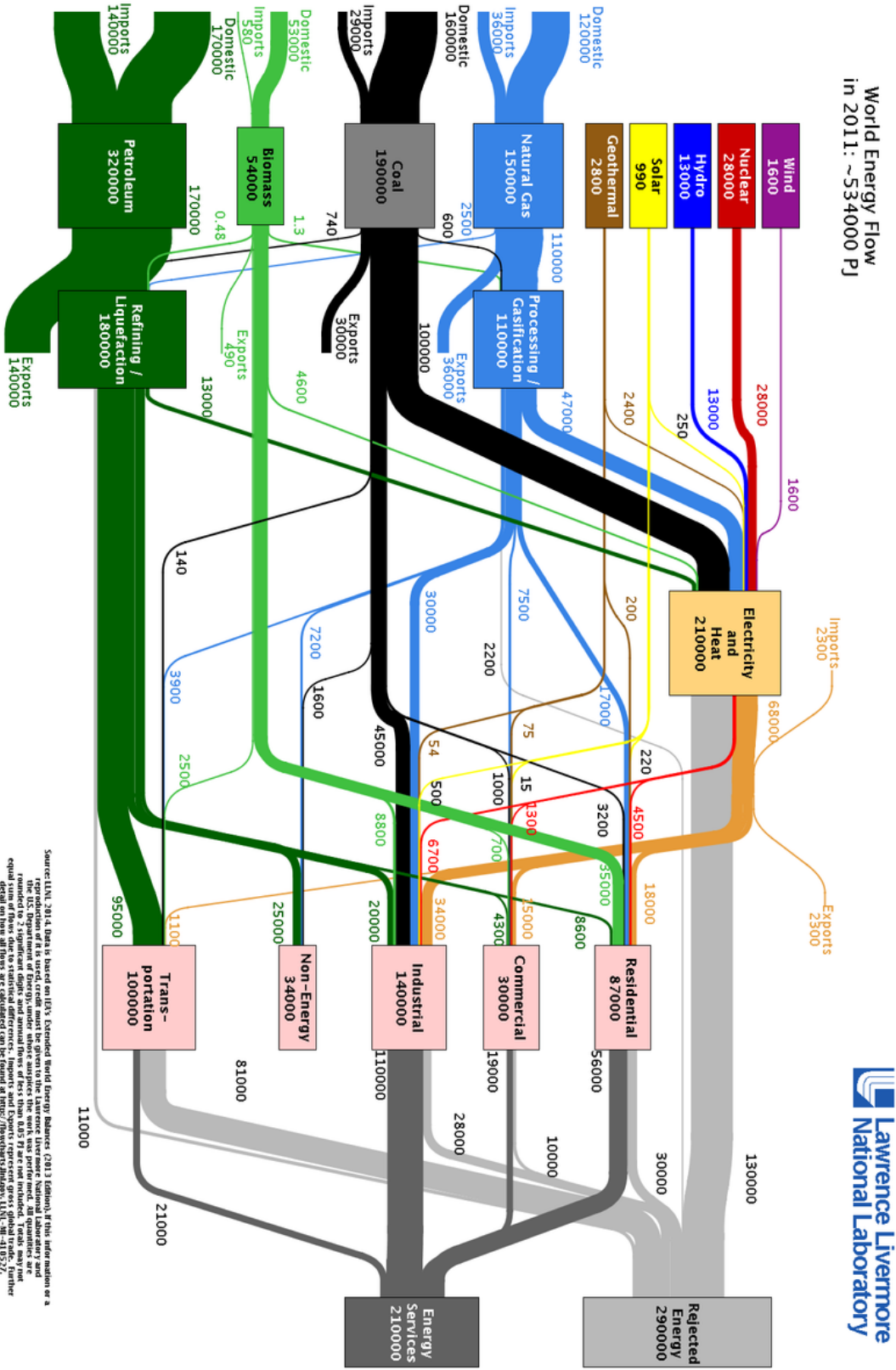


Figure 1.1: Estimated energy use in the world in 2011 (1 PJ = 10^{15} J), showing the energy production from key energy sources and showing the energy consumption by sectors [5].

Background and motivation

would provide a means of reducing the rate at which non-renewable energy resources are being depleted, as well as mitigating any environmental (human or natural) impact associated with the use of these resources.

For example, it is estimated that recovering and re-using waste-heat streams has the potential to provide an additional 8 EJ of energy towards the annual energy consumption in Europe, thereby reducing the annual primary-energy use by over 15% [11]. This would manifest as a direct reduction of the rate at which fossil fuels are being consumed and at which associated (carbon dioxide) emissions are being produced. This example highlights the important opportunities that exist for suitable technologies that can be deployed for heat recovery, re-use and energy integration, *e.g.*, by conversion to useful mechanical, hydraulic or electrical work. In plants that are already in operation the implementation of various waste-heat recovery technologies can lead to important boosts in overall efficiency and utility expenditure savings [12], and in newly built facilities that incorporate the most up-to-date technologies these savings can potentially be even higher according to theoretical predictions.

In summary, a number of challenges and opportunities continue to act as important drivers behind a strong interest in the utilisation of renewable heat and in the recovery and re-utilisation of waste heat. The development of high-performance and affordable heat-to-power conversion technologies features prominently as an enabling component of this effort. At the same time, combined heat and power (CHP) is being promoted in various applications, and at different scales, in the interest of improving overall fuel-use efficiency. The main challenge in this case, once again, is the economic viability of a particular project that relies heavily on the upfront (capital) cost of the CHP unit, along with operational performance amongst other factors.

1.1.2 Low-grade-heat conversion technologies

Beyond the conversion of low- and medium-grade waste-heat, increased attention is being directed at technologies capable of utilising heat in this temperature range that promise to alleviate the challenges relating to energy and the environment, either:

1. by maximising the overall efficiency of fossil-fuel use, examples of which are energy integration through the matching of thermal sources and sinks primarily in industrial and commercial sites, and also co-generation or combined heat and power (CHP) and tri-generation systems in a range of applications across scales; or

2. by circumventing the need for fossil-fuels altogether, such as by harnessing heat from renewable energy sources (*e.g.*, solar, geothermal).

Nevertheless, at least from a purely thermodynamic perspective, the overall efficiency of industrial or urban energy systems can be directly enhanced by recovering and utilising wasted heat.

For the purpose of this discussion, low-grade-heat engines can be divided into two broad classes: Rankine cycle type engines and two-phase oscillating engines. Several Rankine-type thermodynamic cycles have been studied in the context of low-temperature power generation, including the organic Rankine cycle (ORC) [13–19], the Kalina cycle [20–23], the Goswami cycle [24, 25], supercritical carbon dioxide cycles (s-CO₂) [26, 27] and trilateral cycles [28–30]. In particular, a growing interest has been observed in organic Rankine cycle (ORC) systems due to their applicability to the efficient conversion of lower grade heat to useful power. ORC systems generate power by using organic working fluids in a similar manner to conventional steam-cycle power plants. By employing suitably designed ORC systems, power can be generated by utilising a broad range of thermal energy sources, including harvested waste heat in industrial and commercial settings, recovered heat in biomass/biogas cogeneration applications, as well as hot fluid-streams in lower temperature geothermal resources or from non-/low-concentrated solar collectors, amongst many others.

Organic Rankine cycles can be further into classified subcritical, transcritical and supercritical ORCs. These three classes, operating on suitable organic working fluids, are presented on temperature-entropy (T - s) diagrams in Figure 1.2. In subcritical cycles, an organic working fluid is evaporated (and also condensed) at pressures below its critical pressure; in transcritical cycles, the working fluid is evaporated at pressures above the critical pressure and is condensed below the critical pressure; in supercritical cycles, the working fluid is evaporated (and also condensed) at pressures above its critical pressure. While engines with subcritical cycles are easier to design, they have the drawback of their isothermal phase change during evaporation. This leads to large exergetic destruction in the evaporator and condenser. Supercritical and transcritical cycles are interesting because they offer a non-isothermal phase change during the fluid evaporation process and are thus less destructive to exergy transfer in the cycle. Subcritical cycles could also be improved in terms of exergy destruction by employing working fluid mixtures [18] as they provide a non-isothermal phase change during evaporation.

Over the years, other novel cycle configurations have also been proposed for waste-heat recovery applications. These include various thermoacoustic and thermofluidic heat

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engines [31–34] and phase-change heat engines such as the Non-Inertive-Feedback Thermofluidic Engine (NIFTE) [35–41]. More recently, the Up-THERM engine [42] has been proposed by Encontech B.V. [43] and is being developed by a consortium of European researchers and SMEs [44–46]. This engine belongs to a class of unsteady vapour-phase heat engines referred to as ‘two-phase thermofluidic oscillators’ (TFOs). When a steady temperature difference is applied across a TFO, the working fluid within this device experiences sustained thermodynamic-property (*i.e.*, pressure, volume and temperature) oscillations, while undergoing phase change during heat addition and rejection. These sustained oscillations can then be harnessed to drive a generator or a load, where work can be extracted.

1.1.3 Performance indicators for waste-heat recovery engines

As with every and any engineering endeavour, waste heat recovery systems can be evaluated against any of a selection of performance indices from power output, torque, efficiencies, cost *etc.* The performance index attributed to any system generally depends on the goal/function of the engineering project and on the choice of the designer. A number of such indices have been encountered earlier in this chapter and are here listed:

- Engine thermodynamic performance variables such as net power output and net heating resources from CHP systems, including efficiency quantifications such as thermal and/or exergy efficiency;
- Equipment size and space requirements, *e.g.*, heat transfer areas;
- Investment and cost related indices such total investment costs (TIC), operating expenditure, specific investment cost or specific purchased equipment cost (SIC or SPEC) and payback period;
- Economic attractiveness indices such as the internal rate of return, return on investment, electricity sales and annual profits.

A number of these indices are evaluated for the waste-heat recovery systems and case studies presented in Chapters 2, 3 and 5. One generally seeks to maximise engine performance and economic indices such as the power output, efficiencies and sales/profits while those such as capital and operating costs, space requirements and environmental impacts are sought to be minimised. Generally, these objectives are in conflict for waste-heat recovery systems, thus, the question arises as to which of them is most important

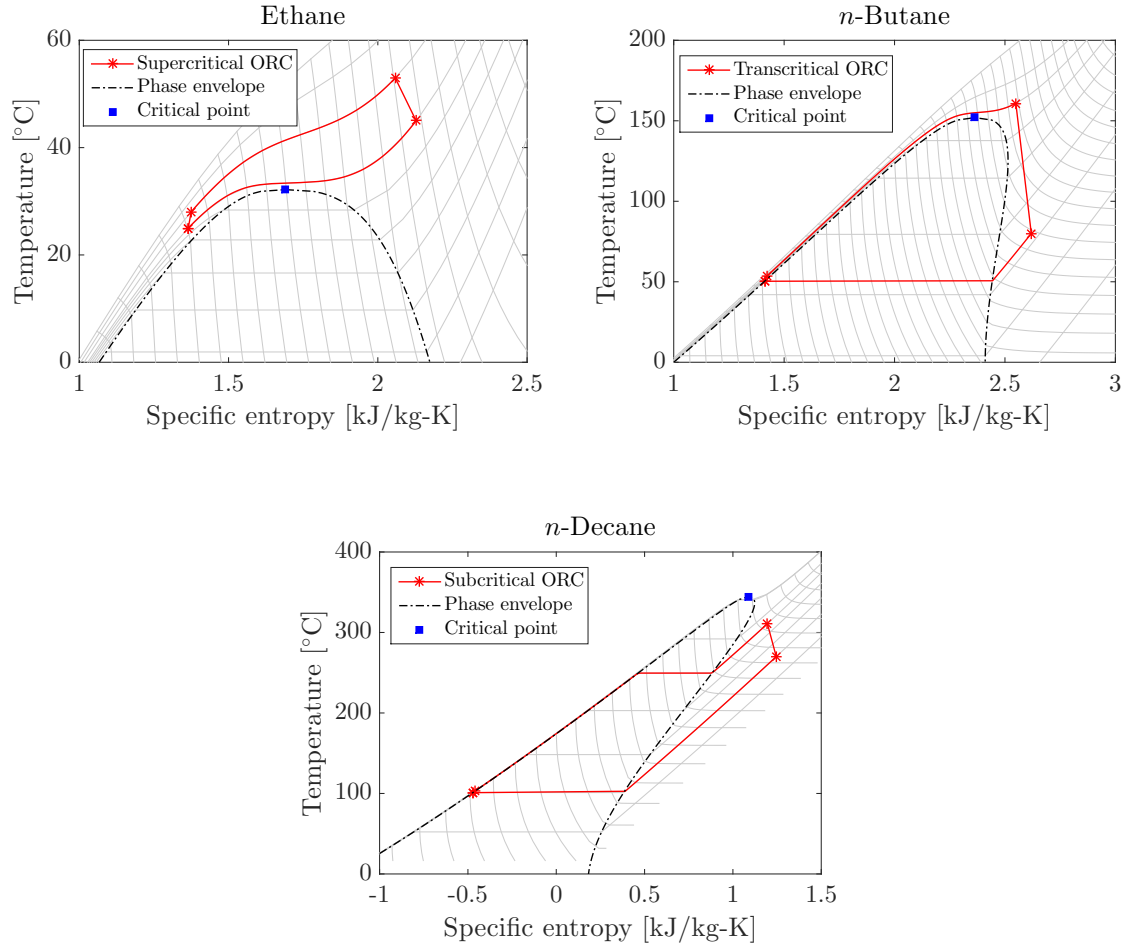


Figure 1.2: Three classes of organic Rankine cycles (ORC) and the phase equilibrium curves of their alkane working fluids on a temperature-entropy (T - s) diagram: a supercritical ORC with a wet working fluid (ethane); a transcritical ORC with an isentropic working fluid (*n*-butane); and a subcritical ORC with a dry working fluid (*n*-decane).

Working fluids for waste-heat recovery engines

to be prioritised. The optimal compromise between performance, size and cost will in practice come from the system purchaser, installer or user. Therefore, outputs from economic evaluations are reported both in terms of absolute costs (in £) and in terms of the cost per unit of power produced from the engine (in £ per kW), in order to provide the broadest possible examination of these results.

These low-grade-heat conversion technologies have lower thermal efficiencies (defined as the ratio of net work-output to the heat input from the heat source) than those associated with conventional large-scale, centralised fossil-fuelled (or nuclear) power plants, due to the lower temperature of the heat sources involved. Nevertheless, the associated energy sources (mentioned above) are typically more easily accessible, abundant and affordable than the fuels used in conventional power plants. The fuel costs in such plants can account for up to two-thirds of the levelized costs (*i.e.*, total costs, including capital expenditure, operation, maintenance, and all overheads) of electricity generation over the lifetime of a plant's operation. Once the regulatory, environmental and legal requirements are satisfied, the power output and investment cost become the key indices against which waste-heat recovery systems are evaluated.

Therefore, the aim in lower grade heat conversion technologies, such as ORC and thermofluidic engines, at least from an economic viability perspective (in terms of the payback period, specific costs and net present value), is one of ***maximising their power output while minimising the dominant investment and capital costs*** [18, 47]. Thermal/Exergy efficiency is important only in as much as it contributes to this aim, and thus, an emphasis is placed on the performance and cost of relevant waste-heat conversion systems. While designing systems to maximise the power output is generally desirable, such designs do not take the associated costs into account and may end up being quite expensive. Similarly, systems designed to minimise the investment costs will result in solutions with the least possible costs, and correspondingly minimal power output. Minimising the SIC (or SPEC) that incorporates both objectives of minimising total costs and maximising power output, seems to strike a good compromise. Another promising option is to carry out multiobjective optimisations during the design of these systems as assessed in Chapters 2 and 5.

1.2 Working fluids for waste-heat recovery engines

Besides the choice of fuel in waste-heat recovery technologies (*i.e.*, low- and medium-grade heat and renewable energy sources *vs.* fossil fuels in conventional power stations), the

thermodynamic cycles in waste-heat recovery systems differ from the steam Rankine cycle chiefly in the choice of working fluids. ORCs utilise organic fluids (*e.g.*, hydrocarbons and refrigerants) and their mixtures, the Kalina cycle utilises a mixture of water and ammonia, while the s-CO₂ cycle utilises supercritical carbon dioxide as the working fluid. One of the features of waste-heat recovery heat engines is the deployment of a broad range of fluids (including hydrocarbons, refrigerants, siloxanes), which allows engineers to select and/or tune certain (combinations of) fluids depending on the characteristics of the heat source, and the heat sink where relevant. While two-phase oscillating engines such as the Up-THERM are newer than Rankine engines and their performances/characteristics are still being studied, one can expect that they can also be operated with suitably designed/selected organic working fluids.

The available working fluids are classified into three categories based on the slope of the dew-point curve in a temperature–entropy (T – s) plot:

- Wet fluids – those that show a negative slope dew-point curve on the T – s diagram, *i.e.*, $\frac{dT}{ds_{\text{dew}}} < 0$, *e.g.*, water and ethane;
- Dry fluids – those with a positive slope dew-point line, *i.e.*, $\frac{dT}{ds_{\text{dew}}} > 0$, *e.g.*, hexane and decane;
- Isentropic fluids – those fluids with a constant entropy, regardless of temperature, along the dew-point line, *i.e.*, $\frac{dT}{ds_{\text{dew}}} \rightarrow \pm\infty$, *e.g.*, benzene and butane.

The phase envelopes of three alkane working fluids are displayed in Figure 1.2 to illustrate the slope of the dew-point curves of wet (ethane), isentropic (n -butane) and dry (n -decane) working fluids. This also illustrates how successive working fluids in a homologous series (the n -alkane family in this case) can get ‘drier’ with increasing molecular weight, transforming from being wet to isentropic and then eventually dry.

Organic working fluids, in comparison with water, are particularly suited to low-grade waste-heat recovery heat engines for a number of reasons:

1. they can generate high-pressure vapours with low-temperature heat sources;
2. at ambient temperatures, they can be condensed above the atmospheric pressure;
3. they have lower enthalpies of vaporisation which could make the heat addition and heat rejection processes more effective;
4. a lot of them are usually dry or isentropic.

Working fluids for waste-heat recovery engines

In the first instance, organic fluids are able to generate higher-pressure vapours at the low-temperatures representative of waste-heat streams. Such pressures are required to drive the turbine and generator assembly as the working fluid expands after being evaporated by the heat source during a heat addition process. As a case in point, the saturation vapour pressure of water at a temperature of 120 °C is 2.0 bar (*i.e.*, 1.0 bar above the atmospheric pressure) while those of the organic fluids *n*-pentane, R-245fa, *i*-butane and ammonia are 9.1 bar, 19 bar, 28 bar and 91 bar respectively. In terms of the gauge pressure (*i.e.*, relative to the atmospheric pressure), the organic fluids are seen to present pressures which are between 8 – 90 times higher than that of water. Thus, organic fluids will generally have much higher vapour pressures than water at such low temperatures, giving them a better ability to drive the expansion machine necessary for power generation. The higher saturation pressures of the organic fluids result in higher vapour densities, which is favourable for the design of compact systems; *e.g.*, compared to water with a saturated vapour density of 1.1 kg/m³ at 120 °C, the saturated vapour densities of *n*-pentane and R-245fa are 25 kg/m³ and 120 kg/m³ respectively.

The organic working fluids also possess an advantage over water during the heat rejection process. Heat rejection (and by extension, working fluid condensation) in heat engines is typically accomplished using cooling water at ambient temperatures, and it is generally advantageous for the working fluid to be condensed at the lowest possible temperature/pressure as this maximises the engine's power output and efficiency. With a cooling water stream at 20 °C, one can expect the working fluid condensation to occur at about 30 °C. At this temperature, the saturation (*i.e.*, condensation) pressures of water, pentane, R-245fa, *i*-butane and ammonia are 0.042 bar, 0.82 bar, 1.8 bar, 4.0 bar and 12 bar respectively. Thus, water will be condensed at a pressure well below the atmospheric pressure and as such, complicated designs, expensive pieces of equipment and hermetic seals will be required to prevent air ingress into the heat engine, leading to considerable capital and operating expenses. In addition, its lower saturation pressure (and correspondingly lower vapour densities) would result in large volumetric flow rates and hence larger system components' sizes. The organic fluids, being condensed at pressures higher than the atmospheric pressure would not require such expensive (nor large) components and thus the engine can be designed, installed and operated at lower costs.

The dry and isentropic nature of organic working fluids is particularly important when one considers the challenges associated with wet expansion in turbo machines. In conventional power plants, in order to avoid expansion through the two-phase region, water must be superheated before expansion to prevent droplet formation and the subsequent

erosion of the turbine blades. This requires that superheaters are installed alongside the boilers (or steam generators), representing additional financial outlay for the project. With organic working fluids however, the superheater is not an essential component of the engine as the working fluid can be expanded from a saturated vapour phase with the working fluid expanding through the turbine in a completely dry state with limited concerns over moisture and droplet formation. Thus, with working fluids such as hydrocarbons and refrigerants which are usually dry or isentropic [48, 49], cost savings can be provided over the duration of the project and the reliability of the turbine can be maintained over the lifetime of the project.

An extensive review of working fluids and their selection for ORC applications according to thermodynamic performance indicators and environmental or safety aspects is given in Bao and Zhao [50]. One advantage of the *n*-alkanes and hydrocarbon working fluids over refrigerant working fluids is their low global warming potential (GWP) [49]. For example, *n*-butane and *n*-pentane have GWPs of 4, while R245fa has a GWP of 1030 and R227ea has a GWP of 3200. However, the flammability of *n*-alkanes (especially the ones with lower molecular weights) limits their applicability, especially for high temperature applications, whereas R227ea and R245fa are non-flammable. One way to overcome this restriction is to mix the hydrocarbons with non-flammable refrigerants, which can act as a retardant [51, 52]. In addition, the refrigerants R227ea and R245fa have been investigated in many studies [48, 53, 54]. For geothermal sources, it was found that the heat recovery engine with R245fa as working fluid has a higher net power output and thermal efficiency than those with *n*-butane or *n*-pentane [54], while that with R227ea was found to have the highest net power output amongst a pool of about 200 working fluids [53]. Furthermore, experimental investigations have been undertaken with those refrigerants and different expander types (*e.g.*, radial turbine and screw expander) [55–57].

1.3 Exergy destruction in waste-heat recovery systems and the use of working-fluid mixtures

Some interesting studies on waste-heat recovery systems focusing on ORC system performance, specifically from a second-law perspective, have revealed that the evaporator and condenser together account typically for over 70% of the total lost work (exergy destruction) in the overall cycle [14, 58–60], with the exergy loss in the evaporator amounting to approximately 1.5 – 2 times that lost in the condenser. The thermodynamic loss in these components arises from the irreversibility associated with the heat transfer between the

Exergy destruction in waste-heat recovery systems and the use of working-fluid mixtures

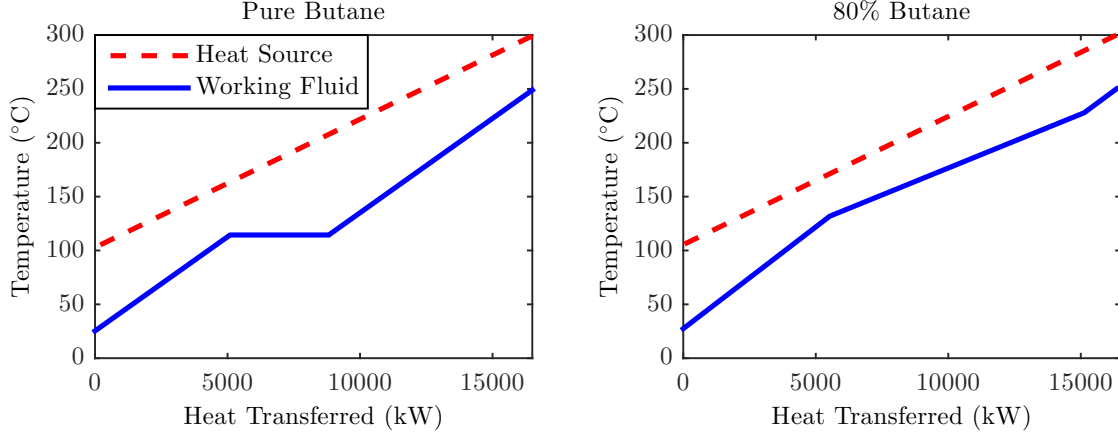


Figure 1.3: Temperature profiles of the heat-source stream and the working fluid (LHS: pure working fluid; RHS: working-fluid mixture) through the evaporator of an ORC system showing the isothermal phase-change process of pure fluids and an idealised temperature glide (and thermal match) of the working-fluid mixture during evaporation. This is also described on a T - s diagram in Figure 2.1.

external heat source (or sink) stream and the working fluid across a finite temperature difference. In most cases, this loss is additionally compounded when employing single-component working fluids due to the isothermal nature of the isobaric phase-change process through the evaporator (and condenser) as depicted in Figure 1.3. (In practice, small pressure drops are observed in these heat-exchange components, but these are not associated with any significant temperature changes.) This gives rise to the well-known pinch-point, away from which the temperature differences between the heat source/sink stream and the working fluid are considerably higher, thereby increasing the exergy losses.

The aforementioned shortcomings of using pure working fluids in ORCs have been motivating research into the deployment of zeotropic fluid mixtures as working fluids. These fluid mixtures do not suffer from such a temperature limitation since they are known to undergo non-isothermal phase change (a so-called ‘temperature glide’) at constant pressure (see Figure 1.3, and Figure 2.1). This gives rise to an increasing boiling temperature during heat addition in the evaporator, resulting in an improved thermal match between the heat-source and working-fluid mixture streams (*i.e.*, a reduced average temperature difference between the two streams) in this heat exchanger and, consequently, a reduced associated thermodynamic (exergy) loss in the process and an improved thermal efficiency and net power output from the cycle [13, 16, 61–63]. Such an improved overall thermodynamic performance, arising from improvements to this heat-exchange process, can offer benefits in terms of comparatively smaller (and more affordable) ORC systems [16, 62], while shifting the dominant component of the cycle’s exergy losses to the expander [61] as

opposed to the case of a pure (single-component) working fluid where the heat-addition process dominates the exergy losses, as mentioned earlier.

A number of experimental and theoretical studies have demonstrated the potential benefits of exploiting the temperature glide of refrigerant [64–67], hydrocarbon [49, 68] and siloxane [69, 70] working-fluid mixtures in designing more efficient and power-dense cycles. Specifically, suitable binary working-fluids have been shown to increase the power output of ORC systems in specific applications by up to 30% and thermal efficiencies by over 15% relative to single-component fluids [71]; second law analyses have also shown significant potential benefits [14, 72, 73]. An experimental study of a solar-ORC engine with R245fa + R152a working fluid [62] led to the conclusion that the mixture offers improved collector/cycle thermal efficiencies and expander-size reductions when compared to an equivalent cycle operating with pure R245fa. Other working-fluid mixtures investigated include isobutene + isopentane and R227ea + R245fa with geothermal-ORCs [65, 68], the quaternary mixture of R125 + R123 + R124 + R134a in the case of a heat recovery application [74], and a number of others in the study by Lecompte *et al.* [14], and others. These efforts also suggest that working-fluid mixtures can be more effective with low-temperature heat sources than with higher-temperature sources.

These benefits derived from working-fluid mixtures are magnified in applications with limited cooling-water supply, *e.g.*, combined heat and power (CHP) systems where the non-isothermal temperature profiles of the condensing fluid mixtures provide a good thermal match to the temperature profile of the heated cooling stream [13]. In these cases, efforts to consider fluid mixtures with large temperature glides are important, for example, where ORC systems are being considered in applications with limited quantities of cooling water [75, 76], which is actually a desirable feature in itself, in CHP applications [77, 78] and in energy integration [79–83] where the heat sink stream has been pre-identified and is associated with a significant temperature variation, thus requiring a temperature glide with a similar magnitude on the condensing side of the power cycle.

However, some exceptions to these general trends have also been reported [13, 84], especially in cases where there is an adequate supply of a cooling stream, limiting the benefits accruable to employing working-fluid mixtures. In such cases, small glides during condensation will always be preferred for best performance. Additionally, from an environmental perspective, the physical, chemical and safety-related properties of promising working fluids can also be altered by selecting and varying the composition of appropriate fluid mixtures [61]. Thus the global-warming and ozone-depletion potentials of prospective ORC working fluids can be significantly reduced. At the same time, some in-

Exergy destruction in waste-heat recovery systems and the use of working-fluid mixtures

investigators have begun to develop and apply advanced computer-aided molecular design (CAMD) methodologies [15, 85–87] with a view towards identifying or designing optimal fluids for ORC applications.

Although these studies have highlighted some of the potential benefits of employing working-fluid mixtures in ORC systems, research into the exact benefits of the employment of working-fluid mixtures and the identification of application-specific optimal fluids is still in its early stages. In addition, many of the associated conclusions have been derived from thermodynamic cycle analyses that do not fully consider the expected heat transfer performance between the heat source/sink and working-fluid streams in the heat exchangers of ORC engines. In particular, the heat transfer and (importantly) the cost implications of using working-fluid mixtures have not been properly addressed and are in need of further consideration. Refrigerant mixtures are known to exhibit reduced heat-transfer coefficients (HTCs) compared to their pure counterparts [88–94]. Specifically, HTCs for refrigerant mixtures are usually lower than the ‘ideal’ values, linearly interpolated between the mixture components [95–98]. This, coupled with the reduced temperature difference between the heat source/sink (wherever this applies) and the working-fluid mixture, will invariably lead to larger and more expensive heat exchangers in an ORC system. Therefore, although working-fluid mixtures may allow a thermodynamic advantage over single-component working fluids, they may also lead to higher system costs owing to a deterioration in their thermal performance and increased component size.

This deterioration in the HTCs of working-fluid mixtures, especially during the phase change processes, is ordinarily not accounted for with simple HTC correlations developed for pure fluids or those developed using (averaged/weighted) thermodynamic properties of the mixtures. Thus, and, by extension, the overall effect of these working-fluid mixtures on the ORC system components’ (heat exchangers, expanders and pumps) sizes and costs will not be adequately accounted for by these HTC models or by simple cost functions that are based on aggregated properties of ORC systems such as heat-exchanger duties or power output. Therefore, there is the need to go beyond these efforts in order to qualify the precise effect of working-fluid mixtures against their pure counterparts, on the design and economics of ORC plants. The reduced heat transfer performance of the fluid mixtures needs to be expressly accounted for, including the subsequent effect on the exact physical sizes (*e.g.*, heat transfer areas of heat exchangers, and volumes of expanders and pumps) and costs of the individual components of the ORC system, leading to a well-defined analysis of the benefits and drawbacks of employing working-fluids mixtures (in comparison with pure working fluids) in ORC systems.

By presenting a method for evaluating the HTC's of working-fluid mixtures, the effects of using such mixtures on the overall heat transfer processes and component sizing in ORC engines is explored, which are important in understanding the role that these fluids play on the overall system performance and cost. An ORC engine model is presented that incorporates a suitable heat transfer description of the heat exchangers used for the heat addition and heat rejection processes. The heat exchangers are discretised along their lengths into segments (accounting for phase-change and single-phase regions), with suitable estimates of the HTC's in the different segments. Overall HTC's and heat-transfer areas (HTAs) are then evaluated for the ORC system heat exchangers. Furthermore, the expanders and working-fluid pumps are sized based on their power requirements as their sizes are also affected by the working-fluid selection. Simple cost models are then used to estimate the relative costs of the components, and, by extension, of the entire engine. Using a selection of alkane and refrigerant working-fluid mixtures, the heat transfer characteristics and ORC-system equipment/component costs are thus investigated.

1.4 Thermodynamic and transport property prediction for working fluids

An essential design feature of all heat engines is the working fluid design. Traditional Rankine cycle engines utilise water because of its abundance and the high temperatures generated by burning coal. For novel heat recovery engines however, the design and/or selection of working fluids is critical to the engine effectiveness and plant economics. The choice of organic working fluid has a considerable impact on the performance, component design, size, cost and operational procedures of waste-heat recovery systems, thus, a larger percentage of ORC research papers are dedicated to the study of suitable fluids [64, 99]. However, with increasing concerns over global warming and air pollution, certain fluids such as CFCs have already been phased out, whilst fluids such as HCFCs and HFCs are set to be phased out in the coming years [100]. From the perspective of an end-user, technical solutions are required that are not constrained by such legislation, in addition to being economically feasible. This demands the identification of both novel working fluids that meet all legislated requirements, and heat conversion systems that are optimised in terms of performance indicators such as payback period or levelised cost of energy.

An inherent challenge in this endeavour concerns the availability of and access to accurate thermodynamic (and transport) property data and phase-behavior information, especially in the case of mixtures of dissimilar fluids that would exhibit large temper-

ature glides. Databases such as the NIST WebBook [101, 102] and fluid-data software packages (*e.g.*, REFPROP [103] and CoolProp [104]) have been commonly used in designing single-component working fluids for ORC systems. REFPROP and CoolProp employ ‘fitted’ equations of state that contain large numbers of parameters, enabling excellent correlations of experimental data, and thereby these software packages provide outstanding descriptions of the thermodynamics of fluids that have undergone extensive experimental study and for which data are plentiful. On the other hand, the success of multi-parameter, correlative equations is less clear when applied to fluids for which data are scarce, especially in terms of thermodynamic states outside the regions of the experiments from which the correlations were made; moreover, this situation may be exacerbated when using mixing rules (which introduce an added level of uncertainty) to obtain mixture properties. A particular difficulty lies in the reliable evaluation of heat transfer coefficients and specific heat capacities for such working-fluid mixtures, especially as these quantities can depend on mixture compositions in a non-trivial fashion.

The present understanding of the challenges and potential benefits of using advanced working fluids in ORCs can be vastly improved by the development of powerful, more accurate and readily accessible whole-system optimisation platforms, featuring accurate and reliable property-prediction models for both pure fluids and fluid mixtures. To this end, computer-aided molecular design (CAMD) offers a viable and promising approach for the simultaneous optimisation of both the working fluid (including mixtures) and the design of the ORC system [85, 86], extending to the design of novel fluid substances and mixtures, the specification of optimal cycle conditions, as well as the implementation of innovative, advanced system architectures. For this purpose, reliable and simple descriptions of the working fluids at the molecular level are much desired. Recently, research groups have begun to explore the use of advanced molecular models (*e.g.*, PC-SAFT [105, 106]) for fluids with this in mind (*e.g.*, [53, 99, 107, 108]), but more work is needed before we are in a position to understand fully the role of working-fluid selection (and ultimately true molecular design, leading to novel fluids) in determining key thermodynamic properties and system variables, and thereby in maximising the overall techno-economic indicators of ORC systems [18].

With the primary objective of developing reliable molecular models for working fluids, the SAFT-VR Mie equation of state [109] – a recent version of the statistical associating fluid theory (SAFT) for molecules interacting through potentials of variable range [110] – is deployed to investigate the selection of working-fluid mixtures. In particular, mixtures of two relatively dissimilar fluids are specifically investigated in order to test

the potential of the present approach in predicting thermodynamic properties in this particularly challenging scenario. The molecular models of the working fluids of choice (alkanes and perfluoroalkanes) are then developed using SAFT-VR Mie, after which the thermodynamic-property calculations carried out for the fluid mixtures are validated against available experimental data. These fluids are known to be environmentally benign with zero ozone-depletion potentials (ODPs) and low global-warming potentials (GWPs) compared to high-performance alternatives, *e.g.*, CFC-12 [111, 112]. The perfluoroalkanes, in particular, are stable, have high autoignition temperatures [113, 114], and have been recommended as replacements of fluids with high ODP and GWP [112]. These aspects are of significant importance in the ultimate selection (or design) of working fluids for waste-heat recovery applications. These set of working-fluid mixtures (specifically, the perfluorocarbons) for which experimental vapour-liquid equilibria and calorific data does not yet exist, are selected as a direct demonstration of the strength of the proposed SAFT-VR Mie approach. The application of SAFT-VR Mie to the new chemical class (perfluorocarbons) and the validation of all fluid-property predictions is also expanded by comparing to experimentally obtained values in the temperature-density (T - ρ) and temperature-heat capacity (T - c_p) spaces for the pure components.

By employing the SAFT-VR Mie equation of state [109], molecular-based models for organic working fluids would be developed such that their thermodynamic properties are accurately calculated. SAFT-VR Mie is shown (by comparison with experimental data) to predict accurately both single-phase and saturated properties of these fluids, and their mixtures, including their second-derivative properties (*e.g.*, the specific heat capacities), which are more challenging and less reliably calculated by cubic equations of state. These would enable an accurate description of important working-fluid properties (entropies, enthalpies, heat capacities) and thus of the performance of the heat recovery engines. These working fluid models would then form an essential component of CAMD tools for the development of innovative architectures and whole-system optimisation of such systems, including the design of novel cycles and working-fluids.

1.5 Working-fluid and system design via CAMPD techniques

In Sections 1.2 – 1.4, various studies on working fluids for waste-heat recovery systems (in particular, the ORC systems) were highlighted. The general approach in these studies has been to investigate a large array of known working fluids with available thermo-physical

properties in different ORC system configurations, based on predefined screening criteria. Subsequently, system-level optimisation studies are completed and the optimal working fluid is selected by comparing the results of these individual optimisations [115, 116]. Such approaches, however, can lead to sub-optimal system designs and limits the flexibility in the design of working fluids for ORCs, especially when one considers the possible use of fluid mixtures. In addition, they cannot be used to identify new and potentially novel working fluids, and therefore more holistic approaches are required. The development of advanced fluid theories rooted in interactions on the molecular scale provides an opportunity for the intelligent design of working fluids for any waste-heat recovery system configuration [108]. This has naturally led to the development of computer-aided molecular (CAMD) design techniques for waste-heat recovery systems. With the application of CAMD, the working fluid and thermodynamic system can be simultaneously optimised in a single optimisation framework, and hence bypassing the pre-emptive screening criteria entirely.

In CAMD, several molecular groups are defined (*e.g.*, $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $>\text{C}<$, $=\text{CH}_2$, $=\text{CH}-$) which can be combined according to a series of rules in order to form a large number of different hydrocarbon molecules. Theoretically, any arbitrary molecule can be described as a collection of such groups, given that all relevant groups are incorporated in the decision space. Initially, CAMD was applied to solvent design and used to identify molecules with specific solvent properties [117]. More recently, this has developed further and involves coupling CAMD methods with process models (hence, CAMPD), facilitating the integrated design and optimisation of the solvent and the separation process [118–121]. 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 [122–124], whilst a group-contribution equation of state (EoS) determines the fluid properties of a molecule based on the molecular groups from which it is composed. Early examples of such EoS are the empirical Joback and Reid group-contribution method [125] and the UNIFAC method [126]. However, an alternative to these empirical methods is the use of molecular-based equations of state based on statistical associating fluid theory (SAFT) [127, 128], for which group-contribution methods have recently become available [129–140]. With such a group contribution EoS, capable of predicting fluid properties based on its functional groups, the molecular structure of the working fluid can be simultaneously optimised alongside the system, potentially identifying novel working fluids which may otherwise been overlooked.

A number of authors have investigated the design of power systems (in particular, ORC systems) using ideas from CAMPD. Papadopoulos *et al.* [85] identified potential working-fluid candidates for ORC systems, paying particular attention to their safety and environment characteristics, before completing a more conventional ORC process simulation using molecular thermodynamic and transport properties as objectives, and later investigated the optimal design of working-fluid mixtures [86]. In Brignoli and Brown [141], a cubic equation of state was coupled to group-contribution methods and used to investigate the effect of a working-fluid’s critical point on the thermodynamic performance of the ORC systems while Palma-Flores *et al.* [142] similarly demonstrated the potential of using CAMD techniques to identify new working fluids with better safety characteristics and leading to waste-heat recovery ORC systems with higher thermal efficiencies. Su and Deng [143] also developed ORC thermodynamic models with group-contribution methods with accuracies of $\pm 10\%$ in comparison with experimental data from REFPROP and subsequently used CAMD techniques in the system design [144], while Cignitti *et al.* [145], in addition to optimising the thermodynamic performance, also considered the heat exchanger requirements as objectives.

However, these previous studies have generally relied on empirical group-contribution methods, such as the Joback and Reid method [125], to obtain working-fluid parameters including the critical temperature and pressure from which thermodynamic properties can be calculated using cubic equations of state. More advanced group-contribution equations of state, which use statistical associating fluid theory (SAFT) [127, 128] molecular-based equations of state have also been applied to the design of ORC systems via CAMPD. For example, Lampe *et al.* [53, 146] used the PC-SAFT equation of state [105, 106] to optimise an ORC system for a geothermal application with a two-stage continuous-molecular targeting CAMD (CoMT-CAMD) technique. Being a ‘non group contribution’ process, the optimisation process was split into two-stages: a hypothetical optimum working-fluid is identified via a non-linear programming (NLP) problem, while real working-fluids that exhibit similar performance to the hypothetical optimum are identified in a second stage. The problem was later reduced to a single mixed-integer non-linear programming (MINLP) optimisation problem to identify promising working fluids from existing databases and to generate novel molecular structures [147]; the model being recently extended to include transport properties and cost correlations, enabling system cost evaluations [148]. Oyewunmi *et al.* and White *et al.* applied a CAMD-ORC optimisation approach for basic ORC systems, using the SAFT-VR Mie and (group contribution) SAFT- γ Mie equations of state respectively for both pure and mixture working

fluids [13, 18, 149, 150]. These authors performed thermodynamic optimisations, maximising the power generation for waste-heat recovery applications.

With a few exceptions, the major limitation of previous CAMPD efforts in ORC system design has been a focus on optimising the cycle and its thermodynamic performance; however, achieving the successful commercialisation of ORC systems across a range of applications requires a consideration of thermoeconomic performance [13, 151, 152]. Quoilin *et al.* [153] evaluated the specific-investment cost (SIC) of small-scale waste-heat driven ORC units, whilst Lecompte *et al.* [154] optimised the design of ORC units for large-scale CHP plants and waste-heat recovery. Multi-objective optimisation studies can be also found in the literature [152, 155–157], where the authors considered the trade-off between maximising power output whilst minimising the SIC. However, all of these previous thermoeconomic studies consider only predefined working fluids, and conduct a separate optimisation for each specific fluid; thermoeconomic methods have not been previously applied to CAMPD-ORC models, partly due to the requirement of group-contribution methods for determining transport properties to size the system heat exchangers.

Another limitation to previous CAMPD efforts is that they typically focus only on a basic, non-recuperated, subcritical ORC system. However, there exist opportunities to improve the thermodynamic performance of this basic ORC by changing the cycle architecture. For example, using a working-fluid mixture instead of a pure fluid results (as discussed in Section 1.3) in non-isothermal, isobaric phase change processes, which facilitates a better thermal match between the working fluid and heat source, and between the working fluid and heat sink, thus reducing irreversibilities and improving the thermodynamic performance of the cycle [14, 16, 152]. Alternatively, operating a partially-evaporated cycle, in which expansion occurs from a two-phase state, can also be used to increase the power output from the system [30, 158].

Previously, Oyewunmi *et al.* [13] evaluated an alternative formulation of SAFT, SAFT-VR Mie [109], to optimise working-fluid mixtures for ORC systems. The group-contribution counterpart, SAFT- γ Mie [140], has been shown to provide a good description of fluid-phase thermodynamic properties of *n*-alkanes and a variety of other fluids; in particular, calculated saturation properties exhibit good agreement with experimental or pseudo-experimental data [87, 140, 159, 160]. The aim here is to formulate a computer-aided molecular and process design (CAMPD) framework for heat recovery and conversion engines, using the SAFT- γ Mie equation of state and to apply this to industrially relevant waste-heat recovery applications focusing on ORC systems. The results obtained are expected to not only identify optimal working-fluids, but to also contribute

important information regarding the characteristics that an optimal working-fluid should possess. While working-fluids' thermodynamic properties are provided by SAFT- γ Mie, their transport properties are predicted by empirical group-contribution methods which were validated against experimental data from NIST REFPROP [103]. These transport property prediction methods are in turn combined with detailed heat exchanger and equipment sizing models and system cost correlations, and integrated into the CAMPD framework. In addition, the framework is extended with an ORC system thermodynamic model, such that recuperated, partially-evaporated and working-fluid mixture cycles can all be considered. Overall, the developed framework allows the thermoeconomic assessment and optimisations of the heat conversion systems to be conducted, and therefore allows for simultaneous system optimisation and optimal working fluid design based on thermoeconomic performance indicators.

1.6 Thesis structure and objectives

Due to the large amounts of thermal energy being wasted from various domestic, commercial and industrial sources, the recovery and conversion of wasted heat using applicable technologies has been identified as a major pathway towards a high efficiency, low-carbon and sustainable energy future. A review of the relevant literature on the design of heat recovery and conversion engines has revealed a number of knowledge gaps as identified in the concluding paragraphs of Sections 1.3, 1.4 and 1.5. These relate to the use of working-fluid mixtures in organic Rankine cycle systems, the design of thermofluidic oscillators such as the Up-THERM converter and the computer-aided molecular and process design of waste-heat recovery engines. Hence, the subsequent chapters of this thesis are dedicated to addressing these challenges.

1.6.1 Aims and objectives

A key component of these heat engines is the working fluid that undergoes the described thermodynamic cycle. Hence the overarching aim of the research described in this thesis is the optimal design of the working fluid and the economical design of these engines. To this end, the following objectives are identified and hereby summarised:

- to develop mathematical models capable of predicting the performance of heat recovery and conversion technologies, in particular the ORC and the Up-THERM heat engines, with pre-selected organic working fluids;

Thesis structure and objectives

- to investigate and optimise the thermodynamic and economic performance of both engines with a focus on the influence of the selected working fluid and working fluid properties including working-fluid mixtures and their limitations;
- to go beyond the pre-selection of working fluids for these heat engines by developing a computer-aided molecular and process design (CAMPD) framework containing models capable of the simultaneous design of optimised processes and optimal working fluid design without recourse to pre-selection;
- to validate all aspects of the framework, starting with the SAFT-VR Mie molecular equation of state (EoS) and the SAFT- γ Mie group contribution EoS, the empirical transport property prediction methods, as well as the thermodynamic and economic results predicted by the CAMPD framework;
- to use the validated CAMPD framework to assess the performance and investment costs of a number of waste-heat recovery ORC systems via a series of NLP, MINLP and multiojective optimisation studies with a view to design novel optimal working fluids for these systems.

1.6.2 Thesis structure

In Chapter 2, a thermoeconomic mathematical model of an organic Rankine cycle system is developed. The model consists of three sub-models: a thermodynamic description of the (organic) Rankine cycle; equipment sizing models for the heat exchangers with suitable heat transfer correlations to address single phase heat transfer and two-phase heat transfer with pure fluids and working-fluid mixtures; equipment cost and system economic evaluation models. Further in Chapter 2, using a selection of alkane and refrigerant working-fluid mixtures, the role of working-fluid mixtures on the overall heat transfer processes, component sizing, system performance and cost of ORC engines is explored for a number of industrial and commercially viable waste heat sources.

Using an experimentally validated model of the Up-THERM engine [42], a characterisation of the engine with respect to optimal working-fluids is presented in Chapter 3. In the first instance, the nominal engine configuration, the optimal characterisation of its load, and the effects of key working-fluid properties on the performance indices of the engine are explored. In addition, a series of potentially viable working fluids are assessed for the engine; important heat transfer characteristics (*e.g.*, boiling and condensation heat transfer coefficients and areas) and thermodynamic performance indices such as the power

output and the exergy efficiency are highlighted. The discussion is concluded by exploring the viability of the engine for power generation at off-design conditions by considering the effect of the variations in heat-source temperature on the optimal working-fluid(s) selection. Ultimately, these will provide guidance on working fluid(s) selection based on the characteristics of the heat source, heat sink and operating conditions (including the application and location) of the Up-THERM heat conversion engine.

In Chapter 4, the topic of the computer-aided molecular and process design (CAMPD) of heat recovery and conversion engines is introduced. A CAMPD framework, with its constituent interlinked parts, is presented. A key part of the framework is the equation of state necessary for the prediction of the thermodynamic properties of working fluids. A typical model development procedure for SAFT-based equations of state (such as SAFT-VR Mie and SAFT- γ Mie) is presented for typical working fluids in waste-heat conversion engines. The models and the molecular feasibility constraints necessary for the group contribution SAFT- γ Mie equation of state, as well as the group-contribution transport property prediction methods are validated against available experimental data. The accuracy and reliability of the framework is explored by validating the constituent process models, component sizing and system costing models and optimisation algorithms with references from literature and commercial systems.

The CAMPD framework is put to work in Chapter 5 where it is applied to the problem of the simultaneous design of the optimal working fluids and process systems of waste-heat recovery engines. Of the two systems considered in this thesis, the (organic) Rankine cycle engine is a more mature technology, with years of experience and more component validation data from steam and nuclear power plants; the Up-THERM heat converter is newer in comparison. Thus, of the two engine models, the ORC model is more reliable with a higher degree of confidence as there are less uncertainties associated with it, making it a better choice for integration into the CAMPD framework. Furthermore, ORC systems are currently being designed by traditional heuristic working-fluid selection rules. In a move towards a holistic approach via CAMPD, case studies on the design of ORC engines operating with heat sources at three different temperatures, via a series of NLP, MINLP and multi-objective thermoeconomic optimisations, are explored in Chapter 5.

The main ideas from the thesis are pulled together in a final concluding chapter, Chapter 6, where further outcomes of the thesis as well as prospective avenues for future research endeavours are discussed.

Chapter 2

Working-Fluid Mixtures in ORC Systems

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2.1 Introduction and modelling ORC systems

As previously highlighted, a non-recuperative organic Rankine cycle (ORC), similarly to the steam cycle, consists of four processes (pumping, heat addition, expansion and heat rejection) carried out by an organic working fluid. Each of these processes requires a separate dedicated component. Two of these are heat exchangers, one for high-pressure heat addition to the working fluid from the heat source (in the evaporator), and another for lower-pressure heat rejection from the cycle to the heat sink (in the condenser). An expander/turbine generates power by expanding the working fluid from the high (evaporator) pressure to the low (condenser) pressure. Finally, a pump is required for working-fluid circulation and re-pressurisation from the low-pressure in the condenser to the higher pressure in the evaporator.

A typical ORC system set-up with the associated temperature-specific entropy (T - s) diagram is shown in Figure 2.1, with the states of the working fluid at labelled points through the system indicated on the T - s diagram for the ORC with a single-component (pure) working fluid and that for a multi-component (mixture) working fluid. These four processes are modelled from a thermodynamic perspective and a heat transfer perspective is also provided for the heat addition and heat rejection processes. Depending on the application, additional components may be required in practice, including waste-heat/process stream and/or coolant-fluid pumps, along with equipment items such as motors, alternators, separators, tanks, seals, piping and instrumentation. The models for evaluating the ORC systems are hereby presented.

2.1.1 Thermodynamic model of the cycle

With the assumption that the engine is operating at steady state, dynamic relations are not necessary and steady-state energy balances will suffice for the thermodynamic cycle analysis. It consists of four interacting sub-models for the main components of a typical ORC system: the pump, the evaporator (with preheater), the expander and the condenser (with desuperheater). The resulting model equations for the processes depicted in Figure 2.1 are stated briefly below, for completeness.

Working fluid pump (State 1 $\rightarrow$ State 2)

The pump delivers working fluid from a pre-specified condensing pressure to a pre-specified evaporating pressure. State 1 (in Figure 2.1) is determined by the condensing

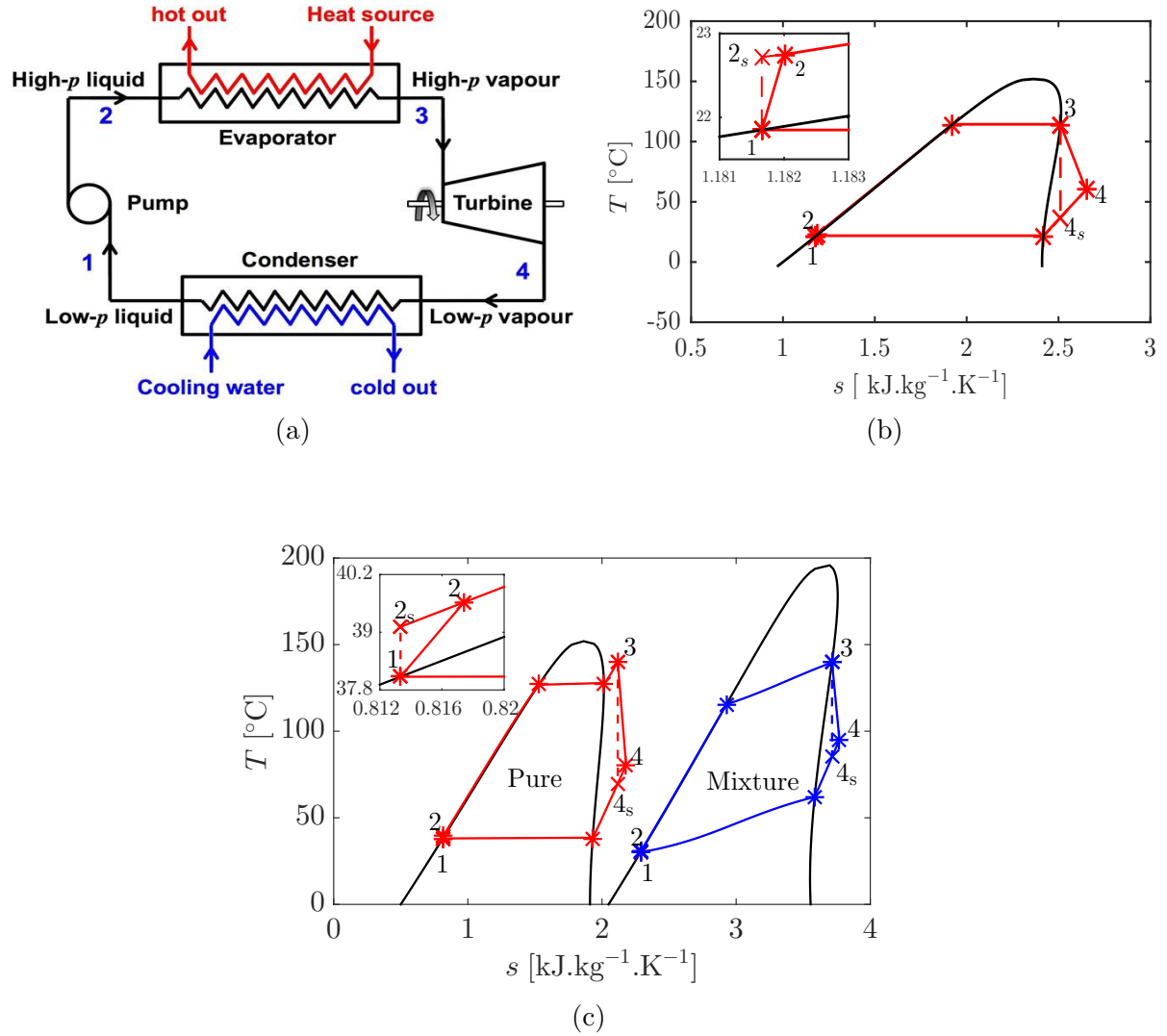


Figure 2.1: (a) The schematic diagram of a non-recuperative organic Rankine cycle engine highlighting the four key process equipment. (b) A temperature-specific entropy (T - s) diagram of an organic Rankine cycle with n -butane as working fluid; inset features an enlargement of the working-fluid pumping process. (c) A T - s diagram of an ORC for a dry single-component (pure) working fluid with superheating and a multi-component (mixture) working fluid without superheating, showing the temperature glides during the evaporation and condensation of the working fluid.

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pressure under the assumption that there is no sub-cooling of the working fluid (*i.e.*, saturated liquid). The fluid properties (temperature, T , specific entropy, s , and specific enthalpy, h) for State 1 are thus functions of the condensing pressure and working-fluid composition, x only:

$$\{T_1, s_1, h_1\} = f(P_{\text{cond}}, x). \quad (2.1)$$

State 2 can be determined by considering the imposed evaporating pressure P_{evap} (P_{23}) and a given isentropic efficiency value for the pump defined as:

$$\eta_{\text{is,pump}} = \frac{h_{2s}(P_{\text{evap}}) - h_1}{h_2 - h_1}, \quad (2.2)$$

where h_{2s} is the enthalpy of the working fluid following an isentropic process from State 1 to the evaporating pressure P_{evap} at State 2s. The fluid properties at State 2 are then calculated from:

$$\{T_2, s_2\} = f(P_{\text{evap}}, h_2, x), \quad (2.3)$$

with h_2 having been previously evaluated from Equation (2.2).

Thus, the power required to pump the working fluid from P_{cond} to P_{evap} (*i.e.*, State 1 to State 2) is given by the working-fluid enthalpy change through the pump:

$$\dot{W}_{\text{pump}} = \dot{m}_{\text{wf}}(h_2 - h_1), \quad (2.4)$$

where $\dot{m}_{\text{wf}}$ is the mass flow-rate of the working fluid through the pump.

Heat addition (State 2 $\rightarrow$ State 3)

The working fluid in the liquid state (State 2) is heated in the evaporator using heat extracted from the heat source and leaves the evaporator as a saturated vapour (at its dew point at the evaporating pressure) or a superheated vapour (State 3). This is taken to be an isobaric process, which is justified by assuming a relatively small pressure drop in the flow through the heat exchanger relative to the pressure in this component, *i.e.*, P_{evap} . The temperature of the working fluid at State 3 is fixed as the dew point temperature ($T_{\text{dew},P_{23}}$) at the evaporating pressure, P_{evap} , plus a variable superheat temperature difference (ΔT_3) from the dew point, set by the degree of superheating.

In order to study the role of superheating on the thermo-economic performance of the ORC systems considered here, the working fluid is allowed to exit the process with varying levels of superheat in order to quantify the optimal degree of superheating for

Introduction and modelling ORC systems

the different working fluids. For convenience, a normalised (and dimensionless) degree of superheating (θ_{SH} , which varies between 0 and 1 irrespective of the fluid, cycle and the external conditions), as opposed to a fixed value (*e.g.*, 5 °C or 10 °C) above the dew-point temperature, is defined as:

$$\theta_{\text{SH}} = \frac{T_3 - T_{\text{dew}}(P_{\text{evap}})}{(T_{\text{hs}} - \Delta T_{\text{min}}) - T_{\text{dew}}(P_{\text{evap}})} . \quad (2.5)$$

In transcritical cycles, the working fluid is vaporised without going through a two-phase region and thus no dew point is encountered. In this case, the degree of superheat is defined with respect to the critical temperature (T_{crit}) as:

$$\theta_{\text{SH}} = \frac{T_3 - T_{\text{crit}}}{(T_{\text{hs}} - \Delta T_{\text{min}}) - T_{\text{crit}}} . \quad (2.6)$$

Thus, the temperature of the working fluid at State 3 can vary between saturated (dew point) temperature at evaporation pressure (no superheating, $\theta_{\text{SH}} = 0$) and the maximum temperature when the pinch point is at the heat source inlet (maximum superheating, $\theta_{\text{SH}} = 1$), corresponding to the maximum degree of superheating. Here, ΔT_{min} is the minimum temperature difference allowed in the heat exchanger such that $T_{3,\text{max}} = T_{\text{hs}} - \Delta T_{\text{min}}$ is the maximum possible superheat temperature.

Once State 3 has been defined from either Equation (2.5) or (2.6), all other properties of the working fluid at the evaporator exit (and expander/turbine inlet) can be found from:

$$\{s_3, h_3\} = f(P_{\text{evap}}, T_3, x) \quad (2.7)$$

Assuming no heat losses, the heating rate required to evaporate the working fluid and raise its temperature from T_2 to the bubble point, and to superheat it from the dew point to T_3 , is equal the rate of heat extraction from the heat source, $\dot{Q}_{\text{in}}$:

$$\dot{Q}_{\text{in}} = \dot{m}_{\text{wf}}(h_3 - h_2) = \dot{m}_{\text{hs}}c_{\text{p,hs}}(T_{\text{hs,in}} - T_{\text{hs,out}}) , \quad (2.8)$$

where $\dot{m}_{\text{hs}}$ is the mass flow-rate of the heat source stream, $c_{\text{p,hs}}$ is its specific heat capacity, and $T_{\text{hs,in}}$ and $T_{\text{hs,out}}$ are the inlet and outlet temperatures of this stream at the evaporator.

Expansion process (State 3 → State 4)

A real expansion process is not isentropic due to irreversible thermal and mechanical loss mechanisms. This is accounted for by defining an isentropic efficiency for the expander:

$$\eta_{\text{is,exp}} = \frac{h_3 - h_4}{h_3 - h_{4s}(P_{\text{cond}})}, \quad (2.9)$$

where h_{4s} would have been the enthalpy of the working fluid following an ideal, isentropic expansion process from State 3 down to the condensing pressure P_{cond} . Having calculated h_4 from Equation (2.9), and given a knowledge of the condensing pressure, all other State 4 properties are then calculated at the end of the non-isentropic expansion process:

$$\{T_4, s_4\} = f(P_{\text{cond}}, h_4(\eta_{\text{is,exp}}), x). \quad (2.10)$$

Furthermore, the power generated by the expansion of the working fluid from P_{evap} to P_{cond} is:

$$\dot{W}_{\text{exp}} = \dot{m}_{\text{wf}}(h_3 - h_4). \quad (2.11)$$

Heat rejection (State 4 → State 1)

The low-pressure (P_{cond}) expanded fluid is condensed to a liquid state at constant pressure typically using water at ambient conditions as a heat rejection medium. The expression for the rate of heat rejection in the condenser is similar to that of the heat input in the evaporator:

$$\dot{Q}_{\text{out}} = \dot{m}_{\text{wf}}(h_4 - h_1) = \dot{m}_{\text{cs}}c_{p,\text{cs}}(T_{\text{cs,out}} - T_{\text{cs,in}}). \quad (2.12)$$

The conditions in the condenser are imposed to ensure that: (i) the pressure in this component remains at or above atmospheric pressure (1 bar), thus preventing air ingress into the system and the use to expensive expanders; while, (ii) the corresponding temperature remains above the cooling stream temperature (*e.g.*, 20 °C) plus a specified minimum pinch temperature-difference (*e.g.*, 10 °C) to permit heat rejection. The selection of the heat-rejection conditions (in particular, of the condensation pressure and cooling stream flow rate) is described in Chapter 2; in cases where the working fluid is expanded below the atmospheric pressure, the cost of the expansion device is suitably modified to reflect the use of special designs and seals to keep the system air tight.

Degrees of freedom and thermodynamic cycle solution

Equations (2.1) to (2.12) represent the thermodynamic model of the subcritical, non-recuperative ORC system under consideration. The equations relating to the working-fluid pump (Equations (2.1) to (2.4)) are solved by specifying the composition (x) and mass flow-rate ($\dot{m}_{\text{wf}}$) of the working fluid, the evaporating and condensing pressures (P_{evap} , P_{cond}), and the pump's isentropic efficiency ($\eta_{\text{is,pump}}$). The degree of superheating (θ_{SH}) and the heat source characteristics present a consistent set of variables for the heat addition process (Equations (2.5) to (2.8)). In a similar manner, the expander's isentropic efficiency and the coolant characteristics represent consistent variable sets for the expansion process and the heat rejection process, respectively. Finally, the thermal efficiency of the ORC is calculated as the ratio of the net power output from the system (expander/turbine minus pumping power) to the rate of heat input from the source:

$$\eta_{\text{th,ORC}} = \frac{\dot{W}_{\text{exp}} - \dot{W}_{\text{pump}}}{\dot{Q}_{\text{in}}} . \quad (2.13)$$

2.1.2 Heat exchanger sizing model

Feasibility of heat exchangers

The thermodynamic model described above captures the thermodynamic characteristics of the ORC. Equations (2.8) and (2.12) maintain the overall heat-transfer balance between the hot-side and cold-side streams in the two heat exchangers. However, it is important to impose relationships between the hot-side and the cold-side fluid temperatures in the two heat-exchanger arrangements in order to ensure that the second law of thermodynamics is not violated at any point along the length of the heat exchangers (*i.e.*, that heat is always transferred from the higher- to the lower-temperature fluid, across a finite temperature difference), thereby maintaining the feasibility of the overall heat transfer design represented in the equations above. Specifying a (positive) minimum pinch-point temperature difference between the hot-side and cold-side fluid streams along the length of the heat exchangers maintains the feasibility of both heat exchangers and hence the validity of the solution of the model equations.

First, the evaporator is conceptualised as comprising three sections, one each for the preheating, evaporation and superheating processes of the working fluid.

$$\dot{Q}_i = \dot{m}_{\text{wf}} c_{\text{p, wf}}^{P_{\text{evap}}} (T_i - T_{i-1}) = \dot{m}_{\text{hs}} c_{\text{p, hs}} (T_{\text{hs}, i+1} - T_{\text{hs}, i}) . \quad (2.14)$$

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The pinch point in the heat exchanger is the segment with the lowest temperature difference ($\Delta T_{pp} = \min\{T_{hs,i} - T_i\}, \forall i$) between the heat source and the working fluid. The feasibility of the heat exchanger is thus ensured by specifying that the pinch-point temperature difference is not lower than the stated minimum (*e.g.*, of 10 °C).

The condenser is treated as comprising two sections: the desuperheating section, and the condensing section. Both of these are discretised into segments in a similar manner to the sections in the evaporator, and the pinch-point temperature difference is specified to be not less than the minimum (*e.g.*, of 10 °C). Constant specific heat capacities are assumed for both the heat source and the cooling fluids.

Heat transfer areas

The heat transfer effectiveness of both the pump and the expander are approximated with their isentropic efficiencies as earlier stated. The heat exchangers are however modelled with a knowledge of their heat transfer coefficients which are derived experimentally and from correlations. The heat exchangers used are assumed to be tube-in-tube heat exchangers, which are cost effective for small- to medium-scale applications [161].

The heat addition process is carried out in two heat exchangers: (1) the preheater (PH), used to pre-heat the working fluid to saturated liquid; and (2) the evaporator (Ev), used to evaporate the working fluid to the saturated vapour state and to also superheat the working fluid when necessary. Similarly, the heat rejection process is carried out in the desuperheater (DSh) and the condenser (Cn). All heat exchangers are discretised into 100 (variable-sized) segments, i ($= 1 - 100$), each segment having an equal heat transfer/duty, *i.e.*, $\dot{Q}_{in}/100$ or $\dot{Q}_{out}/100$. A typical segment is illustrated in Figure 2.2. In all heat exchangers, the working fluid flows through the tube-side (tb), while the heat source and sink streams are the shell-side (sh) fluids.

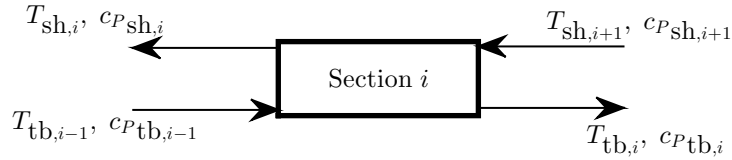


Figure 2.2: Heat exchanger segment showing flow directions on the shell (sh) and tube (tb) sides. The working fluid flows through the tube-side (tb), while the heat source and sink streams are the shell-side (sh) fluids.

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Thus, the total rates at which heat is transferred to/from the working fluid in relation to Equations (2.8) and (2.12), respectively, are given by:

$$\dot{Q}_{\text{in}} = \dot{Q}_{\text{PH}} + \dot{Q}_{\text{Ev}} = \sum_{i=1}^{100} \dot{Q}_i + \sum_{i=1}^{100} \dot{Q}_i \quad (2.15)$$

and

$$\dot{Q}_{\text{out}} = \dot{Q}_{\text{DSh}} + \dot{Q}_{\text{Cn}} = \sum_{i=1}^{100} \dot{Q}_i + \sum_{i=1}^{100} \dot{Q}_i. \quad (2.16)$$

An energy balance across each segment gives the heat transferred across the segment as:

$$\dot{Q}_i = \dot{m}_{\text{sh}} (T_{\text{sh},i+1} c_{P\text{sh},i+1} - T_{\text{sh},i} c_{P\text{sh},i}) = \dot{m}_{\text{tb}} (T_{\text{tb},i} c_{P\text{tb},i} - T_{\text{tb},i-1} c_{P\text{tb},i-1}) \quad (2.17)$$

or

$$\dot{Q}_i = \dot{m}_{\text{sh}} (h_{\text{sh},i+1} - h_{\text{sh},i}) = \dot{m}_{\text{tb}} (h_{\text{tb},i} - h_{\text{tb},i-1}). \quad (2.18)$$

Furthermore, for each segment an overall heat-transfer coefficient, U_i , can be defined:

$$\dot{Q}_i = U_i A_i \Delta T_{\text{lm},i}, \quad (2.19)$$

where

$$\Delta T_{\text{lm},i} = \frac{(T_{\text{sh},i+1} - T_{\text{tb},i}) - (T_{\text{sh},i} - T_{\text{tb},i-1})}{\ln[(T_{\text{sh},i+1} - T_{\text{tb},i}) / (T_{\text{sh},i} - T_{\text{tb},i-1})]} \quad (2.20)$$

and

$$U_i^{-1} = h_{\text{sh},i}^{-1} + dx/k + h_{\text{tb},i}^{-1}. \quad (2.21)$$

In these equations, ΔT_{lm} is the log-mean temperature difference between the ‘hot’ fluid and ‘cold’ fluid in the heat exchanger, h is the local heat transfer coefficient, dx is the tube thickness and k is the thermal conductivity of the tube material. From these sets of equations, the heat transfer area for each segment is calculated and summed up to derived the total heat transfer area for the heat exchanger.

Calculating heat transfer coefficients

Depending on the heat-transfer region, different Nusselt-number correlations are applied to determine the local heat-transfer coefficient. Single-phase local heat transfer coefficients (HTCs, h_{sh} , h_{tb}) can be calculated from the Reynolds number (Re) and Prandtl number (Pr), using the Dittus-Boelter Nusselt number ($\text{Nu}_{i,\text{sp}}$) correlation:

$$\text{Nu}_{i,\text{sp}} = 0.023 \times \text{Re}_i^{0.8} \text{Pr}_i^n, \quad (2.22)$$

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where $n = 0.4$ for a fluid being heated and $n = 0.3$ for a fluid being cooled. For evaporation, the correlations proposed by Cooper [161] and Gorenflo [162] have been used for nucleate-boiling conditions, whereas the asymptotic correlations by Dobson [163] and Zuber [161] have been used to account for the convective-heat-transfer phenomena. For condensation inside tubes, the correlations proposed by Shah [164] and Dobson [163] have been considered, accounting for both gravity-driven and shear-driven condensation.

For systems involving working-fluid mixtures, two-phase HTC's can be calculated by suitably modifying $Nu_{i,sp}$ with empirical functions of the Martinelli parameter, X_{tt} [88, 165]. In the present work, this modification was fitted specifically to results from experiments involving horizontal turbulent-flow boiling of refrigerant mixtures, as:

$$Nu_{i,tp} = F(X_{tt}) Nu_{i,sp}, \quad (2.23)$$

where

$$F(X_{tt}) = 1 + 1.8X_{tt}^{-0.82} \quad (2.24)$$

and

$$X_{tt} = \left(\frac{1-q}{q} \right)^{0.9} \left(\frac{\rho_v}{\rho_l} \right)^{0.5} \left(\frac{\mu_l}{\mu_v} \right)^{0.1}. \quad (2.25)$$

Equations (2.23) – (2.25) can be applied directly for pure fluids using the overall mixture composition for the liquid and vapour-phase properties. For the fluid mixtures, X_{tt} is calculated using the equilibrium liquid and vapour-phase compositions (not the overall composition) at the saturation temperature and corresponding vapour quality, q on mass basis [88]. The HTAs of all segments are then calculated from Equation (2.19) and summed to give the total HTA (A_{HX}) for the heat exchanger of interest.

Pressure drop

A key consideration when estimating the required heat-transfer area is the pressure drop along the full length of the heat exchanger. The heat exchanger systems are assumed to be horizontally placed and thus gravitational pressure drops are neglected. The single-phase frictional pressure drop per unit heat exchanger length (L) is calculated as a function of the fluid velocity inside the tubes by:

$$\left(\frac{dP}{dL} \right)_f = -\frac{4f_0}{D} \times \left(\frac{\rho u^2}{2} \right), \quad (2.26)$$

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with $f_0 = 0.046\text{Re}^{-0.2}$. Here, ρ is the fluid density, u is the fluid velocity, D is the tube diameter or characteristic length, μ is the dynamic viscosity and f_0 is a friction factor.

The two-phase frictional pressure drop is calculated using the correlations proposed by Chisholm [161]. By multiplying the required length of each subsection with the differential pressure drop, ΔP_f for the two-phase sections is obtained. The acceleration pressure drop (ΔP_a) during the complete phase change can be calculated by:

$$\Delta P_a = G^2 \times \left(\frac{1}{\rho_{\text{out}}} - \frac{1}{\rho_{\text{in}}} \right), \quad (2.27)$$

where ρ_{in} and ρ_{out} denote the density of the working fluid at the inlet and outlet of the heat exchanger, respectively, and G is the mass flux.

2.1.3 ORC system costing and economic evaluation

Generally, there are uncertainties inherent in the estimation of costs of process equipment and plants (and also in the estimation of heat-transfer coefficients, albeit to a lesser degree), with preliminary cost estimation techniques being accurate up to $\pm 25\%$ [166, 167]. While these uncertainties do exist, the qualitative information derived from using a particular costing technique for comparison of plants/systems of different sizes will not be influenced to a large degree by such uncertainties. Thus, it is important to use a single and consistent source of information for the comparison of the ORC systems employing different working fluids.

The first estimate of the capital cost of the ORC system is made by adding the costs of its major constituent components (the working-fluid pump, the expander and the heat exchangers) with the ultimate goal of investigating the role of the working fluid (mixtures) in affecting the capital costs of these engines. Not only are the effects of working-fluid choice on plant costs being manifested directly in the costs of these units, the costs of the aforementioned components represent the largest contribution to the total installed costs of a typical engine in a waste-heat application; typically 50% – 70% [17, 168]. Thus, the costs of these components are added to give an estimate of the plant cost.

Various techniques are available for estimating the installation/capital costs of process equipment and units. Data for such techniques are usually obtained from surveys of equipment manufacturers during a particular time period. An example is the C -value method, used in combination with the ESDU 92013 Chart [169], produced in 1994, for estimating the cost of different types of heat exchangers. Another technique available is the capital equipment-costing (CAPCOST) program from Turton *et al.* [167] which

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contains the capital costs of a large variety of process equipment, benchmarked in the year 2001. Similar to the CAPCOST program, logarithmic correlations are presented for a wide range of process equipment in Seider *et al.* [166]; the data used for these correlations were gathered in the year 2006. Generally, conversions from the publication years (1994, 2001 or 2006) to the current year can be carried out using the Chemical Engineering Plant Cost Index (CEPCI).

The C -value method

The cost of a heat exchanger is a strong function of its size, which is related to the area available for heat transfer, A . Various empirical methods and relationships (typically power laws) have been developed to estimate heat-exchanger costs in terms of a cost per unit area. A challenge of such methods lies in the complex definition of the heat transfer area for different types of heat exchangers. The C -value [169] method seeks to circumvent this limitation by estimating the costs using the knowledge of the heat load, $\dot{Q}$, and the average available temperature difference ΔT_{lm} . Here, a cost factor, C is defined as the cost per unit UA or per unit $\dot{Q}/\Delta T_{lm}$, which avoids the challenges of separately quantifying the area and overall heat-transfer coefficients involved.

For each heat exchanger, the C -value is estimated separately for each section (*e.g.*, the desuperheating and condensing section of the condenser) since a linear temperature profile is required in the definition of ΔT_{lm} . By applying Equation (2.19) to each section, the UA value (and hence the C -value) is evaluated from the knowledge of $\dot{Q}$ and ΔT_{lm} . The cost of the heat exchanger is then estimated with the C -value, combined with the ESDU 92013 chart that contains cost correlations for different heat-exchanger types. The ESDU 92013 chart contains tabulated values of overall heat-transfer coefficients, U , and cost factors, C , for different cold-side and hot-side fluids at fixed values of $\dot{Q}/\Delta T_{lm}$. Once $\dot{Q}/\Delta T_{lm}$ is known, the required ‘ U [W/m²K]’ and ‘ C [£/(W/K)]’ values are obtained using the logarithmic interpolation:

$$C = \exp \left(\ln C_1 + \ln(C_1/C_2) \frac{\ln \left[(\dot{Q}/\Delta T_{lm})/(\dot{Q}/\Delta T_{lm})_1 \right]}{\ln \left[(\dot{Q}/\Delta T_{lm})_1/(\dot{Q}/\Delta T_{lm})_2 \right]} \right), \quad (2.28)$$

where the subscripts ‘1’ and ‘2’ correspond to the tabulated values of $\dot{Q}/\Delta T_{lm}$ (and C) that span the $\dot{Q}/\Delta T_{lm}$ of interest.

The C -value is then multiplied by $\dot{Q}/\Delta T_{lm}$ (and adjusted for inflation) to obtain the cost of the heat exchangers. On the ESDU 92013 chart, the C -values under ‘Low

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Viscosity Organic Liquids’ and ‘Low Pressure Gas’ are used for the cold fluid side (working fluid) and hot fluid side (flue gas) respectively for the evaporator. For the condenser, the C -values under ‘Low Viscosity Organic Liquids’ and ‘Process Water’ are used for the hot-fluid side (working fluid) and cold-fluid side (cooling water), respectively. The total cost of a heat exchanger is thus derived by summing together the cost of its sections. This is especially useful for cases where the actual heat transfer areas are not required.

Component costs from correlative equations

While the costs of the heat exchangers can be derived as previously described, there are only a limited number of ORC applications worldwide, and as such, system cost data are not publicly available. Thus, the cost correlations originating from the chemical industry are commonly used in the literature as an alternative to estimating component costs for ORC systems.

These correlations provide the costs of the individual components based on a specific sizing attribute (*e.g.*, heat-transfer area for heat exchangers and power output/requirement for expanders and pumps *etc.*). Here, the cost correlations given by Seider *et al.* [166] and Turton *et al.* [167] respectively are used:

$$\ln(C_p^0) = \ln(F) + [Z_1 + Z_2 \ln(X) + Z_3 \ln(X)^2 + Z_4 \ln(X)^3 + Z_5 \ln(X)^4] , \quad (2.29)$$

$$\log_{10}(C_p^0) = \log_{10}(F) + [Z_1 + Z_2 \log_{10}(X) + Z_3 \log_{10}(X)^2] . \quad (2.30)$$

Due to their more recent dates of production, the variations introduced by year-on-year conversions with the Chemical Engineering Plant Cost Index (CEPCI) are minimised.

In these equations, C_p^0 is the component base-cost in £; F is a material factor accounting for the component manufacturing; Z_i is the cost coefficient; and X is the sizing attribute. Both Z_i and X vary depend on the type of the equipment selected and the values used to estimate the purchase cost of each piece of equipment are summarised in Table 2.1. It is assumed that the pump is a centrifugal pump, whilst the heat exchangers are of tube-in-tube construction. A number of expanders are considered including a radial turbine and a vacuum expander. For these components, the cost is described as a function of the power output.

In reality, the pressure ratio across the expander will impact both the efficiency and cost of the expander. Within this work these effects have been neglected owing to the complexities of requiring a more detailed expander model, and because correlations that consider these effects are either not currently available, or not sufficiently validated.

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However, these effects should be considered in future studies. Annual average exchange rates of 1.427 \$/£, 1.843 \$/£ and 1.648 \$/£ for 2001, 2006 and 2014, respectively, are used to convert the costs from USD to GBP. Finally, the CEPCI (CEPCI₂₀₀₁ = 397, for Turton *et al.* [167]; CEPCI₂₀₀₆ = 500, for Seider *et al.* [166]; CEPCI₂₀₁₄ = 576.1, for Toffolo *et al.*) is used to convert the cost to today's values (CEPCI₂₀₁₇ = 562.1) by multiplying the the base-cost with a ratio of the current CEPCI to the reference CEPCI.

Total costs and specific costs

The capital cost estimation technique developed by Guthrie relates all process costs back to the costs of major equipment units [172, 173]. Thus, once the cost of the components are evaluated, these can be summed together to obtain the total equipment costs (*i.e.*, $\sum_i C_{p,i}^0$). The total investment cost (TIC) is determined by adding contingency factors to the equipment costs:

$$\text{TIC} = 1.18 \times \sum_i C_{p,i}^0, \quad (2.31)$$

where the 18% factor contains a 15% contingency factor, to account for inaccuracies introduced by using correlations for equipment costs and pressure factors, and a 3% contractor fee factor [174].

A common indicator used for preliminary economic assessment of ORC systems are the specific investment costs (SIC). This metric represents the total investment costs of the system per net-kilowatt of electrical power generated, thus:

$$\text{SIC} = \frac{\text{TIC}}{\dot{W}_n}. \quad (2.32)$$

The specific purchased equipment costs (SPEC), often used in place of the SIC, is also employed by various authors in describing ORC systems. The SPEC is lower than the SIC as it is derived by dividing the total equipment costs by the net power generated.

2.1.4 Case study and optimisation problem

A wide variety of fluid streams can be used as ORC-system heat sources, including thermal oil (*e.g.*, in solar applications), process/waste-heat streams (*e.g.*, in industrial applications), geothermal water/steam, exhaust/flue gases, *etc.* Thus it is important that initial simulation results be presented with case studies based on the typical heat sources found in such industrial settings. These have been sub-divided into three classes: low- ($\leq 100^\circ\text{C}$), medium- ($\leq 300^\circ\text{C}$) and high-temperature ($\geq 300^\circ\text{C}$) heat sources.

Table 2.1: Cost correlation coefficients for ORC system components. Correlations from Ref. [166] are used in Equation (2.29); correlations from Refs. [167] and [170] are used in Equation (2.30).

Component	X	F	Z_1	Z_2	Z_3	Z_4	Z_5	Ref.
Pump	$S^{*,1}$	2.7	9.0073	0.4636	0.0519	–	–	[166]
Pump motor	$\dot{W}_{\text{pump}}$ [hp]	1.4	5.8259	0.1314	0.0533	0.0286	0.00355	[166]
Radial turbine	$\dot{W}_{\text{exp}}$ [kW]	3.5	2.2486	1.4965	–0.1618	–	–	[167]
Expander	$\dot{W}_{\text{exp}}$ [kW]	1.0	6.5106	0.8100	–	–	–	[166]
Expander ²	$\dot{W}_{\text{exp}}$ [kW]	1.0	7.3194	0.8100	–	–	–	[166]
Generator ³	$\dot{W}_{\text{exp}}$ [kW]	1.5	2.4396	0.9400	–	–	–	[170]
Heaters/Coolers	A [m ²]	1.0	10.106	–0.4429	0.0901	–	–	[166]
Evaporator/Condenser	A [m ²]	1.0	9.5638	0.5320	–0.0002	–	–	[166]

¹ $S^* = \dot{V}\sqrt{H}$, where $\dot{V}$ is the pump volumetric flow rate in m³/s and H is the pump head in metres.

² Sub-atmospheric pressure discharge expander (*e.g.*, applicable to $P_{\text{cond}} < 1\text{atm}$).

³ The costs of the generator gearbox is estimated as 40% of the generator costs [171].

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With the aim of investigating the advantages and challenges of deploying working-fluid mixtures in ORC systems, it is more appropriate to consider systems with liquid-phase heat-source and heat-sink streams as gaseous streams would dominate the thermal resistances on the source and sink sides of the heat exchangers, thereby overshadowing the thermal resistances on the working-fluid vapour and liquid streams, and limiting the information one hopes to derive by employing different working-fluid mixtures. Thus, while gaseous heat source/sink streams may also be of interest, a low-temperature heat source stream is selected in the first instance.

Thus, the heat source selected here is a hot-water stream from the 80-kW_e Birdsville geothermal ORC power-plant in Birdsville, Australia [175], with an inlet temperature ($T_{\text{hs,in}}$) of 98 °C and a flow-rate of 27 kg·s⁻¹. This is typical of what is obtainable from (low-pressure) geothermal reservoirs and also (low-grade) waste-heat streams in industrial processes. The heat sink is a water stream at ambient conditions (in at 20 °C, out at 30 °C). The required thermodynamic and transport properties of the working-fluid mixtures and the heat source and sink are calculated by using REFPROP 9.1 [176], while the pump and expander isentropic efficiencies ($\eta_{\text{is,pump}}$ and $\eta_{\text{is,exp}}$) are taken as 75%.

With these external heat-source and heat-sink conditions, an optimisation problem is set up to maximise the net power output ($\dot{W}_{\text{net}}$) from the ORC system for the selection of working fluids:

$$\begin{aligned}
 & \underset{P_{\text{evap}}, P_{\text{cond}}, \theta_{\text{SH}}, \dot{m}_{\text{wf}}}{\text{maximise}} && \{\dot{W}_{\text{net}}\} \\
 & \text{subject to:} && 0 \leq \theta_{\text{SH}} \leq 1 \\
 & && P_{\text{cond}} \leq P_{\text{evap}} \leq P_{\text{crit}} \\
 & && T_{4\text{v}} \leq T_4 \\
 & && \Delta T_{\text{pinch, min}} \leq \Delta T_{\text{pinch}} .
 \end{aligned} \tag{2.33}$$

In this problem, defined to maximise the net power output, the heat exchangers are designed such that their pinch-point temperature difference (ΔT_{pinch}) is greater than a set minimum ($\Delta T_{\text{pinch, min}}$) of 10 °C. In addition, the amount of superheating provided, θ_{SH} , is controlled by the first constraint while the cycles are kept subcritical with the second constraint (*i.e.*, $P_{\text{cond}} \leq P_{\text{evap}} \leq P_{\text{crit}}$). A further constraint ($T_{4\text{v}} \leq T_4$) is added to ensure that the working fluid exits the expander as superheated vapour, avoiding the challenges associated with wet expansion (*i.e.*, expansion through the two-phase region).

2.2 Optimal cycles with working-fluid mixtures

To start with, the ORC system is optimised to maximise $\dot{W}_{\text{net}}$ as described in Equation (2.33), using the Interior Point algorithm [177]. Two sets of working-fluid mixtures are considered: the *n*-hexane + *n*-pentane alkane system; and the R-245fa + R-227ea refrigerant system; other fluid mixtures will be considered in Section 2.3.3. Earlier studies have shown that these mixtures can provide significant thermodynamic benefits in ORC systems [14, 71, 178, 179], which has motivated their consideration in the present study. Furthermore, pentane and the selected refrigerants are presently being used in actual installations, especially in geothermal ORC plants, such as the one considered here. The optimal power outputs and associated operating pressures are presented in Figure 2.3, and the expander performance parameters are presented in Figure 2.4. All other cycle parameters are given in Tables 2.2.

From Table 2.2, the total rate of heat inflow to the cycle (in all cases) varies between 3.2 MW and 4.0 MW. Of this total, about 85% is used to evaporate the alkane working fluids ($\dot{Q}_{\text{Ev}}$, 70%–85% for the refrigerants) and the rest is used to pre-heat the fluids to their bubble points ($\dot{Q}_{\text{PH}}$). On average, about 3.5 MW is rejected from the cycles, 85% of which is rejected in the condensation process. For the *n*-pentane + *n*-hexane system, a working-fluid mixture with an *n*-hexane mass fraction of 0.5 (*i.e.*, $x_{\text{C}_6\text{H}_{14}} = 0.5$) results in the cycle with the highest net-power output and thermal efficiency. The (pure) *n*-hexane cycle has the lowest power output (Figure 2.3a), followed closely by the *n*-pentane cycle; their power outputs are about 26% lower than that of the optimal mixture. For the R-245fa + R-227ea system, the mixture with $x_{\text{R-227ea}} = 0.4$ is the optimal working fluid (Figure 2.3b).

The working-fluid mixtures with *n*-hexane fractions between 40% and 60% have the highest specific work-outputs (defined as $w_{\text{exp}} = \dot{W}_{\text{exp}}/\dot{m}_{\text{wf}}$), with $x_{\text{C}_6\text{H}_{14}} = 0.5$ having the highest, and the highest working-fluid flow-rates (from Table 2.2) and therefore also the highest net power-outputs in the considered application. While the pure fluids have the lowest mass flow-rates, they result in cycles with the lowest specific work outputs due to their lower net power outputs. Their specific work outputs are about 12% lower than that of the optimal fluid mixture. For the R-245fa + R-227ea system, the optimal working fluid flow-rate increases monotonically from pure R-245fa to pure R-227ea, and R-227ea has the cycle with the lowest specific work.

As expected, the temperature glides (Figure 2.3c) are smaller in the evaporator than in the condenser. In both heat exchangers, these follow a parabolic variation with x ,

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Table 2.2: Cycle parameters for ORC systems operating on a low-temperature heat source at 98 °C, optimised for maximum net power output using *n*-pentane + *n*-hexane and R-245fa + R-227ea working-fluid mixtures.

$x_{\text{C}_6\text{H}_{14}}$	$\dot{W}_{\text{net}}$ kW	η_{th} %	w_{exp} kJ·kg ⁻¹	$\dot{W}_{\text{pump}}$ kW	$\dot{m}_{\text{wf}}$ kg·s ⁻¹	θ_{SH} [-]	$\dot{m}_{\text{cs}}$ kg·s ⁻¹	$\dot{Q}_{\text{PH}}$ MW	$\dot{Q}_{\text{Ev}}$ MW	$\dot{Q}_{\text{DSh}}$ MW	$\dot{Q}_{\text{Cn}}$ MW
0.0	161	5.00	21.1	2.17	7.74	0.45	73.1	0.47	2.75	0.30	2.75
0.1	179	5.25	21.8	2.20	8.29	0.18	77.2	0.53	2.88	0.23	3.00
0.2	193	5.43	22.5	2.16	8.68	0.00	80.5	0.57	2.99	0.18	3.19
0.3	204	5.55	23.3	2.05	8.86	0.00	83.2	0.59	3.09	0.19	3.29
0.4	211	5.61	23.7	1.92	8.98	0.00	84.9	0.61	3.15	0.20	3.35
0.5	214	5.64	23.9	1.78	9.03	0.00	85.8	0.62	3.18	0.20	3.38
0.6	213	5.61	23.8	1.62	9.02	0.00	85.8	0.62	3.18	0.21	3.38
0.7	208	5.55	23.4	1.44	8.94	0.00	84.7	0.60	3.15	0.20	3.34
0.8	198	5.44	22.7	1.26	8.77	0.00	82.4	0.58	3.06	0.20	3.24
0.9	183	5.28	21.7	1.06	8.48	0.00	78.4	0.53	2.93	0.19	3.09
1.0	161	5.05	20.2	0.85	8.02	0.00	72.3	0.47	2.71	0.17	2.85

$x_{\text{R-227ea}}$	$\dot{W}_{\text{net}}$ kW	η_{th} %	w_{exp} kJ·kg ⁻¹	$\dot{W}_{\text{pump}}$ kW	$\dot{m}_{\text{wf}}$ kg·s ⁻¹	θ_{SH} [-]	$\dot{m}_{\text{cs}}$ kg·s ⁻¹	$\dot{Q}_{\text{PH}}$ MW	$\dot{Q}_{\text{Ev}}$ MW	$\dot{Q}_{\text{DSh}}$ MW	$\dot{Q}_{\text{Cn}}$ MW
0.0	163	4.97	11.5	4.05	14.5	1.00	74.7	0.50	2.78	0.48	2.64
0.1	187	5.17	11.8	5.18	16.2	1.00	82.1	0.60	3.01	0.52	2.92
0.2	204	5.30	11.7	6.44	18.0	0.84	87.1	0.70	3.15	0.49	3.15
0.3	214	5.39	11.1	7.88	19.9	0.54	90.1	0.78	3.20	0.41	3.36
0.4	219	5.42	10.3	9.66	22.3	0.11	91.6	0.87	3.17	0.25	3.58
0.5	219	5.40	9.79	11.0	23.5	0.12	91.7	0.91	3.14	0.26	3.57
0.6	213	5.33	9.02	12.7	25.1	0.00	90.6	0.95	3.05	0.21	3.57
0.7	204	5.21	8.29	14.3	26.3	0.00	88.6	0.97	2.94	0.22	3.48
0.8	191	5.06	7.52	15.9	27.5	0.00	85.9	0.98	2.81	0.22	3.37
0.9	179	4.89	6.80	17.9	29.0	0.00	83.3	0.99	2.67	0.23	3.25
1.0	170	4.76	6.19	20.2	30.7	0.00	81.4	1.02	2.55	0.24	3.17

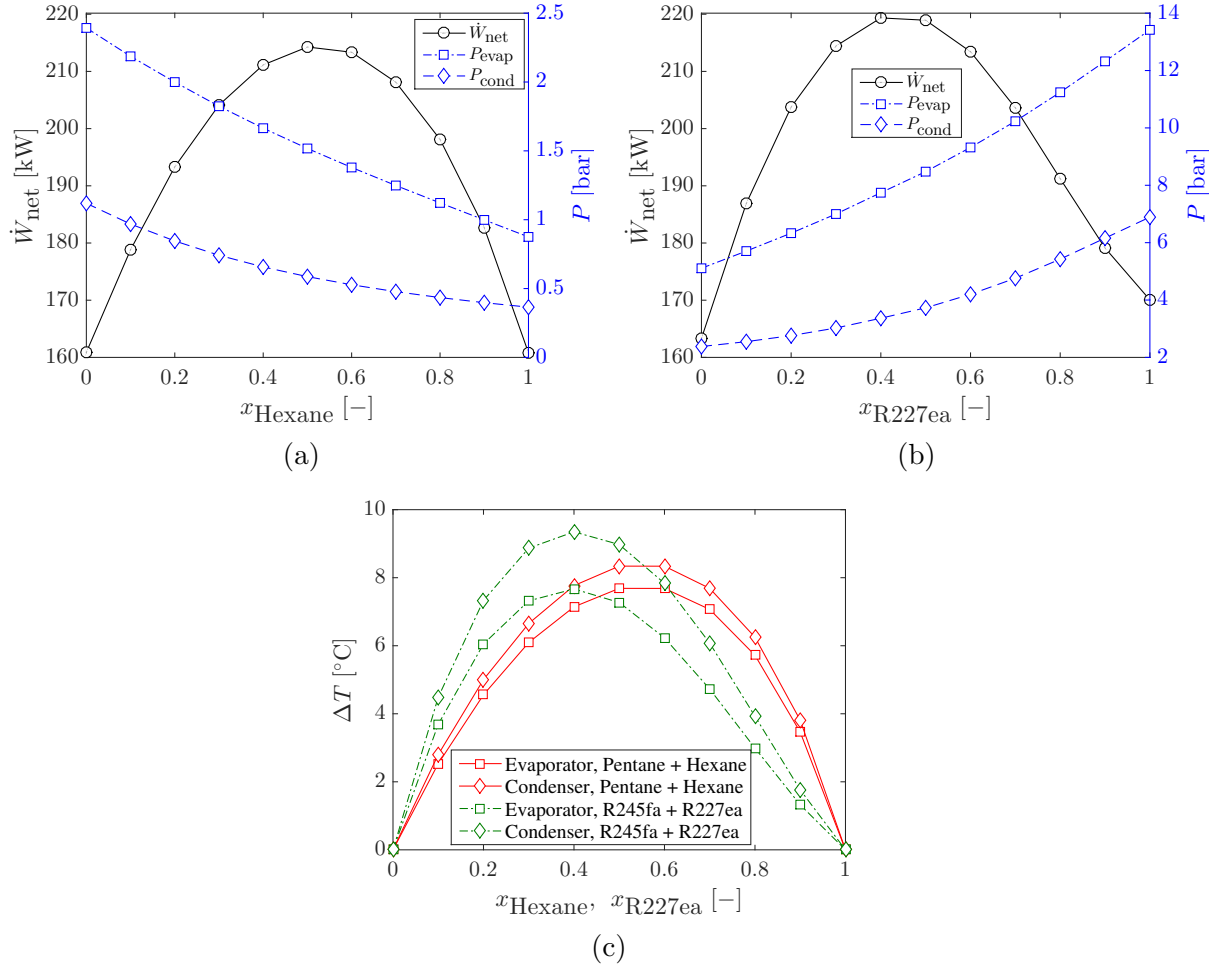


Figure 2.3: Optimal net power-output (maximum $\dot{W}_{\text{net}}$) of ORC systems operating on a low-temperature heat source at 98 °C, with corresponding operating phase-change pressure, and evaporation and condensation temperature glides at optimal operating conditions, as functions of the n -hexane or R-227ea mass fraction. (a) n -pentane + n -hexane; (b) R-245fa + R-227ea; (c) temperature glides.

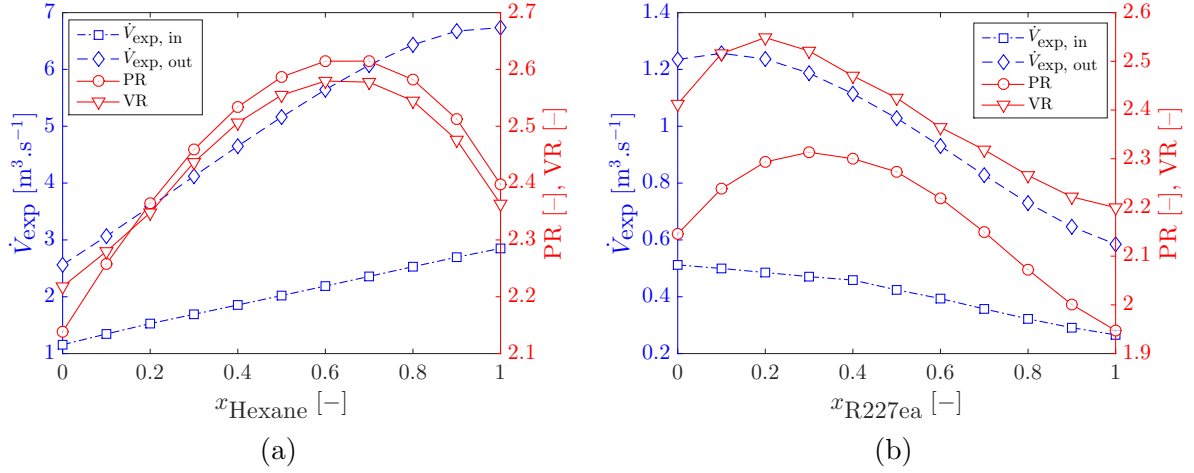


Figure 2.4: Expander volumetric flow-rate, volume and pressure ratio for optimised ORC systems operating on a low-temperature heat source at 98 °C. (a) n -pentane + n -hexane; (b) R-245fa + R-227ea.

reaching a maximum of 7.5 °C – 8.0 °C at $x_{\text{C}_6\text{H}_{14}} = 0.5$ (n -pentane + n -hexane) and 7.5 °C – 9.0 °C at $x_{\text{R-227ea}} = 0.4$ (R-245fa + R-227ea). These directly correspond to the optimal mixtures, leading to a conclusion that the temperature glide is a reasonably good predictor of the maximum power output, since high-power-output mixtures have relatively high temperature glides, which are also closer to the external heat sink temperature changes (10 °C). Although this holds true for closely related binary mixtures, it has been suggested that mixtures of highly dissimilar fluids may not follow this trend [13, 18, 84].

From the values of θ_{SH} in Table 2.2, it is clear that most of the optimal cycles are achieved with zero superheat, $\theta_{\text{SH}} = 0$ (*i.e.*, expanding from a saturated vapour state, without superheating) or minimal superheat. This is because these working fluids are slightly dry in nature (*i.e.*, on the T - s diagram, they have a dew-point curve with a large positive slope) and, as such, superheating is detrimental to cycle performance [13]. Only cycles with mixtures with high proportions of R-245fa are optimised while employing high values of superheat, due to their almost isentropic nature (*i.e.*, almost vertical dew point line on the T - s diagram).

On average, the mass flow-rate of the cooling water needed to condense the working fluids is $85 \text{ kg} \cdot \text{s}^{-1}$. It should be noted that the cooling-water flow-rates are over three times larger than the heat-source flow-rate and about ten times larger than the working fluid flow-rates due to the low temperature change (10 °C) imposed on the cooling stream.

The optimal evaporation and condensation pressures (Figures 2.3a and 2.3b, RHS axes) reduce linearly from n -pentane (R-227ea) to n -hexane (R-245fa). This is because

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the saturation pressure of *n*-pentane (or R-227ea) is higher than that of *n*-hexane (or R-245fa) at the same temperature, since the critical temperature of *n*-pentane (or R-227ea) is lower than that of *n*-hexane (or R-245fa). In the R-245fa + R-227ea system, the entire condensation process occurs at above atmospheric pressures, whereas in the *n*-pentane + *n*-hexane system, only *n*-pentane condenses at above atmospheric conditions (the other working fluids condense at sub-atmospheric pressures). The pumping power (while being negligible compared to the expander output) mirrors the behaviour of the optimal evaporation pressure in both working-fluid systems.

Similarly, the volumetric flow rate through the expander, $\dot{V}_{\text{exp}}$ (Figure 2.4, LHS axes) increases linearly from pure *n*-pentane (or R-227ea) to pure *n*-hexane (or R-245fa) due to the reduction in the saturation pressure during evaporation and condensation at higher concentrations of *n*-hexane (or R-245fa). The pressure ratio (PR), and volumetric expansion ratio (VR), (Figure 2.4, RHS axes) follow similar trends, with a minimum observed for one of the pure-fluid components (*n*-pentane and R-227ea, respectively), and a maximum observed for a specific fluid mixture. The low expansion ratios and volumetric flow rates for pure components suggests that they would require smaller expanders than the mixtures, potentially leading to cost savings. In addition, they would require fewer expansion stages as volumetric expanders are produced with a fixed ratio, further increasing the potential cost savings.

2.3 Sizing and costing of optimal ORC systems

In the previous section, using a specific choice of working fluids in a low-temperature ORC system, the thermodynamic benefits of employing working-fluid mixtures in ORCs, especially for cases when the heat source and sink profiles are constrained is demonstrated. As expected, some working-fluid mixtures produce higher power outputs and achieve higher efficiencies than both pure fluids, as a result of the matching temperature glides during the phase change processes. The associated expansion and pressure ratios of such working-fluid mixtures are comparable to those of the pure working fluids.

However, these results were derived purely from a thermodynamic perspective; the effects of such mixtures on the heat transfer processes in the heat exchangers, and especially the evaporator and the condenser, have not yet been considered. Experimental investigations have shown that working-fluid mixtures are likely to experience lower heat transfer coefficients (HTCs) than pure fluids under similar conditions. Thus, it is imperative to examine the consequences of selecting fluid mixtures on the heat transfer processes

in an ORC system, with a view towards determining the sizes and costs of the main system components, and therefore their contributions to overall system cost. The pump and expander costs depend on their power ratings and volume/pressure ratios, which were derived from the thermodynamic optimisation and thus need no further treatment. The costs of the heat exchangers, on the other hand, depend on their sizes, which cannot be obtained from thermodynamic calculations alone, and require appropriate heat transfer models as presented in Section 2.1.2.

2.3.1 Heat exchanger sizing for optimal ORC systems

First, the overall heat-transfer coefficients (HTCs) calculated using equations presented in Section 2.1.2, especially for the heat exchangers involving phase change (evaporator and condenser) are verified. The overall HTCs at the 20th, 50th and 80th segments of these heat exchangers, and for the single-phase heat exchangers, are presented in Figure 2.5 for the R-245fa + R-227ea system. The calculated values are generally in good agreement with experimental data obtained for flow boiling of refrigerant mixtures found in Jung *et al.* and Shin *et al.* [88, 165]. Also in agreement with experimental observations, the HTCs for the fluid mixtures at each of the segments appear lower than the linearly interpolated values between the two pure-fluid components that make up the mixture. While various explanations have been proposed for this phenomenon, most authors contend that it is due to mass-transfer effects caused by the composition differences between the vapour and liquid phases during the phase-change process [88, 165].

In the single-phase heat exchangers (preheater and desuperheater), the overall HTCs for the mixtures are also lower than the linearly interpolated values, although this deviation is less pronounced for the R-245fa + R-227ea mixtures. Overall, the HTCs are highest in the evaporator, followed by the condenser, and lowest in the desuperheater. Higher HTCs are achieved in the condenser and evaporator due to change of phase. The working-fluid vapour results in low HTC values in the desuperheater. It should be noted that, in some cases, the evaporator also serves to superheat the working fluid (for cases where $0 \leq x_{\text{R-227ea}} \leq 0.5$) and, as such, the working fluid exists as a superheated vapour in later segments of the evaporator. The HTCs in these superheating segments are similar to those exhibited in the desuperheater in Figure 2.5. Furthermore, the HTCs presented here are those for the R-245fa + R-227ea system; similar conclusions can be drawn from those of the *n*-pentane + *n*-hexane.

Based on the knowledge of the HTCs and associated heat-transfer rates, the heat transfer areas (HTAs) for all segments of the heat exchangers can be calculated from

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Equation (2.19). The HTAs of the segments in the evaporator and the condenser (for R-245fa + R-227ea) are presented in Figure 2.6; similar observations can be made by considering *n*-pentane + *n*-hexane. As the mass fraction of R-227ea is increased in the mixture, the HTA is seen to increase and then decrease such that the systems with pure fluids (R-245fa and R-227ea) have heat exchangers with the lowest HTAs. This is the case across all of the segments and in both the evaporator and condenser, as a direct result of the lower HTC of the working-fluid mixtures, with the only exception being that of the evaporator for R-245fa + R-227ea where some mixtures (*e.g.*, $x_{\text{R-227ea}} = 0.8$) have lower HTAs than pure R-245fa; systems with pure R-227ea still has the lowest areas across all of the sections.

From Figure 2.6, the HTA variations are less pronounced in the evaporator than in the condenser, where large differences exist between the pure fluids and the mixtures. The pure fluids have the smallest heat transfer areas primarily due to their higher HTC values. While the variation in HTA with choice of working fluid (pure and mixtures) across both types of equipment is a result of their varying heat-transfer coefficients, there are larger variations in the condensers due to the larger heat duties (see Table 2.2) and larger working-fluid volumetric flow-rates (see Figure 2.4) handled by the condensers. Another factor that contributes to this is the large mass flow-rate of cooling water (average of $\sim 80 \text{ kg}\cdot\text{s}^{-1}$ from Table 2.2) compared to that of the heat source ($27 \text{ kg}\cdot\text{s}^{-1}$).

The total HTAs for each of the heat exchangers with the different working-fluid mixtures are presented in Figure 2.7, in normalised form with respect to (based on parameters in Table 2.3):

$$A_n = (A_{\text{HX}} - A_{\text{min}})/(A_{\text{max}} - A_{\text{min}}). \quad (2.34)$$

The absolute total heat-transfer area gives a direct indication of the size of the heat exchanger, while the normalised form facilitates the comparison between the different fluid mixtures. As expected by considering their thermal duties (see Table 2.2), the evaporators are generally 2 to 3 times larger than the preheaters, while the condensers are 5 to 6 times larger than the desuperheaters. Although the condenser thermal-duties are only about 15% higher than those of the evaporators, the condensers are twice (or more) as large as the evaporators in most instances. This is due to the lower overall HTCs and the lower temperature differences across the condensers. This is further magnified by the lower pressures in the condensers (compared to the evaporators), leading to higher working-fluid volumetric flow-rates ($\dot{V}_{\text{exp,out}} > \dot{V}_{\text{exp,in}}$, see Figure 2.4) and, hence, much larger condenser sizes.

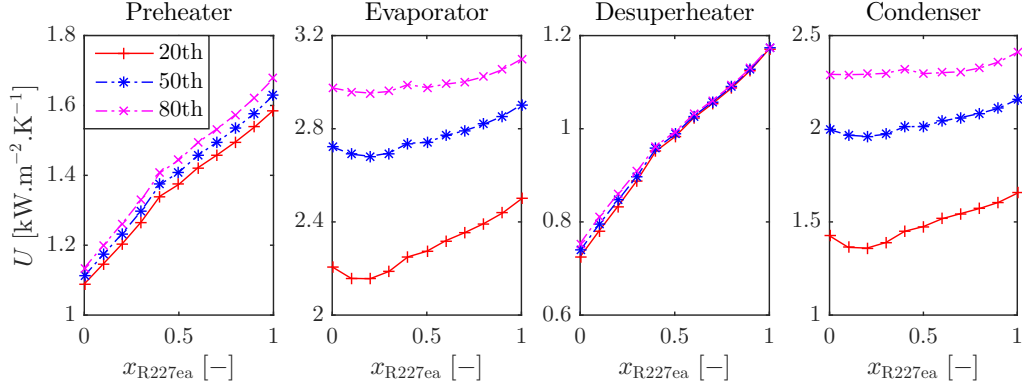


Figure 2.5: Overall heat transfer coefficients of heat exchangers in ORC systems operating on a low-temperature heat source at 98 °C and optimised for maximum net power output, at segments along the heat exchangers for systems with R-245fa + R-227ea working-fluid mixtures.

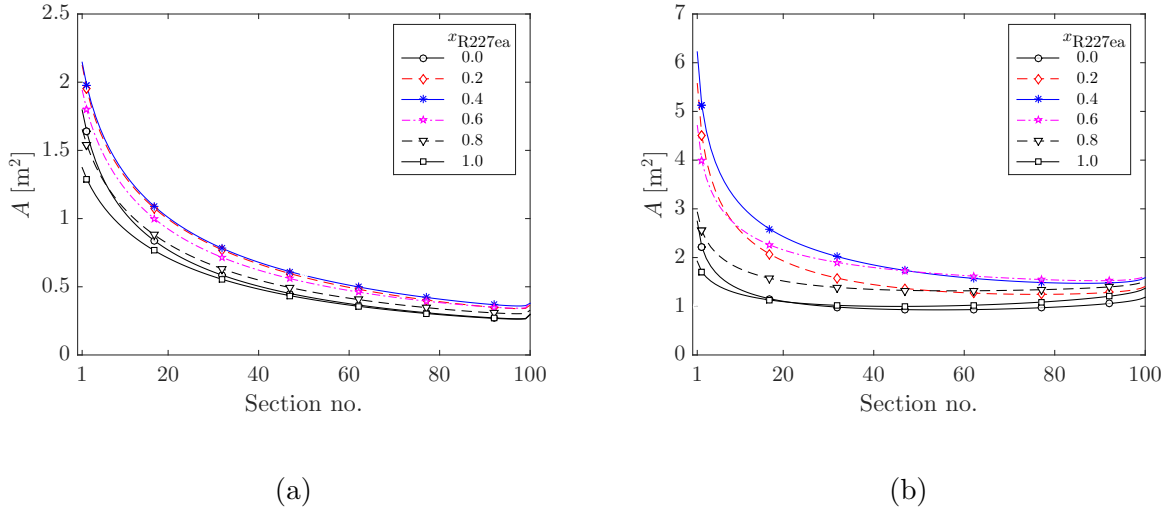


Figure 2.6: Heat-transfer areas along the phase-change heat exchangers (evaporator and condenser) in ORC systems operating on a low-temperature heat source at 98 °C and optimised for maximum net power output, with R-245fa + R-227ea working-fluid mixtures. (a) Evaporator; (b) Condenser.

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Table 2.3: Heat exchanger area normalisation parameters used in Equation (2.34).

Pentane + Hexane	PH	Ev	DSh	Cn	R-245fa + R227ea	PH	Ev	DSh	Cn
$A_{\min}$ (m ²)	21.8	48.5	15.8	80.8	$A_{\min}$ (m ²)	24.5	51.1	15.2	109
$A_{\max}$ (m ²)	25.8	65.3	23.4	150	$A_{\max}$ (m ²)	37.2	82.6	29.9	204

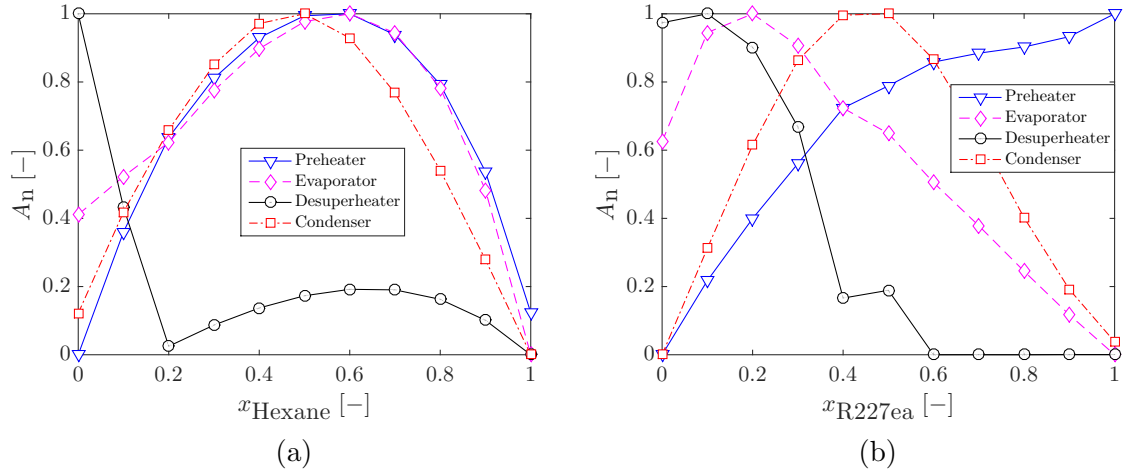


Figure 2.7: Normalised total heat-transfer areas for heat exchangers in ORC systems operating on a low-temperature heat source at 98 °C and optimised for maximum net power output, with the different working-fluid mixtures. Normalisation parameters are given in Table 2.3. (a) *n*-pentane + *n*-hexane; (b) R-245fa + R-227ea.

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From the thermodynamic optimisation results in Table 2.2, it can be seen that although most of the optimal cycles are achieved without superheating ($\theta_{SH} = 0$), a few ($x_{C_6H_{14}} = 0, 0.1$, and $x_{R-227ea} \leq 0.5$) do however involve varying degrees of superheat ($\theta_{SH} > 0$), and thus would require a superheating section to be added to their evaporators. The effect of this addition, is that these systems (with high degrees of superheat) will require larger evaporators as is noticeable for both sets of fluid mixtures in Figure 2.7. For the *n*-pentane + *n*-hexane mixtures, ORC systems with $x_{C_6H_{14}} = 0$ or $x_{C_6H_{14}} = 0.1$ do not follow the general parabolic trend established with the other mixtures. Their evaporator HTAs are seen to be larger than expected from the trend due to this additional superheating section. This effect is even more pronounced for the R-245fa + R-227ea mixtures, which exhibit optimal cycles with larger degrees of superheat. The evaporator HTAs for ORC systems with $0.1 \leq \theta_{SH} \leq 1$ (*i.e.*, those with $x_{R-227ea} \leq 0.5$) are much larger than those with $x_{R-227ea} > 0.5$ that do not require a superheating section.

Furthermore, in systems that require an additional superheating section, the working-fluid vapour exits the evaporator and, therefore, enters the expander at higher temperatures, and subsequently exits the expander with higher degrees of superheat and at higher temperatures. This requires a larger amount of heat to be rejected to the cooling stream in the desuperheater, as a consequence of which these systems (with $\theta_{SH} > 0$) typically require larger desuperheaters (Dsh) than the systems with $\theta_{SH} = 0$. This inference can be seen in Figure 2.7 for both the *n*-pentane + *n*-hexane and R-245fa + R-227ea working-fluid systems, accounting for the two regimes in the normalised desuperheater HTA. The ORC systems with $\theta_{SH} > 0$ (*i.e.*, $0 \leq x_{C_6H_{14}} < 0.2$ and $0 \leq x_{R-227ea} < 0.5$, see Table 2.2) have larger normalised DSh areas than those with $\theta_{SH} = 0$. Thus, superheating the working fluid in ORC evaporators not only increases the size (*i.e.*, HTA) of the evaporator, but also the size of the desuperheater and eventually the cost of the engine as a whole.

As the concentration of R-227ea in the refrigerant-mixture system increases, the PH heat duty increases, and so does its total HTA. The PH areas for the *n*-pentane + *n*-hexane systems are also directly governed by their heat duties. It should, however, be noted that these variations in HTA with working-fluid mixtures (maximum range of 13 m² and 15 m² for the preheaters and desuperheaters, respectively) are much smaller than those associated with the two-phase heat exchangers (maximum range of 32 m² and 95 m² for the evaporators and condensers respectively). This is important, in that it suggests that working-fluid mixtures have a more profound effect on the evaporator and condenser sizes than they do on the single-phase heat-exchangers, at least in the present study.

Sizing and costing of optimal ORC systems

From Figure 2.7, it is clear that the pure working-fluids have smaller evaporator HTAs compared to the mixtures. The only minor exception is found in the R-245fa + R-227ea system, where fluid mixtures with $x_{\text{R-227ea}} \geq 0.9$ have lower Ev areas than pure R-245fa. Furthermore, due to the deterioration of HTC during condensation, the condensers for the working-fluid mixtures are much larger than those for the pure fluids. In the case of the R-245fa + R-227ea system, the condenser HTAs range from 109 m² ($x_{\text{R-227ea}} = 0$) to 204 m² ($x_{\text{R-227ea}} = 0.5$). This implies an increase in HTA of 85% when a working-fluid mixture is *substituted for* a pure working fluid (or, conversely, a decrease in HTA of 45% when a working-fluid mixture is *substituted with* a pure working fluid). Such large differences in HTAs between working-fluid mixtures and pure fluids can lead to considerable differences in plant size and cost, in favour of the pure working fluids.

2.3.2 Cost estimation of optimal ORC systems

With the heat transfer areas of the heat exchangers determined, all the equipment size factors required in Table 2.1 for the estimation of the ORC component costs are now defined. With these size factors, the costs of the ORC components can now be evaluated. The calculated component-base costs of the optimal ORC systems are presented in Figure 2.8 (LHS axes). It should be noted that the costs presented are the capital costs; an investment decision will require the analysis of the associated operating costs, expected profits and payback periods.

The pumps (combined with their motors) cost around £6,000, with the cost reducing monotonically from pure *n*-pentane (R-227ea) to *n*-hexane (R-245fa) as a direct result of the lower evaporation pressures as the concentration of *n*-hexane (R-245fa) in the working fluid is increased (in line with Figure 2.3). Similarly, the costs of the single-phase heat exchangers (PH and DSh) are low (£9,000 – £10,000). However, the evaporator and condenser costs are well in excess of £80,000. The expander costs fall into two classes: (i) sub-atmospheric pressure (vacuum) discharge expanders that cost between £65,000 – £75,000; and (ii) standard expanders with a considerably lower cost between £25,000 – £35,000. From these results, it is clear that the expander and the phase-change heat exchangers present the dominant costs of the ORC system considered here.

The pure fluids (pure *n*-pentane and *n*-hexane; R-245fa and R-227ea) generally have the lowest-cost evaporators and condensers, while the mixtures ($x_{\text{C}_6\text{H}_{14}} = 0.6$ and $x_{\text{C}_6\text{H}_{14}} = 0.5$; $x_{\text{R-227ea}} = 0.2$ and $x_{\text{R-227ea}} = 0.5$, respectively) have the highest costs. This is a direct result of the pure working fluids having higher heat-transfer coefficients (due to the deterioration of heat transfer behaviour of the mixtures) than the working-fluid

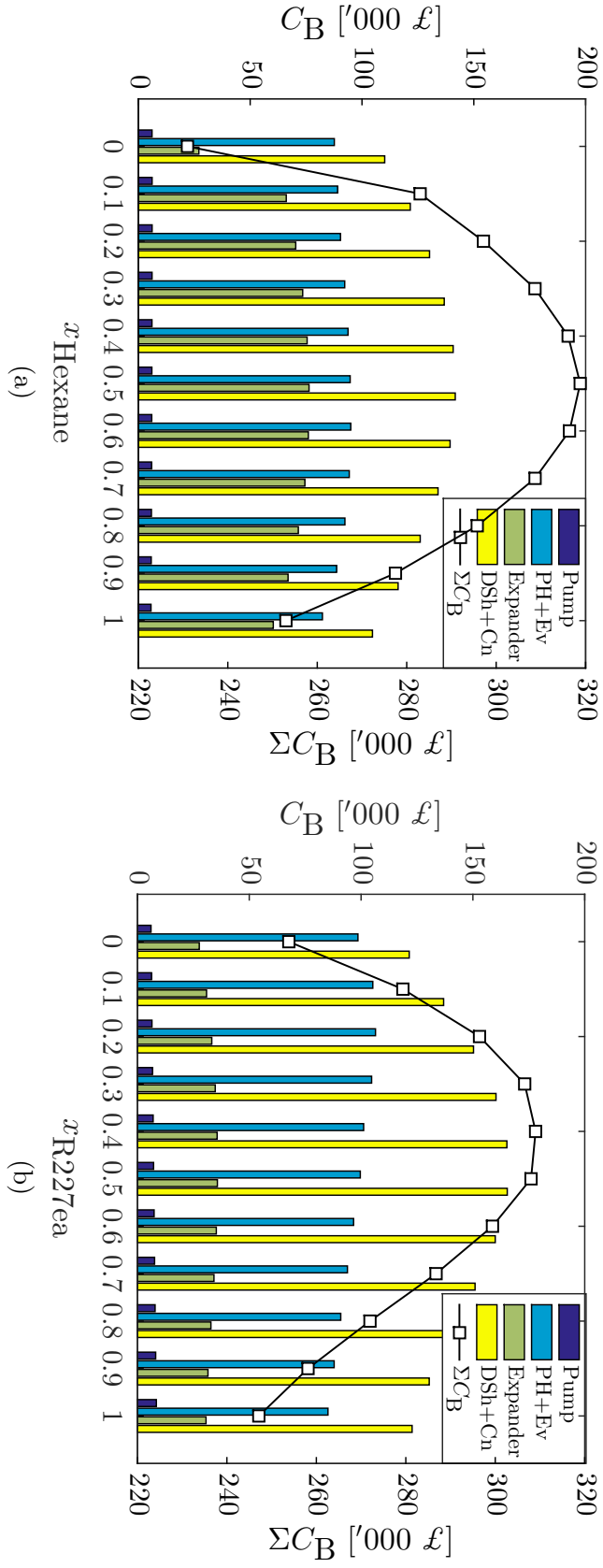


Figure 2.8: Optimal ORC systems' component costs (bars; LHS axes) and total component costs (line; RHS axes) for ORC systems operating on a low-temperature heat source at 98 °C, optimised for maximum net power. Component-base costs, C_B are indexed in year 2006, with the following currency conversions: £1 $\equiv$ €1.47, \$1.84. (a) n -pentane + n -hexane; (b) R-245fa + R-227ea.

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mixtures and thus their lower heat transfer areas and subsequent lower costs. In addition, the higher power output produced by the mixtures is achieved partly by their high heat duties (see Table 2.2), contributing to their larger HTAs and heat exchanger costs and resulting in cheaper heat exchangers for the ORC systems with pure working fluids.

From Figure 2.8, it is clear that the expander costs mirror the trend exhibited by the optimal power output in Figure 2.3 especially as they are correlated with the power output. However, for the *n*-pentane + *n*-hexane system, the expander cost for pure *n*-pentane ($x_{\text{C}_6\text{H}_{14}} = 0$) is over 50% lower than those of the other working fluids. After expansion, the *n*-pentane vapour exits the expander at above atmospheric pressure while all the other working fluids exit at sub-atmospheric pressures (*i.e.*, below 1 atm) and had their expander costs calculated with the sub-atmospheric pressure discharge expander correlation in Table 2.1. This, in turn, makes the cost of the *n*-pentane expander much lower than the rest in the *n*-pentane + *n*-hexane system. On the other hand, all the working fluids in the R-245fa + R-227ea system exit the expander above atmospheric pressure; this makes the expanders and the ORC engines (total cost on RHS axes of Figure 2.8) of the R-245fa + R-227ea system cheaper than those of the *n*-pentane + *n*-hexane system.

It should be noted that the cost figures presented here in Figure 2.8 (and subsequently in Figures 2.9 – 2.12) are preliminary, simple estimations based on the specific costing exercise presented in Section 2.1.3, and therefore subject to the assumptions and accuracy of this exercise. It is inevitable that the final cost values are more difficult to quantify rigorously, and are associated with uncertainties that are larger than those in the thermodynamic analysis. Specifically, the cost figures can be expected to vary by about $\pm 25\%$ as stated in Section 2.1.3, and the actual capital costs of the associated plants can be different from those presented by a similar margin. Furthermore, employing any of the other cost correlations mentioned in Section 2.1.3 would result in new cost figures, different in magnitude from those in this work. Nevertheless, the qualitative (relative) comparisons derived from these figures (Figures 2.8 – 2.12), with regards to the effect of the choice of working fluid (*i.e.*, pure or working-fluid mixtures) are less sensitive to the absolute cost figures and should remain as presented herein. This is to be expected since the component cost calculations were based on the physical sizes of the equipment, that are directly affected by the choice of working fluid.

The total base cost for the ORC systems is presented on the RHS axes in Figure 2.8. By comparing the individual component-base costs to the total cost, one can arrive at a component cost distribution for typical ORC systems. The pumps generally have the

lowest proportion of the total cost, usually less than 3% while the expander (depending on the type) can contribute between 10% and 25% to the total cost. Due to their special construction, vacuum discharge expanders are more expensive than standard ones and thus they can contribute up to 25% of the total cost. The heat addition heat exchangers (preheater and evaporator) make up about 35% of the total costs, while the heat rejection heat exchangers (desuperheater and condenser) make up between 45% and 55% of the total cost. This implies that the heat exchangers can make up to 90% of the combined component cost of ORC systems, highlighting the consequence of employing (or not) working-fluid mixtures on the overall ORC plant cost and the need to investigate the compromise between the thermodynamic benefits and the cost implications of more working-fluid mixture systems.

2.3.3 Heat input limitations and other working-fluid mixtures

While the benefits and drawbacks of working-fluid mixtures in ORCs have been demonstrated, albeit with two pairs of fluids (*n*-pentane + *n*-hexane and R-245fa + R-227ea), it is important to investigate other working fluid systems of practical interest. Along with the four initial pure fluids, mixtures of the following alkanes and refrigerants are also considered: *n*-butane, R-134a, R-236fa and R-245ca. Although this list is not an exhaustive selection of the huge number of mixture combinations possible, it will give some indication of the behaviour of mixtures with ORCs in general. In addition, alternative ORC system designs are investigated. Here, the heat input to the cycle is fixed as may be practically required, *e.g.* due to retrofits or a need of the heat source for other purposes such as heating or otherwise, presenting another basis of comparison of pure working fluids and working-fluid mixtures in ORCs.

This is done by limiting the heat extracted from the heat source such that $\dot{Q}_{\text{in}} \leq \dot{Q}_{\text{in,lim}}$ and Equation (2.33) can be rewritten as:

$$\begin{aligned}
 & \underset{P_{\text{evap}}, P_{\text{cond}}, \theta_{\text{SH}}, \dot{m}_{\text{wf}}}{\text{maximise}} && \{\dot{W}_{\text{net}}\} \\
 & \text{subject to:} && \dot{Q}_{\text{in}} \leq \dot{Q}_{\text{in,lim}} \\
 & && 0 \leq \theta_{\text{SH}} \leq 1 \\
 & && P_{\text{cond}} \leq P_{\text{evap}} \leq P_{\text{crit}} \\
 & && T_{4\text{v}} \leq T_4 \\
 & && \Delta T_{\text{pinch, min}} \leq \Delta T_{\text{pinch}} .
 \end{aligned}
 \tag{2.33 revisited}$$

Sizing and costing of optimal ORC systems

Three cases are provided:

1. $\dot{Q}_{\text{in,lim}} = \infty$, such that $\dot{Q}_{\text{in,lim}}$ is allowed to attain a maximum possible value; this is the case in Section 2.2 where the optimal cycle heat input ($\dot{Q}_{\text{in}}$) for different working fluids is seen to vary between 3.2 MW and 4.0 MW.
2. $\dot{Q}_{\text{in,lim}} = 2.5$ MW.
3. $\dot{Q}_{\text{in,lim}} = 1.0$ MW.

In all the cases, the cycles are optimised to maximise the net power output, subject to the heat exchangers' pinch conditions. Cases 2 and 3 are further limited by the heat input constraints ($\dot{Q}_{\text{in}} \leq \dot{Q}_{\text{in,lim}}$), corresponding to heat source outlet temperatures of 76.0 °C and 89.2 °C, respectively. In particular, the case of 1.0 MW heat input is replicative of the conditions in the original plant. The maximum net power output for the three cases, using different working fluid mixtures are presented in Figures 2.9 – 2.11, respectively. Here also, the component costs of the optimal ORC systems are reported in terms of their 'rated costs', *i.e.*, cost per kilowatt of net power generated ($\Sigma C_{\text{B}}/\dot{W}_{\text{net}}$). This is done such that high power output fluids (especially the fluid mixtures which will have higher total costs) are not unnecessarily penalised.

The working-fluid mixtures are seen to produce higher power outputs than the pure fluids in all three cases. In Case 1 ($\dot{Q}_{\text{in,lim}}$ is unconstrained), the fluid mixtures generally lead to systems with lower rated costs (in pounds per kW) than the pure fluids with only a few exceptions (R-245ca + R-245fa where R-245ca has the least cost and R-236fa + R-245fa where R-245fa has the least cost). This is due to the higher net power derived from cycles with mixtures over those with pure fluids, keeping their rated costs lower (although they have higher total costs as in Figure 2.8). It should, however, be noted that the objective here was to maximise the net power output from the cycle. Thus, the systems with working-fluid mixtures, with their much higher power output, will be expected to have lower rated costs in comparison with the pure working fluids. In Section 2.4, a multi-objective cost–power optimisation is considered.

For Cases 2 and 3 (Figures 2.10 and 2.11), the working-fluid mixtures still result in cycles with the highest power output, but these systems are, however, more expensive (both in terms of the total costs in pounds and the rated costs in pounds per kW) than those with the pure working fluids. A clear exception to these trends is the *n*-butane + *n*-hexane working-fluid system, where the working-fluid mixtures are seen to provide lower net power outputs than the constituent pure fluids. Due to the lower

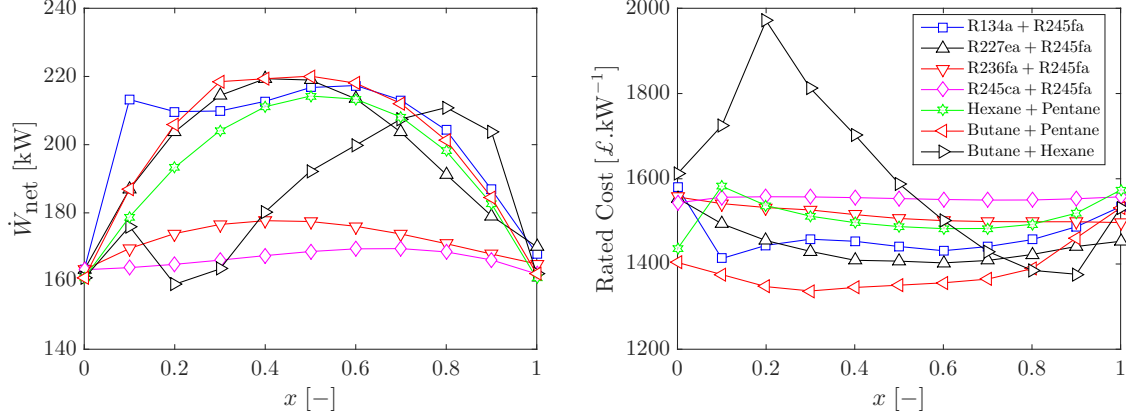


Figure 2.9: Maximum net power output and related rated costs (in pounds per kW) for ORC systems operating on a low-temperature heat source at 98 °C, with working fluid mixtures. Cycle heat input is not restricted, *i.e.*, $Q_{\text{in,lim}}$ is allowed to attain a maximum possible value; ‘ x ’ represents the mass fraction of the first component fluid in each working-fluid mixture pairing. Component-base costs, C_B , are indexed in the year 2006, with the following currency conversions: £1 $\equiv$ €1.47, \$1.84.

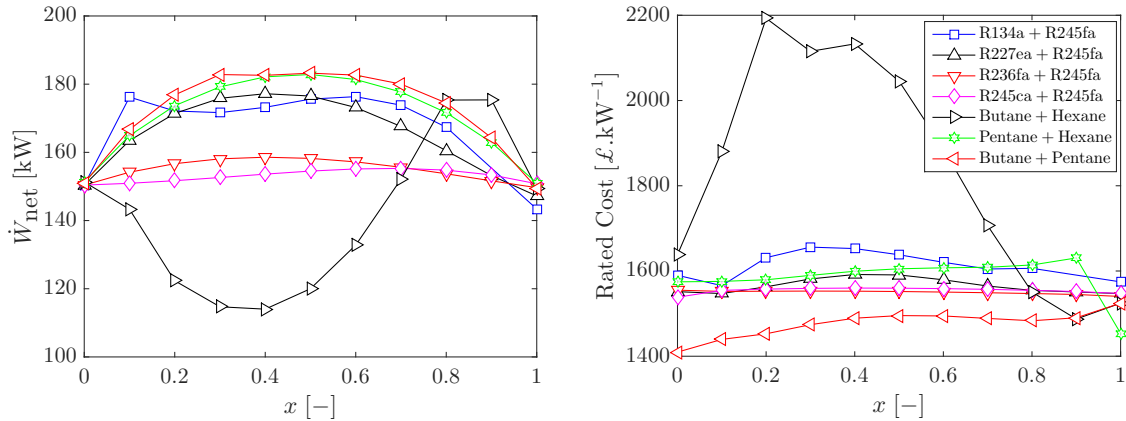


Figure 2.10: Maximum net power output and related rated costs (in pounds per kW) for ORC systems operating on a low-temperature heat source at 98 °C, with working fluid mixtures. Cycle heat input is restricted to 2.5 MW, *i.e.*, $Q_{\text{in,lim}} = 2.5$ MW; ‘ x ’ represents the mass fraction of the first component fluid in each working-fluid mixture pairing. Component-base costs, C_B , are indexed in the year 2006, with the following currency conversions: £1 $\equiv$ €1.47, \$1.84.

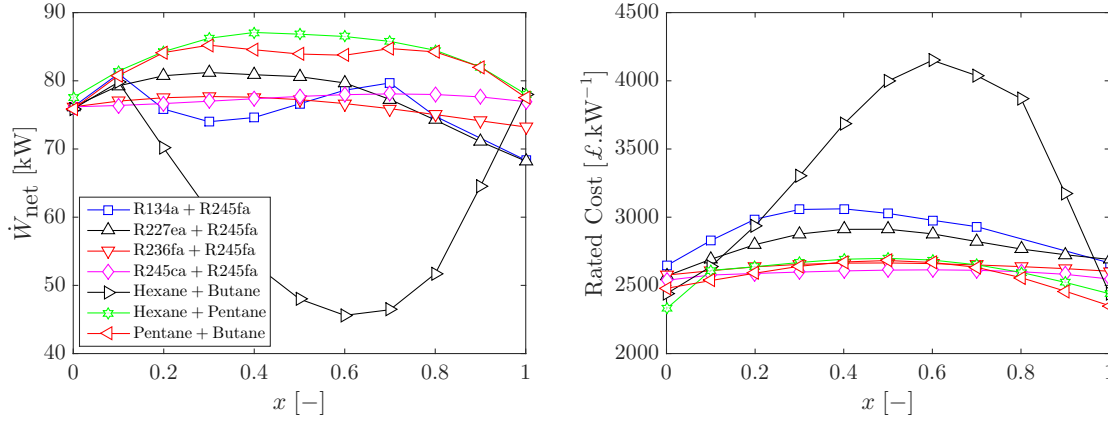


Figure 2.11: Maximum net power output and related rated costs (in pounds per kW) for ORC systems operating on a low-temperature heat source at 98 °C, with working fluid mixtures. Cycle heat input is restricted to 1.0 MW, *i.e.*, $\dot{Q}_{\text{in,lim}} = 1.0$ MW; ‘ x ’ represents the mass fraction of the first component fluid in each working-fluid mixture pairing. Component-base costs, C_B , are indexed in the year 2006, with the following currency conversions: £1 $\equiv$ €1.47, \$1.84.

isobaric specific heat-capacities of the mixtures compared to the pure fluids, they are expected to result in lower power output [72]. Their lower net power output is made more pronounced as they also have lower optimal mass flow-rates than the constituent pure working fluids. These invariably translate to the much higher rated costs for ORC systems with *n*-butane + *n*-hexane working fluids than those with other working-fluid systems. For most of the fluid pairings, the mixture with the highest net power output usually leads to the most expensive ORC system, while the systems with the pure fluids are usually the cheapest. Here, the gain in power output achieved by the mixtures is not sufficient to overcome the additional cost incurred in the use of larger expanders and heat exchangers due to their poor heat transfer performance.

As a specific example (for Case 3, $\dot{Q}_{\text{in,lim}} = 1.0$ MW) in the *n*-pentane + *n*-hexane system, the ORC system with *n*-pentane as the working fluid has the lowest rated cost (£2,300 per kW) due to its very low expander cost compared to the other working fluids, while the system with $x_{\text{C}_6\text{H}_{14}} = 0.5$ has the highest rated cost at £2,700 per kW. For the R-245fa + R-227ea system, the ORC system with pure R-245fa has the lowest rated cost (about £2,500 per kW) while that with $x_{\text{R-227ea}} = 0.5$ has the highest rated cost. The thermodynamically optimal fluid mixtures ($x_{\text{C}_6\text{H}_{14}} = 0.4$ and $x_{\text{R-227ea}} = 0.3$) have ORC system rated costs of £2,700 per kW and £2,900 per kW, respectively. On the other hand, the cost optimal working fluids are *n*-pentane and R-245fa, which give rated cost reductions of 14.8% and 13.8%, respectively, over the thermodynamically optimal working fluids.

2.4 Multi-objective cost–power optimisation

So far, the costs of ORC systems optimised to achieve the maximum net power output have been considered. The analysis on the low-temperature heat source ORC system is concluded with a brief investigation of the simultaneous cost and performance optimisation of these systems with pure fluids and working-fluid mixtures. This is carried out in a similar manner to the problem in Equation (2.33), with no restriction on the heat input into the cycles. The only addition here is change in the objective function to a multi-objective optimisation of the net power output (maximisation) from the cycles and the rated costs (minimisation) of the ORC systems; the constraints remain as earlier stated. The results are presented in Figure 2.12 for the n -pentane + n -hexane and the R-245fa + R-227ea systems, in form of the pareto optimal curves.

The pareto curves reveal that the two objectives (maximising the cycles’ net power output and minimising their systems’ rated costs in pounds per kW) are fairly complementary functions; the cycles with the maximum net power output are the ones that have ORC systems with the minimum rated costs. Ordinarily, the net power output and the total component-base costs (in £) will be competing functions such that ORC systems that maximise the power output will be expensive while the cheap systems (*i.e.*, those with minimum costs) will produce minimal power. This highlights the importance of *normalising* the total component-base costs with the cycle net power to derive the rated ORC system costs, thereby making both objectives complimentary. This also reveals the economies of scale in the design of ORC plants; plants with higher power outputs will cost less (in pounds per kW) than those with lower power output—in this instance, ORC systems with net power below 50 kW cost in excess of £5000 per kW while those with power above 150 kW cost below £2000 per kW.

Thus, with reference to the plots in Figure 2.12, the ORC systems that simultaneously maximise the net power output and minimise the rated costs are those located towards the top-left corner of the plots. Furthermore, the pareto curves are colour coded to distinguish the mixture compositions of the various working-fluid mixtures and pure fluids used in the cycles. From both subplots in Figure 2.12, one can observe that the working-fluid mixtures always result in cycles with the maximum net power. This directly replicates and reinforces the conclusions from Section 2.2. These ORC systems are, however, not the ones with the least rated costs; the systems with the pure working fluids are the ones that minimise the rated costs.

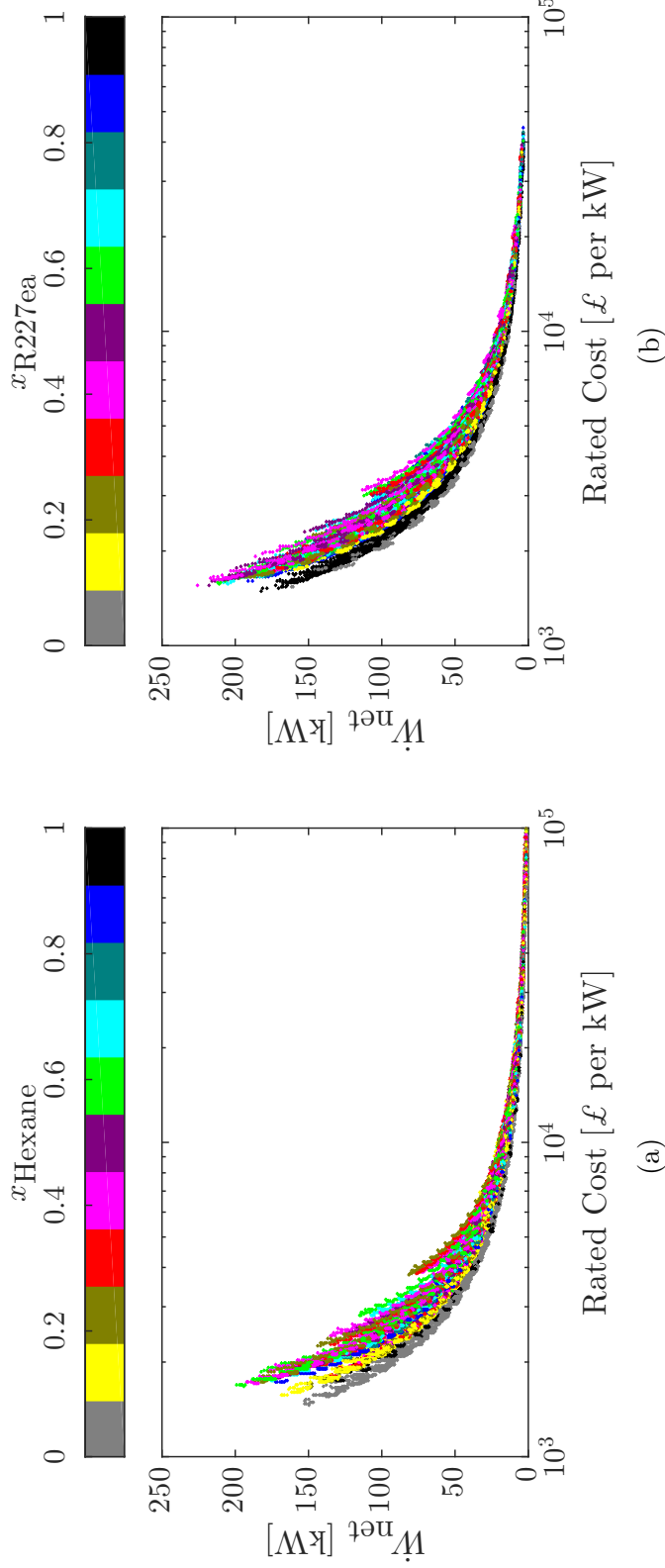


Figure 2.12: The pareto optimal curves for the multi-objective optimisation (maximum net power and minimum rated costs in pounds per kW) of ORCs operating on a low-temperature heat source at 98 °C, with two sets of working-fluid mixtures. Component-base costs, $\bar{C}_B$, are indexed in the year 2006, with the following currency conversions: £1 $\equiv$ €1.47, \$1.84. (a) n -pentane + n -hexane; (b) R-245fa + R-227ea. The colour range in these plots reflect the composition of the working fluid for the different ORC systems. (For interpretation of the references to colour in this figure legend, the reader is referred to a web or PDF version of this thesis.)

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At the net power levels where systems with pure working fluids are feasible, they are much cheaper than the systems with working-fluid mixtures. For example, in the case of the *n*-pentane + *n*-hexane system, at a net power output of 100 kW, systems with pure *n*-pentane and/or systems with pure *n*-hexane as working fluid cost below £2000 per kW while those with the working-fluid mixtures can cost up to £3000 per kW, representing a 50% increase in rated cost in using working fluid mixtures. Similarly, in the R-245fa + R-227ea system, ORC systems with the pure working fluids (R-245fa or R-227ea) are generally cheaper than those with the fluid mixtures. These illustrate that, while the working-fluid mixtures may deliver plants with higher power ratings, they do so with considerable additional cost incurred. The pure working fluids on the other hand will produce slightly less power but with the advantage of smaller sized process units and at considerably lower costs.

Previous research efforts into the deployment of working-fluid mixtures (also referred to as multi-component working fluids) in ORC systems [13, 14, 16, 18, 49, 61, 62, 64–66, 68, 69, 71, 84] have generally considered the thermodynamic benefits of such mixtures in comparison with pure (single component) working fluids, and as shown in Section 2.2, the mixtures do give better performance (in terms of net power output and/or thermal/exergy efficiencies) than the pure fluids. These mixtures have, however, been shown to suffer a deterioration in their heat transfer performance, especially during the phase-change processes. The overarching consequences on the size and costs of ORC systems with such mixtures were not explored in the references listed above. The results presented in this section are an attempt to quantify and qualify these consequences, in comparison with ORC systems employing pure working fluids.

In other works investigating working-fluid mixtures in ORC systems, Andreasen *et al.* [155] concluded that a 500-kW ORC system with the R32 + R134a working-fluid mixture is cheaper than that with pure R32 as working fluid. However, Heberle and Brüggemann [180, 181] showed that ORC systems with pure *i*-butane as working fluid has a lower specific cost (in $\text{€}\cdot\text{kW}^{-1}$) than those with the *i*-butane + *i*-pentane working-fluid mixtures. Similarly, ORC systems with pure *n*-pentane or pure R-227ea were found to be cheaper than those with mixtures of *n*-pentane + *n*-hexane or R-245fa + R-227ea, respectively, as presented in this chapter and in Oyewunmi and Markides [152, 182, 183]. It should be noted that the ORC systems in Refs. [152, 181, 182] have lower ratings of about 300 kW and 100 kW, respectively; thus, one may make a case that ORC systems with mixtures may become more cost effective at higher plant ratings. However, in this chapter, a more extensive set of working-fluid mixtures has been investigated across

A high-temperature gaseous heat source case

varying ORC plant sizes, and (in line with the recent findings in Refs. [152, 181, 182]) one can summarise that working-fluid mixtures, although attaining a better thermodynamic performance in ORC systems, lead to larger and more expensive systems. Thus, it is important to point out that while working-fluid mixtures may result in a thermodynamic benefit, the ORC systems with pure working fluids are more cost effective.

2.5 A high-temperature gaseous heat source case

A number of industrial processes, *e.g.*, cement kilns and glass furnaces, release waste heat to the environment in the gaseous form. In this case, flue gas from a refinery gas-fired boiler – with a flowrate of 560 kg.s^{-1} , temperature of $330 \text{ }^{\circ}\text{C}$ and an average specific-heat capacity, c_p , of $1.07 \text{ kJ.kg}^{-1}.\text{K}^{-1}$ – is used as an example waste-heat stream. The cooling stream is water provided at $20 \text{ }^{\circ}\text{C}$ and it is assumed that it is available in large quantities; this is different from the low- and medium-temperature heat source cases where the cooling stream is constrained to an outlet temperature of $30 \text{ }^{\circ}\text{C}$. Applying such a constraint to this case will only serve to reinforce previous conclusions from Section 2.4 and from the medium-temperature heat source case in Oyewunmi *et al* [13]. This ‘unlimited’ cooling set-up is reminiscent of what applies in large power station where cooling is provided by a river for example, and it provides a different set-up and (perhaps) conclusions from those encountered earlier. Thus the cooling water flowrate is suitably adjusted to ensure the condenser pinch conditions (set at a minimum of $10 \text{ }^{\circ}\text{C}$) are satisfied.

Such high temperature heat sources offer the possibility of designing the ORC system to operate at higher evaporation pressures, higher than those possible with lower temperature heat sources, as higher evaporation temperatures (and thus, pressures) can be attained before the pinch conditions in the evaporator is violated. In addition, working-fluid mixtures that result in larger temperature glides can be employed in the cycle. Thus, the ORC systems here are designed to maximise the net power output at different evaporation pressures and Equation (2.33) is thus rewritten as:

$$\begin{aligned} & \underset{P_{\text{cond}}, \theta_{\text{SH}}, \dot{m}_{\text{wf}}}{\text{maximise}} && \{\dot{W}_{\text{net}}\} \\ & \text{subject to:} && 0 \leq \theta_{\text{SH}} \leq 1 \\ & && P_{\text{cond}} \leq P_{\text{evap}} \leq P_{\text{crit}} \\ & && T_{4\text{v}} \leq T_4 \\ & && \Delta T_{\text{pinch, min}} \leq \Delta T_{\text{pinch}}. \end{aligned} \tag{2.33 revisited}$$

First, using the SAFT-VR Mie EoS, the working fluid thermodynamic properties are calculated as functions of pressure, temperature and working-fluid composition. These properties are then stored in look-up tables and accessed by the ORC model via interpolation. Using two sets of working-fluid mixtures offering the expected large phase-change temperature glides – *n*-butane + *n*-decane and *n*-perfluorobutane + *n*-perfluorodecane – the ORC model is simulated in order to investigate the role of changes to the working fluid composition on system performance, as described below.

2.5.1 Thermal efficiency, specific power and expansion ratio

Presented in Figure 2.13 are the specific work output ($w_{\text{exp}} = \dot{W}_{\text{exp}}/\dot{m}_{\text{wf}}$), the thermal efficiency η_{th} and the volumetric expansion ratio ($\text{VR} = \dot{V}_{\text{exp,out}}/\dot{V}_{\text{exp,in}}$) as functions of the mass fraction of the more volatile component – *n*-butane (or *n*-perfluorobutane) – in the working-fluid mixture, at different evaporating pressures (P_{evap}). These properties are independent of the working-fluid mass flowrate ($\dot{m}_{\text{wf}}$) and thus enable a direct comparison between the ORC configurations. The specific work, w_{exp} , gives an indication of the energy density of each configuration and how this varies with the working fluid mixture used, while the expansion ratio provides an indication of the size (and/or number of stages) of the expander required. Large or multi-stage expanders must be used to achieve high expansion ratios, which, in turn, leads to high costs. By and large, both sets of working-fluid mixture exhibit similar trends in the performance indicators.

For the two sets of working fluids, the pure components (at $x = 0$ or $x = 1$) generally give rise to cycles of higher thermal efficiency than the working fluid mixtures, as evidenced in Figure 2.13a for the alkanes. At evaporation pressures lower than 10 bar, cycles with pure *n*-decane or *n*-perfluorodecane working fluids are the most efficient, whereas, at higher evaporation pressures, cycles with pure *n*-butane or *n*-perfluorobutane exhibit the highest thermal efficiency. Cycles with working-fluid mixtures exhibit lower efficiencies varying between these extremes. One might have expected the mixtures to lead to cycles with higher thermal efficiencies, especially as they have higher average heat addition temperatures (compared to single-component fluids) due to their non-isothermal heat evaporation. However, systems with mixtures also exhibit a higher average heat-rejection temperature, which is detrimental to the thermal efficiency. The pure working fluids on the other hand can be condensed at lower temperatures and pressures since there is no restriction on the cooling stream and thus have lower average heat-rejection temperature, and subsequently higher thermal efficiencies.

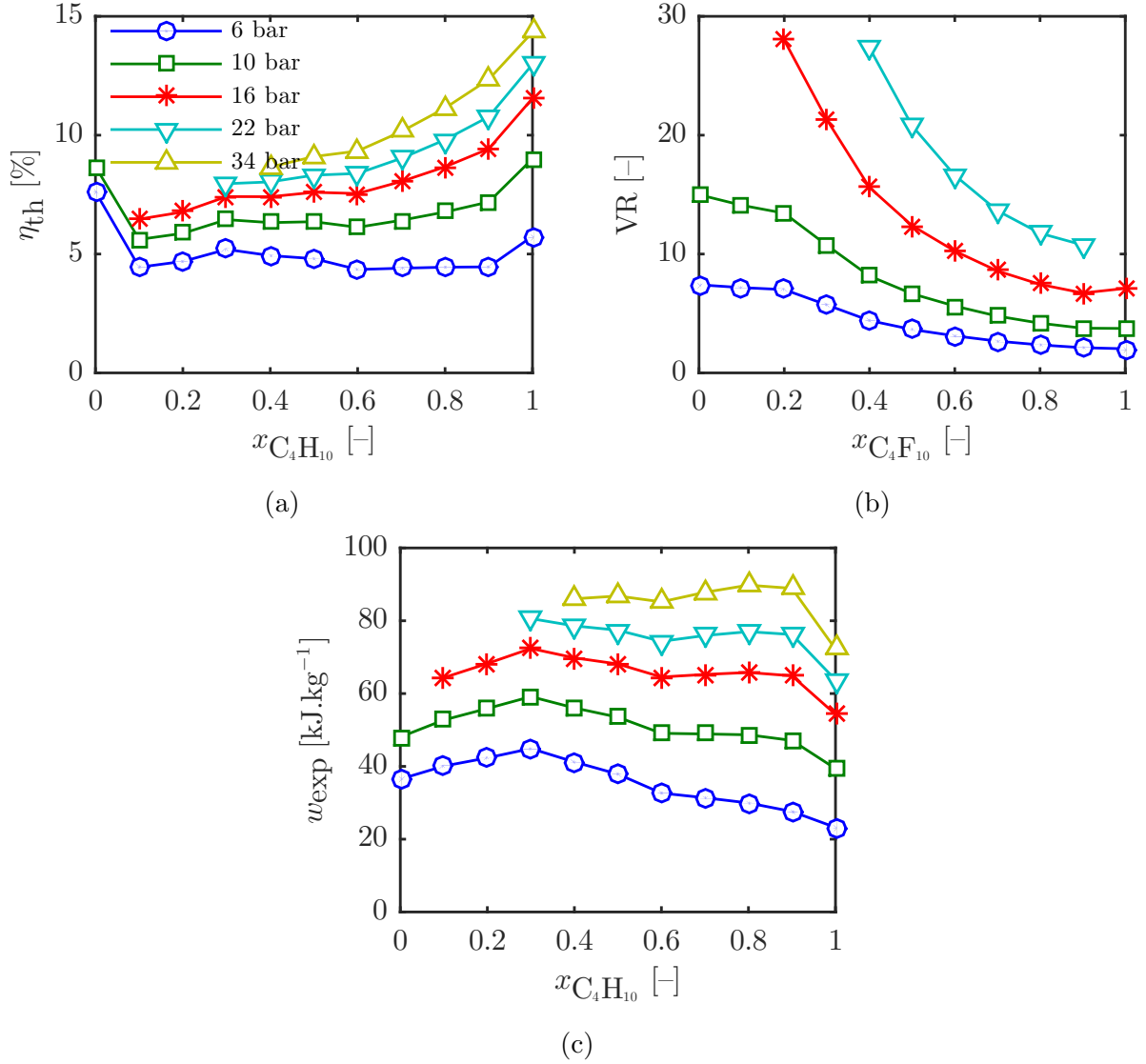


Figure 2.13: Performance indices of optimal ORC systems (maximum net power output) operating on a high-temperature heat source at 330 °C, with n -butane + n -decane (n -C₄H₁₀ + n -C₁₀H₂₂) and n -perfluorobutane + n -perfluorodecane (n -C₄F₁₀ + n -C₁₀F₂₂) working fluid mixtures. The indices are indicated at evaporation pressures of 6, 10, 16, 22 and 34 bar. (a) Thermal efficiencies of ORCs with alkanes; (b) Expansion ratios of ORCs with perfluoroalkanes; (c) Specific power output of ORCs with alkanes.

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For cost minimisation, a cycle with a lower expansion ratio is preferred to one with a higher ratio. The expansion ratios for the working fluids are illustrated in Figure 2.13b for perfluoroalkanes. It is clear that the working fluid mixtures rich in the more-volatile component (*i.e.*, *n*-butane or *n*-perfluorobutane) lead to cycles with the lowest expansion ratios. At evaporating pressures lower than 6 bar, the cycles with *n*-butane or *n*-perfluorobutane working fluids have the lowest expansion ratios; cycles with *n*-decane or *n*-perfluorodecane working fluids have the highest expansion ratios and thus may lead to costlier systems even though they are more efficient. Cycles with a working-fluid mixture with 90 mol% of *n*-butane or *n*-perfluorobutane generally have the lowest expansion ratios and may be the most cost effective.

In Figure 2.13c the variation in w_{exp} with the working fluid concentration is illustrated. While the single-component working fluids show a better performance in terms of η_{th} , the mixtures perform considerably better than their pure counterparts in terms of this performance index. For the perfluoroalkanes, a cycle of 20 mol% *n*-perfluorobutane consistently delivers the highest specific power at all evaporation pressures. For the alkanes, a cycle with 30 mol% *n*-butane working fluid mixture performs best at most conditions. At very high evaporating pressures (≥ 34 bar), a cycle with 90 mol% *n*-butane working fluid mixture performs best.

2.5.2 Absolute power output

From the previous results, ORC power systems are seen to have lower thermal efficiencies than those typically associated with large-scale, centralised fossil-fuelled power plants, due to the low temperature of the heat input involved. However, the ORC waste-heat energy source is more easily accessible, abundant and much more affordable than the fuel(s) used in conventional power plants. Fuel costs in such plants can, in some cases, account for up to 60 – 70% of the levelized costs of generating electricity over the lifetime of the plant's operation. Therefore, the aim in low-grade heat-conversion technologies, at least from an economic viability perspective, becomes one of maximising their power output while driving the dominant investment and capital costs of the systems down. Efficiency and other indices are important in as much as they contribute to this aim.

By optimising the cycle (through maximising the absolute power output) at different evaporation pressures, one arrives at the maximum power output achievable from the heat source using an ORC engine with the selected working fluids. The ORC absolute power outputs with the working fluids are presented in Figure 2.14a (for *n*-butane + *n*-decane) and Figure 2.14b (for *n*-perfluorobutane + *n*-perfluorodecane). The heat source

A high-temperature gaseous heat source case

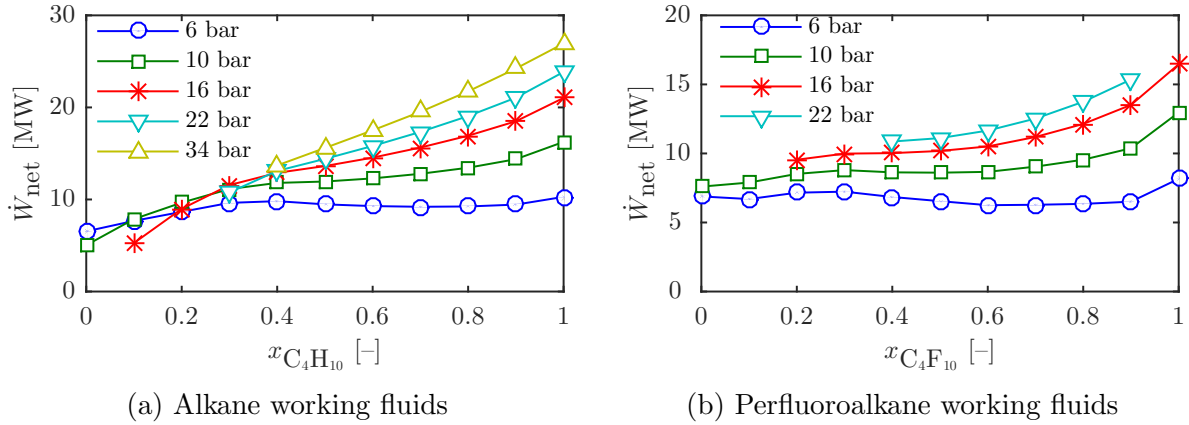


Figure 2.14: The maximum net power output ORC systems operating on a high-temperature heat source at 330 °C, with *n*-butane + *n*-decane (*n*-C₄H₁₀ + *n*-C₁₀H₂₂) and *n*-perfluorobutane + *n*-perfluorodecane (*n*-C₄F₁₀ + *n*-C₁₀F₂₂) working fluid mixtures, at evaporation pressures of 6, 10, 16, 22 and 34 bar.

used is seen to have the potential to deliver in excess of 20 MW of electricity when the alkanes (and their mixtures) are employed as the ORC working fluid; the perfluoroalkane cycles deliver a maximum of about 16 MW. This presents a low-cost and viable energy source for most high-temperature process industries especially as no cost is incurred in fuel (*i.e.*, the heat source).

For both sets of working fluids, as with the thermal efficiencies, the more-volatile component of the mixture generates the highest power output in the majority of the investigated cases as evidenced in Figure 2.14. Amongst the alkanes, the ORC with pure *n*-butane delivers the highest power output while pure *n*-perfluorobutane delivers the highest amongst the perfluoroalkanes. The cycle with the less-volatile component of the binary mixtures (*n*-decane and *n*-perfluorodecane respectively) generally delivers the least power output. At evaporating pressures less than 6 bar (Figure 2.14a), a working fluid mixture with 40 mol% *n*-butane performs best in comparison with other mixtures and the pure components. Similarly, for the perfluoroalkanes, a mixture with 30 mol% *n*-perfluorobutane performs best (at low evaporation pressures).

2.5.3 The question of the optimal working fluid design

From the absolute power output (the primary selection index) results in Figure 2.14, it would seem that the more-volatile pure components (*n*-butane or *n*-perfluorobutane) represent the optimal ORC working fluids, especially for high-pressure and high power-output systems. However, cycles with working fluid mixtures are seen to deliver higher

CHAPTER 2. WORKING-FLUID MIXTURES IN ORC SYSTEMS

power outputs at low evaporation pressures or in low- and medium- temperature ORCs, especially when the cooling resources are (realistically) constrained (see Figure 2.3); the mixtures also lead to cycles with higher power densities. Furthermore, using such working fluid mixtures at such low pressures limits the maximum allowable pressure of the ORC setup thus leading to a sizeable reduction in the ORC installation costs since high-pressure systems are generally known to be much more expensive than low-pressure systems. Also, in cases where low-pressure process requirements are dictated by other upstream/downstream processes in a facility, the working fluid mixtures provide an avenue to meet prescribed power demands as they deliver a higher power output than their single-component counterparts.

Therefore, the working fluid design (*i.e.*, the choice between a mixture and a single-component working fluid including the choice of the particular number of components and their compositions) is largely influenced by the cycle design – the heat source, the operating pressures and temperatures, the power output target and the intended application(s). This has been demonstrated with the ORC simulation results for the investigated cases of the sets of single-component working fluids and their mixtures as presented in this chapter. The cycle design may also be constrained by the choice of working fluid – for instance, its operating pressures or temperatures may be restricted due to flammability and degradability of the working fluid. Considering the numerous individual hydrocarbons and refrigerants from which such fluid mixtures can be designed, the eventual number of combinations grows exponentially with each additional fluid component, leading to a largely intractable problem. This presents a highly interwoven design problem that is best solved simultaneously with a structured approach.

Group-contribution equations of state (EoS) present a realistic opportunity to addressing this challenge [85, 108, 184]. In such EoS, properties of compounds are determined by the additive contributions from the individual molecular groups contained in the compound – individual group contributions are modelled separately. ORC working fluids generally contain molecular groups that occur frequently in hydrocarbons and refrigerants (*e.g.*, $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CF}_2$, $>\text{CH}-$, $>\text{CCl}_2$). These groups form a much smaller set than the set of individual fluids they constitute – for example, the entire fluid family of normal alkanes (excluding methane) is composed of only two groups, *i.e.*, $-\text{CH}_3$, and $>\text{CH}_2$ groups. Thus with an efficient group-contribution approach, one can effectively design the combination of such molecular groups to generate working fluids while at the same time optimising the ORC system design. For this problem design and solution, the

Summary

latest version of the SAFT group-contribution theories – the SAFT- γ Mie EoS – will be employed as presented later on in Chapter 4 and Chapter 5.

2.6 Summary

The thermodynamic benefits of employing working-fluid mixtures in organic Rankine cycle (ORC) systems has been investigated, with specific focus on applications involving a varying range of heat source temperatures from various industrial settings. Mixtures can provide an improved thermal match to the heat source and sink by exhibiting non-isothermal phase change behaviour. This way, the average temperature differences (and associated exergy losses) during heat addition and rejection are minimised, which can lead to an enhancement of the power output and efficiency. The effects of selecting such mixtures on the sizes and costs of the resulting ORC engines was also investigated. Initially, two sets of fluid mixtures, namely *n*-pentane + *n*-hexane and R-245fa + R-227ea, were used for this investigation due to their common use in subcritical and non-recuperative ORC installations; five other pairs of mixtures were later investigated, as well as ORC systems of different sizes. Fluorocarbon and alkane mixtures (*n*-perfluorobutane + *n*-perfluorodecane; *n*-butane + *n*-decane) providing larger phase change temperature glides are also employed in higher-temperature ORC systems.

The thermodynamic optimisation (maximum net power output) resulted in optimal working-fluid mixtures, especially when the cooling resources are limited, as in most realistic applications. The analyses revealed that the temperature glides of the working-fluid mixtures during evaporation and condensation resulted in higher power output and thermal efficiencies for fluid mixtures. The ORC simulations revealed that in order to recover the maximum power output from a waste-heat source it is beneficial in most cases to limit the amount of superheating applied during the heat addition process. Specifically, cycles without superheating, when the fluids are expanded from their saturated-vapour states without superheating, were observed to produce higher power outputs and also to be more efficient than cycles with superheating.

However, when larger cooling resources are available, the pure fluids result in ORC systems with higher thermal efficiencies and power outputs than the mixtures. For example, in the high-temperature ORC case, the heavier pure component (*n*-decane or *n*-perfluorodecane) was the most thermally efficient working fluid at low evaporation pressures and the lighter pure component (*n*-butane or *n*-perfluorobutane) was the most efficient at higher pressures. The lighter pure components also generally led to the ORC

CHAPTER 2. WORKING-FLUID MIXTURES IN ORC SYSTEMS

systems with the highest power output; it is only at evaporation pressures below 6 bar that the mixtures become favourable.

For the low-temperature ORC systems, mixtures containing 50% of *n*-hexane and those with 40% R-227ea had the highest net-power output, delivering up to 30% more power than either set of pure fluids. The pure fluids did however result in smaller expanders due to their low volumetric flow-rates and expansion ratios. Due to their poor phase-change heat transfer characteristics, ORC systems with fluid mixtures appeared to have the largest evaporators and condensers (with their condenser areas up to 80% higher than those of the pure fluids), requiring more expensive heat exchangers than the pure fluids. Moreover, due to sub-atmospheric (vacuum) expansion, the expander costs in the case of the *n*-pentane + *n*-hexane working-fluid mixtures (and *n*-hexane) were much higher than those for pure *n*-pentane. Generally, and in consonance with recent efforts from other investigators, equipment sizes and costs were larger for both sets of mixtures than for the constituent pure fluids. Thus, the working-fluid mixtures would require larger plant layout areas, contributing significantly to their overall installation costs.

Although the mixtures were found to have the highest power output, they also had the highest rated cost (equipment cost per net kilowatt power generated). On the other hand, a multi-objective cost–power optimisation revealed that ORC systems with pure *n*-pentane working fluid had the lowest rated cost followed by those with *n*-hexane. For the case of R-245fa + R-227ea working fluids, the ORC system with pure R-227ea had the lowest rated costs, about 14% less than the system with 40% R-227ea working fluid. These observations imply that the thermodynamic benefits derived from using the working-fluid mixtures may be outweighed by the increased costs incurred. The fact that these insights were only possible from a direct consideration of thermal and cost factors, as exemplified here, underlines the importance of employing a combined thermodynamic, thermal and cost approach in the selection of optimal working-fluid (mixtures) for ORC systems.

Chapter 3

The Up-THERM Heat Converter: Model Development and Working-Fluid Design

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3.1 Introduction

Over the years, other novel cycle configurations have also been proposed for waste-heat recovery (WHR) applications. One particular class of engine suitable for the affordable utilisation of low-grade heat is the thermofluidic oscillator. The simple construction (few moving parts or dynamic seals) of thermofluidic oscillators allow these devices to have low capital and maintenance costs, in addition to long lifetimes. Single-phase thermofluidic oscillators include Sondhauss tubes [185, 186], standing-wave thermoacoustic engines [31, 33, 187, 188], and liquid-piston Stirling engines [189]. The ‘Non-Inertive-Feedback Thermofluidic Engine’ (NIFTE) [35–41] is an example of a two-phase thermofluidic oscillator [32, 34, 190–192], which can operate over temperature differences as low as 30 °C. In the NIFTE, a steady external temperature difference generates and sustains regular thermodynamic oscillations of temperature and pressure that drive fluid flows in the engine from which power can be extracted. Models of NIFTE have been developed and validated against experimental data. It was found that the model predictions were in close agreement with the experimental measurements of oscillation frequency f_0 , temperature gain k and exergy efficiency η_{ex} [38, 39].

More recently, the Up-THERM engine has been proposed by Encontech B.V. [43] and is being developed by a consortium of European researchers and SMEs [44–46]. This engine belongs to a class of unsteady vapour-phase heat engines referred to as ‘two-phase thermofluidic oscillators’ (TFOs). When a steady temperature difference is applied across such a TFO, the working fluid within this device experiences sustained thermodynamic-property (*i.e.*, pressure, volume and temperature) oscillations, while undergoing phase change during heat addition and rejection. These sustained oscillations can then be harnessed to drive a generator or a load, where work can be extracted. The Up-THERM engine, due to its few moving parts and dynamic seals, has been shown to deliver comparable thermodynamic and economic performance with respect to established technologies such as the organic Rankine cycle engines [11, 193]. Thus, this technology is being envisioned as an affordable prime mover in combined heat and power (CHP) and/or other cogeneration applications.

In this chapter, a summary of the dynamic mathematical model of the Up-THERM heat engine is presented. This is based on the modelling approach taken for the NIFTE as it serves as an excellent starting point for the study of similar two-phase unsteady/oscillatory heat engine concepts. Both linear and non-linear engine component contributions are accounted for in the model. In Kirmse *et al.* [42], the complete model is

Modelling the Up-THERM heat engine

presented, including experimental measurements of the temperature profile of the working fluid as it flows over the heat exchanger surfaces of the two-phase thermofluidic oscillator. In addition, the model prediction of the oscillation frequency of the Up-THERM engine is validated against experimental data from a similar engine, and the heuristic parameters of the model are adjusted by considering the differences between these two devices. Here, a characterisation of the engine with respect to optimal working fluids and to the optimal external load design is presented. Specifically, the effects of key working-fluid properties on the performance indices (such as the power generated and the exergy efficiency) of the engine are investigated, including an investigation of a series of potentially viable working fluids that can be employed in the engine and the optimal operation of the engine in off-design conditions.

3.2 Modelling the Up-THERM heat engine

3.2.1 Device description and operation

The key components of the Up-THERM heat engine are depicted in Figure 3.1. It consists of hot and cold heat-exchanger sections, which are part of the vertical displacer cylinder on the left-hand side of the device as it appears in this figure. This is where heat is either added from or rejected to an external source or sink, respectively. The device contains a working fluid in both the liquid and vapour phases; working fluid in the vapour phase is present at the top part of the displacer cylinder as shown in the inset of Figure 3.1 where the piston is at the bottom dead centre (BDC), while the rest of the engine is filled with working fluid in the liquid phase. In particular, the quantity of vapour at the top of the displacer cylinder acts as a gas spring, which is periodically compressed and expanded as the vapour-liquid interface (or, liquid level) below it, and the so called ‘liquid piston’ in the displacer cylinder, oscillate vertically, thus contacting the hot and cold heat-exchanger surfaces where evaporative and condensing phase-change heat transfer occurs in an alternating manner. Within the displacer cylinder is also a solid piston; the position of this piston, together with the inner wall of the displacer cylinder, forms the piston valve arrangement that separates the displacer cylinder into upper and lower chambers. Beneath the piston valve sits a slide bearing. A mechanical spring just below the solid piston connects the bottom of the piston to the bottom of the displacer cylinder, which is also connected to a liquid connection-tube. At the other side of the connection tube the flow is split into two ends of the same closed fluid-loop that forms

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the load arrangement. This contains two check valves, two hydraulic accumulators, and a hydraulic motor where work is generated.

It is assumed that the cycle starts with the piston at the top dead centre (TDC) position, as in Figure 3.1. In this position, the vapour-liquid interface in the displacer cylinder is in contact with the hot heat exchanger (HHX) surface, which causes the liquid working fluid to evaporate, thus increasing the pressure in the gas (vapour) spring above it. This, together with the force from the upper section of the mechanical spring that is initially fully compressed, forces the piston and vapour-liquid interface downwards. As this takes place, the piston valve closes, thereby preventing fluid from flowing from the upper to the lower chamber. From this point, the pressure in the upper chamber continues to increase, while the piston continues to move downwards with the valve closed. After a certain vertical (downwards) displacement of the piston, the piston valve opens, which suddenly re-connects the two (upper and lower) chambers of the displacer cylinder; the large pressure differential between the chambers causes fluid to flow quickly from the upper into the lower chamber. Due to inertia, the vapour-liquid interface and solid piston overshoot their equilibrium position – which lies between the HHX and cold heat exchanger (CHX) surfaces, and equivalently, at the mean vertical position of the vapour-liquid interface in the displacer cylinder – bringing the interface and the vapour directly above in contact with the cold surface of the CHX and compressing the lower section of the mechanical spring.

This causes working-fluid vapour to condense, thereby decreasing the pressure in the gas (vapour) spring, and therefore in the entire displacer cylinder. The resulting suction force pulls the solid piston and the vapour-liquid interface upwards (with the aid of the force in the compressed lower mechanical spring) and, eventually, closes the piston valve after a certain vertical (upwards) displacement of the piston. The valve remains closed as the piston continues to move upwards, within a certain range. For as long as the valve is closed, and since condensation continues to occur, the pressure in the upper chamber of the displacer cylinder continues to decrease. At some point, the piston valve re-opens and a sudden flow of working fluid from the lower chamber into the upper chamber allows the pressures of the two chambers to equalise once again. The piston and vapour-liquid interface reach the HHX and the cycle is complete.

The oscillating (zero-mean) fluid flow in the displacer cylinder is transmitted via the connection tube to the load arrangement, where it is transformed into a unidirectional flow with the use of two check valves. The two hydraulic accumulators act to dampen the amplitudes of the pressure and flow oscillations in the load arrangement. Hence, a more

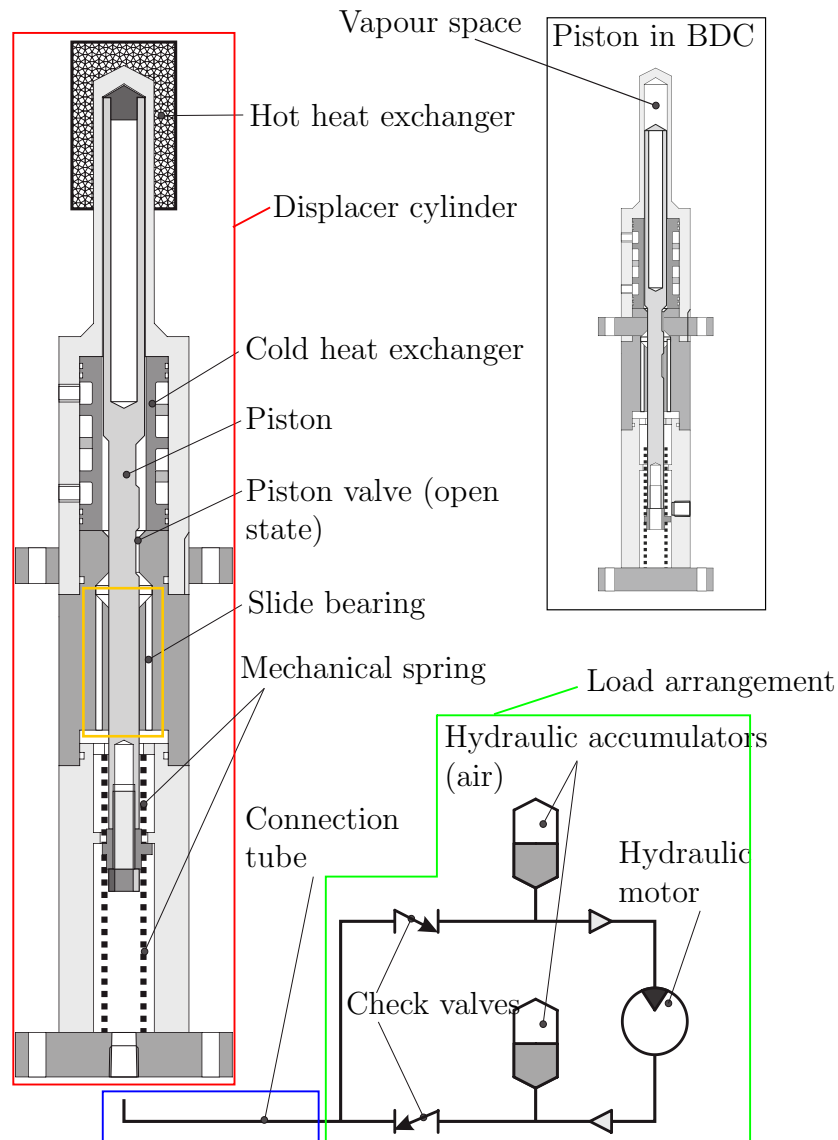


Figure 3.1: Schematic of the Up-THERM heat engine with hot and cold heat exchangers, piston, valve, mechanical springs and hydraulic motor with piston at the top dead centre (TDC) and at the bottom dead centre (BDC, inset). The top space of the hydraulic accumulators is filled with air.

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steady flow can be supplied to the hydraulic motor, where useful work can be extracted from the device at higher efficiency (thanks to the dampened unsteadiness).

3.2.2 Mathematical model development

The Up-THERM engine model development, presented in detail by Kirmse *et al.* [42], follows previous approaches for thermoacoustic and thermofluidic devices by Ceperley [31], Huang and Chuang [32], Backhaus and Swift [33, 34] and, in particular, Smith and Markides [35, 190–192] who developed various models for the NIFTE device [35–40] to which the Up-THERM engine has some similarity. These authors reported that the operating oscillation frequency, f , thermal gain (related to the temperature or heat gradient along the walls of the heat exchangers of the device), k , and exergy efficiency, η_{ex} , predicted by the NIFTE models were in good agreement with experimental data from an early-stage NIFTE prototype that took the form of a thermally powered fluid-pump. Since the thermal energy exchanged between the HHX/CHX walls and the working fluid in both the NIFTE and the Up-THERM engine are dominated by alternating phase-change (evaporation and condensation) heat transfer, the modelling approach used for the NIFTE is a suitable starting point for the Up-THERM engine model development.

Briefly, the *dominant* thermal or fluid process in each spatially lumped component of the Up-THERM is described to first-order by an ordinary differential equation (ODE). This allows electrical analogies to be drawn such that thermal and fluid resistances can be represented by equivalent electrical resistances (R), liquid inertia represented by inductances (L), and hydrostatic pressure and vapour compressibility represented by capacitances (C). The models for the vertical motion of the solid piston and the flows in the slide bearing, liquid column, connection tube, hydraulic accumulators and the hydraulic motor are linearised based on the assumption of small variations around their time-mean values, which define the operating equilibrium point (detailed later in this section on Page 75). The temperature profile along the heat exchangers' walls is assumed to follow a (non-linear) hyperbolic tangent ($\tanh\{.\}$) function; this assumption has been validated experimentally in Kirmse *et al.* [42]. The piston valve and check valves exhibit inherently and strongly non-linear behaviour with large variations around their equilibrium points; they are thus modelled as non-linear components (detailed later in this section on Page 76).

Linear components

The solid piston (and surrounding fluid flow inside the displacer cylinder) are modelled by combining the force balance equation on the piston with the Navier-Stokes equation for the fluid. The Navier-Stokes equation is reduced by assuming fully-developed, incompressible and axi-symmetric flow. Below the piston valve (which is modelled non-linearly; see Section 3.2.2) the piston and liquid are separated. The piston moves through a slide bearing, lubricated by a thin liquid film while the bulk of the liquid flows through a number of small channels. The electrical analogies for the piston, liquid, and slide bearing are:

$$\begin{aligned} R_{l,1} &= \frac{128c_2h_p\mu}{\pi c_1 c_3}; & R_{l,2} &= \frac{128c_2h_p\mu}{\pi c_1 (c_1 - 2c_2d_p^2)}; & C_1 &= \frac{\pi^2 c_1 (c_1 - c_2d_p^2)}{64c_2^2 k_{ms}}, \\ L_1 &= \frac{64c_2^2 m_p}{\pi^2 c_1 (c_1 - 2c_2d_p^2)}; & R_p &= \frac{64h_p\mu}{\pi d_p^2 c_1}; & C_p &= \frac{\pi^2 d_p^2 c_1}{32k_{ms}c_2}; & L_p &= \frac{32m_p c_2}{\pi^2 d_p^2 c_1}, \\ R_{b,p} &= \frac{16\mu h_b}{\pi^2 d_p^3 \delta}; & L_{b,p} &= \frac{4\rho_{ss} h_b}{\pi d_p^2}; & L_{b,l} &= \frac{4\rho h_b}{\pi d_b^2}; & R_{b,l} &= \frac{128\mu h_b}{\pi d_{b,l}^4}. \end{aligned} \quad (3.1)$$

In Equation (3.1), $c_1 = d_c^2 - d_p^2$, $c_2 = \ln(d_c/d_p)$, and $c_3 = c_2(d_c^2 + d_p^2) - c_1$ are geometric constants, h_p and d_p are the height/length and diameter of the solid piston, and m_p and ρ_{ss} its mass and density, respectively. In addition, the slide bearing has length l_b and diameter d_b , and the spring constant is k_{ms} .

Liquid columns are modelled by applying the Navier-Stokes equation, simplified with the same assumptions as for the modelling of the liquid surrounding the piston. Based on this approach, the resistance, inductance and capacitance of each liquid column are given by:

$$R = \frac{128\mu l_0}{\pi d_0^4}; \quad L = \frac{4\rho l_0}{\pi d_0^2}; \quad C = \frac{\pi d_0^2}{4\rho g}, \quad (3.2)$$

where the length of the liquid column is represented by l_0 , its diameter by d_0 , the viscosity and density of the liquid in the column by μ and ρ , and g is the gravitational acceleration. It should be noted that the hydrostatic pressure difference only applies for the liquid column in the displacer cylinder, as the other cylinders are completely filled with liquid and thus have constant liquid-column height.

The hydraulic accumulators are modelled as linear gas springs. It is assumed that the gas at the top of the accumulators is compressed/expanded isentropically and there-

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fore, based on an ideal-gas approximation, the process observes $PV^{\gamma_a} = \text{const.}$, and the capacitance of each accumulator gas spring is:

$$C = \frac{V_0}{\gamma_a P_0}, \quad (3.3)$$

where V_0 and P_0 respectively are the equilibrium volume and pressure of the gas in the accumulators, and γ_a is the heat capacity ratio of air in the accumulators.

A torque balance is applied on the motor (with an assumed efficiency of 80%), which leads to the frictional losses and inductance of the motor:

$$R_{\text{hm}} = \frac{16\mu_{\text{lub}}d_{\text{sh}}^3 l_{\text{sh}}}{\pi\epsilon d^4 d_{\text{hm}}^2}; \quad L = \frac{8m_{\text{hm}}}{\pi^2 d^4}, \quad (3.4)$$

where μ_{lub} is the viscosity of the lubricant around the shaft, l_{sh} and d_{sh} the length and diameter of the shaft, ϵ the gap between the motor and the shaft, d the diameters of the inlet and outlet pipes of the motor, and d_{m} and m_{m} the diameter and homogeneously distributed mass of the motor. The useful *instantaneous* mechanical power that can be extracted from the device is dissipated in a further electrical resistance R_{gen} :

$$\dot{W} = R_{\text{gen}} U_{\text{hm}}^2, \quad (3.5)$$

where U_{hm} is the (volumetric) fluid flow-rate through the hydraulic motor, and R_{gen} is determined empirically to maximise the power output from the Up-THERM converter, as described in Section 3.3.2. The power output from the engine can be utilised in both mechanical and/or electrical forms.

Other performance indices useful in characterising the Up-THERM engine, in particular a few efficiency measures, are defined in Section 3.2.3. A detailed description of the modelling approach for the hydraulic motor and the other linear components can be found in Kirmse *et al.* [42].

Non-linear components

In the thermal domain, the temperature profile along the HHX-CHX heat exchanger surfaces that are in contact with the working fluid is modelled by using a $\tanh\{.\}$ function that saturates when the vapour-liquid interface position (y) moves far away from the equilibrium position at $y = 0$, as shown in Figure 3.2 [39]:

$$T_{\text{hx}} = \alpha \tanh(\beta y). \quad (3.6)$$

Modelling the Up-THERM heat engine

In Equation (3.6), α is half of the maximum temperature difference between the HHX and CHX, and the product $\alpha\beta$ is the gradient of the temperature profile at and close to the origin, as defined in Figure 3.2.

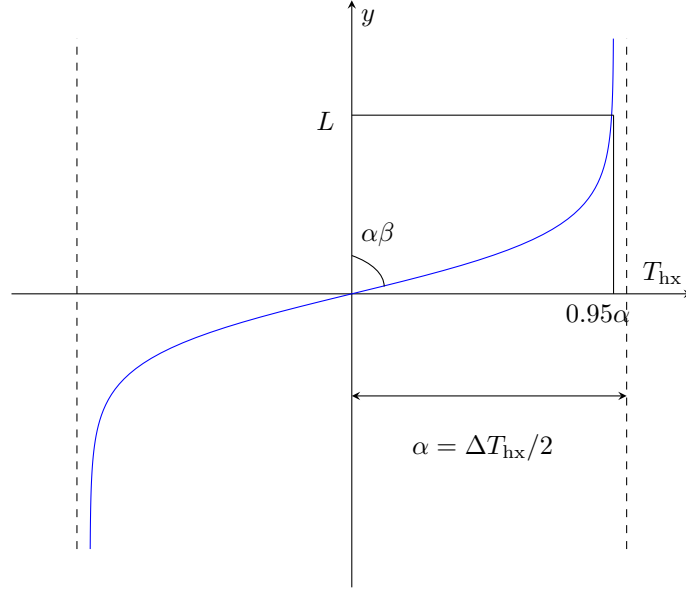


Figure 3.2: Imposed non-linear temperature profile in the heat exchanger walls. At length L of the heat exchanger the temperature saturates at 95% of $\Delta T_{hx}/2$.

The (rate of) thermal energy exchanged between the heat exchangers and the working fluid can be described via a convective (phase-change) heat transfer coefficient h ,

$$\dot{Q} = hA_{hx} (T_{hx} - T_{wf}) \approx T_0 \dot{S}, \quad (3.7)$$

with T_0 the equilibrium temperature, $\dot{S}$ the corresponding entropy flow-rate, A_{hx} the area over which phase-change heat transfer occurs, and T_{wf} the working fluid temperature.

The thermal domain must be coupled to the fluid domain, as the rest of the engine is described in the fluid domain. Two coupling equations are employed for this purpose [35]:

$$\dot{S} = \rho_g s_{fg} U_{th}, \quad (3.8)$$

$$T_{hx} = \left(\frac{dT}{dP} \right)_{sat} P_{th}; \quad T_{wf} = \left(\frac{dT}{dP} \right)_{sat} P_{C,v}. \quad (3.9)$$

In the above equations, ρ_g is the density of the working fluid in the vapour phase, s_{fg} is the phase-change specific entropy, U_{th} is the volumetric flow rate, $(dT/dP)_{sat}$ is the rate of change of temperature with pressure in the saturation region of the working fluid, and

CHAPTER 3. THE UP-THERM HEAT CONVERTER: MODEL DEVELOPMENT AND WORKING-FLUID DESIGN

P_{th} and $P_{C,v}$ are the pressures in the thermal domain and the gas (vapour) spring at the top of the displacer cylinder, respectively.

Thus, the volumetric flow-rate due to heat exchange (leading to evaporation and/or condensation) becomes:

$$U_{th} = \frac{P_{th} - P_{C,v}}{R_{th}}; \quad R_{th} = \frac{\rho_g s_{fg} T_0}{h A_{hx} (dT/dP)_{sat}}, \quad (3.10)$$

where R_{th} is the thermal resistance.

The piston valve in the displacer cylinder is modelled by using a combination of two Heaviside step functions to account for the two instances in the cycle where the valve opens/closes:

$$R_{pv} = R_{min} + \frac{1}{2} R_{max} (-H\{P_{C,d} - \rho_{wfl}gh\} + H\{P_{C,d} + \rho_{wfl}gh\}). \quad (3.11)$$

In Equation (3.11), R_{min} is a constant minimum resistance due to viscous drag when the valve is open and R_{max} a large pre-set constant resistance applicable when the valve is closed. In addition, $P_{C,d}$ is the hydrostatic pressure of the liquid column inside the displacer cylinder, ρ_{wfl} is the density of the working-fluid liquid and h is the distance of the *solid* piston from its time-mean equilibrium position.

The check valves in the load arrangement are also modelled using a Heaviside step function. Each check valve remains open when there is a positive fluid flow rate U through it and closes at the moment when the flow rate becomes negative:

$$R_{cv} = R_{max} H\{U\}. \quad (3.12)$$

A third non-linear resistance is introduced to ensure that the amplitudes of the piston and liquid flow in the displacer cylinder are not larger than the geometric dimensions (height) of the displacer cylinder:

$$R_{nl} = R_{max} (-H\{P_{C,d} - \rho_{wfl}gh_3\} + H\{P_{C,d} + \rho_{wfl}gh_3\}), \quad (3.13)$$

where h_3 is the maximum allowable amplitude by this expression. Finally, the models of all individual components are then interconnected in the same way as they are in the physical engine, resulting in the circuit diagram shown in Figure 3.3.

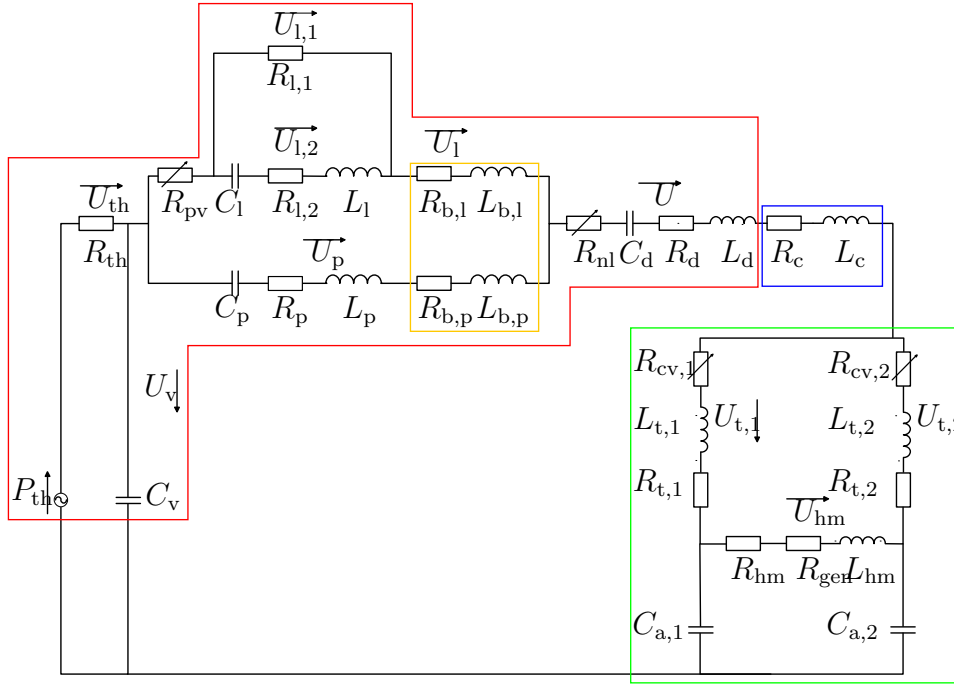


Figure 3.3: Circuit diagram of the Up-THERM heat engine; colours correspond to the engine components in Figure 3.1. R_i denotes a resistance, L_i an inductance and C_i a capacitance. U_i is the volumetric flow rate through a component. The subscript ‘th’ denotes the thermal domain. The single components of the fluid domain are the leakage flow denoted by ‘l’, the piston ‘p’, the fluid flow in the slide bearing ‘b,l’, the piston in the slide bearing ‘b,p’, the connection tube ‘c’, the liquid column ‘d’ and the gas spring ‘v’ in the displacer cylinder, and the non-linear valve formed by the piston and cylinder ‘pv’. The load comprises the two check valves ‘cv,i’, two pipes ‘t,i’, hydraulic accumulators ‘a,i’ and hydraulic motor ‘hm’.

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Heat transfer coefficients

Equation (3.7) describes the heat input from the heat source to the working fluid. This process involves boiling heat transfer, and is taken as a pool-boiling process in this work. Thus, a key parameter to be evaluated for this process is the pool-boiling heat transfer coefficient, h . The heat transfer coefficient h can be calculated by using the reference heat transfer coefficient for a specific fluid h_0 and a correlation for the reduced heat transfer coefficient [162]:

$$\frac{h}{h_0} = F_q F_p F_w. \quad (3.14)$$

For most fluids experimental values of h_0 exist, and are available from Table 1 of Section H2 in the VDI Heat Atlas [162]. For fluids for which experimental values do not exist, a calculation procedure is presented in the VDI Heat Atlas. In Equation (3.14) the functions F_i are non-dimensional and independent of the fluid. They take into account the heat flux, the reduced pressure ($P_r = P/P_c$) of the fluid, and the properties of the heat exchanger wall. The function F_q is dependent on the heat flux q , the reference heat flux $q_0 = 20 \text{ kW.m}^{-2}$, and an exponent n that is dependent on the reduced pressure and the fluid properties:

$$F_q = \left(\frac{q}{q_0} \right)^n, \quad (3.15)$$

where n is given by:

$$n = \begin{cases} 0.9 - 0.3p_r^{0.15}, & \text{for water} \\ 0.95 - 0.3p_r^{0.3}, & \text{for organic fluids} \end{cases}. \quad (3.16)$$

The function F_p takes the pressure dependability of the reduced heat-transfer coefficient into account. It is calculated as:

$$F_p = \begin{cases} 1.73p_r^{0.27} + 6.1p_r^2 + \frac{0.68p_r^2}{1-p_r^2}, & \text{for water} \\ 0.7p_r^{0.2} + 4p_r + \frac{1.4p_r}{1-p_r}, & \text{for organic fluids} \end{cases}. \quad (3.17)$$

The function F_w takes the properties of the heat-exchanger material into account. It can be split into a function F_{wr} , which considers the surface roughness of the heat-exchanger wall, and a function F_{wm} that considers the wall material, so that $F_w = F_{wr}F_{wm}$. F_{wr} can be calculated by:

$$F_{wr} = \left(\frac{R_a}{R_{a0}} \right)^{2/15}, \quad (3.18)$$

Modelling the Up-THERM heat engine

where $R_{a0} = 0.4 \mu\text{m}$ is the reference surface roughness for metal surfaces. R_a is the measured surface roughness. If this value is not known then $R_a = R_{a0} = 0.4 \mu\text{m}$, so that $F_{\text{wr}} = 1$ [194]. The function F_{wm} accounts for the wall material by using the ratio of the effusivity $b = \sqrt{\lambda\rho c}$ of the wall material to the effusivity of the reference material, copper $b_0 = 35.35 \text{ kW}\cdot\text{s}^{0.5}\cdot\text{m}^2\cdot\text{K}$:

$$F_{\text{wm}} = \left(\frac{b}{b_0} \right)^{0.5}. \quad (3.19)$$

3.2.3 Performance indices and efficiency definitions

Four indicators—oscillating frequency (f), power output ($P = \dot{W}$), exergy efficiency (η_{ex}) and thermal efficiency (η_{th})—are used to describe the performance of the Up-THERM device. Of these, the oscillating frequency is unique to unsteady thermofluidic heat-engines such as the NIFTE and the Up-THERM. The power output and efficiencies, on the other hand, are commonly encountered performance indicators used in describing heat engines in general. The frequency of operation of the Up-THERM is determined by examining the cyclic steady-state time profiles of the pressure oscillation in the displacer cylinder. The period of oscillation is determined as the time between three successive points with zero amplitude (*i.e.*, the time for one full cycle). The frequency is thus calculated as the inverse of this period.

The instantaneous power output from the Up-THERM heat engine has been introduced in Equation (3.5) (Section 3.2.2) as the product of the generator resistance (R_{gen}) and the square of the instantaneous volumetric flow-rate through the hydraulic motor (U_{hm}). The power generated over a cycle is calculated as:

$$\dot{W} = \oint R_{\text{gen}} U_{\text{hm}} dV_{\text{load}} = \oint P_{\text{load}} dV_{\text{load}}, \quad (3.20)$$

where $V_{\text{load}} = \oint U_{\text{hm}} dt$ is the volume in the load and $P_{\text{load}} = R_{\text{gen}} U_{\text{hm}}$ is the pressure in the load.

The exergy efficiency is calculated as the ratio of the power generated to the exergy input to the cycle:

$$\eta_{\text{ex}} = \frac{\oint P_{\text{load}} dV_{\text{load}}}{\oint P_{\text{th}} dV_{\text{th}}}. \quad (3.21)$$

Here, P_{th} is the thermal pressure (referred heat-exchanger temperature) and V_{th} is its thermal volume (referred entropy flow due to heat transfer), with $V_{\text{th}} = \oint (U + U_v) dt$.

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A measure of the thermal efficiency follows as a product of the exergy efficiency and Carnot efficiency:

$$\eta_{\text{th}} = \eta_{\text{ex}} \cdot \left(1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}\right). \quad (3.22)$$

where T_{cold} is the minimum temperature of the heat sink, and T_{hot} is the maximum temperature of the heat source; T_{cold} and T_{hot} correspond respectively to the supply temperatures of the cooling stream (heat sink) and the heating stream (heat source) to the engine. It must be noted that this thermal efficiency is slightly overestimated as the heat-source and heat-sink temperatures do not remain constant in the heat exchangers.

3.3 Nominal Up-THERM engine configuration

The Up-THERM engine was conceived primarily for solar power and waste heat recovery applications. The first prototype of this engine was proposed by the company Encontech B.V. [43] and this was followed by an Up-THERM prime-mover designed to convert heat to power as part of a gas-fired micro-CHP unit in EU-funded project ‘Up-THERM’. The initial working fluid considered for these engines was water. In the CHP prototype, thermal energy is transferred from the hot combustion gases in the gas boiler to the HHX of the Up-THERM with a flow of diathermal oil Therminol 68 at a flow rate of 0.6 kg.s^{-1} . The oil stream (heat source) temperature (T_{hs}) is raised to 360°C , while the heat-sink (cooling-water stream) temperature (T_{sink}) is around 10°C . The working-fluid equilibrium temperature lies approximately midway between the heat-source and sink temperatures:

$$T_{\text{sat}} = T_{\text{eq}} = \frac{T_{\text{hs}} + T_{\text{sink}}}{2}, \quad (3.23)$$

and the equilibrium pressure is the saturation pressure at this temperature.

The working fluid extracts thermal energy from the heat source for subsequent conversion to mechanical work. The amount of heat delivered to the working fluid is governed by Equations (3.6) – (3.10), which are all influenced by the thermodynamic properties of the working fluid, the heat-source temperature and the heat exchanger design. It is to be expected that different working fluids will extract different amounts of heat from the heat source. For example, at the nominal design conditions (see Section 3.5.2), water extracts 42.7 kW from the heat source while toluene extracts 9.4 kW; R113 extracts the highest amount of heat from the heat source (180 kW) and subsequently delivers the highest power output. The performance of the engine at varying source temperatures is investigated in Section 3.5.3.

3.3.1 Engine nominal parameters and nominal performance

The optimal physical dimensions of the Up-THERM engine were considered in Kirmse *et al.* [42], with water as the working fluid. Here, in Table 3.1, the resulting nominal electrical parameters (resistances, capacitances and inductances) from that work are listed. These parameters directly correspond to those in Figure 3.3 and most of them remain unchanged in the present work. Those that depend on the heat-source temperature and the thermodynamic properties of the working fluid (highlighted by “*” in Table 3.1), change accordingly. A numerical simulation of the model (using ODE solvers in MATLAB [39, 195, 196]) with the nominal parameters in Table 3.1 results in the nominal performance of the engine presented in Table 3.2.

The time-varying volumetric flow-rates in key engine sections during nominal operation are shown in Figure 3.4a. It can be observed that a limit cycle is attained from about 2.5 s; after initial transients in pressures and flow rates, the oscillations are sustained at a constant frequency and amplitude. In this figure, U is the volumetric (liquid) flow-rate through the displacer cylinder and into the connection tube (which is also equal to the flow-rate from the connection tube to the load arrangement) and U_{pist} represents the movement of the piston in the displacer cylinder. Both of these flow rates are seen to oscillate about a mean value of zero, with U_{pist} having larger amplitudes than U due to leakage around the piston and through the slide bearings. Furthermore, U_{phm1} is the volumetric (liquid) flow-rate through the check valve that ‘feeds’ the hydraulic motor. This flow is always positive with the same peak amplitude as U due to the non-return action of the valve that prevents U_{phm1} from having a significant negative amplitude since only a small amount of liquid can flow back before the valve closes. When the valve is fully open, the flow rates U_{phm1} and U are identical. This means that all the liquid from the displacer cylinder and via the connection tube flows through the check valve into the accumulator and the hydraulic motor. Downstream of the accumulator, the volumetric (liquid) flow-rate U_{hm} is equal to the flow-rate through the hydraulic motor, which is always positive due to the action of the check valves providing uni-directional flow. It does, however, experience reduced amplitudes of oscillation due to the dampening action of the two hydraulic accumulators.

Time-varying pressures in important engine sections are shown in Figure 3.4b. In particular, $P_{\text{C,l,dc}}$ is the hydrostatic pressure of the liquid column in the displacer cylinder below the piston, and is thus a measure of the height of the liquid column below the piston. The amplitude of $P_{\text{C,l,dc}}$ is smaller than that of the piston pressure $P_{\text{C,pist}}$ and that of the pressure in the hydraulic accumulator $P_{\text{C,acc1}}$. $P_{\text{C,pist}}$ is the pressure exerted

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Table 3.1: Values of electrical analogy parameters at the nominal Up-THERM engine configuration. Superscript * denotes parameters that are directly dependent on heat-source/sink temperature and working-fluid thermodynamic properties.

Electrical parameter	Thermal-fluid effect	Nominal value	Units
C_d^*	Displacer cylinder capacitance	1.81×10^{-8}	$\text{m}^4 \cdot \text{s}^4 \cdot \text{kg}^{-1}$
C_l	Leakage flow capacitance	1.78×10^{-10}	$\text{m}^4 \cdot \text{s}^4 \cdot \text{kg}^{-1}$
C_p	Piston capacitance	6.02×10^{-10}	$\text{m}^4 \cdot \text{s}^4 \cdot \text{kg}^{-1}$
C_v^*	Linear gas spring displacer cylinder	3.38×10^{-9}	$\text{m}^4 \cdot \text{s}^4 \cdot \text{kg}^{-1}$
L_c^*	Connection tube inductance	2.03×10^5	$\text{kg} \cdot \text{m}^{-4}$
L_{hm}	Hydraulic motor inductance	3.09×10^6	$\text{kg} \cdot \text{m}^{-4}$
L_d^*	Displacer cylinder inductance	8.44×10^6	$\text{kg} \cdot \text{m}^{-4}$
L_l	Leakage flow inductance	6.45×10^7	$\text{kg} \cdot \text{m}^{-4}$
$L_{t,i}^*$	Fluid flow in load pipes	2.02×10^6	$\text{kg} \cdot \text{m}^{-4}$
L_p	Piston inductance	5.96×10^6	$\text{kg} \cdot \text{m}^{-4}$
$L_{b,l}^*$	Fluid flow inductance in slide bearing	9.18×10^6	$\text{kg} \cdot \text{m}^{-4}$
$L_{b,p}$	Piston inductance in slide bearing	3.01×10^6	$\text{kg} \cdot \text{m}^{-4}$
R_c	Connection tube resistance	5.81×10^2	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
R_{hm}	Hydraulic motor resistance	5.67×10^7	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
R_d	Displacer cylinder resistance	8.68×10^5	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
$R_{l,1}$	Leakage flow resistance (1)	6.24×10^7	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
$R_{l,2}$	Leakage flow resistance (2)	1.28×10^6	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
$R_{t,i}$	Fluid flow in load pipes	7.44×10^4	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
R_p	Piston resistance	9.86×10^4	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
$R_{b,l}$	Fluid flow resistance in slide bearing	5.31×10^7	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
$R_{b,p}$	Piston resistance in slide bearing	7.74×10^5	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$
R_{th}^*	Thermal resistance	6.36×10^7	$\text{kg} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$

Nominal Up-THERM engine configuration

by the compressed mechanical springs and therefore it represents the piston position in the displacer cylinder. The highest pressure amplitude can be observed in the piston as it is directly connected to the displacer cylinder where the phase change and resultant pressure forcing arises.

3.3.2 Optimal load characterisation

While the nominal electrical analogy parameters (RLC s) of the Up-THERM engine have been defined, the load resistance R_{gen} is yet to be determined as it is external to the engine. This is the resistance presented by the employed generator, and the power extracted from the engine is strongly correlated with this parameter. It would be expected that there is a value of R_{gen} that optimises some performance criterion of the engine. Thus, the optimal R_{gen} needs to be defined relative to the performance criterion, *e.g.*, maximum power output or maximum efficiency; in this case, the maximum power output. This is especially important in waste-heat recovery applications, where the aim is to maximise power output per unit cost [13].

The power output from the engine is defined in Equations (3.5) and (3.20). From these relations, one would expect higher power outputs at higher values of R_{gen} , as the power output appears to be directly proportional to R_{gen} . However, this increase is not sustained due to the dependence of the power output on the flow rate through the hydraulic motor (U_{hm}). At higher values of R_{gen} , when the resistance to the flow through the motor is higher, U_{hm} decreases since $U_{\text{hm}} = P_{\text{load}}/R_{\text{gen}}$, as well as the power output, that appears to have a direct proportionality to the square of U_{hm} . Thus, the power output varies non-monotonically with R_{gen} , and the optimal R_{gen} that maximises the power output is a compromise between these two factors.

In order to determine the optimal generator resistance, the engine is simulated at different cycle heat-source temperatures and with a selection of working fluids (*n*-pentane, water, ammonia and R245fa), over a range of R_{gen} values. In Figure 3.5a and 3.5b the oscillating frequency and power output, respectively, are plotted as functions of R_{gen} for four working fluids at a heat-source temperature of 200 °C. In addition, power outputs when using different heat-source temperatures are plotted in Figure 3.5c. For some working fluids and at lower heat-source temperatures (*e.g.*, water at 200 °C and pentane at 100 °C), there are no sustained oscillations in the engine due to the very low flow rates caused by the high generator resistances ($R_{\text{gen}} > 5 \times 10^8 \text{ kg.m}^{-4}.\text{s}^{-1}$).

From the figures, it can be seen that the oscillating frequency remains largely invariant to the generator resistance, whereas the power output is strongly affected by the value

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Table 3.2: Performance indices for nominal operation of Up-THERM heat engine.

Index:	Power output	Exergy efficiency	Thermal efficiency	Frequency
	2.64 kW	11.2%	6.18%	1.67 Hz

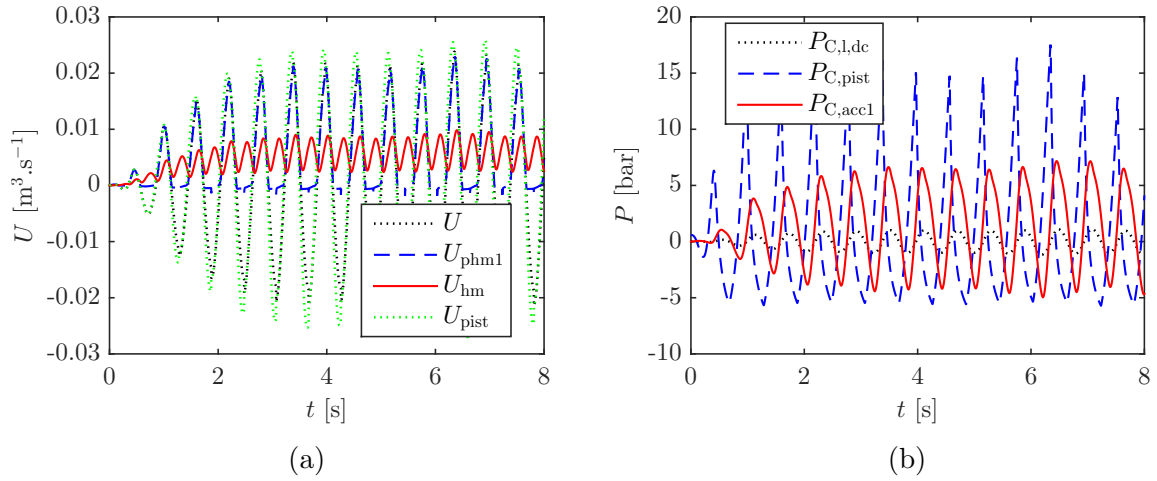


Figure 3.4: Variations in volumetric flow-rate (U) and pressure (P) in key engine sections. (a) Volumetric flow-rates through the connection tube (U), the forward check-valve (U_{phm1}), the hydraulic motor (U_{hm}) and the piston (U_{pist}). (b) Pressure variations in the displacer cylinder ($P_{\text{C,l,dc}}$), of the piston ($P_{\text{C,pist}}$) and in one of the hydraulic accumulators ($P_{\text{C,acc1}}$).

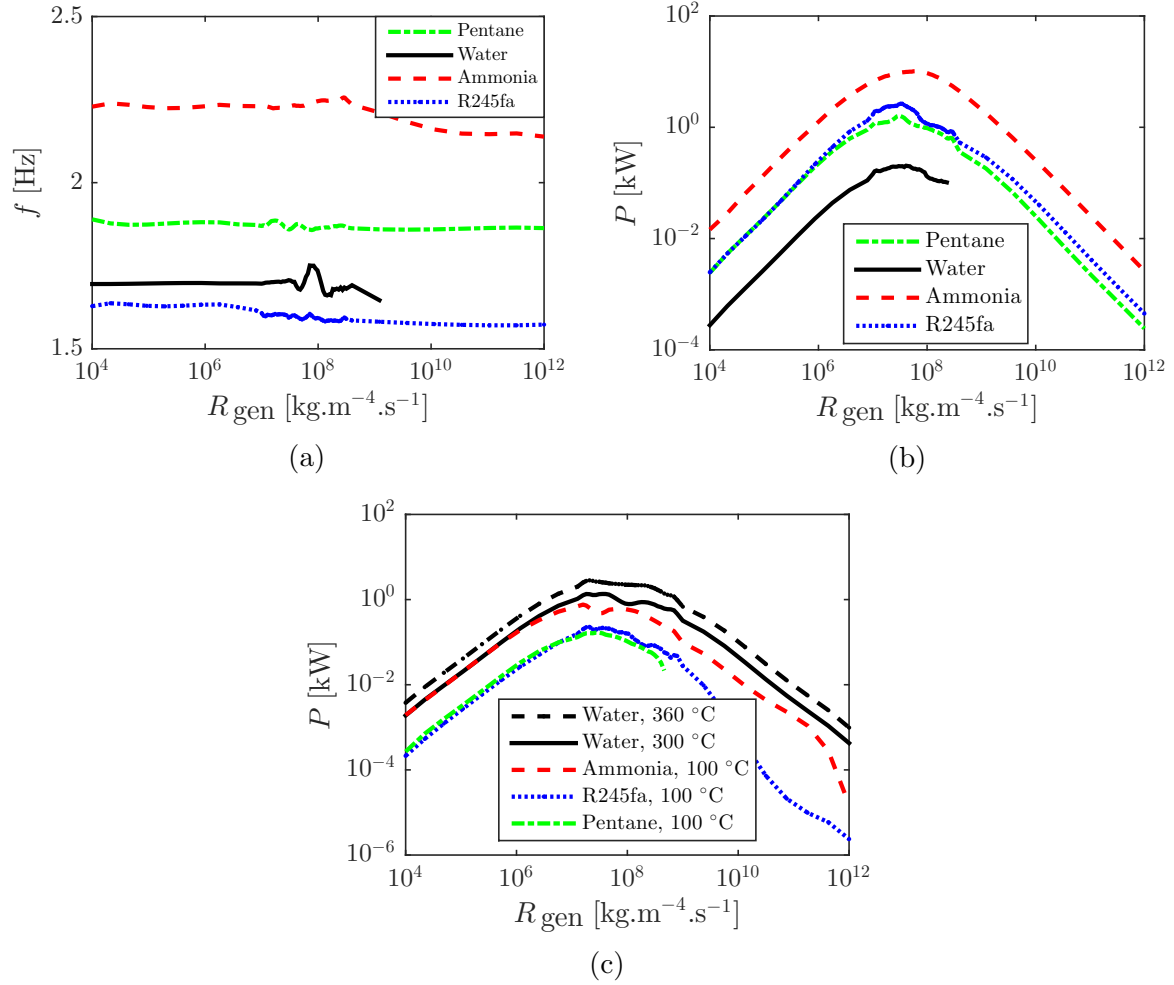


Figure 3.5: Up-THERM engine performance as a function of generator resistance (R_{gen}). (a) Engine oscillating frequency (f) with four working fluids and heat-source temperature of 200 °C. (b) Engine power output ($P = \dot{W}$) with four working fluids and heat-source temperature of 200 °C. (c) Engine power output ($P = \dot{W}$) with four working fluids and various heat-source temperatures.

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of R_{gen} . As expected, the power output is almost negligible at low values of R_{gen} ($< 10^6 \text{ kg.m}^{-4}.\text{s}^{-1}$) and also at high values of R_{gen} ($> 10^{10} \text{ kg.m}^{-4}.\text{s}^{-1}$). The power output peaks in the range $2 \times 10^7 \text{ kg.m}^{-4}.\text{s}^{-1}$ to $7 \times 10^7 \text{ kg.m}^{-4}.\text{s}^{-1}$, irrespective of the working fluid employed or the heat-source temperature. For most of the simulations, the maximum power is generated at a value of $R_{\text{gen}} = 5.6 \times 10^7 \text{ kg.m}^{-4}.\text{s}^{-1}$, and thus this value of R_{gen} is employed as the optimal value for the subsequent simulations in this work. For a few of the working fluids, (*e.g.*, some siloxanes), the optimal R_{gen} differs from the above value, but only slightly, usually in the range of $\pm 5\%$. The optimal value of R_{gen} is therefore generally insensitive to the choice of the working fluid but mainly a function of the engine configuration and component sizes. Thus, the selection of the optimal R_{gen} is key in designing an optimal engine configuration.

3.4 Thermodynamic property characterisation of the Up-THERM engine

Having fully characterised the optimal configuration of the Up-THERM heat engine with respect to the imposed external conditions, it is of interest to investigate the performance of the engine with various working fluids, and to attempt to characterise the engine's performance in relation to the thermodynamic properties of suitable working fluids. This can enable a determination of the properties that have the most significant effects on the engine performance and aid in the screening of working fluids in future selection processes, similarly to what was attempted for another TFO device (the NIFTE) by Markides *et al.* [40].

In order to determine the most important thermodynamic properties, a parametric investigation on the engine's exergy efficiency and power output is carried out, where each thermodynamic property (or property combination) is varied separately and independently while the others are set to their nominal values at the nominal saturation temperature. The *independent* properties investigated are: the saturation temperature (T_{sat}); the entropy change during vaporisation (s_{fg}); the vapour-phase heat-capacity ratio (γ_{g}); the vapour-phase density (ρ_{g}); the liquid-phase density (ρ_{l}); and the saturation pressure (P_{sat}). The enthalpy change during vaporisation (h_{fg}) and volume change during vaporisation (v_{fg}), although dependent on T_{sat} & s_{fg} and ρ_{g} & ρ_{l} (*i.e.*, $h_{\text{fg}} = T_{\text{sat}} \times s_{\text{fg}}$ and $v_{\text{fg}} = \rho_{\text{g}}^{-1} - \rho_{\text{l}}^{-1}$) respectively, are also investigated in the first instance.

Water is used as the reference working fluid here, due to its larger thermodynamic property variations, *e.g.*, in h_{fg} and s_{fg} , over organic fluids. The nominal point is set

Thermodynamic property characterisation of the Up-THERM

at an equilibrium/saturation temperature of 185 °C, which corresponds to heat-source and heat-sink temperatures (from Equation (3.23)) of 360 °C and 10 °C respectively. The nominal values of the investigated thermodynamic properties are thus calculated at 185 °C. T_{sat} is varied from 20 °C through the nominal point to the critical temperature. The values of s_{fg} , h_{fg} and v_{fg} generally decrease with increasing T_{sat} , becoming zero at the critical temperature. The liquid-phase density ρ_l also decreases with increasing T_{sat} , but at the critical temperature it becomes equal to ρ_g , which increases with T_{sat} . Both P_{sat} and γ_g also increase with increasing T_{sat} , with γ_g increasing very rapidly closer to the critical temperature. These trends are illustrated in Figure 3.6.

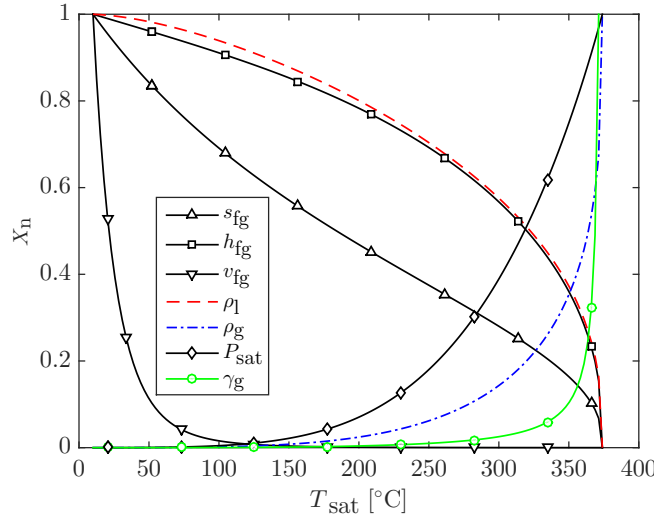


Figure 3.6: Variations in normalised working-fluid thermodynamic properties (X_n)—entropy change during vaporisation (s_{fg}), enthalpy change during vaporisation (h_{fg}), volume change during vaporisation (v_{fg}), liquid-phase density (ρ_l), vapour-phase density (ρ_g), saturation pressure (P_{sat}) and vapour-phase heat-capacity ratio (γ_g)—with saturation temperature (T_{sat}) for water as the working fluid. Each thermodynamic property is normalised between 0 and 1 using the formula $X_n = [X - X_{\text{min}}]/[X_{\text{max}} - X_{\text{min}}]$, where X represents any of the aforementioned thermodynamic properties.

3.4.1 Individual thermodynamic property variations

The results of varying each of the aforementioned thermodynamic properties independently are presented in Figure 3.7. The oscillating frequency, f , is generally insensitive to these variations (Figure 3.7a), although deviations from the nominal frequency can be seen with changes to the volume change during vaporisation v_{fg} and saturation pressure P_{sat} . The increase in f at higher (and slight decrease at lower) P_{sat} is to be expected as

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larger pressures correspond to larger driving forces, generating more frequent oscillations (and *vice versa*).

The influence of the thermodynamic properties on the exergy efficiency, η_{ex} , and the power output $P = \dot{W}$ are presented in Figures 3.7b and 3.7c. Amongst the *independent* properties, P_{sat} and ρ_g have the greatest combined effect on the exergy efficiency and power output from the Up-THERM engine. The volume and entropy changes during vaporisation, v_{fg} and s_{fg} , and the saturation temperature T_{sat} also have some effect on these indices, while γ_g , ρ_l (the only liquid-phase property) and h_{fg} are less-important properties in affecting performance in this analysis. The fact that T_{sat} has only a slight effect on the engine performance (the power output decreases slightly as T_{sat} is increased) may suggest that it is not a key thermodynamic property with respect to power output and exergy efficiency. It does however play a key role in the initial screening and selection of working fluids as detailed in Section 3.5.1.

In particular, v_{fg} (a function of ρ_g and ρ_l), is seen to have a profound effect on the exergy efficiency, especially at low saturation temperatures (corresponding to higher values of v_{fg} ; see Figure 3.6). Also, high values of v_{fg} (at low T_{sat}) lead to very low power outputs from the engine, in contrast to the fact that higher oscillating frequencies are experienced at these high values. When v_{fg} is large, there is a larger volume of working-fluid vapour generated during evaporation over the hot heat exchanger per unit heat (and exergy) input, which translates to increased positive-displacement work per unit heat input, *i.e.*, higher efficiency such as seen in Figure 3.7b. At the same time, the heat/exergy input to the engine is very low, which eventually translates to reduced power outputs.

From Figure 3.7c, the engine is seen to produce higher power outputs at low values of ρ_g (at low T_{sat}) and to produce lower power outputs at higher values. This can be attributed to the influence of these properties on the thermal resistance R_{th} . Referring to Equation (3.10), P_{sat} varies directly with ρ_g and T_{sat} ; thus low values of ρ_g and T_{sat} lead to low thermal resistances, which enable more heat to be exchanged between the working fluid and the heat exchangers. This eventually makes more thermal energy available for subsequent conversion to power in the load arrangement. Similarly at low values of s_{fg} (corresponding to high T_{sat}), a lower thermal resistance is experienced leading to higher power outputs from the engine.

The saturation pressure, P_{sat} , has the greatest influence of all varied properties on the power output in Figure 3.7c. The power output increases with P_{sat} from low values to values above the nominal, beyond which a maximum is observed at a pressure of 69.6 bar

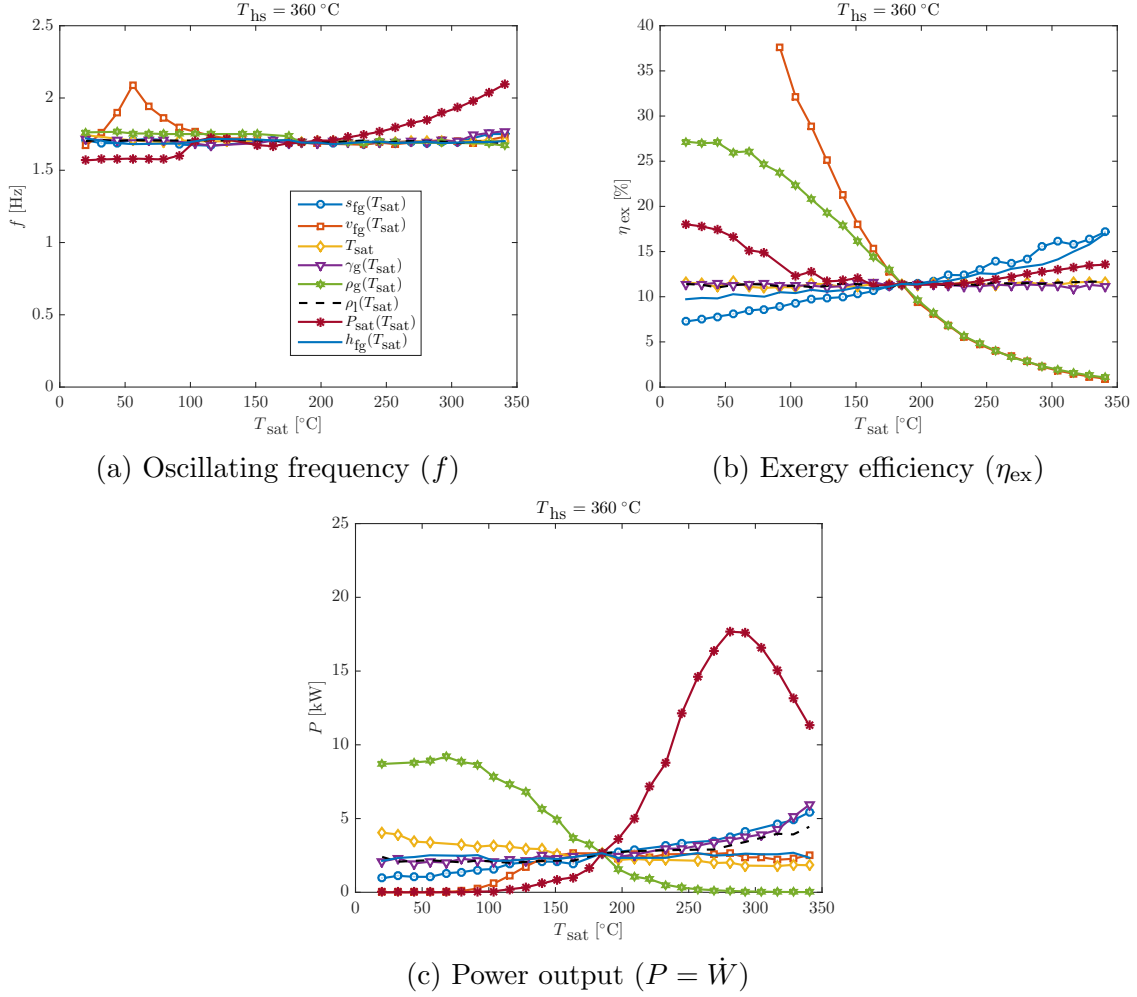


Figure 3.7: Performance indices of the Up-THERM heat engine with water as the working fluid on independently varying its thermodynamic properties—entropy change during vaporisation (s_{fg}), volume change during vaporisation (v_{fg}), saturation temperature (T_{sat}), vapour-phase heat-capacity ratio (γ_{g}), vapour-phase density (ρ_{g}), liquid-phase density (ρ_{l}), saturation pressure (P_{sat}) and enthalpy change during vaporisation (h_{fg}). Each property is varied between the indicated saturation temperature (T_{sat}) range while others are set to their respective nominal values at a saturation temperature of 185 °C.

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(corresponding to a reduced pressure and temperature of 0.315 and 0.863 respectively). While ρ_g is equally important, it has an opposite effect to that of P_{sat} . Higher values of P_{sat} lead to higher power outputs, while lower values of ρ_g also lead to higher power outputs. For any single working fluid, it is almost impossible to simultaneously achieve a high value of P_{sat} and a low value of ρ_g since both properties increase (or decrease) with increasing (or decreasing) T_{sat} . Therefore, in most cases a compromise has to be reached between these properties; this relationship is further explored in the next subsection by simultaneously varying groups of thermodynamic properties.

3.4.2 Combined thermodynamic property variations

In the previous section, the saturation pressure, P_{sat} , and the vapour-phase density, ρ_g , were identified as very significant properties in describing the Up-THERM engine performance. Combinations of (two, three and four) properties are now varied, to investigate any synergies that may exist between property groups and to also identify which of P_{sat} or ρ_g is more important in affecting performance. The resulting performance predictions are presented in Figure 3.8 for the exergy efficiency and the power output. Some combined variations (*e.g.*, of s_{fg} and γ_g) result in higher efficiencies and/or power outputs over the individual properties.

From the results, the key role of varying P_{sat} in affecting performance persists when it is varied in combination with other properties. In particular, the simultaneous variation of P_{sat} and s_{fg} has a stronger effect on both the power output and exergy efficiency than varying P_{sat} alone. Efficiency and power output (up to a point) are both seen to increase with the combination of high P_{sat} and low s_{fg} . Interestingly, however, the combination of high P_{sat} and T_{sat} causes a reduction in power output from that previously attained at higher P_{sat} alone. Thus, a combination of high saturation pressures and low equilibrium/saturation temperatures is needed to maximise power output from the engine. This suggests that one needs a fluid with as high a P_{sat} as possible at any corresponding T_{sat} to maximise the power output.

Similarly, the performance trends in the variations of ρ_g are seen to persist when other thermodynamic properties are simultaneously varied. As expected, the improvements on performance due to simultaneous variations of T_{sat} and ρ_g or γ_g and ρ_g are insignificant compared to those of varying ρ_g alone. There is, however, a slight increase in power output at combinations of low ρ_g and low T_{sat} .

The simultaneous variation of combinations of P_{sat} and ρ_g is seen to result in very different trends from those obtained when these properties are varied individually. In fact,

Thermodynamic property characterisation of the Up-THERM

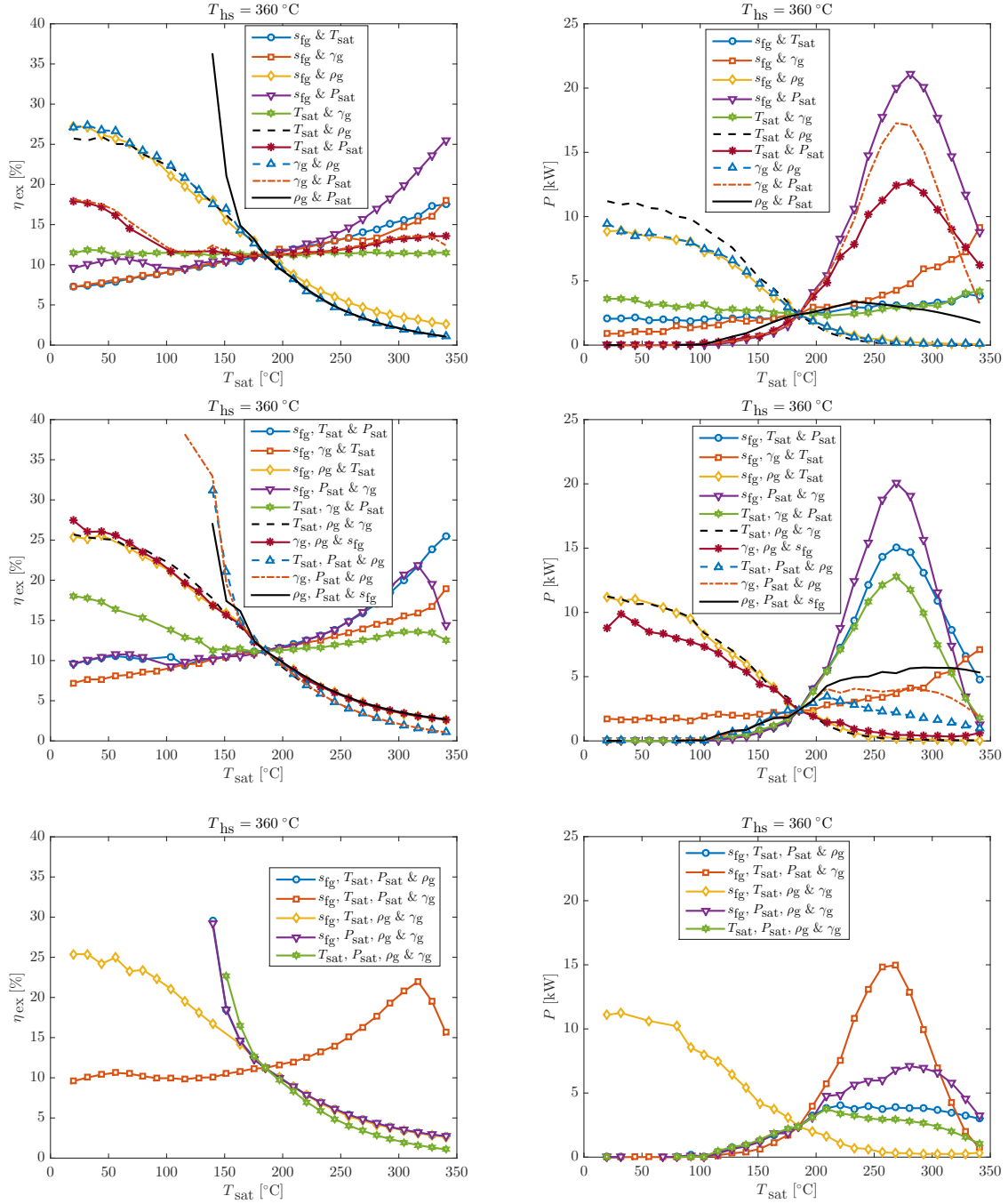


Figure 3.8: The exergy efficiency (η_{ex} , LHS) of and the power output ($P = \dot{W}$, RHS) from the Up-THERM heat engine with water as the working fluid on varying combinations of its thermodynamic properties (see legends for combinations). Each property combination is varied between the indicated saturation temperature (T_{sat}) range while others are set to their respective nominal values at a saturation temperature of 185 °C .

CHAPTER 3. THE UP-THERM HEAT CONVERTER: MODEL DEVELOPMENT AND WORKING-FLUID DESIGN

variation in each property tends to nullify the effect of the other on the power output; they do, however, reinforce each other in terms of the exergy efficiency, with η_{ex} increasing rapidly from the nominal value at lower values of ρ_g and P_{sat} . Thus, for a high-power design one needs a combination of a high P_{sat} and high ρ_g fluid (low ρ_g should be avoided), whereas for a high-efficiency design a combination of low ρ_g and low P_{sat} is needed. In order to simultaneously achieve a high power output and a high exergy efficiency, one needs a combination of high P_{sat} and low ρ_g , which is not physically realisable for most known fluids as both P_{sat} and ρ_g increase with T_{sat} . This suggests that power output and efficiency are competing performance objectives; high power designs will generally have lower exergy efficiencies and *vice versa*.

The simultaneous variation of combinations of three or four properties serve to further confirm the earlier findings, since the general trends (in variations of P_{sat} and ρ_g) from both the single-property and two-property variations are found to persist when three or more properties are varied simultaneously. When either T_{sat} , γ_g or s_{fg} are varied in combination with P_{sat} and ρ_g the previous trends in power and efficiency persist, especially the sharp increase in efficiency below the nominal point. This supports the earlier inference of the competition between power output and exergy efficiency, and further highlights the conflicting importance of ρ_g and P_{sat} . The identification of these key combinations of thermodynamic properties is particularly important and informative for the computer-aided molecular and process design (CAMPD) of these engines.

3.4.3 Comparison with an ideal two-phase and other thermofluidic devices

As earlier stated, the Up-THERM engine and the Non-Inertive-Feedback Thermofluidic Engine (NIFTE), both belong to the same class of two-phase oscillatory heat engines, known as thermofluidic oscillators. These two-phase engines can be characterised by a *working fluid thermal efficiency*, η_{wf} . This is a theoretical ideal thermal efficiency relating to the useful work done in transferring a working-fluid across two constant pressure (and temperature) reservoirs, employing only positive-displacement phase-change processes and ignoring any exergy destruction via valves and thermal losses [40]. This generally characterises any two-phase heat engine as no information about the physical engine (Up-THERM or NIFTE or otherwise) is required in its definition. A *working fluid exergy efficiency* $\eta_{\text{wf,ex}}$ can be further defined by dividing η_{wf} by the Carnot efficiency corresponding to the hot and cold temperature reservoirs.

Working fluids for the Up-THERM engine

An investigation of the effect of working fluids and their thermodynamic properties on η_{wf} was carried out by Markides *et al.* [40], to highlight the working fluids with the highest *potential* to convert heat to work in any two-phase heat engine. It was reported that η_{wf} generally increases with the heat-addition temperature irrespective of the working-fluid employed, as expected. However, its exergetic component, $\eta_{\text{wf,ex}}$, decreases with heat-addition temperature. Also, the organic working fluids (pentane and R245ca) were seen to exhibit higher $\eta_{\text{wf,ex}}$ and lower η_{wf} in comparison to the hydrogen-bonding fluids (water and ammonia) at the same reduced temperatures. Furthermore, amongst the working-fluid thermodynamic properties, the volume change during vaporisation (v_{fg}) had the strongest effect on the η_{wf} , with η_{wf} decreasing with decreasing v_{fg} (increasing T_{sat}). The saturation pressure (P_{sat}) leads to second largest deviation, with η_{wf} increasing with P_{sat} . Other thermodynamic properties had less significant effects on the working fluid efficiencies.

These results are replicated in both the NIFTE and the Up-THERM where changes in v_{fg} have the greatest influence on the exergetic efficiencies of both devices. In the Up-THERM, the exergy efficiency decreases with decreasing v_{fg} . In the NIFTE however, the exergy efficiency increases with decreasing v_{fg} in the first instance, until a maximum and then decreases [40]. P_{sat} and the entropy change during vaporisation (s_{fg}) are also seen to have significant effects on the exergy efficiency of the Up-THERM and its power output. In addition, thermodynamic properties such as the liquid-phase density (ρ_l), the vapour-phase heat-capacity ratio (γ_g) and the saturation temperature (T_{sat}) are seen to have less significant effects on the exergy efficiencies of both the NIFTE and the UP-THERM engine. Finally, while the effect of the vapour-phase density (ρ_g) on the working fluid efficiency and the exergy efficiency of the NIFTE was not reported, it is seen to have significant effects on the efficiencies and power output of the Up-THERM.

3.5 Working fluids for the Up-THERM engine

3.5.1 Available working fluids

Currently, there are a number of publications on working-fluid selection for different heat engines, especially for the ORC variants. It is generally accepted that it is challenging to select an optimal working-fluid for all cycle configurations, operating conditions and heat-source temperatures, which makes it difficult to generalise working-fluid selection rules across different cycles. Chen *et al.* [197], in an investigation of 35 pure working fluids

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(refrigerants, hydrocarbons and ammonia) in ORCs, suggested that the critical temperature and the slope of the saturated vapour curve (on a $T - s$ diagram) of working fluids are important characteristics to consider when designing cycles and selecting operating conditions. Furthermore, siloxanes (MM, MDM, MD₂M, MD₃M and MD₄M) have been investigated as suitable working fluids for medium- and high-temperature cycles [16, 99].

Various other factors influence the selection of (organic) working fluids, including the stability, material compatibility, safety, environmental impact and purchase cost of the prospective fluids. Organic working fluids are known to suffer chemical and physical deterioration at high temperatures, thus the stability of the fluid at the maximum temperature in the cycle should be considered before selection. The selected working fluid should also be non-corrosive and compatible with the engine materials and lubricants. Various authors [70, 198–201] have presented techniques for studying the thermal and chemical stability of various refrigerant-fluid systems. It is also important to ensure that the selected fluid has a negligible environmental imprint in terms of its ozone depletion potential (ODP), atmospheric lifetime and global warming potential (GWP). Refrigerants such as R-11, R-12, R-113, R-114, and R-115 have been phased out while others such as R-21, R-22, R-123, R-124, R-141b and R-142b are in the process of being phased out due to their detrimental environmental impact [197]. A few of these fluids are considered in this work for comparison purposes.

The working fluids considered in this work are listed in Table 3.3, and include hydrocarbons (straight alkanes, branched alkanes and aromatics), water and ammonia, refrigerants (halogenated alkanes) and siloxanes. The properties of these fluids are taken from the REFPROP program [103], which contains experimentally validated data of various fluids. Other approaches for providing working-fluid thermodynamic property values do exist, notably from a molecular perspective including the statistical associating fluid theory (SAFT) equations of state (EoS) [13, 15, 18, 53, 109, 127, 140, 159]. While these EoS have been demonstrated to predict accurately the thermodynamic properties of relevant fluid systems, current databases are not yet exhaustive, and since the REFPROP program contains a larger set of fluids, it is preferred for the purposes of the present study. The molecular-based EoS will however play an important role in the computer-aided molecular and process design (CAMPD) of working fluids for waste-heat recovery systems in general [87] and the Up-THERM heat engine in particular.

For a two-phase thermofluidic-oscillator engine like the Up-THERM, it is important that the working fluid is able to undergo phase change at the externally imposed cycle temperatures. This makes the critical temperature of the working fluid a very important

Working fluids for the Up-THERM engine

Table 3.3: List of investigated working fluids for the Up-THERM heat engine; phased-out and soon to be phased out fluids are italicised.

Dry fluids:	<i>n</i> -Butane, <i>i</i> -Butane, Pentane, <i>n</i> -Hexane, <i>i</i> -Hexane, Heptane, Octane, Nonane, Decane, <i>R-113</i> , <i>R-114</i> , <i>R-115</i> , <i>R-123</i> , <i>R-141b</i> , R-218, R-236fa, RC-318, D4, D5, D6, MM, MDM, MD ₂ M, MD ₃ M, MD ₄ M.
Isentropic fluids:	Propane, Benzene, Toluene, <i>R-11</i> , <i>R-124</i> , R-134a <i>R-142b</i> , R-227ea, R-236ea, R-245ca, R-245fa.
Wet fluids:	Water, Ammonia, Propylene (Propene), <i>R-12</i> , <i>R-22</i> , R-32, R-41, R-125, R-143a, R-152a.

thermodynamic selection criterion. Specifically, the equilibrium temperature of the engine (which corresponds to the time-mean saturation temperature of the working fluid) should be below the critical temperature of the working fluid ($T_{\text{eq}} \leq 0.95 T_c$) to ensure the formation of a vapour phase and present a significant volume change for sustained physical oscillations. A 95% cut-off is employed to ensure that the saturation temperature is well below the critical temperature. Thus, working fluids with $0.95 T_c < T_{\text{eq}}$ are deemed infeasible in the present work.

The considered fluids are also presented in Figure 3.9, where they have been plotted based on their critical pressure (on the vertical axis) and critical temperature (on the lower horizontal axis). Also, the corresponding heat-source temperature (on the upper horizontal axis), $T_{\text{hs}} = 2T_{\text{eq}} - T_{\text{sink}}$ with T_{sink} set to 10 °C, is displayed such that fluids suitable for feasible operation with the Up-THERM can be easily identified and those that are not feasible can be easily removed from consideration. The two temperature axes have been evaluated such that working fluids that fall to the left of a particular heat-source temperature are infeasible; for these fluids the heat-source and also the equilibrium temperatures exceed the imposed critical limit on the saturation temperature. For example, with reference to Figure 3.9, at a heat-source temperature of 360 °C (633.15 K), the equilibrium temperature is 185 °C (458.15 K). The fluids R-113, *i*-C₆H₁₄ and others to the right of the dotted line are applicable whereas R-141b, R-11 and those falling on the left of the line are not applicable since the oscillations in the engine would lead to near-critical or supercritical operation.

3.5.2 Working fluids for nominal design

As stated earlier, the Up-THERM engine was nominally designed for a heat-source temperature of 360 °C and for cost, safety, availability and environmental-impact reasons,

Working fluids for the Up-THERM engine

with water as the working fluid. With a selected heat-sink temperature of 10 °C, this gives an equilibrium (and working-fluid time-mean saturation) temperature of 185 °C, from Equation (3.23). For water, this results in a saturation pressure of 11.2 bar. In this section, alternative working fluids are considered for use in the Up-THERM engine at the nominal heat source/sink temperatures; the fluids are listed in Table 3.3. Not all the working fluids in Table 3.3 are feasible for the nominal settings of the engine. Fluids with a critical temperature T_c below 209 °C ($T_{\text{sat}}/0.95$) will operate near or over the critical region of the phase diagram and will be unable to generate two-phase flow and are thus not considered as feasible. These fluids are pre-screened and excluded from the simulations by utilising Figure 3.9, which has the heat-source temperatures and the corresponding cut-off critical temperatures superimposed.

From the pre-screening exercise, only the working fluids to the right of $T_{\text{hs}} = 360$ °C, as indicated by the dotted line in Figure 3.9, are considered feasible for operation with the Up-THERM when a heat-source temperature of 360 °C is used. It can be seen that heavier alkanes with increasing chain lengths have progressively higher critical temperatures, and that the siloxanes generally have high critical temperatures. The applicable fluids thus shortlisted for the subsequent simulations are: R113, hexane and other higher-molecular-weight alkanes, benzene and toluene, water, and the siloxanes, for a total of 18 working fluids.

Using the properties of these fluids, the Up-THERM engine model is simulated with the nominal heat source/sink conditions and all other system parameters (*e.g.*, related to the geometry/size of the device) kept constant. The results of these simulations are presented in Figure 3.10; in Figure 3.10a the resulting thermal efficiency, oscillating frequency and the operating pressure (saturation pressure) of the engine with the different working fluids arranged in decreasing magnitude of power output are shown, while a plot of the power output against the exergy efficiency of the engine for a given working fluid is shown in Figure 3.10b.

When using the different pre-selected working fluids, the operating/oscillating frequency of the Up-THERM engine generally varies between 1.5 Hz and 2 Hz with the refrigerant R113 having the lowest frequency and nonane the highest one. Also, the higher-molecular-weight fluids, such as the siloxanes, are seen to exhibit lower frequencies than the lighter working fluids, such as the alkanes. Overall, the oscillating frequency is not strongly affected by the choice of working fluid. Also, in this analysis, the exergy efficiency and the thermal efficiency are, in fact, proportional and will show identical

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trends, since the heat source and heat sink temperatures (and therefore, the Carnot efficiency in Equation (3.22)) are identical.

One of the most apparent inferences from Figure 3.10a is the link between the power output (and/or efficiency) and the saturation pressure. While all the working fluids are operating at the same equilibrium/time-mean saturation temperature of 185 °C, they have different saturation pressures based on their vapour-liquid equilibrium curves. There is a strong positive correlation between P_{sat} and the power output and a negative correlation between P_{sat} and the exergy and thermal efficiencies; the fluids with higher P_{sat} , such as R113 and the hexanes, have higher power outputs and lower efficiencies than the fluids with lower P_{sat} , such as decane and MD4M. Thus, a competition arises between the engine's power output and its exergy and/or thermal efficiency, which appear as conflicting design objectives.

An obvious trend from Figure 3.10b is the inverse and multi-objective relationship between the power output from the Up-THERM engine and its exergy efficiency; working fluids with a high power output have a low efficiency, and *vice versa*. This follows from the results in Figure 3.10a and Section 3.4, where higher working-fluid saturation pressures are associated with higher power outputs, while lower values of vapour-phase density ρ_g lead to higher power outputs and higher exergy efficiencies. As these two thermodynamic properties both vary directly with the saturation temperature T_{sat} , both scenarios (high P_{sat} and low ρ_g) cannot be simultaneously achieved. The working fluids that lead to high-power engine designs are R113, *i*-hexane and *n*-hexane with correspondingly low exergy/thermal efficiencies. Similarly, the working fluids that lead to high-efficiency engine designs are the siloxanes in general, decane and nonane with correspondingly low power outputs. The existence of an inverse relationship between power output and efficiency confirms the earlier inference that one cannot simultaneously achieve high power and high efficiency engine designs.

It is also important to highlight the performance of the engine within and amongst the chemical classes of working fluids present. Most of the applicable screened fluids are dry fluids; only water is a wet fluid and the aromatic compounds (benzene and toluene) are the only isentropic fluids (see Table 3.3). Interestingly, the dry fluids dominate the results in Figure 3.10; dry fluids lead to the engines with the highest power output (R113 and the hexane isomers) and also to the highest efficiencies (the siloxanes). This conclusion may, however, not be applicable at lower heat-source temperatures as more working fluids become 'feasible' as discussed in Section 3.5.3. Furthermore, within a particular chemical class of working fluids, *e.g.*, the straight-chain alkanes, the shorter-chain and lighter-

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molecular-weight compounds result in designs with higher power outputs (and lower efficiencies) while the longer-chain and heavier compounds result in higher efficiencies (and lower power outputs). This is illustrated by the alkanes and the siloxanes. Engines with fluids from *n*-hexane, *n*-heptane to *n*-decane progressively have lower power outputs and higher efficiencies. Similarly, from MM to MD4M and from D4 to D6, the fluids progressively display higher efficiencies and lower power outputs. This suggests that the power output and the efficiencies correlate negatively and positively respectively with the molecular weight of the working fluids. As the critical properties (T_c and P_c) are related to the molecular weights as seen in Figure 3.9 – within a chemical class, *e.g.*, the alkanes or siloxanes, heavier compounds have lower P_c and higher T_c and *vice versa* – the performance of the engine may also be dependent on the critical properties of the working fluids; this is investigated in Section 3.5.4.

The performance of the engine with *n*-hexane and *i*-hexane as working fluids also reveals a reciprocal relationship between isomers. The branched alkane (*i*-hexane in this case) results in a higher power output and slightly lower efficiency than the straight-chain alkane. The branched alkane could be interpreted as behaving like its corresponding lighter alkane, exhibiting a higher power output and a lower efficiency. This relation is further encountered in Section 3.5.3 when more isomer pairs are considered. Also, between the aromatic compounds, the substitution of the hydrogen atom in benzene with the methyl group in toluene (the heavier compound) results in an engine with a lower power output and higher efficiencies. Furthermore, a closer inspection of Figure 3.10 reveals that the compounds with higher molecular weights, especially the siloxanes, are concentrated on the high-efficiency (and low-power-output) end of the graph while those with lower molecular weights are concentrated on the high-power end of the graph. This highlights the compromise necessary between the power output and the efficiency with molecular weight.

3.5.3 Working fluids for varying heat-source temperature

In Sections 3.4 and 3.5.2 the challenge inherent in selecting working fluids to simultaneously maximise both the power output and efficiency of the Up-THERM engine was established. In this section, the working-fluid selections for off-design conditions at different heat-source temperatures are investigated. The performance of various working fluids when used with the engine at lower heat-source temperatures of 100 °C and 200 °C is presented in Figure 3.11. Similarly, in Figure 3.12 results are presented for heat-source temperatures of 300 °C and 400 °C. In both sets of figures, the working fluids are arranged

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in order of decreasing engine power output. These simulations were all carried out with a heat-sink temperature of 10 °C, as before.

The investigated working fluids are once again taken from Table 3.3. At the lower heat-source temperatures of 100 °C and 200 °C, more fluids become available for consideration as more refrigerants now have critical temperatures above these equilibrium temperatures, enabling the necessary two-phase flow in the device. Also available for consideration are the lighter hydrocarbons such as pentane and butane, and ammonia. At the higher heat-source temperature of 400 °C, working fluids such as R113 and *i*-hexane are excluded from consideration as the equilibrium temperature is now greater than their critical temperatures.

Most of the findings from the nominal-design case with heat-source temperature of 360 °C are replicated at heat-source temperatures from 100 °C to 400 °C as shown in Figures 3.11 and 3.12. Fluids with higher equilibrium saturation pressures are seen to produce higher power outputs (with lower efficiencies), while those with lower saturation pressures produce lower power outputs. Also, within the alkane homologous series the lighter compounds produce higher power output and lower exergy/thermal efficiencies than the heavier compounds, highlighting the respective positive and negative correlation of efficiency and power output with molecular weight. The oscillating frequency remains largely unaffected by the choice of working fluid.

As observed earlier with the hexane isomers, the performance of the engine with butane isomers also exhibits a reciprocal relationship. From Figure 3.11, the branched alkane (*i*-butane in this case) results in a higher power output and slightly lower efficiency than the straight-chained alkane (*n*-butane). This is also observed with *i*-hexane and *n*-hexane at higher heat-source temperatures. Also interesting here is the comparison between saturated and unsaturated alkanes (C_3H_8 and C_3H_6 respectively) at the low heat-source temperature of 100 °C. The alkene results in a higher power output (and slightly lower efficiencies) than the alkane, agreeing with an expectation based on their respective molecular weights.

The availability of more working fluids at lower heat-source temperatures introduces a more interesting comparison amongst the chemical classes of working fluids present. A close inspection of Figure 3.11 for the heat-source temperatures of 100 °C and 200 °C reveals that the wet fluids—R32, R143a, propene and ammonia—occupy the high power (and low efficiency) end of the figures, whereas the dry fluids occupy the high exergy-efficiency end of the figures; this is quite different from the result in Figures 3.10 and 3.12 where the dry fluids are dominant. This finding is, however, directly influenced and

Working fluids for the Up-THERM engine

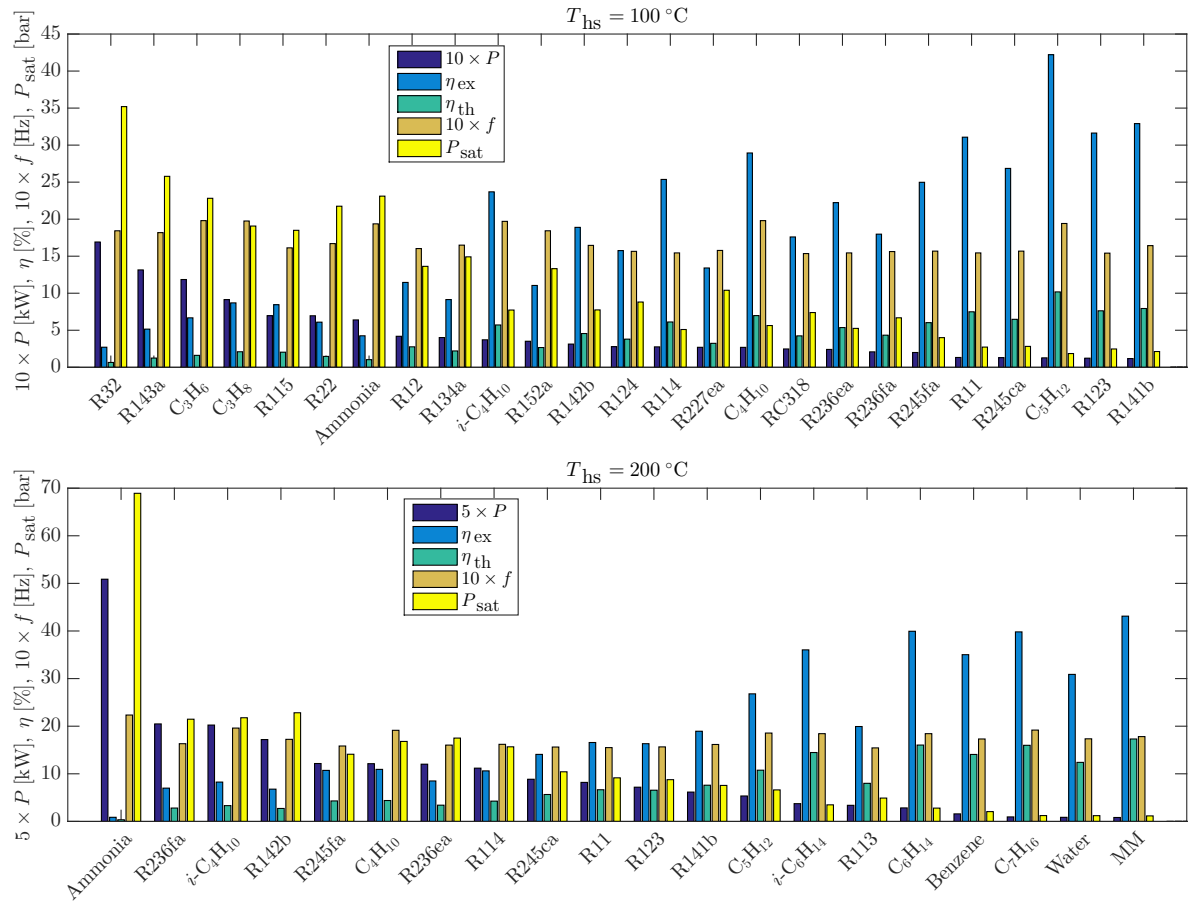


Figure 3.11: Power output ($P = \dot{W}$), exergy efficiency (η_{ex}), thermal efficiency (η_{th}), oscillating frequency (f) and equilibrium pressure (P_{sat}) of the Up-THERM heat engine with water and various organic working-fluids at low heat-source temperatures of 100 °C and 200 °C, and a heat-sink temperature of 10 °C. The working fluids are arranged in order of decreasing power output. The alkane formulae, where given and where not indicated otherwise, refer to the normal (straight-chain) alkane.

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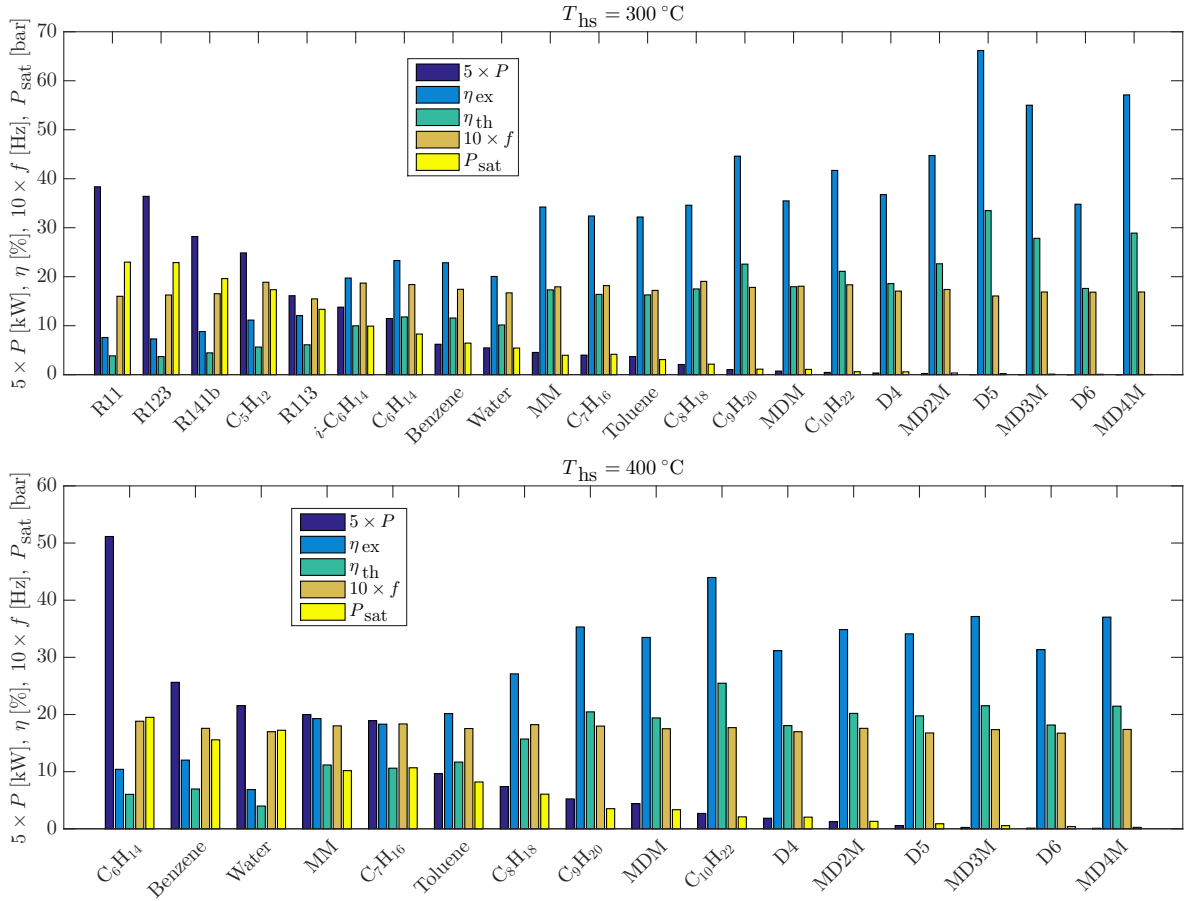


Figure 3.12: Power output ($P = \dot{W}$), exergy efficiency (η_{ex}), thermal efficiency (η_{th}), oscillating frequency (f) and equilibrium pressure (P_{sat}) of the Up-THERM heat engine with water and various organic working-fluids at higher heat-source temperatures of 300 °C and 400 °C, and a heat-sink temperature of 10 °C. The working fluids are arranged in order of decreasing power output. The alkane formulae, where given and where not indicated otherwise, refer to the normal (straight-chain) alkane.

subject to the low critical temperatures of most of the wet fluids, which is why they were excluded by pre-screening at the high heat-source temperatures. These results suggest that, when available, wet fluids are more suitable for the high power-output designs, while the dry fluids are more suitable to the high efficiency designs.

3.5.4 Effect of critical properties

In Section 3.4, it was concluded that the working-fluid (equilibrium) saturation pressure P_{sat} and its (equilibrium) vapour-phase density are important thermodynamic properties in controlling the performance of the Up-THERM heat engine. It was also established that the power output and exergy efficiency correlate strongly with P_{sat} from Figure 3.10 through Figure 3.12. The molecular weight of working fluids also appeared to be significant in optimising the engine output, especially within a homologous series of working fluids as in Section 3.5.2. These indicate that the critical properties of the fluid will play an important role in working-fluid selection and performance optimisation of the Up-THERM engine.

Therefore, it is important to investigate the relationship between the engine performance and the critical temperature and pressure of the working fluids. In particular, the power output is compared to the reduced and critical properties of the applicable working fluids, while minding the fact that the power output and the thermal/exergy efficiency are inversely correlated. This is done at heat-source temperatures of 200 °C and 360 °C and the results are presented in Figure 3.13 and Figure 3.14, respectively; the corresponding working fluids in this results are the same as those in Figure 3.11 and Figure 3.10. In these figures, the reduced pressure is defined as $P_r = P_{\text{sat}}/P_c$ and the reduced temperature is defined in a similar manner.

The correlation between the engine performance and the working-fluid critical properties is evident in both figures. From Figure 3.13, the engine's power output is seen to decrease as the working-fluid critical temperature increases. This implies that its thermal/exergy efficiency increases with the critical temperature. Since the equilibrium saturation temperature ($T_{\text{sat}} = (200 \text{ °C} + 10 \text{ °C})/2$) is the same across all the working fluids, it is indeed expected and not surprising that the engine's power output will increase (while the efficiencies will decrease) with the working-fluid reduced temperature due to its definition. Thus, not only is the critical temperature, T_c , important in the pre-screening process of excluding non-applicable working fluids at different heat-source temperatures as used in Figure 3.9, it also has a telling impact on the power output

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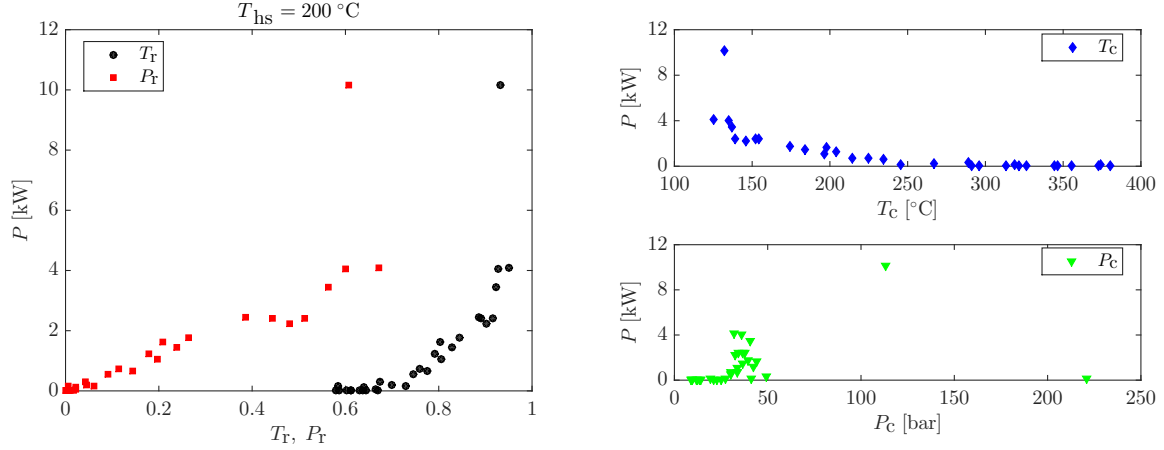


Figure 3.13: Power output ($P = \dot{W}$) as function of working-fluid critical properties—reduced temperature and pressure (T_r & P_r), critical temperature and pressure (T_c & P_c)—at a heat-source temperature of 200 °C; the heat-sink temperature is 10 °C. The corresponding working fluids can be found in Figure 3.11.

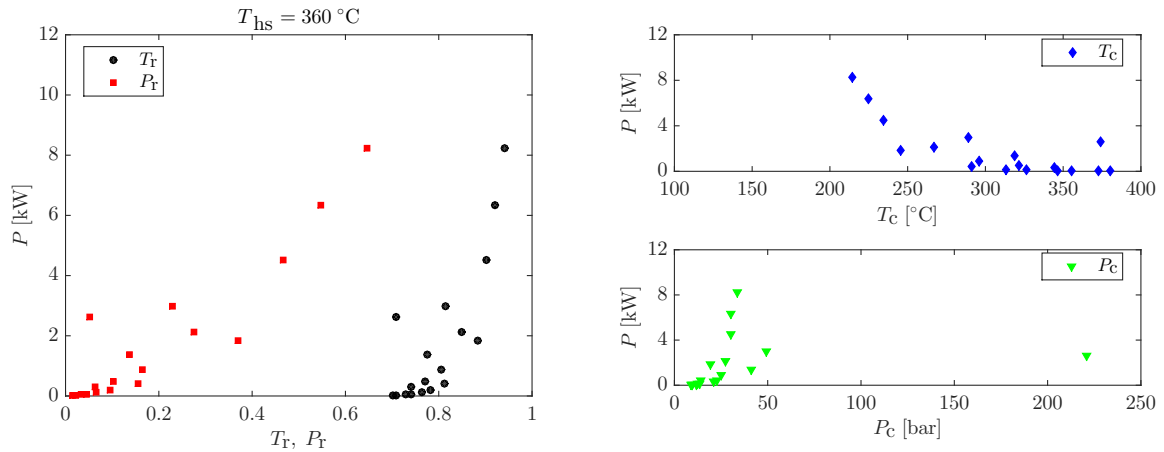


Figure 3.14: Power output ($P = \dot{W}$) as function of working-fluid critical properties—reduced temperature and pressure (T_r & P_r), critical temperature and pressure (T_c & P_c)—at a heat-source temperature of 360 °C; the heat-sink temperature is 10 °C. The corresponding working fluids can be found in Figure 3.10.

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and/or the efficiency of the engine. High power designs will require working fluids with low (but still feasible) T_c , whereas high efficiency designs will require fluids with high T_c .

While the critical temperature clearly dictates working-fluid selection and the performance of the engine, the role of the critical pressure, P_c , is less obvious, although higher critical pressures do tend generally to result in higher power outputs amongst working fluids from the same family. Also, while all working fluids have the same T_{sat} , they all have different saturation pressures, P_{sat} , based on their vapour-liquid equilibrium (VLE) curves. The normalisation of the working-fluid critical pressure based on the equilibrium saturation pressure in the definition of the reduced pressure, P_r , does however result in a more definite trend with respect to the engine's performance. In Figure 3.13 it is clear that the engine's power output increases as the reduced pressure increases. Conversely, high efficiency designs will be favoured by low reduced pressures.

In summary, working fluids with low critical temperatures or high reduced temperatures and high reduced pressures can result in engines that will deliver a high power output. This is particularly well demonstrated by ammonia (see Figure 3.9) at a heat-source temperature of 200 °C in Figure 3.11, which delivers more than double the power output of the closest neighbour, R236fa. This is further explored in the next section. In Figure 3.14, the engine's performance at a heat-source temperature of 360 °C is presented against the working-fluid critical properties. These results appear more scattered than in Figure 3.13, but similar conclusions can be drawn and be generalised for different heat source/sink temperatures.

3.5.5 Optimal working-fluid selection

In Figure 3.15a, the maximum power output from the Up-THERM heat engine over all working fluids is plotted against the corresponding heat-source temperature. The 'optimal' working fluid responsible for this maximum power output is also indicated at the different heat-source temperatures. As the heat-source temperature is varied, the optimal working-fluid changes, with R32 being optimal at 100 °C and hexane being optimal at 400 °C. Noticeable in this figure are the discontinuities as the heat-source temperature is varied. These are a result of the exclusion of working fluids when the condition $T_{\text{sat}} > 0.95 T_c$ is imposed, as dictated by Figure 3.9. A few of the optimal working-fluids are seen to be very versatile especially at low heat-source temperatures, being optimal across large ranges of heat-source temperatures.

At heat-source temperatures below about 210 °C, it is found that the optimal working-fluids are predominantly wet fluids. This supports the earlier inference that, where appli-

CHAPTER 3. THE UP-THERM HEAT CONVERTER: MODEL DEVELOPMENT AND WORKING-FLUID DESIGN

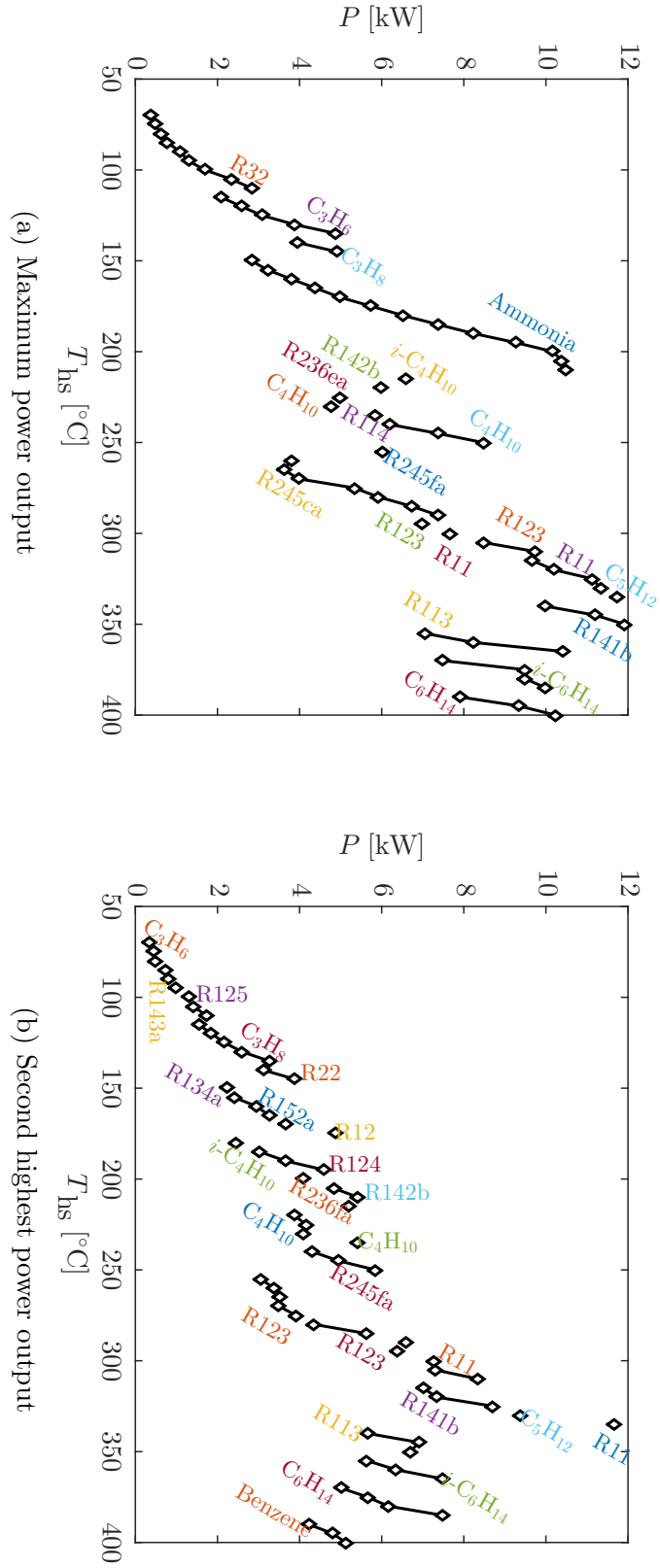


Figure 3.15: Maximum power output ($P = \dot{W}$) from the Up-THERM heat engine as a function of the heat-source temperature (T_{hs}). The heat-sink temperature is 10 $^{\circ}\text{C}$. The corresponding optimal working-fluids are displayed alongside the heat-source temperatures. The alkane formulae, where given and where not indicated otherwise, refer to the normal (straight-chain) alkane.

Working fluids for the Up-THERM engine

cable, Up-THERM designs with wet working-fluids produce higher power outputs (and correspondingly lower efficiencies). Ammonia in particular is the most versatile of the working fluids, being the optimal fluid between heat-source temperatures of 150 °C and 210 °C. This is a direct result of its low critical temperature and high critical pressure as highlighted in the previous section. At higher temperatures however, there are more frequent discontinuities in the optimal curve, with dry and isentropic working-fluids being optimal between 215 °C and 300 °C, while only dry fluids are feasible and optimal at higher heat-source temperatures.

Finally, Figure 3.15a can be used as a working-fluid selection map for the Up-THERM engine. From this figure, an optimal working-fluid can be selected as a function of the available heat source(s). A few of these fluids (those italicised in Table 3.3), especially at higher heat-source temperatures, are already or are soon to be phased out due to the Montreal protocol [202]. For this reason, a second map, Figure 3.15b, is provided alongside the optimal map. This contains the working fluids that are second best in providing the maximum power output from the Up-THERM engine. These fluids can thus serve as second-best alternative substitutes for the phased out and soon to be phased out optimal working-fluids, where relevant.

3.5.6 Comparison with existing heat engines

At this stage, it is important to compare the Up-THERM engine with other established concepts in terms of both performance and economical viability. Suitable technologies for comparison at the relevant power output and heat-source temperature ranges are the organic Rankine cycle (ORC) and the Stirling engine, both of which already form the basis of known micro-CHP prime-mover systems [203, 204]. ORC systems [13, 14, 16, 53, 99] are a relatively mature technology capable of utilising low-grade heat, while Stirling engines [31, 33, 34] are also able to utilise low-grade heat for subsequent conversion to electricity. ORCs are based on a conventional (two-phase) Rankine cycle but incorporating an organic working fluid, whereas Stirling engines are based on an inherently unsteady but single-phase thermodynamic cycle whereby the cyclic compression and expansion of a gaseous working fluid at different temperatures leads to a net conversion of thermal energy to mechanical work.

While the scope for comparison of these engines is quite wide, the discussion here is limited to engines with the same power output as the Up-THERM engine investigated in this work, *i.e.*, in the 1 kW – 10 kW range. A waste-heat recovery ORC engine operating on a refinery flue gas (at a source temperature of 330 °C), and delivering power output

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in excess of 10 kW is predicted to have a maximum thermal efficiency of about 15% [13]. Also, its specific investment cost (at power outputs between 1 kW and 10 kW) is predicted to range between €3000 and €7500 per kW of mechanical power produced. From the results in Figures 3.10 and 3.12, it is clear that the high power designs of the Up-THERM engine have thermal efficiencies between 5% and 12%. Although these thermal efficiencies are lower than those of ORCs above (about 15%), they have the same order of magnitude and are thus comparable. As discussed previously in Sections 3.5.2 and 3.5.3, the power output of the Up-THERM engine can be sacrificed in order to improve its efficiency; this can lead to Up-THERM engine designs with thermal efficiencies as high as those of ORC and Stirling engines, although one is of the opinion that this is hardly desirable.

Furthermore, it is envisaged that the Up-THERM engine will be much more affordable than ORC and Stirling engines due to its simple construction and operation, and small number of moving parts and dynamic seals – the Up-THERM contains only a single moving part, its solid reciprocating piston. Such single-piston engines have a number of advantages when compared to state-of-the-art Stirling engines, namely simplicity, adequate high temperature sealing, elimination of heat losses, very low leakage rates and much easier balancing [44]. These, amongst others, will allow lower capital and operating costs for the Up-THERM engine with longer operating lifetimes. In addition, prototypes similar to the Up-THERM engine have been developed at costs of €200 – €500 per kW of power generated; these are much cheaper than €2500 – €4500 per kW for Stirling-type engines [46].

Thus, the Up-THERM engine can be said to offer an economically and technologically viable alternative to ORCs and Stirling engines in waste-heat recovery, solar, and combined heat and power (CHP) applications, especially for small-scale power generation in remote and/or off-grid locations.

3.6 Summary

A synopsis of a non-linear lumped dynamic model for a novel two-phase thermofluidic oscillator heat engine named Up-THERM has been presented in this chapter. This engine relies on the periodic evaporation and condensation of its working fluid and the vertical motion of a single solid-piston. The oscillatory motions of the piston and working fluid are transformed to a unidirectional flow of the working fluid through a hydraulic motor to extract power. With its few moving parts, the resulting device requires low capital and maintenance costs. While the engine is specifically conceived for heat-recovery ap-

Summary

plications, it is also relevant in low-power applications especially in remote or off-grid locations where low investment and maintenance costs are crucial for favourable returns, and economic viability.

The performance of the Up-THERM engine is defined here in terms of its exergy or thermal efficiency and its power output. In its nominal configuration with water as the working fluid and a heat-source temperature of 360 °C, the Up-THERM engine delivers 2.64 kW at an exergy efficiency of 11.2%. This can be compared with the nominal exergy efficiency of a similar device known as the NIFTE, which was reported by Markides *et al.* [40] as being of the order of 1%, and the maximum exergy efficiency value of 6% attained by varying working fluids but with a nominal geometric NIFTE design, although it is noted that the target heat-source temperatures in the case of the NIFTE are lower (< 200 °C). However, the performance of the Up-THERM engine (at this nominal configuration) can be considerably improved by employing organic working fluids such as R113 and isomers of hexane, delivering up to 8 kW of power. The Up-THERM converter is also shown to offer an economically and technologically viable alternative to established technologies such as ORCs and Stirling engines in waste-heat recovery, solar and CHP applications, especially for small-scale power generation in remote and/or off-grid locations.

A key element of the Up-THERM engine's design is the specification of the generator mounted to the hydraulic motor. The generator is characterised by its resistance, R_{gen} , with its value determined empirically as the one that maximises power output. Simulations revealed that the power output varies over orders of magnitude with respect to this resistance, making its determination very important in characterising the engine. The optimal value of R_{gen} is however found to be generally insensitive to the external conditions of heat-source and heat-sink temperatures, and the employed working fluid.

The effects of several working-fluid thermodynamic properties on the performance of the engine were investigated. This was carried out using water as the reference working fluid at a nominal engine design, by varying combinations of the respective properties as functions of the saturation temperature, T_{sat} , which revealed that the saturation pressure, P_{sat} , and the vapour-phase density, ρ_g , are the most dominant independent thermodynamic properties in terms of their effects on the power output and exergy efficiency of the engine. The entropy change during vaporisation s_{fg} also has a marginal effect on the engine's performance. Higher values of P_{sat} and lower values of ρ_g lead to higher power outputs. This particular combination of P_{sat} and ρ_g is virtually impossible for real

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working fluids as both properties increase (or decrease) with increasing (or decreasing) T_{sat} , suggesting a compromise has to be reached between both properties.

An important aspect of this work concerns the working-fluid selection for the Up-THERM engine. Due to its nature as a two-phase engine, it is important that the employed working fluid is capable of generating two-phase flow at the combinations of the heat-source and heat-sink temperatures. Only fluids with critical temperatures higher than the resulting equilibrium temperature will satisfy this condition. At the nominal design, R113 and *i*-hexane are the most promising fluids in furnishing a high-power-output engine, delivering more than double the output with water as working fluid. These fluids do however lead to low-efficiency designs as the engine's efficiency and power output were found to be inversely related. Siloxanes and higher members of the alkane family result in high-efficiency engine designs, however with much lower power output.

A total of 46 working fluids including aliphatic and aromatic hydrocarbons, refrigerants and siloxanes were considered for use in the Up-THERM engine. Simulations with these fluids at various external (heat source) conditions revealed that the critical properties of the fluids have a profound effect on the engine's performance. High-power designs were generally favoured by working fluids with low critical temperatures; the critical temperatures still need to be greater than the equilibrium temperature for feasible designs. Furthermore, working fluids with high reduced temperatures and pressures also favour high-power designs. Conversely, fluids with high critical temperatures and low reduced temperature/pressure will favour high-efficiency engine designs. Thus, in a chemical family such as the alkanes, lower-molecular-weight members will favour high-power designs while heavier members will favour high-efficiency designs.

Finally, an optimal working-fluid selection map is presented in Figure 3.15. This figure contains the working fluid(s) that maximise the engine's power output at different heat-source temperatures. From this map, the engine is seen to deliver power output in excess of 10 kW especially at higher heat-source temperatures. Wet fluids were found to be optimal at heat-source temperatures below 210 °C, and dry fluids were optimal at higher heat-source temperatures. Working fluids such as ammonia (in particular, owing to its low critical temperature and high critical pressure), R245ca, R32, propene and butane feature prominently on this map, generating high power-outputs over large heat-source temperatures ranges. This makes them suitable and adaptable to variations in heat source and sink temperatures while the engine is in operation. These working fluids are therefore good candidates for the Up-THERM heat engine.

Chapter 4

Computer-Aided Molecular and Process Design of Heat Recovery and Conversion Systems

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4.1 Introduction

An integral part in the design of heat engines is the evaluation of thermo-physical properties of working fluids at different points in the engine and across its individual components. These properties include those such as enthalpies and entropies that are required in the thermodynamic evaluation of the engine as presented in the case of an organic Rankine cycle engine in Section 2.1 and in the case of the Up-THERM engine in Section 3.2. In addition, transport properties such as thermal conductivities and viscosities, and surface tensions are also required when evaluating the heat transfer characteristics and interactions of these working fluids in the engines. The evaluation of component and system costs, and other economic indices also relies on the accurate prediction of these working-fluid properties.

Previously in Chapters 2 and 3, such working fluid properties are derived from the NIST/REFPROP database [101–103, 205], which contains (pseudo-)experimental thermodynamic, critical and transport properties of a variety of fluid systems (including those of hydrocarbon and refrigerant working fluids). Another source of such experimental data is the CoolProp [104]. The use of such databases relies on the availability of experimental data for well-known fluids which in turn requires that the working fluid of interest in the design of a heat engine should be known beforehand. Thus, a large amount of research has gone into the performance testing of a large number of known working fluids for use in engines such as the organic Rankine cycle (ORC) engine; working fluids for which little or no experimental data exist are usually not considered by default and as such, novel and/or non-conventional working fluids (which are excluded from the problem by default) cannot be identified or suggested for use in ORC engines or other suitable heat engines.

However, in terms of optimisation, this pre-selection of a working fluid is a constraint on the optimisation problem; thus in Equation (2.33) for example, where the working fluids are selected *a priori*, the optimal solution is constrained by this selection. This is evidenced by the different *sub-optimal* solutions obtained for the different working fluids considered (see Section 2.2). Therefore, there is a possibility of obtaining a better solution to the design problem if the selection of the working fluid is relaxed and formulated as part of the optimisation problem. This integration of the optimal working-fluid design into the optimal process design problem is the essence of the computer-aided molecular and process design (CAMPD) as explored in this chapter. With respect to Equation (2.33), a CAMPD optimisation problem would have to include variables, models and constraints that address the working-fluid design problem. This will provide added flexibility in the

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working-fluid design and also in the process design, preventing the usual pre-selection, and thus lead to truly optimal systems, with the possibility of the identification of non-conventional and novel working fluids.

A general CAMPD structure for power systems' design is illustrated with the flowchart in Figure 4.1. This is unlike conventional optimisation studies where a large array of working fluids are evaluated based on predefined screening criteria; then for each screened working fluid a system-level optimisation is completed and the optimal working fluid is selected by comparing the results of these individual optimisations. However, this conventional method can lead to sub-optimal system designs since optimal working fluids could be excluded based on the subjective screening criteria. As illustrated, the CAMPD framework consists of four parts which are the process model, a working-fluid model represented by a molecular equation of state (EoS), process/molecular constraints and an optimisation solver. Process models for the ORC engine and the Up-THERM engine are discussed in Chapters 2 and 3, while typical process constraints are presented in Equation (2.33). The molecular equations of state (based on the Statistical associating fluid theory, SAFT) and the corresponding molecular constraints are presented in this chapter.

A key feature of this structural approach is the incorporation of the working fluid design and the heat engine design in a single mixed-integer non-linear optimisation problem (MINLP) for which solution algorithms are readily available; an example of such is the outer approximation with equality relaxation and augmented penalty (OAERAP) solver [206] available in the gPROMS software package [207]. Such a formulation would thereby result in simultaneous optimal working fluid and optimal cycle configuration satisfying all process (heat source/sink, pinch conditions, downstream requirements) constraints; where applicable, environmental constraints (global warming potential – GWP, ozone depletion potential – ODP, toxicity, *etc.*) can be included in the problem definition. Additionally, molecular groups that favour higher cycle performance would be identified for further investigation. Furthermore, sensitivity analyses can be provided for such optimal working fluid and cycle designs with the view to capturing changes in optimal solutions/configurations with unforeseen fluctuations in process conditions (*e.g.*, heat source/sink temperature and flowrate variations).

The connected parts of the CAMPD framework, starting with the thermodynamic and transport property prediction methods, are discussed in this chapter. After its development, the framework is also validated in this chapter, and it is applied to case studies in organic Rankine cycle systems design in Chapter 5.

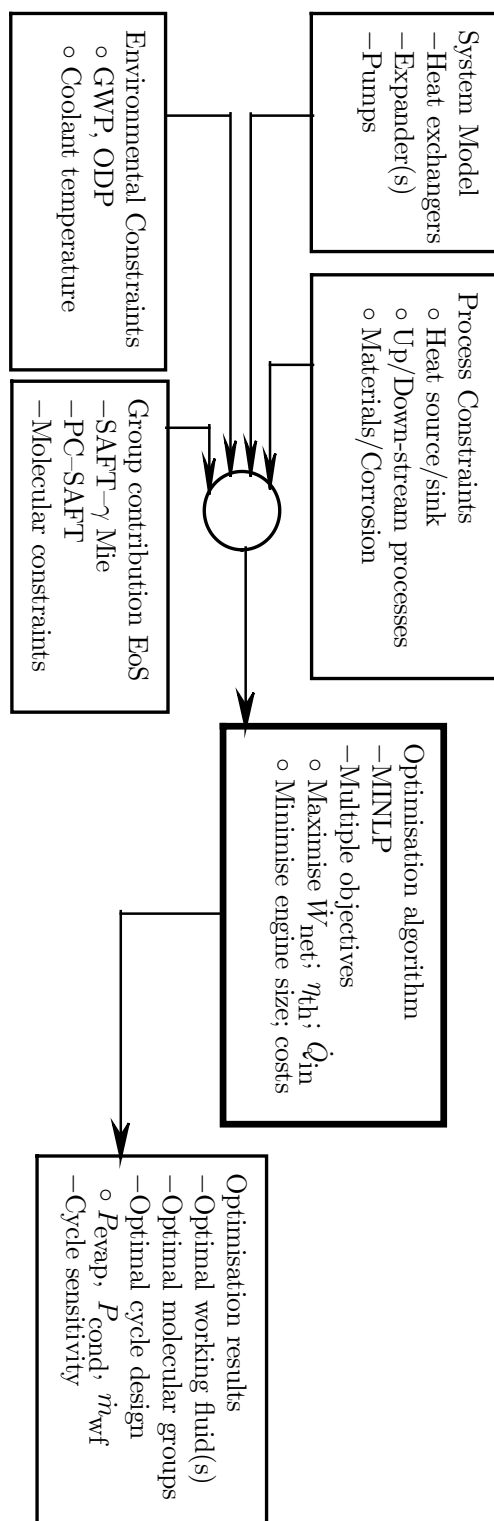


Figure 4.1: A computer-aided molecular and process design (CAMPD) structure for power systems.

4.2 Working-fluid properties from molecular equations of state

Most of the currently deployed heat engines utilise pure (single-component) fluids, hence the thermodynamic-property modelling of these engines has been historically focused on pure working fluids. Thermodynamic data for pure fluids can be reliably sought from sources such as the NIST/TRC Web Thermo Tables, which contain a wide range of experimental and pseudo-experimental thermodynamic properties for a large set of pure fluids. Experimental thermodynamic properties of fluid mixtures of potential interest, however, are frequently unavailable – particularly properties such as enthalpies, entropies and heat capacities, which are important in describing (low-temperature) thermodynamic power cycles and heat engines; moreover, where they are available, the data are unlikely to represent the particular compositions of interest. Thus, in order to model fluid mixtures of arbitrary composition properly, a means of predicting the necessary thermodynamic information is required. For the purpose of ORCs and other applicable heat engines, an approach to reliably and simultaneously predict both phase-equilibrium and calorific quantities is required.

Cubic equations of state (EoS), such as the Peng-Robinson [208] or the Soave-Redlich-Kwong [209], have been employed over the years for the modelling of phase-equilibrium properties, especially in the oil and gas, and petrochemical industries. These equations are, however, best suited for the prediction of phase-equilibrium properties in P - T - x space, and are less reliable for the prediction of calorific properties (heat capacities, enthalpies) for both pure fluids and fluid mixtures [210]. They are even less accurate for the calculation of second-derivative properties (*e.g.*, coefficient of thermal expansion, isothermal compressibility). These shortcomings are not entirely unexpected as these EoS are semi-empirical in nature and their underlying molecular models (based on a hard spherical core surrounded by a spherically symmetric region of attraction) are usually not sufficiently realistic.

The development of molecular EoS such as those based on the perturbed hard-chain theory (PHCT) and the associated perturbed anisotropic chain theory (PACT) EoS for chain molecules has provided some insight into addressing these deficiencies. Also, advances in statistical mechanics coupled with increased computational capabilities have led to the development of EoS based on molecular principles, which provide more-realistic and accurate descriptions of real fluids and fluid mixtures. Foremost among these is arguably the statistical associating fluid theory (SAFT) EoS [127, 128]. SAFT possesses a

predictive capability lacked by cubic EoS, which it inherits from its firm theoretical foundation in statistical mechanics. This allows confidence in predictions of thermodynamic properties made outside the range of the experimental data used for the adjustment of the model parameters, and (as illustrated with the results presented in Sections 4.2.3 and 4.2.4) even in predictions of properties that were not considered in the process of model refinement.

4.2.1 The SAFT-VR Mie equation of state

Two equations of state based on the statistical associating fluid theory (SAFT) are considered: SAFT-VR Mie and SAFT- γ Mie; both are based on the Mie pair potential [211]. In the first instance, the SAFT-VR Mie EoS is used for the prediction of fluids' thermodynamic properties. A thorough discussion of the adequacy of the SAFT-VR Mie EoS and its advantages compared with cubic EoS and previous versions of the SAFT has been presented in Lafitte *et al.* [109]; in particular, it was shown that the SAFT-VR Mie EoS can be conveniently deployed to produce an accurate description of the thermodynamic properties of each of the classes of fluids considered in this present work – alkanes and perfluoroalkanes. For the specific details of the SAFT-VR Mie EoS the reader is referred to the original reference (*i.e.*, Lafitte *et al.*); here, only a brief description is provided. Similar to other versions of SAFT, SAFT-VR Mie is a molecular-based equation of state that allows the calculation of a fluid's Helmholtz free energy, following the development of its underlying molecular model. The fluid molecules are modelled as chains of m spherical segments that interact through a Mie (generalised Lennard-Jones) pair potential centred on each segment:

$$\phi(r) = \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a} \right)^{\frac{\lambda_a}{\lambda_r - \lambda_r}} \varepsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right]. \quad (4.1)$$

Here, r represents the separation of the two interacting segments, σ is a parameter representing the size of the segment, ε is the depth of the potential well, and λ_r and λ_a are respectively the repulsive and attractive exponents characterising the range of the potential; for the case $\lambda_r = 12$ and $\lambda_a = 6$, Equation (4.1) reduces to the standard Lennard-Jones potential. Thus, the set of parameters comprising m , the chain length, along with the intermolecular pair-potential parameters, σ , ε , λ_r , and λ_a , fully define the underlying model of a non-associating pure fluid (such as an alkane or a perfluoroalkane in the present work).

Working-fluid properties from molecular equations of state

In the SAFT approach, the Helmholtz free energy, a , of the fluid is expressed as a sum of an ideal and a residual contribution; the latter is divided into a sum of terms representing individual contributions due to: the monomer segments; the grouping of the segments into the chains (of length m) that make up the model molecules; and (in the case of associating molecules) association. The generic SAFT free energy can thereby be written as:

$$a = a^{\text{IDEAL}} + a^{\text{MONO}} + a^{\text{CHAIN}} + a^{\text{ASSOC}}. \quad (4.2)$$

Typical working fluids such as hydrocarbons and refrigerants, used in heat engines are non-associating fluids, whereby $a^{\text{ASSOC}} = 0$. The ideal contribution, a^{IDEAL} , is calculated by providing the ideal-gas specific heat capacity c_p^0 for the fluid as a function of temperature. A standard approach is to correlate these using polynomials in temperature [212]; here, the ideal-gas heat capacities from the NIST database [102] are correlated using 3rd order polynomials. Then, a^{IDEAL} is obtained via standard thermodynamic relations, with the integration of c_p^0 (to give the enthalpy) and of c_p^0/T (to give the entropy).

Once the Helmholtz free energy is defined, standard thermodynamic relations are used to derive thermodynamic properties of interest (*e.g.*, pressure, fugacities, activity coefficients and chemical potentials). A particular feature of this version of SAFT is the facility to adjust λ_r to suit the relative softness or hardness of a given molecule, allowing it to provide accurate descriptions of second-derivative properties, such as heat capacities, while maintaining a faithful representation of phase equilibrium [109]. An accurate description of these properties is particularly important in this current work, wherein one seeks to capture (for example) the thermal behaviour of the specific entropy, which is closely related to the heat capacity.

Fluid mixtures are treated using van der Waals one-fluid mixing with standard combining rules and no further adjustments (*i.e.*, binary-interaction parameters are not employed), as per:

$$\left. \begin{aligned} \sigma_{ij} &= \frac{\sigma_{ii} + \sigma_{jj}}{2} \\ \lambda_{k,ij} - 3 &= \sqrt{(\lambda_{k,ii} - 3)(\lambda_{k,jj} - 3)} \\ \varepsilon_{ij} &= \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \end{aligned} \right\}; k = r, a. \quad (4.3)$$

For further details of mixture modelling the reader is directed to the appendix of Ref. [109].

4.2.2 Alkane and perfluoroalkane fluid models

Given the goal of demonstrating the predictive power of the proposed modelling approach, fluorocarbon mixtures of *n*-perfluorobutane and *n*-perfluorodecane ($n\text{-C}_4\text{F}_{10}$ + $n\text{-C}_{10}\text{F}_{22}$)—for which mixture data is not available in the literature—are considered. The results are also compared with alkane mixtures of *n*-butane and *n*-decane ($n\text{-C}_4\text{H}_{10}$ + $n\text{-C}_{10}\text{H}_{22}$), which are corresponding analogue substances that are particularly well-suited fluids for validating the SAFT-VR Mie approach. Firstly, alkanes are common ORC working fluids [14, 16, 61, 68, 71] and, beneficially, extensive experimental property data are readily available for pure butane and decane, as well as of their mixtures. Alkanes are also non-associating molecules, so they present a useful starting point before proceeding to molecules with higher levels of complexity. From Equation (4.2), the ideal contributions to the SAFT free energy are calculated via ideal-gas specific heat capacities, correlated as polynomial functions of temperature; the coefficients of the polynomials for these working fluids are presented in Table 4.1.

Table 4.1: Coefficients of 3rd order polynomials used to correlate the ideal-gas specific heat capacities $c_p^0(\text{J mol}^{-1} \text{K}^{-1}) = a_0 + a_1T + a_2T^2 + a_3T^3$ as functions of absolute temperature (in Kelvin) for $n\text{-C}_4\text{H}_{10}$, $n\text{-C}_{10}\text{H}_{22}$, $n\text{-C}_4\text{F}_{10}$, and $n\text{-C}_{10}\text{F}_{22}$. The heat capacities are taken from the NIST database. The coefficients are valid between 200 K and 800 K.

Fluid	a_0	$a_1 \times 10$	$a_2 \times 10^4$	$a_3 \times 10^7$
$n\text{-C}_4\text{H}_{10}$	9.487	3.313	−1.108	−0.02822
$n\text{-C}_{10}\text{H}_{22}$	−7.913	9.609	−5.288	1.131
$n\text{-C}_4\text{F}_{10}$	46.37	6.197	−5.165	1.479
$n\text{-C}_{10}\text{F}_{22}$	64.95	17.21	−17.29	6.328

The models for the alkanes and $n\text{-C}_4\text{F}_{10}$ are already available [109]; thus a new model is developed for $n\text{-C}_{10}\text{F}_{22}$. Model parameters are obtained via least-squares minimisation to provide the best description of experimental vapour pressures P_{sat} and saturated-liquid densities ρ_{sat} , as well as single-phase densities ρ (both of the condensed-liquid and the superheated-vapour), and the speed of sound, u . In particular, the following

Working-fluid properties from molecular equations of state

least-squares objective function, comprising the sum of the residuals from each of the considered properties, is minimised:

$$\begin{aligned} \min_{\theta} M = & \frac{w_{P_{\text{sat}}}}{N_{P_{\text{sat}}}} \sum_{i=1}^{N_{P_{\text{sat}}}} \left[\frac{P_{\text{sat},i}^{\text{exp}}(T_i) - P_{\text{sat},i}^{\text{calc}}(T_i; \theta)}{P_{\text{sat},i}^{\text{exp}}(T_i)} \right]^2 + \frac{w_{\rho_{\text{sat}}}}{N_{\rho_{\text{sat}}}} \sum_{i=1}^{N_{\rho_{\text{sat}}}} \left[\frac{\rho_{\text{sat},i}^{\text{exp}}(T_i) - \rho_{\text{sat},i}^{\text{calc}}(T_i; \theta)}{\rho_{\text{sat},i}^{\text{exp}}(T_i)} \right]^2 + \\ & \frac{w_{\rho}}{N_{\rho}} \sum_{i=1}^{N_{\rho}} \left[\frac{\rho_i^{\text{exp}}(T_i; P_i) - \rho_i^{\text{calc}}(T_i; P_i; \theta)}{\rho_i^{\text{exp}}(T_i; P_i)} \right]^2 + \frac{w_u}{N_u} \sum_{i=1}^{N_u} \left[\frac{u_i^{\text{exp}}(T_i; P_i) - u_i^{\text{calc}}(T_i; P_i; \theta)}{u_i^{\text{exp}}(T_i; P_i)} \right]^2. \end{aligned} \quad (4.4)$$

Here, θ represents the vector of parameters of the intermolecular model; the N_j are the numbers of experimental data points, the superscripts ‘exp’ and ‘calc’ refer to experimental data points and calculated values respectively. The w_j are weights attached to each property residual; here all properties are assigned equal weight $w_j = 1$.

The thermodynamic conditions considered for the experimental data are provided in Table 4.2; these were chosen to maintain relevance to the typical operation of an ORC system in a waste-heat recovery application. The resulting intermolecular parameters resulting from the optimisation of the objective function (M) are presented in Table 4.3 and are used for modelling the fluids. The corresponding percentage average absolute deviation AAD (%) of the theoretical calculations from the experimental data for the investigated pure-fluid properties are presented in Table 4.4. The AAD (%) is computed as:

$$\text{AAD (\%)} = \frac{1}{N_p} \sum_{i=1}^{N_p} \left[\frac{X_i^{\text{calc}} - X_i^{\text{exp}}}{X_i^{\text{exp}}} \right] \times 100, \quad (4.5)$$

where X_i^{exp} and X_i^{calc} are the experimental and computed properties respectively, and N_p is the number of experimental data points used in the calculation.

It is noted from the results that the overall deviations are generally low for vapour-liquid equilibria and second-derivative thermodynamic properties. The deviations from the critical temperature and pressure are also low; although not of great importance in this current study (in which the focus is on the subcritical region) this is particularly gratifying as such good descriptions of both critical and subcritical regions are difficult to obtain simultaneously.

4.2.3 SAFT-VR Mie predictions *vs.* experimental data

The effectiveness of the SAFT-VR Mie modelling approach in predicting the thermodynamic properties and phase behaviour of the $n\text{-C}_4\text{H}_{10} + n\text{-C}_{10}\text{H}_{22}$ and $n\text{-C}_4\text{F}_{10} + n\text{-C}_{10}\text{F}_{22}$

Table 4.2: Pressure and temperature ranges of the experimental data considered in the determination of average absolute deviation AAD (%) given in Table 4.4. Experimental data points are taken from the NIST Web thermodynamic tables [205]; the number of experimental data points used for each evaluation is given in parentheses.

Fluid	Vapour liquid equilibria (VLE)		Single-phase properties (compressed liquid and superheated vapour)					
	Temperature range [°C]			Temperature range [°C]			Pressure range [bar]	
	P_{sat}	ρ_{sat}	ρ	u	c_p	ρ	u	c_p
$n\text{-C}_4\text{H}_{10}$	−40 to 150 (39)	−40 to 150 (39)	−40 to 150 (819)	−40 to 150 (819)	−40 to 150 (819)	1 to 50	1 to 50	1 to 50
$n\text{-C}_{10}\text{H}_{22}$	0 to 320 (66)	0 to 320 (66)	0 to 320 (1576)	0 to 320 (1576)	0 to 320 (1576)	1 to 50	1 to 50	1 to 50
$n\text{-C}_4\text{F}_{10}$	−40 to 120 (32)	−40 to 120 (32)	−40 to 120 (741)	−40 to 120 (741)	−40 to 120 (741)	1 to 50	1 to 50	1 to 50
$n\text{-C}_{10}\text{F}_{22}$	0 to 270 (56)	0 to 250 (52)	50 to 260 (1035)	—	30 to 260 (46)	0.1 to 5.2	—	0.2 to 12

Table 4.3: Model parameter values for the pure compounds estimated from experimental single phase and phase equilibrium data using SAFT-VR Mie EoS. Values for the alkanes and n -C₄F₁₀ are taken from Ref. [109]. Values for n -C₁₀F₂₂ were generated for this study starting from the same λ_a value as that of n -C₄F₁₀ and tuning the other parameters to best match experimental data.

Fluid	m	σ [Å]	(ε/k_B) [K]	λ_r	λ_a
n -C ₄ H ₁₀	1.8514	4.0887	273.64	13.650	6.0
n -C ₁₀ H ₂₂	2.9976	4.5890	400.79	18.885	6.0
n -C ₄ F ₁₀	2.1983	4.4495	290.49	24.761	5.7506
n -C ₁₀ F ₂₂	2.8693	5.2581	382.63	26.508	5.7506

Table 4.4: Average absolute deviation AAD (%) from experimental values of selected thermodynamic properties of n -C₄F₁₀ and n -C₁₀F₂₂ obtained with SAFT-VR Mie using model parameters in Table 4.3. Properties considered comprise the vapour pressure P_{sat} , the saturated-liquid density ρ_{sat} , single-phase (liquid and vapour) density ρ , speed of sound u , isobaric heat capacity c_p and the critical conditions (T_c , P_c). (Information relating to the experimental data is provided in Table 4.2.)

Fluid	AAD (%)						
	P_{sat}	ρ_{sat}	ρ	u	c_p	T_c	P_c
n -C ₄ H ₁₀	0.38	0.74	0.37	4.19	1.52	1.73	0.22
n -C ₁₀ H ₂₂	0.80	0.68	0.78	2.55	0.46	1.40	2.14
n -C ₄ F ₁₀	0.57	1.75	1.99	6.69	0.78	0.29	0.79
n -C ₁₀ F ₂₂	0.60	1.56	1.94	—	4.60	0.09	4.07

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systems is illustrated in Figures 4.2 – 4.5. In practice, thermodynamic power cycles such as ORCs are analysed using phase diagrams in T - s or P - h spaces, hence experimental data in these spaces would ideally be required for the validation of the SAFT modelling approach. However, only pure-component (and not mixture) phase-equilibrium data are available for these systems in these representations [13]. Moreover, experimental data in any of P - x , T - x or P - T spaces relating to the n -C₄F₁₀ + n -C₁₀F₂₂ mixture system is not available.

Thermodynamic properties of pure working fluids

Figure 4.2(a) presents the vapour-liquid temperature-density (T - ρ) coexistence envelope for n -perfluorobutane calculated with SAFT-VR Mie. Also included are density isobars (at $P = 2, 5, 20$ and 40 bar). In this (and subsequent figures) symbols represent experimental data (here taken from the NIST Web thermodynamic tables [205]), while curves represent calculations. Similarly, the T - ρ coexistence envelope for n -perfluorodecane and its superheated-vapour isobars are plotted in Figure 4.2(c); note that experimental data are available only for the isobars between 1 bar and 4 bar. The description of the fluid density in all the regions of interest – the subcritical condensed-liquid and superheated-vapour phases as well as the supercritical region – is excellent. This degree of agreement is extremely challenging to achieve using an analytical EoS, and such degree of agreement have hitherto not been reported in literature [13, 18]. It is well known that fluorinated hydrocarbons are difficult to describe with traditional intermolecular potentials, due partly to their high polarisability and the repulsive nature of the electronegative fluorine atoms in the molecules [213].

The specific heat capacities of perfluorobutane as functions of temperature are shown in Figure 4.2(b). The four isobars ($P = 2, 5, 20$ and 40 bar) have similarly been chosen to span both subcritical and supercritical regions and both condensed-liquid and superheated-vapour regions. Although slight deviations are recorded close to the critical region, once again the descriptions obtained with the SAFT-VR Mie EoS are in very good agreement with the available experimental data; this highlights the predictive power of the EoS (since these data were not included in the refinement of the model parameters). Experimental data relating to the specific heat capacity of perfluorodecane are available only for the saturated-liquid phase. These have been plotted along with the calculations obtained by SAFT-VR Mie in Figure 4.2(d). Once again, the calculations are in good agreement with the available experimental data.

Working-fluid properties from molecular equations of state

In Figure 4.3 similar thermophysical properties of the alkane analogues—*n*-butane and *n*-decane are presented. Here, the isobaric specific heat capacities and densities (including the vapour-liquid saturation densities) calculated with SAFT-VR Mie are substantiated with experimental data from NIST. The descriptions of these pure-fluid properties provided by SAFT-VR Mie are seen to be consistent with the experimental data. It is clear from Figures 4.2 and 4.3 that SAFT-VR Mie provides an excellent description of the thermodynamic properties of each of the four pure components considered in this study.

Thermodynamic properties of binary-mixture working fluids

The properties of binary mixtures of the two alkanes, and of the two perfluoroalkanes can now be studied. In the first instance, the properties of the mixtures of *n*-perfluorobutane and *n*-perfluorodecane are considered; the compositions of the mixtures are arbitrary and chosen simply to span the range between the two pure components.

First, the SAFT-VR Mie description of the alkane mixtures ($n\text{-C}_4\text{H}_{10} + n\text{-C}_{10}\text{H}_{22}$) in P - T - x space is provided; incorporated with this are the experimental data available in these spaces. Presented in Figure 4.4(a) are the P - T vapour-pressure curves for *n*-butane ($x_{\text{C}_4\text{H}_{10}} = 1$) and *n*-decane ($x_{\text{C}_4\text{H}_{10}} = 0$) calculated with SAFT-VR Mie, interspersed with constant-composition P - T bubble-point curves of their mixtures. The dew-point curves have been omitted to give clarity to the figure. Experimental data from three sources – the NIST database, and from Refs. [214] and [215] – are also included for the purpose of comparison. It should be noted that the experimental bubble-point data for the mixtures (from Refs. [214] and [215]) span only a section of the P - T phase envelopes whereas the SAFT calculations represent the whole of the bubble curve to enable a better description of the transition between the two pure components. Isothermal P - x envelopes were also calculated with SAFT-VR Mie (which captures both bubble- and dew-point descriptions); these are presented in Figure 4.4(b) together with experimental measurements of Ref. [216]. In both Figure 4.4(a) and 4.4(b), the calculations provide an excellent description of the phase equilibria in the P - T and P - x spaces, both for the pure components and their mixtures. The slight disagreement in the critical region is expected here as it is well known (see, *e.g.*, Refs. [217, 218]) that analytical EoS cannot simultaneously capture both the critical and subcritical regions; nevertheless the description from SAFT-VR Mie remains very good.

Vapour-pressure curves for *n*-perfluorobutane ($x_{\text{C}_4\text{F}_{10}} = 1$) and *n*-perfluorodecane ($x_{\text{C}_4\text{F}_{10}} = 0$), and P - T envelopes of their mixtures calculated with SAFT-VR Mie are presented in Figure 4.4(c). Corresponding pure-component experimental data are also

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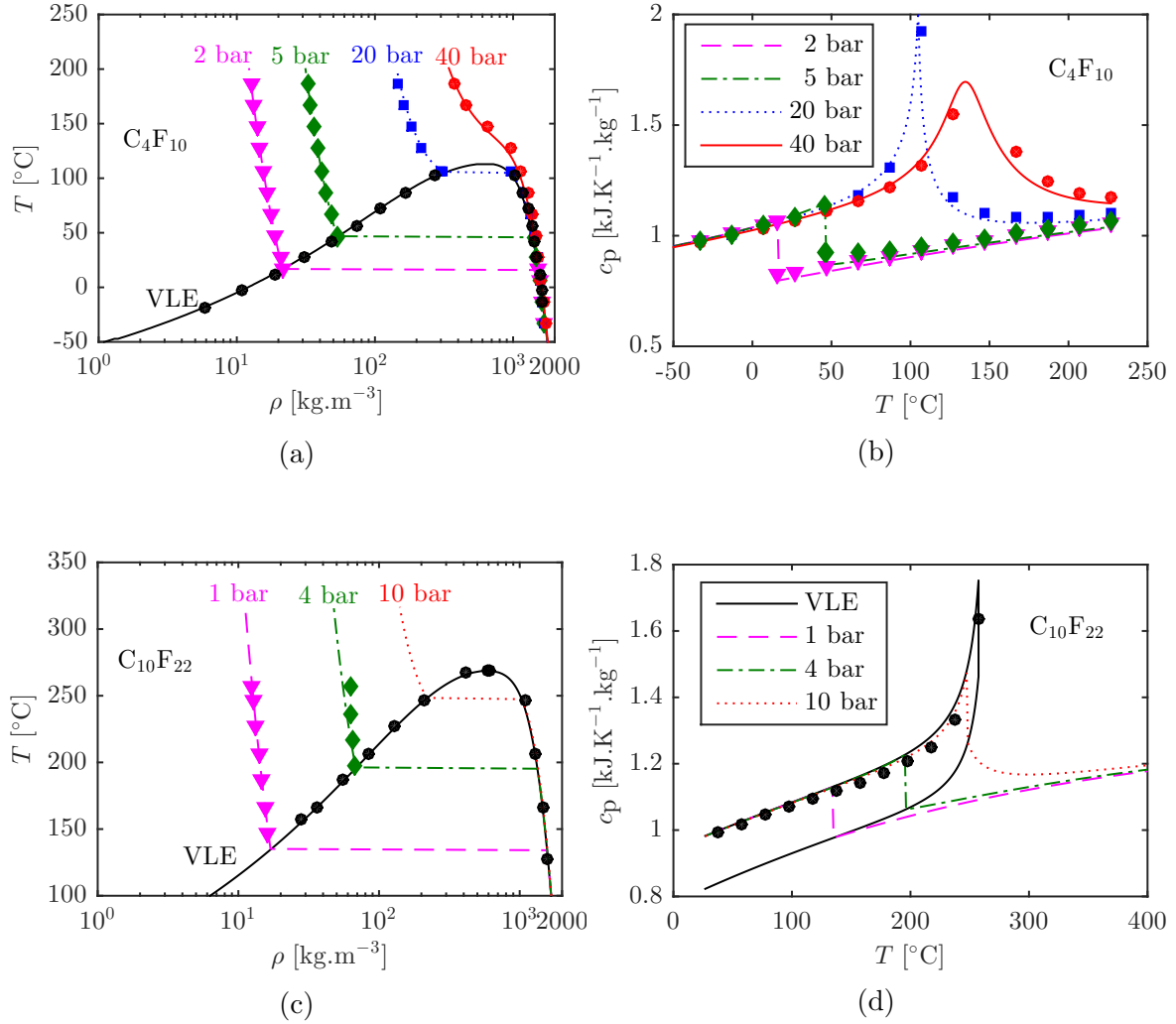


Figure 4.2: Selected thermodynamic properties of n -perfluorobutane and n -perfluorodecane: (a) vapour-liquid T - ρ coexistence envelopes and density isobars (at indicated pressures) for n -perfluorobutane; (b) temperature dependence of the isobaric heat capacity c_p of n -perfluorobutane; (c) vapour-liquid T - ρ coexistence envelopes and density isobars for n -perfluorodecane; (d) vapour-liquid c_p - T coexistence envelopes and temperature dependence of the isobaric heat capacity c_p of n -perfluorodecane. Comparison of experimental data from NIST (symbols) with the description obtained using SAFT-VR Mie EoS (continuous curves).

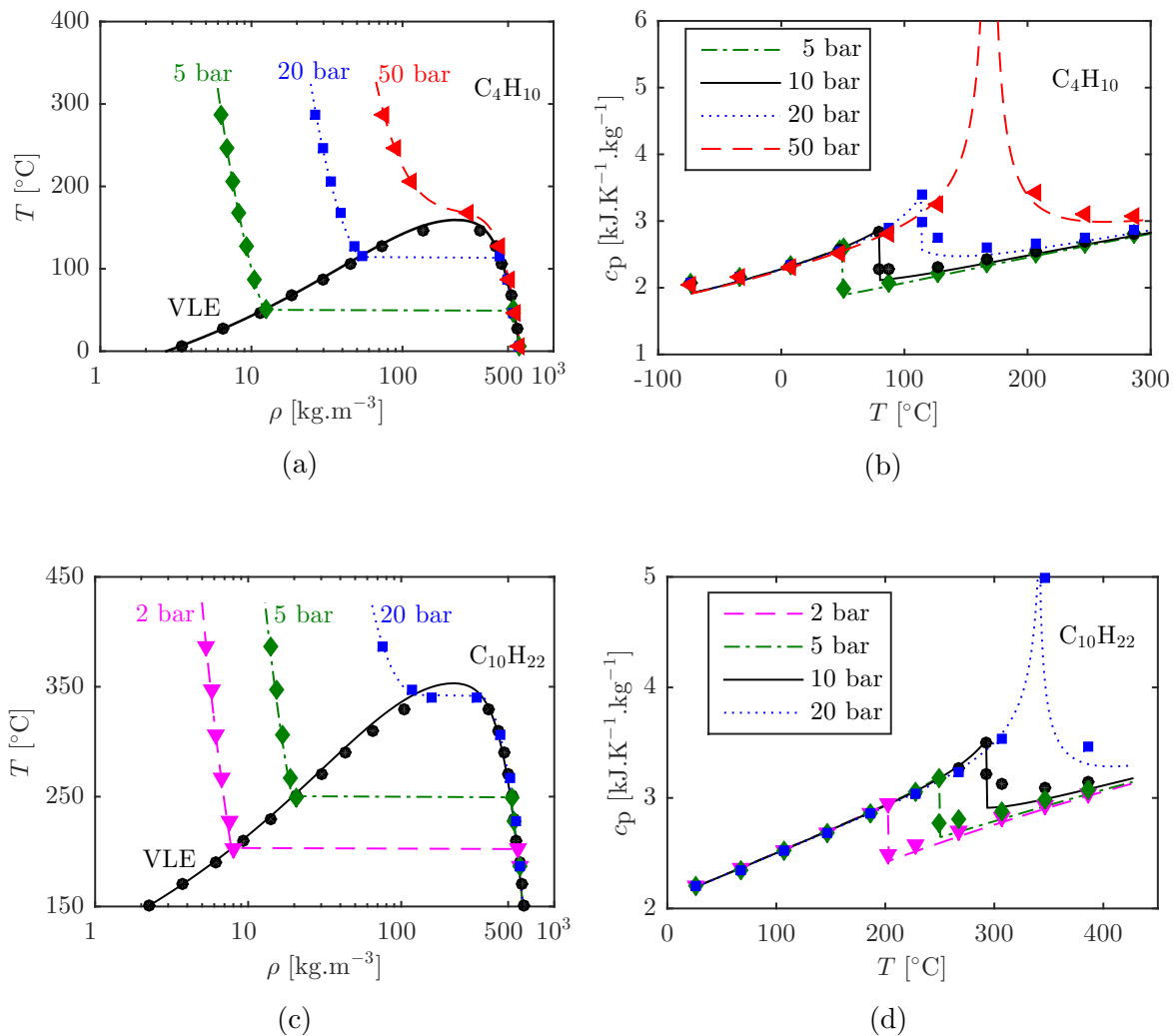


Figure 4.3: Selected thermodynamic properties of n -butane and n -decane: (a) vapour-liquid T - ρ coexistence envelopes and density isobars (at indicated pressures) for n -butane; (b) temperature dependence of the isobaric heat capacity c_p of n -butane; (c) vapour-liquid T - ρ coexistence envelopes and density isobars for n -decane; (d) temperature dependence of the isobaric heat capacity c_p of n -decane. Comparison of experimental data from NIST (symbols) with the description obtained using SAFT-VR Mie EoS (continuous curves).

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provided for comparison; mixture data for these fluids are unavailable at present. The SAFT-VR Mie calculations provide a very good representation of the pure-component phase equilibria in this space. Although there are no experimental data to validate the P - T envelopes of the perfluoroalkane mixtures, one can visually discern (from Figure 4.4(a)) that the plotted envelopes follow a similar trend to that seen for the alkane mixtures, which was substantiated by experimental data. This therefore provides confidence that the vapour-liquid predictions for the perfluoroalkane mixtures provided by SAFT-VR Mie conforms to the same degree of accuracy as the description of their alkane analogues.

This section is concluded by verifying the ability of SAFT-VR Mie in predicting the phase equilibria of the alkane mixtures and their perfluoroalkane analogues in T - s and P - h spaces, which are crucial for the purposes of the thermodynamic analyses required in the description of low-temperature heat engines. In Figure 4.5(a), predicted phase envelopes for both pure n -perfluorobutane and pure n -perfluorodecane are presented in T - s space, together with those of intermediate mixtures comprising 30 mol%, 60 mol%, 80 mol% and 90 mol% n -perfluorobutane in order to illustrate the crossover in the phase behaviour between the two pure components. Also provided are the experimental phase-envelopes for each of the pure components (from the NIST database), as indicated by the symbols. These phase envelopes are also provided in P - h space (for both pure fluids, 30 mol%, 50 mol% and 80 mol% n -perfluorobutane) in Figure 4.5(b), once again incorporating experimental pure-component data from NIST. (N.B.: The reference state for the data in Figure 4.5 is defined by $h = 0$ and $s = 0$ at the saturated liquid temperature $T = 273.16$ K.) The phase envelopes (both calculated and experimental in T - s and P - h) of n -butane, n -decane and their mixtures are also provided in Figure 4.5(c) and 4.5(d). The agreement between the calculated and experimental pure-component phase envelopes in these figures is very promising, especially when one takes into account that these experimental data were not considered during the refinement of the molecular model parameters (*i.e.*, m , σ , ε , λ_r and λ_a).

Overall, the quality and consistency of agreement between the SAFT-VR Mie predictions and the experimental data for the pure components illustrated in Figures 4.2 through 4.5 emphasises the predictive power of the proposed modelling approach, and provides confidence in the reliability of the thermodynamic-property predictions for the mixtures (for which the analogous experimental P - h and T - s phase envelopes are not readily available). Furthermore, the predictive performance of the approach for the alkane mixtures in P - T space is considered excellent, as is the performance for the same fluids in the P - h and T - s spaces. Unfortunately, as stated earlier, carrying out the same validation for the per-

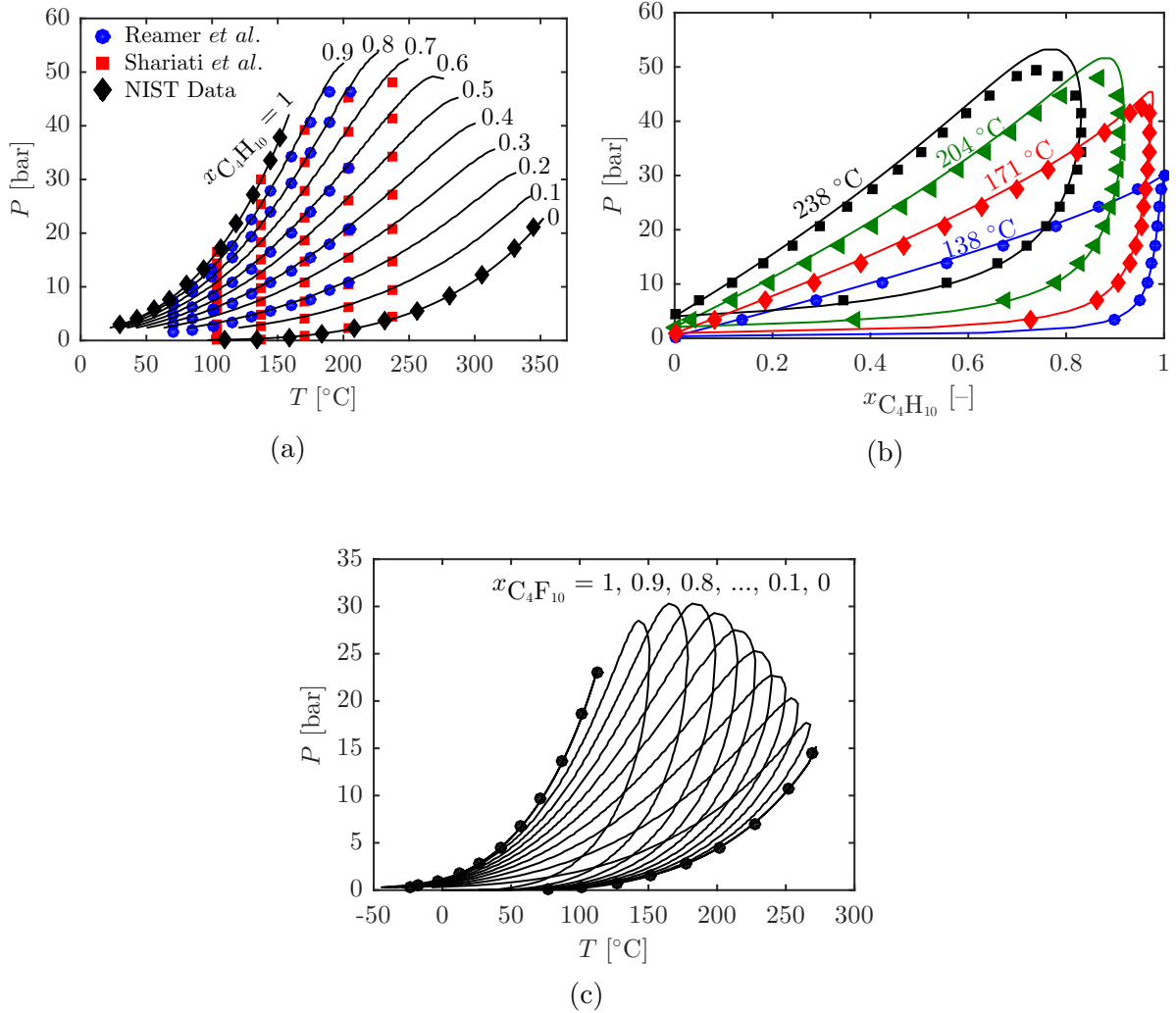


Figure 4.4: Vapour-liquid equilibria of selected fluid mixtures. (a) Constant-composition pressure-temperature (P - T) phase boundaries (bubble-point curves) as predicted using SAFT-VR Mie (curves) for pure n -butane ($x_{C_4H_{10}} = 1$) and n -decane ($x_{C_4H_{10}} = 0$), and intermediate binary mixtures (with composition as indicated). Validation data from the NIST database (for n -butane and n -decane) and from Refs. [214, 215] (for the mixtures) are indicated by the symbols. (b) Isothermal pressure-composition (P - x) phase boundaries (saturation curves) as predicted using SAFT-VR Mie (curves). Validation data for each of the isotherms (from Ref. [216]) are indicated by the symbols. (c) Constant-composition P - T phase boundaries as predicted using SAFT-VR Mie (curves) for pure n -perfluorobutane ($x_{C_4F_{10}} = 1$) and pure n -perfluorodecane ($x_{C_4F_{10}} = 0$), and intermediate binary mixtures with validation data taken from the NIST database.

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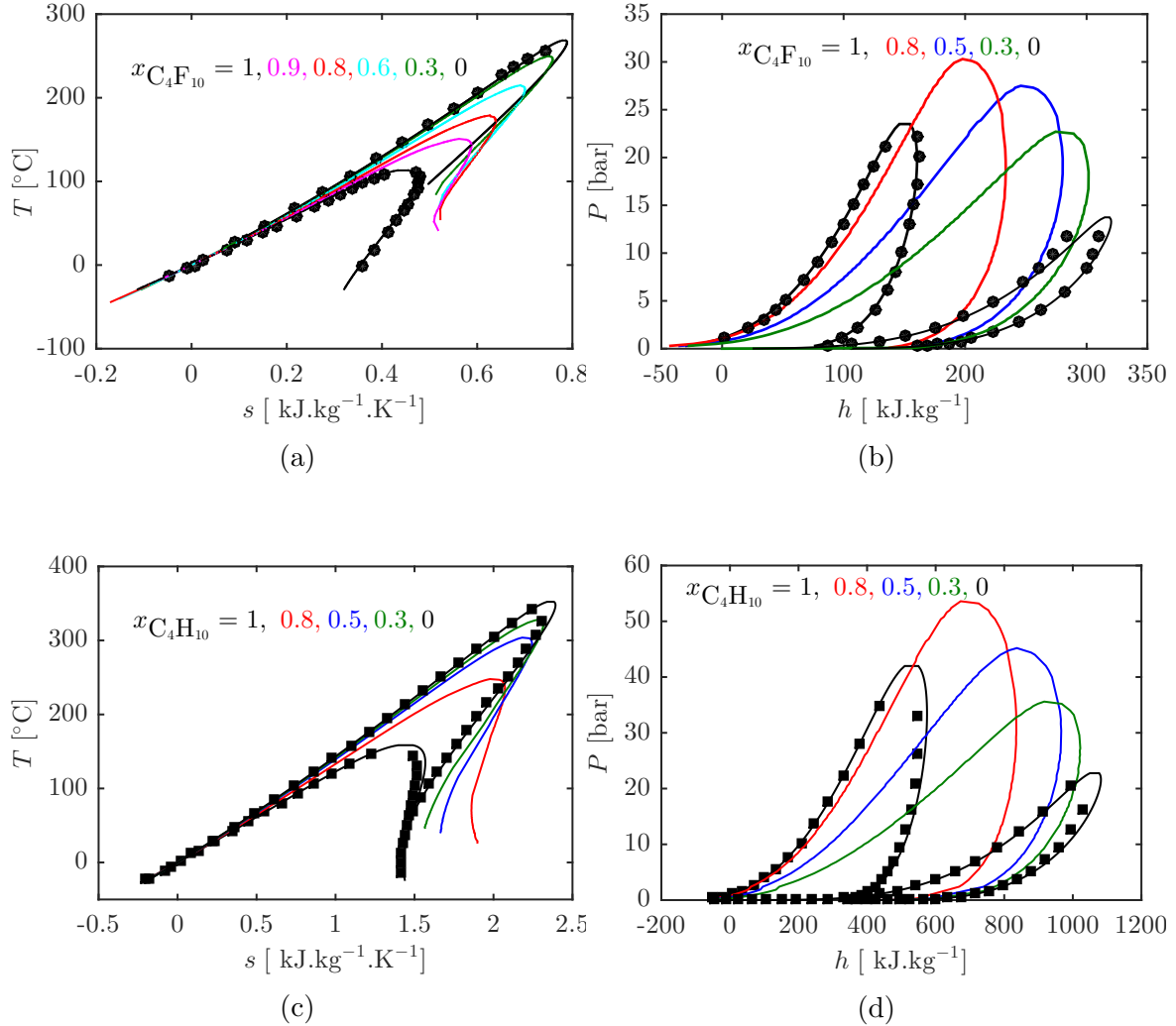


Figure 4.5: Temperature-specific entropy ($T-s$) and pressure-specific enthalpy ($P-h$) phase boundaries (saturation curves) as predicted using SAFT-VR Mie (curves) for pure working fluids and mixtures. (a) $T-s$ envelopes for pure n -perfluorobutane, pure n -perfluorodecane, and intermediate binary mixtures comprising 30 mol%, 60 mol%, 80 mol% and 90 mol% n -perfluorobutane. (b) $P-h$ envelopes for pure n -perfluorobutane, pure n -perfluorodecane, and mixtures comprising 30 mol%, 50 mol% and 80 mol% n -perfluorobutane. (c) $T-s$ envelopes for pure n -butane, pure n -decane, and intermediate binary mixtures comprising 30 mol%, 50 mol% and 80 mol% n -butane. (d) $P-h$ envelopes for pure n -butane, pure n -decane, and intermediate binary mixtures comprising 30 mol%, 50 mol% and 80 mol% n -butane. Validation data for the pure components (from the NIST database) are indicated by the symbols.

fluoroalkane mixtures is not possible due to the lack of experimental data. Nevertheless, given that the perfluoroalkanes are structural analogues of the well-validated alkanes and the similarity exhibited in the results of the two chemical classes throughout Figures 4.2 to 4.5, the results suggest that the predictions of the required thermodynamic data of the perfluoroalkane mixtures will also be appropriate. One of the primary purposes of this study is to provide a method by which predictions of working-fluid properties (pure and mixtures), especially in the T - s and P - h spaces, can be made with relative reliability, even in the absence of experimental data. In summary, the results in this section give confidence that this is the case, at least for the classes of chemical compounds that were considered here as working fluids.

4.2.4 SAFT- γ Mie group-contribution equation of state

With the SAFT-VR Mie EoS, accurate thermodynamic descriptions of working fluids can be achieved once the underlying models have been developed. To use this equation of state in CAMPD problems, the model parameters (*i.e.*, m , σ , ε , λ_r and λ_a) would need to be included in the set of decision variables along with the process design variables in the (non-linear programming, NLP) optimisation problem. While this demonstrates that it may be applicable to CAMPD problems, this equation of state may be limited in application because the set of model parameters (which represents only one working fluid) would in general, not point to any known working fluid. It is only in a rare and exceptional case that the optimal parameters will be close enough to that of a known working fluid. This implies that one needs to go through a process of deciphering the yet unknown working fluid that is being described by those suggested parameters – a particularly onerous task given that a large number of experiments and parameter estimation would be required. Thus, the SAFT-VR Mie EoS does not offer the needed flexibility in deriving non-conventional and novel working fluids.

Alternatively, a group-contribution equation of state predicts the thermodynamic properties of a working fluid based on the molecular groups from which it is composed. Examples of molecular groups relevant to this work are single-bonded hydrocarbon groups such as $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $>\text{C}<$, and double-bonded hydrocarbon groups such as $=\text{CH}_2$, $=\text{CH}-$ and $=\text{C}<$, which can be used to construct a wide range of alkane and alkene working fluids. As highlighted in Section 2.5.3, these groups form a much smaller set than the set of individual fluids they constitute – *e.g.*, the entire fluid family of normal alkanes (excluding methane) is composed of only two groups, *i.e.*, $-\text{CH}_3$, and $>\text{CH}_2$ groups. Group-contribution methods have been available for decades [125]. However,

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these methods only provide important parameters such as the critical temperature and critical pressure, rather than providing all of the thermodynamic properties required to evaluate a thermodynamic system. Instead, the SAFT- γ Mie group-contribution EoS is used here, especially because of its strong foundation in statistical mechanics.

In a similar manner to SAFT-VR Mie, the SAFT- γ Mie EoS describes the interaction between two molecular groups using a Mie potential [140], where the group parameters retain their previous definitions as in the case of SAFT-VR Mie. Additional parameters for the molecular group description are the number of identical segments comprising a group, v^* , and the shape factor, S . The shape factor is a key parameter of the SAFT- γ Mie methodology that characterises the extent to which the segments of a given group contribute to the overall molecular properties [140]. Intermolecular parameters for pure fluids (based on the hetero-nuclear molecular model) are derived from the contributions of the different groups that make up the molecule using combining rules. The required thermodynamic properties of such fluids are then derived via the Helmholtz free energy (see Equation (4.2)) using standard thermodynamic relations.

SAFT- γ Mie parameters (including the ‘like’ and ‘unlike’ interaction parameters) for various molecular groups are available in published literature (*e.g.*, in Dufal *et al.* [159]) including the $-\text{CH}_3$, $>\text{CH}-$ and the $>\text{CH}_2$ groups that are important for the description of hydrocarbon working fluids chosen in the present ORC study. These parameters were derived by regression to experimental pure-component vapour-liquid equilibrium data. In Figure 4.6 thermodynamic properties of pure alkanes and bubble-point curves of the n -butane + n -decane system generated using SAFT- γ Mie are presented; these are compared with experimental data from the NIST database. It is clear that the SAFT- γ Mie group contribution EoS gives an accurate property description of both pure fluids and the mixture thereby giving confidence that the SAFT methodology can be extended to other candidate working fluids for which the molecular/group parameters are yet to be derived. This is especially remarkable as the properties (enthalpies and entropies) plotted in Figure 4.6 were not used in the estimation of the group model parameters.

Important groups yet to be modelled include those associated with refrigerants, other halogenated hydrocarbons and siloxanes (*e.g.*, $-\text{CF}_3$, $>\text{CF}_2$ and $>\text{CCl}-$ groups). Once these are accounted for within the SAFT- γ Mie group contribution framework, they will be included in the database of candidate groups for working fluid design, thus enabling a larger and more rigorous design set for the CAMPD approach.

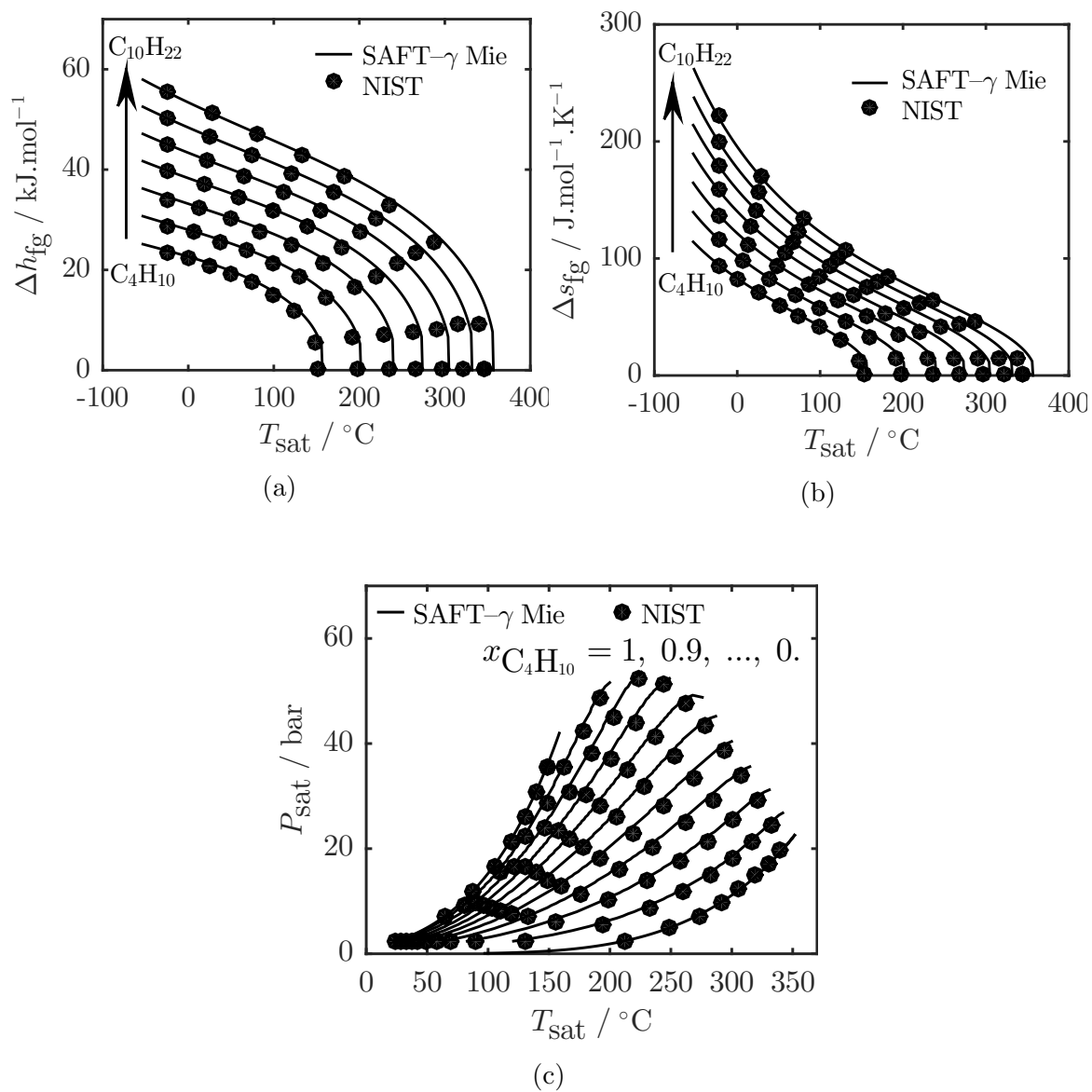


Figure 4.6: Thermodynamic properties of alkanes and their mixtures predicted with the SAFT- γ Mie EoS (curves) in comparison with NIST experimental data (filled circles). (a) Phase change enthalpies of *n*-alkanes from *n*-methane to *n*-decane; (b) Phase change entropies of *n*-alkanes from *n*-methane to *n*-decane; (c) P - T bubble-point curves of pure *n*-butane and pure *n*-decane interspersed with those of their mixtures.

4.2.5 Molecular feasibility constraints

With the SAFT- γ Mie EoS and other group contribution methods in general, there is the flexibility to combine the available molecular groups as one sees fit as these methods will generate results for a number of combinations of groups (*e.g.*, non-integer numbers of groups can be combined to generate an ‘impossible’ molecule). Thus, one has to ensure that the combinations attempted correspond to real molecules; in the first instance, the molecules must be combined in integer quantities. These integer amounts of molecular groups in essence make the CAMPD problem to result in a mixed integer non-linear optimisation problem (MINLP). Aside from the integer requirement on the number of molecular groups, in constructing a molecule from molecular groups, rules of stoichiometry and valence must be obeyed.

To ensure that a generated set of molecular groups represents a genuine molecule, it is therefore necessary to introduce molecular feasibility constraints. In this study, non-cyclic molecules of single and double-bonded hydrocarbon groups are considered. The first constraint—the well-known ‘octet-rule’ [123]—ensures that all free attachments of a group are occupied in a bond. This implies:

$$\sum_i n_i \times (2 - \nu_i) = 2m, \quad (4.6)$$

where n_i is number of group i present, and ν_i is the valency of group i that is defined as the number of other groups to which that group can attach; *e.g.*, the valency of both $-\text{CH}_3$ and $=\text{CH}_2$ is one, whilst the valency of $>\text{CH}_2$ and $=\text{CH}-$ is two and so on ($-$, $>$ and $=$ represent one single bond, two single bonds and one double bonds respectively). $m = 1, 0$ or -1 for non-cyclic, monocyclic and bicyclic groups, respectively. It is also required that each group with a double bond has another double bond to which it can attach, hence:

$$\sum_i n_i d_i = 2j \quad \text{where } j = \{0, 1, 2, \dots\}, \quad (4.7)$$

where $d_i = 1$ if group i contains a double bond, and $d_i = 0$ otherwise.

In addition to this, the number of groups linked by only one double bond (*i.e.*, $=\text{CH}_2$) must be less than or equal to the number of groups linked by one double bond and additional single bonds (*i.e.*, $=\text{CH}-$). In addition to the constraints listed here, molecular constraints for triple-bonded and cyclic molecules have also been developed and implemented within the CAMPD-ORC model. These constraints will become important in

future studies when the analysis presented here is extended to include the groups that make up these molecules.

To validate the molecular feasibility constraints a simple study has been completed in which the number of each group is varied between 0 and 4, and the molecular constraints are applied. Considering the $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $>\text{C}<$, $=\text{CH}_2$ and $=\text{CH}-$ groups this corresponds to a total of $5^6 = 15,625$ combinations. After applying the molecular constraints this results in a total of 320 feasible working fluids. Upon a manual inspection of these results it was observed that these 320 working-fluids included all the expected hydrocarbon families such as *n*-alkanes, methyl alkanes, 1-alkenes, 2-alkenes, alongside less typical, but chemically feasible combinations, thus validating the molecular feasibility constraints.

4.3 Transport property prediction from group contribution methods

A key step in the sizing of heat exchangers is the estimation of the heat transfer coefficients for the different fluid phases as illustrated in Section 2.1.2. This process relies heavily on various experimentally-derived correlations which are functions of well-established dimensionless numbers, *e.g.*, the Nusselt and Prandtl numbers. These numbers are ratios of combinations of thermodynamic and transport properties, including their thermal conductivity and dynamic viscosity. While the SAFT-based equations of state [109, 160] can reliably provide the required thermodynamic properties, they do not allow for the calculation of fluid transport properties.

Thus, the required transport properties, specifically the dynamic viscosity, thermal conductivity and surface tension, have to be predicted by other means. While there are numerous property-estimation methods, for example those detailed in Ref. [212], the methods to be used for this work need to fulfil certain criteria. Firstly, the methods should be applicable to a large number of fluids and homologous series. Also, they should be fairly straight-forward to implement; methods that require solving for roots of equations and/or solving differential equation may not be appropriate here. In particular, transport-property prediction methods that incorporate molecular group-contribution approaches are sought, in line with the motivation and modelling objective and framework in this work. Methods that are found suitable for the hydrocarbon working fluids considered within this study (*n*-alkanes, methylalkanes and alkenes) are summarised below.

4.3.1 Necessary thermodynamic properties

The transport-property prediction methods that will be highlighted below are generally empirical correlations, that incorporate elements of group-contribution approaches, and in some instances rely on thermodynamic quantities such as the normal boiling temperature, molecular weight and molar densities. Also, these methods generally consider the specific fluid phases (liquid or vapour phase respectively) and as such an equation of state will be required for the prediction of these quantities. Correlations for estimating the vapour-phase thermal conductivity require the constant-volume specific heat capacity (c_v) and vapour density which are obtainable from the SAFT- γ Mie equation of state as functions of temperature and pressure (and composition, for mixtures).

Another thermodynamic quantity that is required is the normal boiling temperature, T_b , or its reduced form, $T_{b,r} = T_b/T_{cr}$. While experimental values of T_b are available, they can also be obtained easily from SAFT- γ Mie to a high degree of accuracy. This high degree of accuracy is made possible because experimental P - T saturation data are used for the estimation of model parameters for the molecular groups. Similarly, experimental values of single-phase densities can be accurately predicted by SAFT- γ Mie because these values were used in the estimation of the group-contribution model parameters.

Other required thermodynamic quantities include the critical temperature T_{cr} , pressure P_{cr} and volume V_{cr} , and the acentric factor. When using the SAFT- γ Mie equation of state within gPROMS there is currently no supported method for determining the critical properties; instead, the critical point can be determined manually by constructing the vapour-pressure curve. Therefore it is necessary to implement an alternative group-contribution method. P_{cr} (in bar), T_{cr} (in K) and V_{cr} (in cm^3/mol) are estimated from the Joback and Reid correlations [125]:

$$P_{cr} = \left(0.113 + 0.0032n_A - \sum_i P_{cr,i} \right)^{-2}, \quad (4.8)$$

$$T_{cr} = T_b \left[0.584 + 0.965 \sum_i T_{cr,i} - \left(\sum_i T_{cr,i} \right)^2 \right]^{-1}, \quad (4.9)$$

and

$$V_{cr} = 17.5 + \sum_i V_{cr,i}, \quad (4.10)$$

where n_A is the total number of atoms in the molecule, T_b is the normal boiling temperature obtained from SAFT- γ Mie, and $P_{cr,i}$, $T_{cr,i}$ and $V_{cr,i}$ are the individual critical pressure, critical temperature and critical volume contributions from each molecular group i . The contributions for each group considered can be found in Ref. [125].

The predictions made using the Joback and Reid method have been compared to NIST data for the alkane and alkene working fluids available in the NIST database. Furthermore, the critical pressures of these working fluids have also been obtained manually using SAFT- γ Mie. The results from this analysis are shown in Figure 4.7. In addition, the absolute deviations of the critical properties predicted by the group contribution methods from experimental values are presented in Table 4.5. The critical temperatures is generally predicted to a high degree of accuracy, with the deviations less than $\pm 0.5\%$ for all but three of the hydrocarbon working fluids considered; similarly the critical pressures are predicted to less than 4%.

From Figure 4.7 it is observed that for all the fluids considered the Joback and Reid method agrees with the NIST data to within $\pm 10\%$, thus confirming that the Joback and Reid is sufficiently accurate to determine the critical pressure of alkane and alkene working fluids. The difference between SAFT- γ Mie and NIST is greater, with SAFT- γ Mie, on average, over predicting the critical pressure by 10%. However, this is not considered a problem since SAFT- γ Mie over predicting the critical pressure actually helps the numerical stability of the optimisation process. For example, if a maximum limit of $P_r = 0.85$ is applied during an optimisation and P_{cr} is obtained using the Joback and Reid method, the resulting maximum pressure will be lower than the critical pressure predicted by SAFT- γ Mie, thus ensuring the calculation will not fail.

While other methods exist for estimating the critical properties, they are either less accurate or do not have the same type of group classifications required in this work. An example is the method of Constantinou and Gani [219] which uses olefinic groups of the $\text{CH}_2=\text{CH}-$, $-\text{CH}=\text{CH}-$, $\text{CH}_2=\text{C}<$, $-\text{CH}=\text{C}<$ and $>\text{C}=\text{C}<$ types, as opposed to the $=\text{CH}_2$, $=\text{CH}-$, $=\text{C}<$ and $=\text{C}=\text{C}$ groups considered within this current work. In addition, this method shows large errors in estimating the critical properties of compounds with a low number of carbon atoms such as ethane and propane.

The only other required quantity is the acentric factor (ω), which is estimated by solving the Pitzer vapour pressure expansion:

$$\ln P_{vp,r} = f^{(0)} + \omega f^{(1)} + \omega^2 f^{(2)}, \quad (4.11)$$

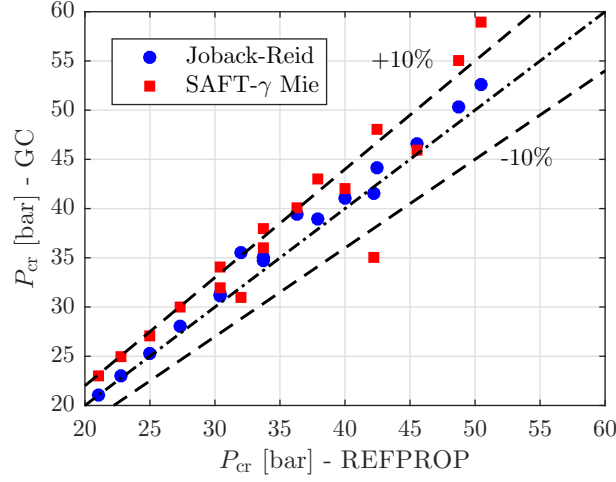


Figure 4.7: A comparison between the critical pressures obtained using Joback and Reid, SAFT- γ Mie and NIST REFPROP for the alkane and alkene working-fluids available in NIST REFPROP.

for ω , at the atmospheric pressure and normal boiling temperature, and ignoring the quadratic term which has been shown to have no effect on the result [212]. This results in the expression:

$$\omega = -\frac{\ln(P_{\text{cr}}/1.01325) + f^{(0)}}{f^{(1)}}, \quad (4.12)$$

where $f^{(0)}$ and $f^{(1)}$, at the normal boiling temperature, are given by Ambrose and Walton [220] as:

$$\begin{aligned} f^{(0)} &= \frac{-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5}{T_{\text{b,r}}}; \\ f^{(1)} &= \frac{-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5}{T_{\text{b,r}}}; \end{aligned} \quad (4.13)$$

with $\tau = 1 - T_{\text{b,r}}/T_{\text{cr}}$ and $T_{\text{b,r}} = T_{\text{b}}/T_{\text{cr}}$.

Using the estimated critical properties from the Joback and Reid correlations (Equations (4.8) and (4.9)), acentric factor predictions from Equation (4.12) were compared with those from the original Pitzer *et al.* definition ($\omega = -\log_{10} \left[\lim_{(T/T_{\text{cr}})=0.7} P_{\text{vp}}/P_{\text{cr}} \right] - 1.0$ [221], also made using the predicted critical properties) for the hydrocarbon fluids in this section. Both sets of predictions were quite close to the true values of ω (*i.e.*, those obtainable from the Pitzer *et al.* definition, but using experimental values of the critical properties), with the percentage deviation less than 5.0% for most of the fluids. However, using Equation (4.12) generally resulted in predicted ω values with lower percentage deviations than those made using the Pitzer *et al.* definition with estimated critical prop-

erties. With these thermodynamic properties provided, the required transport properties can then be estimated.

4.3.2 Dynamic viscosity

Liquid dynamic viscosity

The dynamic viscosities of liquid n -alkanes can be accurately predicted by the Joback and Reid group contribution method [125] which uses a two-parameter equation to describe the temperature dependency of the dynamic viscosity:

$$\eta_L = M \exp \left[\left(\sum_i \eta_{a,i} - 597.82 \right) / T + \sum_i \eta_{b,i} - 11.202 \right], \quad (4.14)$$

where η_L is the liquid viscosity in units of Pa·s and M is the molecular weight of the molecule. The contributions from each group ($\eta_{a,i}$ and $\eta_{b,i}$) considered here can be found in Joback and Reid [125]. This method however gives predictions with large errors for the liquid viscosities of branched alkanes. For these molecules, an alternative method, the Sastri-Rao method [222] is employed. The pure-liquid viscosity in units of mPa·s is calculated with the equation:

$$\eta_L = \sum_i \eta_{B,i} \times P_{vp}^{-[0.2 + \sum_i N_i]}. \quad (4.15)$$

The values for the group contributions to determine the summations above are given in Ref. [222]. The contributions are generally cumulative, except for the case of $\sum_i N_i$ where the contributions from each functional group are taken only once (*e.g.*, in 2-methylpentane, the contributions from the $-\text{CH}_3$ groups are taken once, not three times while those from the $-\text{CH}_2$ groups are also taken once instead of twice). The vapour pressure (P_{vp} , in atm) is calculated as a function of the normal boiling point, T_b :

$$\ln P_{vp} = (4.5398 + 1.0309 \ln T_b) \times \left(1 - \frac{(3 - 2T/T_b)^{0.19}}{T/T_b} - 0.38(3 - 2T/T_b)^{0.19} \ln(T/T_b) \right). \quad (4.16)$$

The switch between the Joback and Reid method and the Sastri-Rao method for alkanes can be easily implemented by employing the Sastri-Rao method when the number of $-\text{CH}_3$ groups is three or greater and using the Joback and Reid method otherwise.

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Vapour dynamic viscosity

For the vapour phases, the dynamic viscosities (in microPoise, 1 Poise = 0.1 Pa·s) are calculated using the corresponding states relation suggested by Reichenberg [223, 224]:

$$\eta_V = \frac{M^{1/2}T}{\sum_i n_i C_i [1 + (4/T_{cr})][1 + 0.36T_r(T_r - 1)]^{1/6}} \times \frac{T_r(1 + 270\mu_r^4)}{T_r + 270\mu_r^4}, \quad (4.17)$$

where n_i represents the number of groups of the i^{th} type and C_i is the group contribution available from Refs. [223, 224]. μ_r is the reduced dipole moment and $T_r = T/T_{cr}$ is the reduced temperature. For high pressure fluids, a correction factor is provided by Reichenberg [225, 226]:

$$\frac{\eta_V}{\eta_{V,0}} = 1 + Q \frac{AP_r^{3/2}}{BP_r + (1 + CP_r^D)^{-1}}. \quad (4.18)$$

The constants A , B , C and D are functions of T_r as shown below and $\eta_{V,0}$ is the vapour viscosity at the same temperature and low pressure from Equation (4.17). $Q = 1 - 5.655\mu_r$; $Q = 1.0$ for non-polar molecules.

$$\begin{aligned} A &= \frac{1.9824 \times 10^{-3}}{T_r} \exp[5.2683T_r^{-0.5767}] ; & B &= A(1.6552T_r - 1.2760) ; \\ C &= \frac{0.1319}{T_r} \exp[3.7035T_r^{-79.8678}] ; & D &= \frac{2.9496}{T_r} \exp[2.9190T_r^{-16.6169}] . \end{aligned} \quad (4.19)$$

These equations should be used with caution as C and D approach infinity at low values of T_r .

Another applicable method for the estimation of vapour viscosity is that of Chung *et al.* [227, 228], including their modification for high-pressure systems. This method however requires special correction factors that are compound specific and, as such, does not fit well with the group-contribution basis of this work.

The predicted dynamic viscosities from the aforementioned group-contribution theories (for both the liquid and vapour phases) are compared with the available pseudo-experimental values from the NIST REFPROP database at temperatures between 0 °C and 400 °C. The comparisons for the n -alkanes, the methyl alkanes and the alkenes are presented in Figure 4.8; only the few methyl alkanes and alkenes available in REFPROP have been presented here. The n -alkanes and methyl alkanes are in the subcooled liquid state at lower temperatures and in the superheated vapour state at higher temperatures (> 200 °C) while the alkenes are in the vapour state at all temperatures. The predic-

tions from the group-contribution methods are seen to be in good agreement with the experimental data from REFPROP. The vapour-phase viscosities are predicted by the Reichenberg relation in Equation (4.17) while the liquid-phase viscosities are predicted with the Joback and Reid method in Equation (4.14), with the exception of those of the methyl alkanes which are predicted with the Sastri-Rao method in Equation (4.15).

4.3.3 Thermal conductivity

Liquid thermal conductivity

Most estimation techniques for the thermal conductivity of liquids are empirical in nature. Two methods, the Latini *et al.* method [229–231] and the Sastri method [232] often appear rather accurate [212]. Latini and coworkers suggested a correlation requiring specific parameters for various classes of organic compound and specific parameters for various compounds [231]. This makes the correlation inconvenient for a group-contribution calculation; the Sastri method, however, allows for group contributions to the thermal conductivity:

$$\lambda_L = \sum_i \lambda_{b,i} \times a^m, \quad (4.20)$$

where:

$$m = 1 - \left(\frac{1 - T_r}{1 - T_{b,r}} \right)^n, \quad (4.21)$$

with $a = 0.856$ and $n = 1.23$ for alcohols and phenols, or $a = 0.16$ and $n = 0.2$ for other compounds, and $\lambda_{b,i}$ (in units of W/(m·K)) is the group contribution to the thermal conductivity at the normal boiling point; these values are available in Ref. [232].

For hydrocarbon compounds when the number of carbon atoms (C_n) is less than 5, a correction of $0.0150(5 - C_n)$ W/(m·K) is added to $\sum_i \lambda_{b,i}$ in Equation (4.20).

Vapour thermal conductivity

Notable methods for estimating the vapour-phase thermal conductivities include the Eucken equation, the modified Eucken correlation [233], the Stiel and Thodos equation [234], and the Chung *et al.* method [227, 228]. These methods usually employ a relation of the dimensionless group, Eucken factor ($\lambda M' / \eta c_v$) as a function of thermodynamic variables such as c_v , T_r and ω . The Eucken factor is close to 2.5 for monoatomic gases but generally expected to be much less for polyatomic gases. The Eucken equation underestimates the conductivity while its modified form overestimates the conductivity and the Stiel and

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Thodos equation yields values between the two Eucken forms [212]; all three forms predict that the Eucken factor should decrease with temperature whereas the factor appears to increase slightly with temperature.

The Chung *et al.* method [227, 228] tends to predict the correct trend of the factor with temperature and yields values close to those reported experimentally [212]. The thermal conductivity relation is given as:

$$\frac{\lambda_V M'}{\eta_V c_V} = \frac{3.75\Psi}{c_V/R}. \quad (4.22)$$

The variables in this equation are expressed in SI units (M' is the molar mass in kg/mol and $R = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$), and c_V (in $\text{J}/(\text{mol}\cdot\text{K})$) is obtainable from an equation of state such as the SAFT- γ Mie. The factor Ψ is calculated as:

$$\Psi = 1 + \alpha \{ [0.215 + 0.28288\alpha - 1.061\beta + 0.26665Z] / [0.6366 + \beta Z + 1.061\alpha\beta] \}, \quad (4.23)$$

where:

$$\begin{aligned} \alpha &= c_V/R - 3/2; \\ \beta &= 0.7862 - 0.7109\omega + 1.3168\omega^2; \\ Z &= 2.0 + 10.5T_r^2. \end{aligned} \quad (4.24)$$

Equation (4.22) is modified to treat materials at high pressures, resulting in the following expression for the thermal conductivity:

$$\lambda_V = \frac{31.2\eta_V\Psi}{M'}(G_2^{-1} + B_6y) + qB_7y^2T_r^{1/2}G_2. \quad (4.25)$$

In the above equation, $y = V_{\text{cr}}/(6V)$ and $q = 3.586 \times 10^{-3}(T_{\text{cr}}/M')^{1/2}/V_{\text{cr}}^{2/3}$, where V_{cr} is the critical volume in cm^3/mol . The molar volume V , in cm^3/mol , is also obtainable from the SAFT- γ Mie equation of state (from the vapour density). The constants G_2 , B_6 and B_7 are provided in Ref. [228]. At low pressures, V becomes large and y approaches zero and G_2 approaches unity, and the above equation will reduce to Equation (4.22) for low pressure vapours.

In a similar manner to the dynamic viscosity, the predicted thermal conductivities are compared with the available experimental values from the NIST REFPROP database and presented in Figure 4.9. The thermal conductivity predictions from the group-contribution methods are also seen to be in good agreement with the experimental data from REFPROP. The vapour-phase thermal conductivities are predicted with the

Chung *et al.* method in Equation (4.22) while the liquid-phase thermal conductivities are predicted with the Sastri method in Equation (4.20).

4.3.4 Liquid surface tension

Several empirical corresponding states correlations are available for the estimation of the surface tension of the various chemical families of fluids. Sastri and Rao [235] present a modification of the corresponding-states methods to deal with polar liquids:

$$\sigma = K P_{\text{cr}}^x T_{\text{b}}^y T_{\text{cr}}^z \left[\frac{1 - T_{\text{r}}}{1 - T_{\text{b,r}}} \right]^m, \quad (4.26)$$

where σ is the surface tension in $\text{mN}\cdot\text{m}^{-1}$, and the pressure and temperature terms are in units of Kelvin and bar respectively. The values of the constants for alcohols and acids are available in Ref. [235] while for all other families of compounds, $K = 0.158$, $x = 0.50$, $y = -1.5$, $z = 1.85$ and $m = 11/9$.

Using the correlation presented in Equation (4.26) the saturated-liquid surface tension of hydrocarbon working fluids can be predicted, and these predictions are compared with the available experimental data from REFPROP. The results are presented in Figure 4.10. It should be noted that there are no experimental surface tension data for 2,2-dimethylpropane and cis-2-butene from REFPROP. For the compounds with available experimental data, the predictions from Equation (4.26) are generally in good agreement with the experimental values, up to the critical point.

The transport properties predicted by the group contribution methods are quantified with respect to available experimental data and the results are presented in terms of the absolute average deviations (AAD) in Table 4.5. In each case, the AAD is evaluated as in Equation (4.5), with 100 data points. The viscosity and thermal conductivity are evaluated at atmospheric pressure with equally-spaced data points between 20 °C and 400 °C while the surface tension is evaluated for the saturated liquid with equally-spaced data points between 20 °C (293.15 K) and 95% of the critical temperature. In comprising with experimental data, the group contribution methods are generally seen to provide good estimates of the required properties as the AAD values were generally less than 4%, 5% and 8% for the viscosity, thermal conductivity and surface tension respectively.

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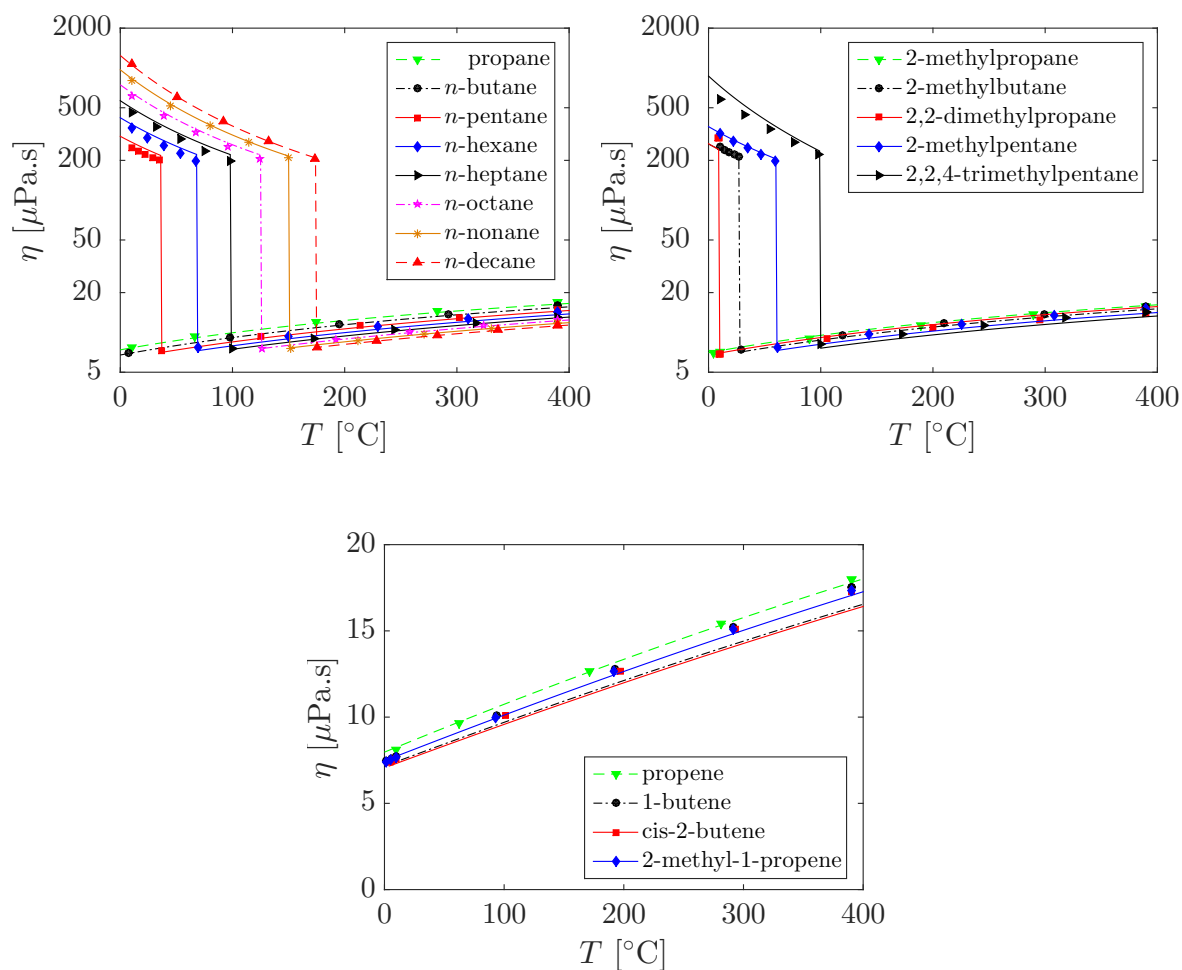


Figure 4.8: Low-pressure dynamic viscosity of n -alkanes, methyl alkanes and alkenes, in the liquid and vapour phases as functions of temperature. Comparison of predicted viscosities from the group-contribution theories (continuous curves) with experimental data from the NIST REFPROP database (symbols).

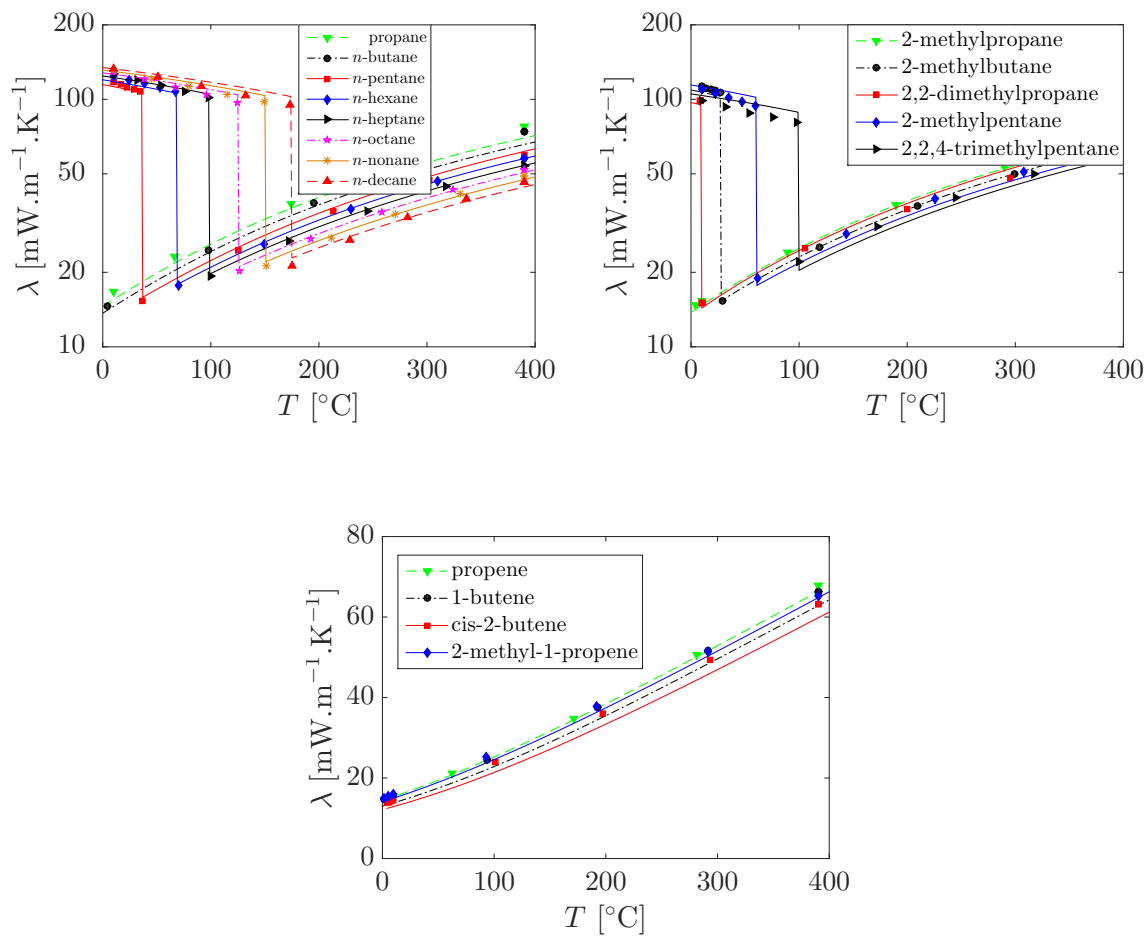


Figure 4.9: Low-pressure thermal conductivity of n -alkanes, methyl alkanes and alkenes, in the liquid and vapour phases as functions of temperature. Comparison of predicted conductivities from the group-contribution theories (continuous curves) with experimental data from the NIST REFPROP database (symbols).

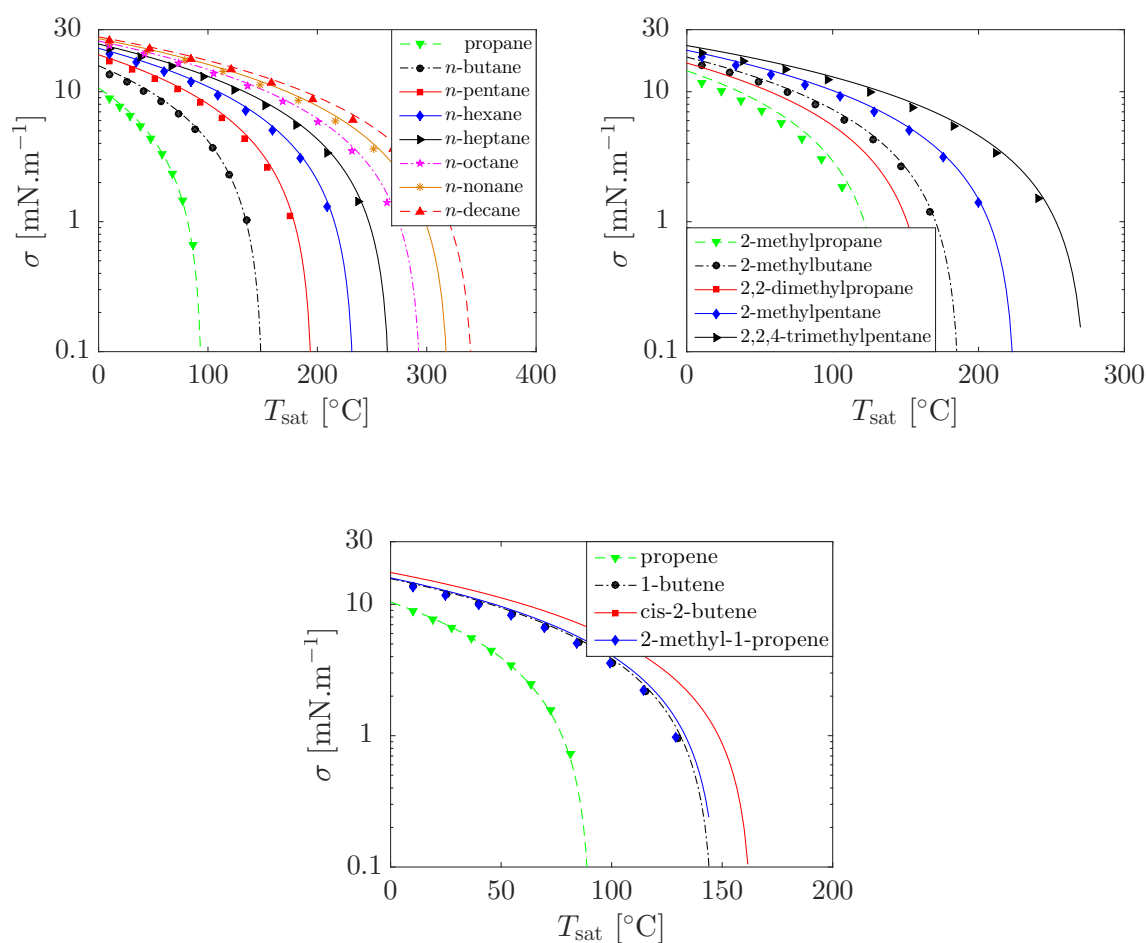


Figure 4.10: Saturated-liquid surface tension of n -alkanes, methyl alkanes and alkenes. Comparison of predicted surface tension from the group-contribution theories (continuous curves) with experimental data from the NIST REFPROP database (symbols).

Transport property prediction from group contribution methods

Table 4.5: Average absolute deviation AAD (%) from experimental values of selected critical and transport properties of selected hydrocarbons obtained with the group contribution approaches in Section 4.3. Properties considered comprise the critical temperature, pressure and volume (T_{cr} , P_{cr} and V_{cr}), liquid and vapour viscosity (η_{L} and η_{V}), liquid and vapour thermal conductivity (λ_{L} and λ_{V}), and surface tension (σ). The AAD is defined in Equation (4.5) and experimental data is taken from NIST REFPROP; the viscosity and thermal conductivity are evaluated at atmospheric pressure with 100 equally-spaced data points between 20 °C and 400 °C while the surface tension is evaluated for the saturated liquid with 100 equally-spaced data points between 20 °C (293.15 K) and $0.95 \times T_{\text{c}}$ (in units of Kelvin).

Fluid	AAD (%)									
	T_{cr}	P_{cr}	V_{cr}	η_{L}	η_{V}	$\eta_{\text{L}} + \eta_{\text{V}}$	λ_{L}	λ_{V}	$\lambda_{\text{L}} + \lambda_{\text{V}}$	σ_{sat}
propane	0.24	3.71	1.75	–	1.84	1.84	–	4.85	4.85	5.54
<i>n</i> -butane	0.47	2.65	1.80	–	1.85	1.85	–	5.67	5.67	3.89
<i>n</i> -pentane	0.31	2.92	1.45	9.79	2.49	2.85	1.78	2.84	2.79	5.08
<i>n</i> -hexane	0.24	2.41	0.52	9.88	5.12	5.74	2.83	0.83	1.09	4.67
<i>n</i> -heptane	0.06	2.32	1.02	10.0	1.55	3.33	1.64	0.67	0.87	4.61
<i>n</i> -octane	0.08	1.54	0.57	5.99	0.84	2.28	3.97	2.12	2.63	4.63
<i>n</i> -nonane	0.02	1.14	2.35	1.81	0.44	0.92	4.45	2.80	3.38	6.03
<i>n</i> -decane	0.03	0.24	2.34	0.61	1.02	0.85	5.58	3.74	4.49	7.51
2-methylpropane	0.71	8.45	1.65	–	2.17	2.17	–	2.85	2.85	19.0
2-methylbutane	0.51	3.65	1.24	4.71	4.66	4.66	4.26	0.26	0.38	3.55
2,2-dimethylpropane	4.02	11.0	0.43	–	5.84	5.84	–	5.34	5.34	N/A
2-methylpentane	0.05	3.12	0.77	1.76	7.14	6.54	6.01	7.24	7.11	4.59
2,2,4-trimethylpentane	0.69	1.31	1.10	12.4	7.69	8.69	9.03	6.69	7.18	9.38
propene	0.11	2.43	0.68	–	0.61	0.61	–	0.58	0.58	1.03
1-butene	0.02	2.60	1.97	–	6.21	6.21	–	6.71	6.71	5.48
cis-2-butene	0.05	1.49	1.64	–	5.71	5.71	–	5.10	5.10	N/A

4.4 Validating the CAMPD framework

Before applying the developed CAMPD framework to case studies in heat recovery and conversion, it is necessary to validate the framework. Earlier in this chapter, the thermo-physical property prediction methods from the SAFT- γ Mie group contribution EoS (for thermodynamic properties) and from the correlative group contribution methods (for the transport properties and surface tension) were presented and validated against experimental data. Here, the CAMPD framework is applied to organic Rankine cycle systems (due to its wealth of technical and economic data over the Up-THERM heat converter) in waste-heat recovery applications and validated. In the first instance, the suitability of the SAFT- γ Mie EoS in the CAMPD framework is ascertained while the optimisation results from the framework are further validated against studies in literature. The ability of the framework to provide accurate results with alternative cycle configurations is also considered while the validation is rounded up by verifying the accuracy of the component size and system costs predictions.

4.4.1 Validation of SAFT- γ Mie within an ORC model

Before applying the CAMPD-ORC model to waste heat recovery case studies, it is necessary to validate that SAFT- γ Mie is suitable for determining the performance of ORC systems. Previously, a comparison between SAFT- γ Mie and the NIST REFPROP database was completed for the saturation properties of normal alkanes [87]. Here, this comparison is extended by solving the ORC model described in Section 2.1 using both SAFT- γ Mie and NIST REFPROP. The assumptions for this study are listed in Table 4.6, and using these assumptions the performance of an ORC system operating with different alkane working fluids has been evaluated over a range of reduced evaporation pressures.

Table 4.6: Model inputs for two validation studies. The NIST study refers to the validation study completed using NIST REFPROP data, as discussed in Section 4.4.1. The PC-SAFT study refers to the validation study discussed in Section 4.4.2. ‘var.’ denotes a variable parameter.

	T_{hi}	$c_{p,h}$	$\dot{m}_h$	η_p	η_e	PP_h	T_1	ΔT_{sh}
	°C	kJ/(kg K)	kg/s	%	%	°C	°C	°C
NIST	200	4.20	1.0	70	80	10	30	10
PC-SAFT [147]	120	4.20	66.0	90	80	10	var.	var.

It should be noted that the heat source is assumed to be a pressurised liquid, with a defined specific heat capacity of $4.2 \text{ kJ}/(\text{kg K})$; such an assumption is valid since the thermodynamic optimum is independent of the heat-source heat-capacity rate (*i.e.*, $\dot{m}_h c_{p,h}$). The results from this analysis are shown in Figure 4.11. It is observed that the two approaches agree well, with very similar trends for both the power output and the thermal efficiency being obtained. Furthermore, both approaches yield the same maximum power point at the same reduced pressure. This therefore validates the SAFT- γ Mie EoS for the performance prediction of ORC systems operating with alkane working fluids.

As an aside, the behaviour observed in Figure 4.11 for the different working fluids can be explained since the molecular complexity (*i.e.*, the number of groups) is approximately proportional to the critical temperature. For example, *n*-pentane consists of two $-\text{CH}_3$ groups and three $>\text{CH}_2$ groups and has a critical temperature of 196.7°C , whilst *n*-heptane has two additional $>\text{CH}_2$ groups and a critical temperature of 267.1°C . Therefore, to obtain a similar evaporating temperature within the ORC, the *n*-heptane cycle must operate at a lower reduced pressure. Furthermore, a lower reduced pressure corresponds to a greater latent heat of vaporisation, which means a greater proportion of the heat absorbed by the working fluid from the heat source is used to evaporate the working fluid. Since evaporation occurs under isothermal conditions, this limits the temperature reduction in the heat source, leading to a higher average heat-source temperature and a higher thermal efficiency. However, this also leads to a lower working-fluid mass flow rate and lower power output. This trade-off between power output and thermal efficiency is a phenomenon that has been well discussed within the literature [236, 237].

4.4.2 Validation of the optimisation model

In addition to comparing SAFT- γ Mie to NIST REFPROP, the developed model has also been compared to another CAMPD-ORC optimisation study taken from the literature [147]. The authors of this previous study used an alternative SAFT equation of state, namely PC-SAFT [105, 106], and for the assumptions listed in Table 4.6, a list of ten optimal working-fluids was obtained. From these ten working fluids, four alkane and three alkene working fluids were identified and using the approach outlined in Section 2.1.4, the ORC system was optimised. The results of the current optimisation in terms of the net power output and the condensation and evaporation pressures are compared to the PC-SAFT results in Figure 4.12.

Overall, similar trends are observed for both the PC-SAFT and SAFT- γ Mie approaches in terms of the optimal evaporation and condensation pressure for each working

fluid. However, when comparing PC-SAFT and SAFT- γ Mie in terms of the absolute power it is observed that SAFT- γ Mie always results in higher values; for propane and propene the percentage difference between SAFT- γ Mie and PC-SAFT is 4.4% and 7.0% respectively, whilst for the remaining fluids the difference is less than 2%. Having said this, in general the rankings of the working fluids from the two studies are similar, with relatively simple working fluids such as propane and propene being favoured over working fluids with increasing molecular complexity, although it also observed that these two fluids do have the highest operating pressures. Therefore, given that both SAFT- γ Mie and PC-SAFT both point towards a similar optimum working fluid, and that the optimal ORC condensation and evaporation pressures are similar, this comparison further confirms the suitability of the SAFT- γ Mie equation of state, the ORC system model, and the optimisation framework.

4.4.3 Alternative cycle configurations

In Section 4.4.1, the CAMPD framework has been validated for a non-recuperated, sub-critical ORC operating with an array of hydrocarbon working fluids, by comparing the results to a similar model that uses the NIST REFPROP program to calculate thermodynamic properties. In this section, a similar validation study will be completed to confirm the suitability of the CAMPD-ORC model to simulate the alternative cycle architectures, namely cycles operating with working-fluid mixtures and partially-evaporated cycles. Although the model is expected to be applicable for the range of heat-source temperatures relevant to ORC systems (*i.e.*, 100–400 °C), for the validation study the heat source is assumed to be at 200 °C, with other cycle parameters given in Table 4.6. These assumed parameters are considered to be representative of a typical ORC system [149].

The purpose of the first validation study is to confirm the suitability of the CAMPD-ORC model for partially-evaporated cycles. For this study, three different working fluids have been considered, namely *n*-pentane, *n*-hexane and isopentane. For these three fluids a parametric study was completed in which z was varied between 0 and 2, and this was repeated at different evaporation pressures. z is closely related to the degree of superheat (θ_{SH}) in the cycle, defined in Equation (2.5); when $z < 1$, the cycle is partially evaporated and the working fluid is expander from a two-phase state entirely through a two-phase region; when $z \geq 1$, the cycle reverts to the basic cycle with expansion from the a saturated ($z = 1$; $\theta_{SH} = 0$) or superheated vapour ($1 < z \leq 2$; $0 < \theta_{SH} \leq 1$) state. The comparison between the results obtained using the CAMPD-ORC model, based on SAFT- γ Mie, and a similar model using NIST REFPROP is given in Figure 4.13.

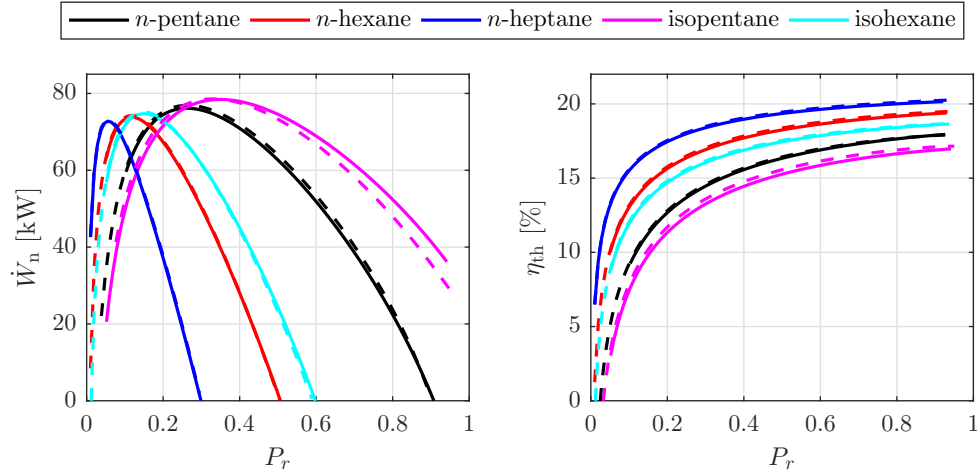


Figure 4.11: Comparison between the net power $\dot{W}_n$ and thermal efficiency η_{th} , as functions of reduced pressure, obtained from the ORC model when using SAFT- γ Mie for working-fluid thermodynamic property prediction (solid) and when using NIST REFPROP thermophysical property database (dashed) for a number of hydrocarbon working-fluids.

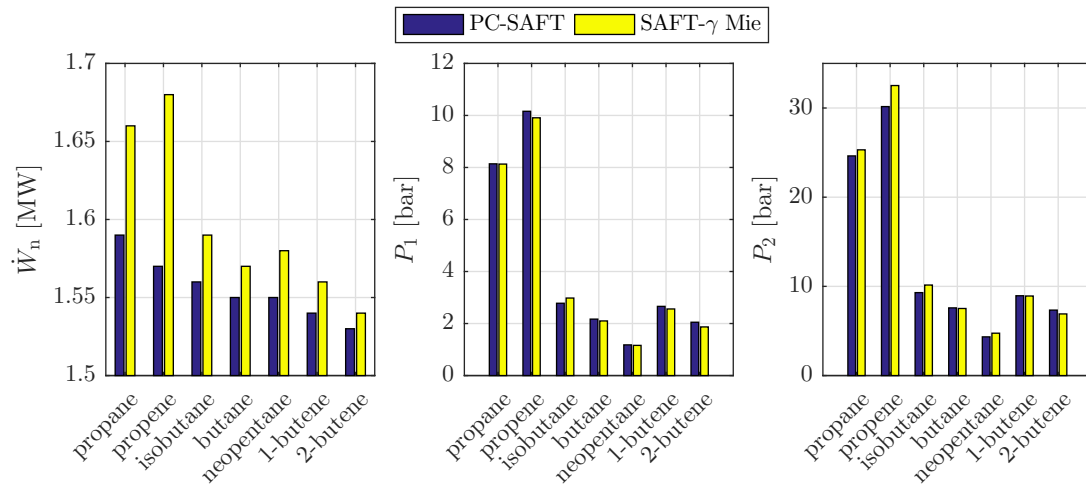


Figure 4.12: Validation of the model against the optimisation study completed using PC-SAFT in Ref. [147] for a set of hydrocarbon working fluids. P_1 is the condensation pressure while P_2 is the evaporation pressure.

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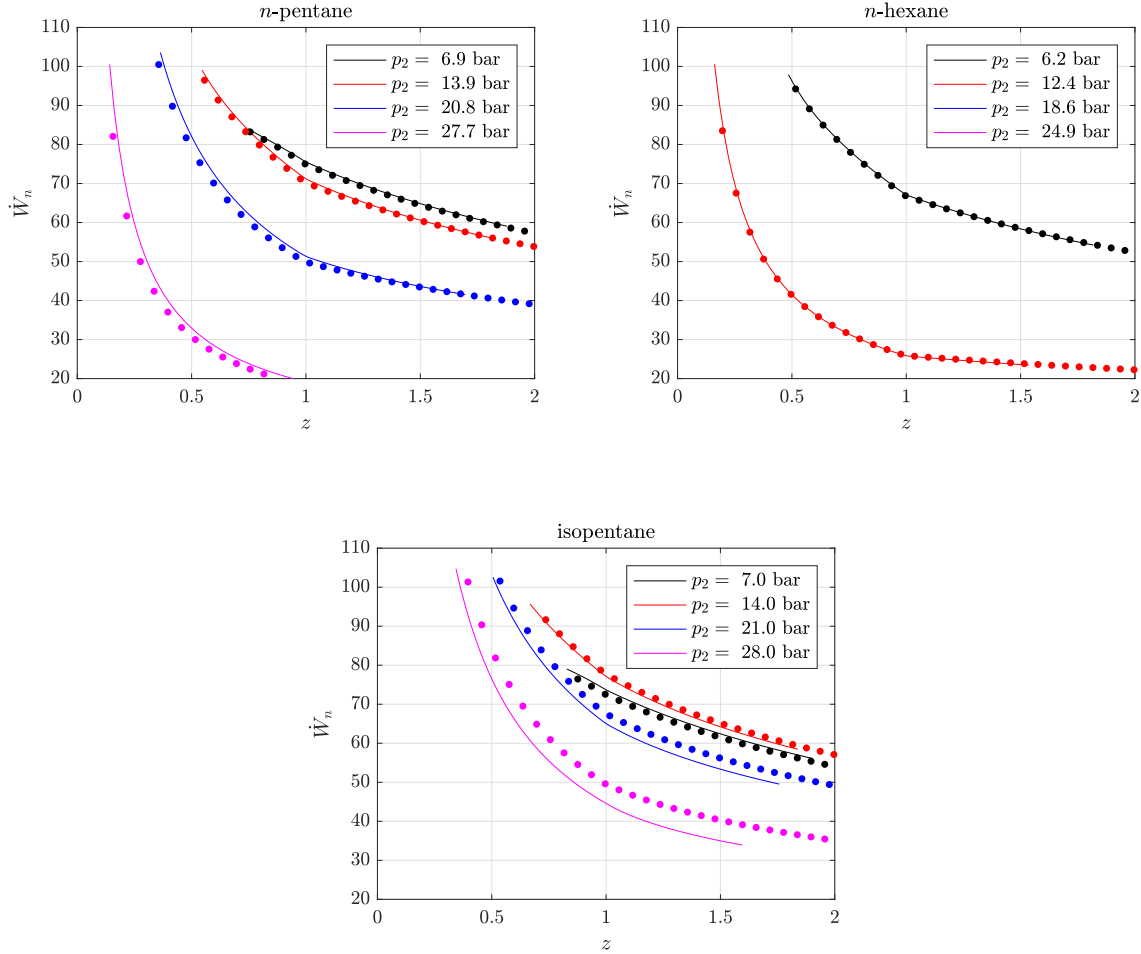


Figure 4.13: Comparison between the power output ($\dot{W}_n$ in kW) predicted by the CAMPD-ORC model (circular markers) and predicted by a model using NIST REFPROP for thermodynamic properties (continuous curves) for three different working fluids operating within a partially-evaporated ($z < 1$) and a superheated ($z \geq 1$) cycle.

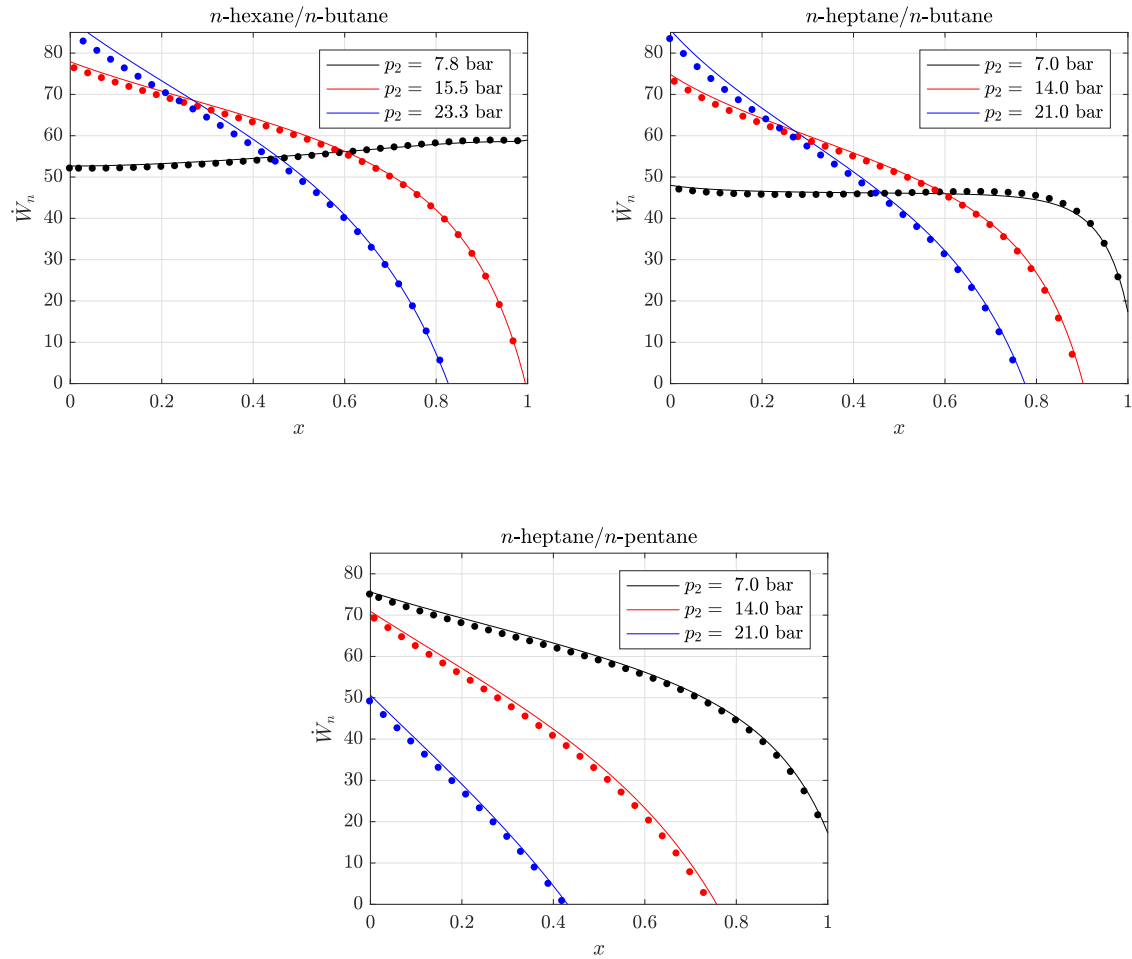


Figure 4.14: Comparison between the power output ($\dot{W}_n$ in kW) predicted by the CAMPD-ORC model (circular markers) and predicted by a model using NIST REFPROP for thermodynamic properties (continuous curves) for three different fluid mixtures. x represents the mass fraction of the first-listed fluid in each mixture, *i.e.*, n -hexane, n -heptane and n -heptane respectively.

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Overall, it is observed that, except for the 28.0 bar case for isopentane, a very good agreement between the two models is obtained and this validates the suitability of the CAMPD-ORC model to simulate these types of cycles. Neglecting this case, the maximum deviations between the CAMPD-ORC model and REFPROP model are below 4%, 1% and 5% for *n*-pentane, *n*-hexane and isopentane respectively. The deviation for the 28.0 bar isopentane case can be explained because at higher pressures the cycle is operating closer to the critical point (33.8 bar), and the deviation between SAFT- γ Mie and NIST REFPROP is found to increase as the critical point is approached. The 18.6 and 24.9 bar cases for *n*-hexane do not appear in Figure 4.13 because the saturation temperature of *n*-hexane at these pressures is higher than the heat-source temperature.

More generally, from Figure 4.13 it is observed that the maximum power is always generated when $z < 1$. This clearly indicates the potential thermodynamic performance benefit of allowing the working fluid to expand from a two-phase state. This is due to the fact that when $z < 1$, the working-fluid expansion takes place inside the two-phase region, such that a larger proportion of the heat transfer during heat addition occurs during preheating, and results in a lower heat-source outlet temperature. This, in turn, means that the ORC is capable of extracting more heat from the heat source, leading to a higher power output. However, it should be noted that the expanders available to ORC systems are usually designed for dry vapours and are thus generally not suited to such partially-evaporated cycles as expanders capable of handling wet vapours are still under research and development.

For the validation of the CAMPD-ORC model for mixtures, three different mixtures have been considered, namely *n*-hexane/*n*-butane, *n*-heptane/*n*-butane and *n*-heptane/*n*-pentane. For each mixture a parametric study was completed in which the mass fraction of the fluid listed first, x , was varied from 0 to 1, and this was repeated at different evaporation pressures. In each case, it was assumed that expansion occurs from a saturated-vapour state (*i.e.*, $z = 1$). The comparison between the results obtained using the CAMPD-ORC model, and the model based on NIST REFPROP is shown in Figure 4.14. Again, a very good agreement is observed for the different case studies; neglecting power outputs below 20 kW, which do not represent good thermodynamic cycles for these case studies, the maximum deviations between the CAMPD-ORC and REFPROP models are 4%, 4% and 8% for the *n*-hexane/*n*-butane, *n*-heptane/*n*-butane and *n*-heptane/*n*-pentane cases respectively. These results therefore validate the CAMPD-ORC model for simulating these types of cycles as well.

4.4.4 Component sizing and system costs

The CAMPD-ORC framework has previously been used to optimise the working fluid and cycle conditions for a non-recuperated, basic ORC, and this process was completed for three different waste-heat streams [149]. Now, using the group-contribution transport-property prediction methods and the heat-exchanger sizing model described in Sections 4.3 and 2.1.2 respectively, it is possible to determine the area requirements of the evaporator and the condenser for these optimum cycles. The full analysis will be described in detail in the case studies in Chapter 5, however, first, it is necessary to validate the developed model.

It should be noted that the other components of the ORC system (*i.e.*, the pump and expander) are sized based on their power requirements which rely only thermodynamic data, specifically the enthalpies of the working fluid at different parts of the cycle. These thermodynamic data are evaluated from the SAFT- γ Mie EoS as presented in Section 4.2 with the subsequent validations with experimental data. In addition, the thermodynamic performance (in terms of the net power output and thermal efficiency) of the framework for ORC systems was also validated in Sections 4.4.1 and 4.4.2. These ensure that the predictions of the expander power output and pump power requirements as derived from the CAMPD framework, are accurate. Thus, only the heat exchangers (*i.e.*, the evaporator and the condenser) are sized and validated here.

For this validation study, the heat-exchanger sizing is first performed using properties obtained using NIST REFPROP. Then, these results are compared to those obtained when the group contribution transport properties are used. Not all of the fluids considered within the initial CAMPD-ORC optimisation study are available within REFPROP, and therefore it is only possible to validate the model for a subset of the fluids considered. This subset of fluids used for the comparison study includes *n*-propane (*n*-alkane), isobutane (methyl alkanes), 1-propene (1-alkene) and cis-2-butene (2-alkene). The heat-carrier fluid for all fluids is Therminol 66[®], entering the evaporator at 150 °C and 1 bar.

In Figure 4.15, the evaporator and condenser area requirements for the four working fluids are presented. In line with the figures, the results obtained using the group-contribution transport property model are in good agreement with those obtained using experimental data from NIST REFPROP. The heat-exchanger area calculations for *n*-propane and isobutane have negligible difference between the two methods. The highest deviation is recorded for cis-2-butene, where the condenser unit surface area is overestimated by the group-contribution method by approximately 18%, being on the conservative side of the heat-exchanger design. It should be noted that the Nusselt number

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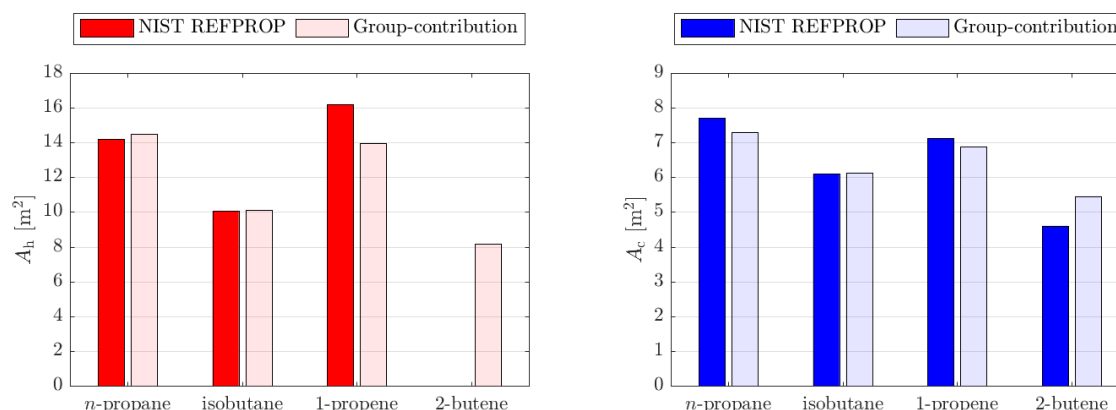


Figure 4.15: Comparison between the evaporator area (LHS, A_h in m^2) and the condenser area (RHS, A_c in m^2) predicted by the CAMPD-ORC model using group-contribution transport properties and that predicted by a model using NIST REFPROP for thermophysical property database for a number of hydrocarbon working-fluids.

correlations for the evaporator area calculation require the use of the working fluid surface tension, which, for *cis*-2-butene, is not available in NIST REFPROP.

Compared to the *n*-propane and isobutane cases, the 1-propene case shows a relatively large deviation of 14% between the total evaporator area predicted using the CAMPD-ORC model and using REFPROP-based model. This deviation occurs, in part, because it is not possible to exactly match the thermodynamic cycle conditions input into the heat-exchanger sizing model, and those output from the CAMPD-ORC model. This, coupled with the 1-propene cycle having a higher amount of superheat, which is 54 °C compared to 18 °C and 0.1 °C for *n*-propane and isobutane cycles respectively, results in the 1-propene superheater load for the REFPROP-based heat-exchanger sizing model being higher than the CAMPD-ORC model. Considering that the heat-transfer coefficient for a vapour is significantly lower than for a liquid or two-phase fluid, this results in the REFPROP-based model predicting a superheater area of 4.37 m^2 , compared to 3.34 m^2 for the CAMPD-ORC model, thus accounting for the relatively large deviation observed.

Ultimately, the deviation introduced by transferring the cycle parameters from the CAMPD-ORC model into the REFPROP heat-exchanger sizing model does not directly represent an issue with the group-contribution transport property prediction methods but is instead a carry-over from the difference between the thermodynamic properties predicted by SAFT- γ Mie within the thermodynamic cycle model and REFPROP. Notwithstanding, neglecting the 2-butene condenser and 1-propene evaporator, the percentage deviation between the CAMPD-ORC model and the REFPROP-based model for the re-

Validating the CAMPD framework

maining heat exchangers are all below 5%. These values are very much in line with the maximum percentage deviations observed between the thermodynamic properties ($< 5\%$), and transport properties ($< 8\%$) discussed in Sections 4.2 and 4.3 respectively. Overall, this gives good confidence in the heat-exchanger sizing model implemented within the CAMPD-ORC model.

The costing methodology used to estimate the component cost and overall system costs of ORC systems is presented in Section 2.1.3. To validate the costing methodology as part of the CAMPD framework, the ‘specific purchased equipment costs’ (SPEC, see Section 2.1.3) values of twelve optimised systems, presented in Chapter 5, are compared to a non-exhaustive list of cost data for commercial waste heat recovery ORC systems available in literature from Refs. [151] and [238]. For each optimised system, the SPEC is calculated using distinct sets of correlations from Seider *et al.* [166] and from Turton *et al.* [167]. The results are presented in Figure 4.16; the cost values from the different sources are normalised to 2017 values using the applicable CEPCI values and exchange rates of 0.898 \$/€, 1.237 \$/€ and 1.330 \$/€ for 2001, 2006 and 2014, respectively.

At low values of $\dot{W}_n$ of around 25 kW, the set of correlations from Turton *et al.* seem to significantly overestimate the SPEC. This can be attributed to the costs of the two-phase sections of the heat exchangers. This correlation for long-tube evaporators is valid in the range of 100 – 10,000 m², whereas the required areas for the two-phase sections as predicted by the model are typically in the range of 2 – 10 m². This illustrates a general weakness of applying correlations to determine costs of equipment: outside of a given capacity range, cost estimations might diverge from actual costs and become increasingly inaccurate. At high capacities, the Seider method seems to slightly underestimate the SPEC. The mixed set of correlations applied in the model seems to lead to SPEC values that agree reasonably well with the cost data for all capacities that are assessed.

In addition, the cost distribution of the ORC system with respect to the individual component is assessed at different capacities. In Figure 4.17, the relative purchased equipment costs of the heat exchangers, pump, generator and expander of a low capacity ORC system (propane, 150 °C heat source, 25 kW) and a higher capacity system (2-heptene, 350 °C heat source, 150 kW) are shown. It can be seen that the contribution of the heat exchangers to the total costs is higher for the low temperature system (69%) than the high temperature system (37%), whereas that of the turbine increases. This agreement is exemplified by a 2 kW system in Liege, Belgium, where 26% of the equipment costs result from the expander and 62% of the costs are related to both heat exchangers [239]. In another commercial 375 kW ORC system setup in Belgium [151], 60% of the

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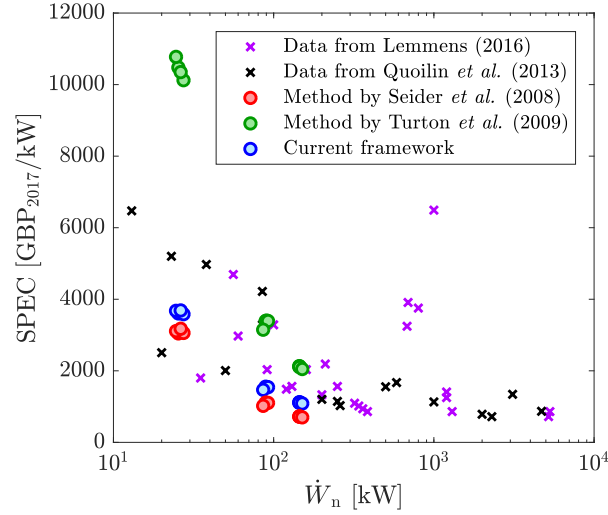


Figure 4.16: Specific purchased equipment costs of ORC waste heat recovery systems. Data of commercial systems, taken from Lemmens [151] and Quoilin *et al.* [238], is denoted by ‘x’. The data in Ref. [238] is presented in Euros (2013), whereas that in Ref. [151] is in Euros (2014); here, both are converted to GBP (2017) using the CEPCI values of 567.3, 576.1 and 556.8 for the years 2013, 2014 and 2017 respectively, with 2013 and 2014 average annual exchange rates of 0.849 £/€ and 0.806 £/€ respectively. Predictions by current framework, determined with correlations are denoted with filled circles ‘o’.

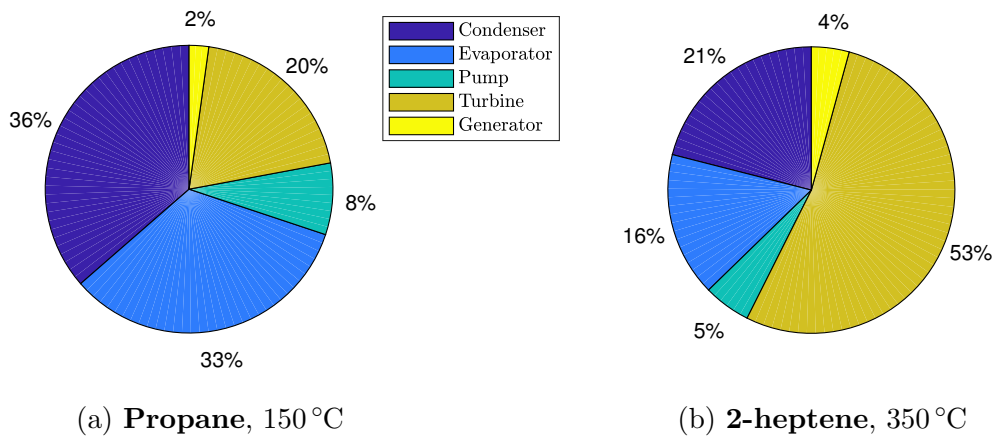


Figure 4.17: Relative equipment costs for two ORC systems at different heat source temperatures. **(a)** Propane working fluid, 150 °C heat source, $\dot{W}_n = 25.6$ kW and SIC of £10,100 per kW. **(b)** 2-heptene working fluid, 350 °C heat source, $\dot{W}_n = 150$ kW and SIC of £2,900 per kW.

Summary

total equipment costs (when the cost of the intermediate thermal oil circuit is excluded) is attributed to the expander, pump and generator, while the condenser and evaporator respectively make up 22% and 13% of the total costs [151].

Furthermore, the costs of the condenser always exceeds that of the evaporator as expected in commercial installations [240]. For both these cases, the capacities of the systems presented in Figure 4.17 differ from the reference cases reported above, thus a direct comparison is not possible. However, the distribution predicted by the model is seen to match those of these systems while accounting the variation in ORC system costs with system size; the trend that a smaller fraction of the costs is attributed to the heat exchangers as the system size increases, while the relative expander costs increase significantly, is correctly predicted. Furthermore, the relative contributions are in the same order of magnitude of these reference cases. Thus, the current model provides reasonable estimates for the equipment costs of small and medium scale ORC systems with capacities between 25 and 150 kW, and is suitable for a comparison between such ORC systems.

4.5 Summary

In this chapter, a computer-aided molecular and process design (CAMPD) framework for the optimisation of waste-heat recovery power systems based on the molecular-based, group-contribution SAFT- γ Mie equation of state (EoS) is presented. The SAFT- γ Mie EoS has not been previously employed in such a framework for organic Rankine cycle (ORC) systems nor for other waste-heat recovery applications. While working-fluid thermodynamic properties are provided from the SAFT- γ Mie EoS, the required transport properties are provided from empirical group contribution (GC) correlations; these GC methods were shown to provide reliable thermodynamic and transport property predictions with respect to available experimental data. This type of CAMPD-ORC framework stands out from conventional modelling approaches in the literature in that it enables the integrated and simultaneous identification of optimal working-fluids, system designs and operational conditions for specific applications.

Other key aspects of the framework have been presented and validated. In particular, ORC performance calculations completed using SAFT- γ Mie agree very well with calculations completed using NIST REFPROP, and with results from another CAMPD-ORC optimisation study available in the literature. The framework also provides for the sizing and costing of ORC systems, as well as providing for the consideration of novel cycle ar-

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chitectures, including recuperated and partially-evaporated cycles, and cycles operating with working-fluid mixtures. Both the heat-exchanger sizing and cost estimation models have been validated against data from NIST REFPROP and commercial systems in literature, and a good agreement is found for the working-fluids and systems considered. The largest deviations observed in the heat-exchanger area were +18% and -13%, when sizing the condenser for 2-butene, and the evaporator for propene respectively. These relatively small deviations confirm the suitability of the group-contribution transport property prediction methods.

Chapter 5

Case Studies in CAMPD of Organic Rankine Cycle Systems

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5.1 Introduction

In Chapter 4, the CAMPD framework was shown to be applicable to the working fluid and process design of organic Rankine cycle (ORC) systems. The SAFT- γ Mie group contribution equation of state was introduced and furthermore, the transport-property group-contribution correlations were coupled to the heat-exchanger sizing model, and the heat-transfer area requirements for a few of the optimal cycles that resulted from the initial thermodynamic study were determined. In practice, the CAMPD framework is applicable to the design of heat engines in general, including the Up-THERM heat converter; however, the ORC system is selected for the case studies as discussed in Section 1.6 and Section 4.4 due to its higher level of market penetration and deployment worldwide. In this chapter, the framework is applied to case studies in ORC systems' design taking into account the thermodynamic performance of various working fluids and their heat-transfer requirements, as well as the total and specific investment costs (TIC & SIC) of the resulting ORC system for each working fluid. This, in turn, allows optimal cycle configurations to be identified based on thermoeconomics.

It should be noted that within these case studies only a basic, non-recuperated ORC has been considered, despite the CAMPD-ORC framework being successfully extended to, and validated for, alternative cycle architectures in Chapter 4. This is because of the uncertainties that are introduced when these novel cycle architectures are considered. Firstly, sizing the heat exchangers for a cycle operating with a working-fluid mixture would require suitable mixing rules to be defined to determine the necessary transport properties. Moreover, there also exist large uncertainties in predicting the local heat-transfer coefficient for a working-fluid mixture. Secondly, whilst partially evaporated cycles are an extremely interesting idea from the point of view of maximising power output, there are currently no commercial expander technologies that are suitable for two-phase expansion. Technologies to efficiently handle two-phase expansion are still in early-stage research [241]; therefore, it follows that cost correlations for two-phase expanders do not exist.

With these in mind, the case studies are evaluated with the basic, non-recuperated ORC system using pure (single component) working fluids. Nonetheless, as more research into working-fluid mixtures and partially-evaporated cycles is conducted, the same tool can be used to evaluate these novel cycles, with minimal changes required to the CAMPD-ORC framework. The three heat-sources considered are each defined by a heat-capacity rate ($\dot{m}c_p$) of 4.2 kW/K, and are defined at 150, 250 and 350 °C respectively. These

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temperatures correspond to typical temperatures at which industrial waste heat is available, and temperatures at which an ORC system could be used. The assumptions for the study are listed in Table 5.1; for all three heat-source temperatures, the heat source is assumed to be the heat-transfer oil Therminol 66[®] at 1 bar, and the heat sink is water.

Four different families of hydrocarbon working fluids are used in the case studies, namely *n*-alkanes, methyl alkanes, 1-alkenes and 2-alkenes. Each of these families consists of a specific set of molecular groups, but can include a variable number of $>\text{CH}_2$ groups. For example, an *n*-alkane is described by two $-\text{CH}_3$ groups and a number of $>\text{CH}_2$ groups, whilst a methyl alkane is described by three $-\text{CH}_3$ groups, one $>\text{CH}-$ group and a number of $>\text{CH}_2$ groups. 1-alkenes and 2-alkenes are similarly described, although a 1-alkene contains a $\text{CH}_2=\text{CH}-$ double bond, whilst a 2-alkene contains a $-\text{CH}=\text{CH}-$ double bond. The molecular structures of these four hydrocarbon families are summarised in Table 5.2; their individual molecular groups are also highlighted and these will be used later on in Section 5.5 for the assessment of more complex molecules in full MINLP formulations.

These molecular groups are used to determine the properties of a particular molecule. For example, the properties of isopentane are derived from the contributions of the three $-\text{CH}_3$ groups, one $>\text{CH}_2$ and one $>\text{CH}-$ group. In a group-contribution method group parameters are only required for the individual groups, which allows the evaluation of novel working fluids for which property prediction would not be possible using conventional approaches. To capture the trade-off between thermodynamic performance and system costs, group-contribution methods are required for both the thermodynamic properties and transport properties. The SAFT- γ Mie equation of state is used for thermodynamic property prediction while empirical group-contribution methods are used for the prediction of the dynamic viscosity μ , thermal conductivity k and surface tension σ . The suitability of SAFT- γ Mie EoS and the empirical correlations for hydrocarbon working-fluid property prediction was discussed and validated against available experimental data in Chapter 4. Thus, the group contribution methods applied in these case studies are summarised in Table 5.3.

Due to the inherent non-linearity in the group contribution methods and equation of state, and in the process model for the ORC system, the CAMPD framework results in a non-linear optimisation problem that requires the specification of both integer and continuous decision variables. Thus, the optimisation problem is classified as a mixed integer non-linear programming (MINLP) problem. If the working fluid is pre-specified, only continuous system parameters need to be optimised and the optimisation problem

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Table 5.1: Model inputs for the three waste-heat recovery case studies used in this work. T_{in} is the temperature of the heat source/sink, $\dot{m}$ is the mass flowrate and c_p is the specific heat capacity. The fluid velocities v are selected to ensure minimal pressure drops in the heat exchangers.

	T_{in} [°C]	$\dot{m}$ [kg/s]	c_p [kJ/kgK]	v [m/s]
Heat source (h)	150/250/350	2.1	2.0	2.0
Heat sink (c)	15	5.0	4.2	1.5

Table 5.2: Four common hydrocarbon families and their constituent molecular groups as used in the case studies. – represents one single bond, > represents two single bonds and = represents one double bond.

S/N	Hydrocarbon family	General formula	Molecular groups
I	<i>n</i> -alkanes	$\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$	–CH ₃ and >CH ₂
II	isoalkanes	$(\text{CH}_3)_2>\text{CH}-(\text{CH}_2)_n-\text{CH}_3$	–CH ₃ , >CH ₂ and >CH–
III	1-alkenes	$\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{CH}_3$	–CH ₃ , >CH ₂ , =CH– and =CH ₂
IV	2-alkenes	$\text{CH}_3-\text{CH}=\text{CH}-(\text{CH}_2)_n-\text{CH}_3$	–CH ₃ , >CH ₂ and =CH–

Table 5.3: Summary of group-contribution methods used within the CAMPD-ORC framework used for the prediction of the thermodynamic and transport properties of working fluids in organic Rankine cycle systems.

Property	Liquid phase	Vapour phase
Thermodynamic (c_p , h , s , ρ)	SAFT- γ Mie [140, 159]	
Critical (T_{cr} , P_{cr} , V_{cr})	Joback-Reid [125]	
Surface tension (σ)	Sastri-Rao [235]	
Dynamic viscosity (μ)	Joback-Reid [125] (<i>n</i> -alkanes) Sastri-Rao [222] (branched alkanes)	Reichenberg [223, 224]
Thermal conductivity (k)	Sastri [232]	Chung [227, 228]

Parametric NLP and MINLP study

reduces to an NLP problem. The set of equations representing the general formulation of the optimisation problem is thus:

$$\begin{aligned} \min_{\mathbf{x}, \mathbf{z}} \quad & \mathbf{f}(\mathbf{x}, \mathbf{z}), \\ \text{subject to:} \quad & \mathbf{h}(\mathbf{x}, \mathbf{z}) = 0, \\ & \mathbf{g}(\mathbf{x}, \mathbf{z}) \leq 0, \\ & \mathbf{x} \in [\mathbf{x}^{\text{lo}}, \mathbf{x}^{\text{up}}] \subseteq \mathbb{R}^n, \\ & \mathbf{z} \in [\mathbf{z}^{\text{lo}}, \mathbf{z}^{\text{up}}] \subseteq \mathbb{N}^m. \end{aligned} \tag{5.1}$$

In Equation (5.1), $\mathbf{x}$ is the vector of n continuous system variables, representing continuous decision variables in the system model, as in the ORC process model in Chapter 2 (Section 2.1), and $\mathbf{z}$ is the vector of m integer variables describing the quantity of each molecular group in the working fluid. Further, $\mathbf{f}$ is the vector of objective functions, which could be the specific investment cost or the net power output¹, or a multi-objective combination of power and cost. The set of equalities $\mathbf{h}$ contains all equations related to the thermodynamic cycle, the group contribution methods, heat exchanger sizing and costing methodology.

The inequality constraints are represented by the vector $\mathbf{g}$; these would generally relate to the inequalities representing the relationships and limits on the evaporation or condensation pressures and the critical pressure, the pinch-point temperature difference and dry expansion, as presented in Chapter 2 (see Section 2.1.4 and Equation (2.33)). The vectors $\mathbf{x}^{\text{lo}}$, $\mathbf{x}^{\text{up}}$, $\mathbf{z}^{\text{lo}}$ and $\mathbf{z}^{\text{up}}$ are lower (lo) and upper (up) bounds imposed on the continuous process variables and integer decision variables of the model. Alongside the integer amounts and types of molecular groups used to describe the working fluids, four other ORC system variables are needed to optimise the system. These optimisation variables are listed in Table 5.4, alongside their lower and upper bounds.

5.2 Parametric NLP and MINLP study

5.2.1 Non-linear programming (NLP) optimisations

Before completing the full CAMPD-ORC MINLP optimisation study, a series of NLP optimisations to maximise the power output are attempted; these are listed below.

¹When the power is the objective of interest, the aim is to maximise the power output or conversely to minimise its negative; thus, $\mathbf{f}$ in Equation (5.1) is $-\dot{W}_n$.

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Table 5.4: Optimisation variables defined for the waste-heat recovery case studies and their lower and upper bounds. $P_{\text{evap},r}$ and $P_{\text{cond},r}$ represent the reduced evaporation and condensation pressures respectively, θ_{SH} is the degree of superheat in the evaporator, $\Delta T_{\text{pinch}, \min}$ is the minimum temperature difference in the heat exchangers and $-(X)_{\text{n-}}$ is the (integer) number of molecular group X present in a working fluid.

Variable	Lower bound	Upper bound	Unit
$P_{\text{evap},r}$	$P_{\text{cond},r}$	0.85	–
$P_{\text{cond},r}$	$0.25/P_{\text{crit}}$	$P_{\text{evap},r}$	–
θ_{SH}	0	1	–
$\Delta T_{\text{pinch}, \min}$	10	200	°C
$-(X)_{\text{n-}}$	0	20	–

- A parametric NLP optimisation study was completed whereby for each hydrocarbon family in Table 5.2 the number of $>\text{CH}_2$ groups was varied parametrically and an NLP optimisation considering only the ORC system variables in Table 5.4 was completed. Thus, the specification $\mathbf{z} \in [\mathbf{z}^{\text{lo}}, \mathbf{z}^{\text{up}}] \subseteq \mathbb{N}^m$ was excluded from Equation (5.1).
- Next, the number of $>\text{CH}_2$ groups was then introduced as a continuous variable and another NLP optimisation was completed. The result from this optimisation should provide the global maximum for that hydrocarbon family.
- Finally, the sensitivity of the global maximum to the number of $>\text{CH}_2$ groups is assessed. This was done to ensure the NLP optimisation successfully finds the global optimum, and to allow the behaviour of the system as the number of $>\text{CH}_2$ groups changes to be investigated.

The results from this study for the four different hydrocarbon families listed in Table 5.2, at the three different heat-source temperatures, are displayed in Figure 5.1.

Firstly, in all instances the NLP optimisation that incorporated the number of $>\text{CH}_2$ groups as a continuous variable always resulted in the highest net power output from the system, thus confirming that when optimising the five variables listed in Table 5.4, the NLP optimisation always finds the global optimum. For the three-defined heat sources this corresponds to maximum net output powers of 36.4, 138.0 and 227.0 kW respectively. For the 150 °C heat source, this optimum was found for a 1-alkene, whilst for the other two heat-source temperatures this optimum was found for a 2-alkene.

Secondly, it is observed that around the optimum number of $>\text{CH}_2$ groups there is often a steep reduction in the power output as the number of $>\text{CH}_2$ groups either increases or decreases from this optimal point, to attain a feasible molecule (*i.e.*, an integer number of $>\text{CH}_2$ groups). For example, considering the 1-alkene family for the 150 °C heat source, the theoretical maximum power is 36.4 kW at $-(\text{CH}_2)_n = 0.3$. However, reducing this to $-(\text{CH}_2)_n = 0.0$ or increasing to $-(\text{CH}_2)_n = 1$ reduces the power output by 4.5% and 8.6% respectively. To understand this behaviour in more detail the results for this hydrocarbon family for this heat-source temperature have been presented in Figure 5.2. Here the optimal ORC system variables, and the resulting net power output are presented against the number of $>\text{CH}_2$ groups. The condensation temperature and evaporator pinch point have not been included since the condensation temperature was found to vary only by a few degrees, whilst the optimal pinch point always sat at the lower bound of 10 °C.

From Figure 5.2, it is observed that the global optimum corresponds to the number of $>\text{CH}_2$ groups that maximises the net power output from the system, whilst having the maximum possible reduced pressure ($P_{\text{evap},r} = 0.85$) and the minimum superheat ($\Delta T_{\text{sh}} = 0.1$ °C). As the number of $>\text{CH}_2$ groups reduces, the critical temperature of the fluid will reduce and therefore the maximum evaporation temperature will also reduce. Therefore, to effectively utilise the heat available it is necessary start superheating the working fluid. Conversely, as the number of $>\text{CH}_2$ groups increases, the critical temperature of the fluid increases, so the reduced pressure will reduce to maintain a similar evaporation temperature and therefore heat-source profile. In other words, during the NLP optimisation in which the integer optimisation variables are relaxed and can take any continuous value, the optimisation converges on an optimum theoretical working-fluid that operates at the maximum bound for the reduced pressure, and minimum bounds for the amount of superheating and the evaporator pinch point.

The results in Figure 5.1 have been replotted in terms of the number of carbon atoms contained within the working-fluid, and these results are shown in Figure 5.3. From this figure, it is clear that for each heat-source temperature there appears to be an optimum number of carbon atoms that the working fluid should contain if one wants to maximise the net power output from the system. It is also observed that as the heat-source temperature increases, increasingly complex working fluids should be favoured. For this study, it appears that the number of carbon atoms should be around 3, 5 and 6 - 7 for heat-source temperatures of 150, 250 and 350 °C respectively. This information can immediately be used to identify likely working fluids for these heat-source temperatures.

CHAPTER 5. CASE STUDIES IN CAMPD OF ORGANIC RANKINE CYCLE SYSTEMS

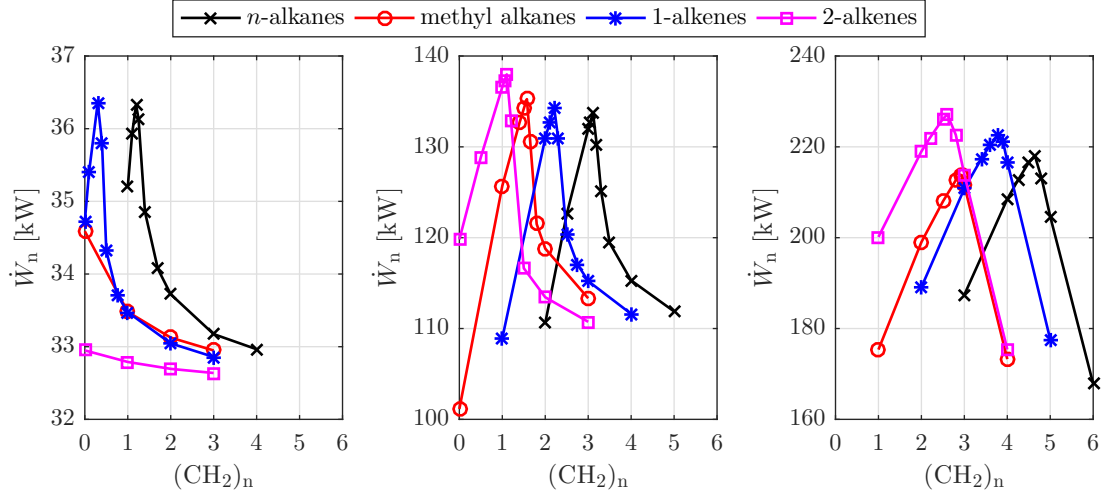


Figure 5.1: The effect of the number of $>\text{CH}_2$ groups on the net power output from the ORC system for the four hydrocarbon families at three different heat-source temperatures; from left to right: $T_{\text{hi}} = 150$, 250 and 350 °C.

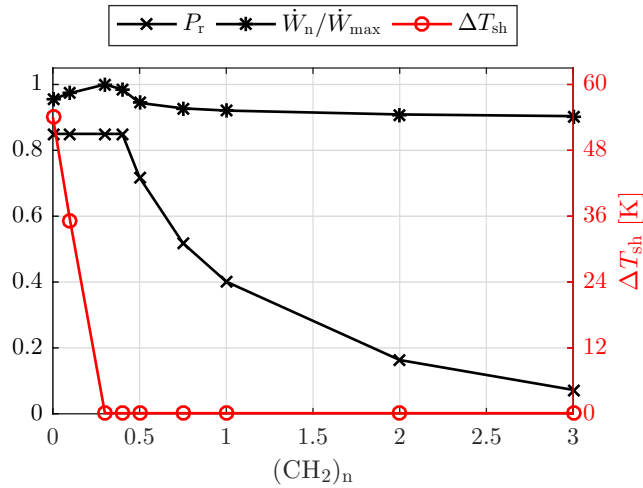


Figure 5.2: The variation in the optimal reduced pressure P_r , the normalised power output $\dot{W}_n/\dot{W}_{\text{max}}$ and the optimal amount of superheating ΔT_{sh} as functions of the number of $>\text{CH}_2$ groups for the 1-alkene family and a heat-source temperature of $T_{\text{hi}} = 150$ °C.

Parametric NLP and MINLP study

Finally to conclude this section it is necessary to discuss the effect of the working fluid on the ORC condensation temperature and pressure. Although not shown in Figure 5.2, the optimal condensation temperature for the 150 and 250 °C heat sources is found to be the minimum condensation temperature that can be obtained without violating the condenser pinch constraint. However, when considering the 350 °C heat source, the condensation temperature is no longer constrained by the condenser pinch point, but instead is constrained by the minimum allowable condensation pressure, defined here as 0.25 bar(a) (see Table 5.4). This is because as the molecular complexity of the working-fluid increases, the saturation temperature at this defined pressure also increases. For example, for the 150 °C heat source the optimal condensation temperatures range between 31.6 and 35.4 °C, with condensation pressures between 2.7 and 9.7 bar(a). However, for the 350 °C heat source all condensation pressures are 0.25 bar(a), whilst the condensation temperatures have increased to values between 46.6 and 47.3 °C. The minimum allowable condensation pressure was defined as 0.25 bar(a) as this value was considered to be a reasonable trade-off between the additional performance benefit that sub-atmospheric condensation offers, and the additional complexity of having to design a sub-atmospheric condenser.

To investigate the effect of the condensation pressure constraint on the cycle the NLP optimisations for the 350 °C heat source were repeated, this time setting $P_{\text{cond,min}} = 0$ bar(a). The results are shown in Figure 5.4.

From Figure 5.4 it is clear that the condensation pressure constraint limits the maximum power output that can be generated from the system. For less complex molecules, with $C_n < 6$, both optimisations result in the same optimal cycle since the condensation temperature is not constrained by the condensation pressure. However, as molecular complexity increases, the 0.25 bar constraint causes a reduction in the power output, and also results in an optimal working fluid that contains less carbon atoms than the optimum obtained from the unconstrained optimisation. For the results shown in Figure 5.4, the condensation pressure constraint reduces the maximum theoretical power output by 6% when compared to the unconstrained optimisation, and ultimately results in the selection of a molecule composed of 6 or 7 carbon atoms, rather than 8 or 9. Therefore, this analysis clearly demonstrates the improved thermodynamic performance that can be achieved for high-temperature heat sources by using more complex molecules, but highlights the complexity of having to operate these fluids under a vacuum in order to realise their potential.

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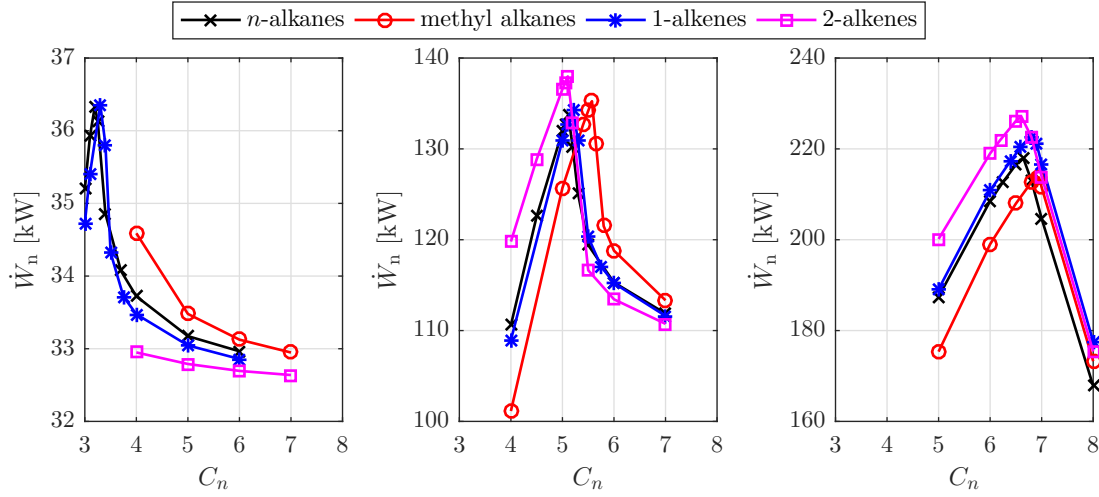


Figure 5.3: The results from Figure 5.1 represented in terms of the number of carbon atoms C_n , rather than the number of $>\text{CH}_2$ groups; from left to right: $T_{hi} = 150, 250$ and 350°C .

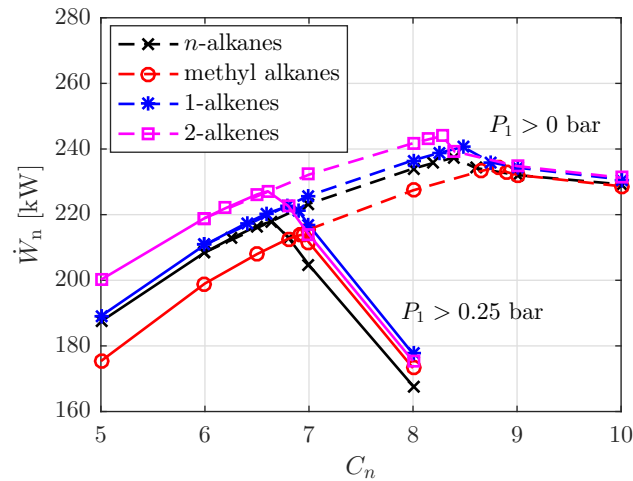


Figure 5.4: The effect of the condensation pressure constraint on the net power output from the cycle for the 350°C heat source. The solid lines correspond to the 0.25 bar absolute constraint, whilst the dashed lines correspond to the unconstrained optimisation cases.

5.2.2 Small scale MINLP optimisations

The final stage of this study was to set the number of $>\text{CH}_2$ groups to an integer decision variable and to run the CAMPD-ORC MINLP optimisation problem for each of the hydrocarbon families. Clearly, the optimal integer number of $>\text{CH}_2$ groups for each hydrocarbon family is already known from either Figures 5.1 or 5.3. However, the purpose of now completing the MINLP optimisation is to confirm the suitability of the MINLP solver for CAMPD-ORC problems. Furthermore, for each hydrocarbon family and heat-source temperature the MINLP optimisation was completed for multiple starting points to ensure that the global optimum was found. These starting points were defined as the optimal points that resulted from the initial parametric NLP optimisation study. For example, for the *n*-alkane family and 150 °C heat source, an optimal ORC system was obtained for *n*-propane, *n*-butane, *n*-pentane and *n*-hexane, and for this case these results were used as the MINLP starting points.

For each hydrocarbon family and heat-source temperature it was found that all starting points converged to the same optimal number of $>\text{CH}_2$ groups and the same values for the ORC system variables. Furthermore, the optimal system that results from the MINLP optimisation also matched the optimal systems identified in the previous parametric NLP study, therefore confirming the suitability of the MINLP solver. The resulting net power output for each case is summarised in Figure 5.5. For the 150, 250 and 350 °C heat-source temperatures optimal net power outputs of 35.2, 136.7 and 219.0 kW are obtained respectively. For the 150 °C heat source this is obtained for propane ($\text{CH}_2\text{--CH}_3\text{--CH}_2$) which is part of the *n*-alkane family, whilst for the 250 and 350 °C heat sources both fluids are part of the 2-alkene family, with 2-pentene ($\text{CH}_3\text{--CH=CH--CH}_2\text{--CH}_3$) and 2-hexene ($\text{CH}_3\text{--CH=CH--(CH}_2)_2\text{--CH}_3$) being the optimal working-fluids respectively.

From Figure 5.5, it is also observed that the percentage reduction in the net power output from the MINLP optimisation studies compared to the theoretical maximums range between 0% and 7.1%. The 0% corresponds to the methyl alkane and 2-alkene families for the 150 °C heat source, in which both the NLP and MINLP both converged on solutions with zero $>\text{CH}_2$ groups. The largest percentage difference corresponds to the methyl alkane family for the 250 °C heat source, and in this case the NLP converged on a solution with 1.57 $>\text{CH}_2$ groups. Since this is not particularly close to either 1 or 2 $>\text{CH}_2$ groups, a significant reduction in power is observed when moving to the MINLP result.

Overall, this study suggests that propane is an optimal working fluid for temperatures below 150 °C, and this agrees well with the study performed using PC-SAFT in Ref. [147].

Furthermore, these results suggest that working fluids that contain a $-\text{CH}=\text{CH}-$ double bond (*i.e.*, 2-alkenes) perform well for heat-source temperatures between 250 and 350 °C. More generally, the results from the present study have confirmed the suitability of a CAMPD-ORC model for the integrated working fluid and thermodynamic optimisation of ORC systems. Instead of running multiple optimisations for a range of different working fluids, one MINLP optimisation can be completed for each hydrocarbon family to determine the optimal working fluid and thermodynamic parameters. This demonstrates the potential of the CAMPD-ORC formulation to drive the search for the next generation of ORC systems.

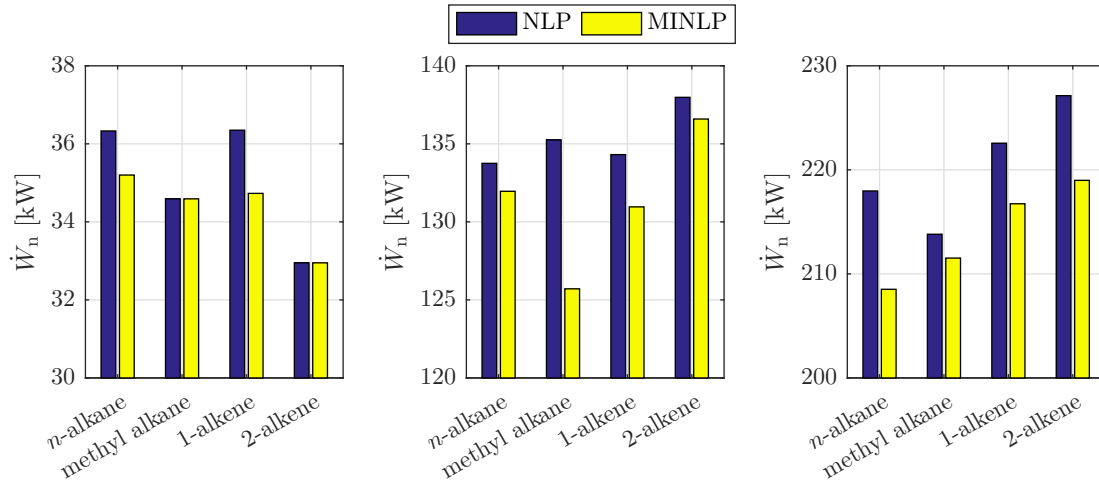


Figure 5.5: The maximum net power output obtained from each heat source with each hydrocarbon family. The NLP results refer to the theoretical maximum obtained from the NLP study, whilst the MINLP results refer to the maximum that can be achieved using a feasible working-fluid; from left to right: $T_{hi} = 150, 250$ and 350 °C.

5.3 Maximum power designs via NLP formulations

In Section 5.2.1, the net power output from the ORC engine is maximised in parametric studies. The NLP optimisation problem is restated here:

$$\begin{aligned}
 \min_{\mathbf{x}} \quad & \mathbf{f}(\mathbf{x}, \mathbf{z}^m) = -\dot{W}_n(\mathbf{x}, \mathbf{z}^m), \\
 \text{subject to:} \quad & \mathbf{h}(\mathbf{x}, \mathbf{z}^m) = 0, \\
 & \mathbf{g}(\mathbf{x}, \mathbf{z}^m) \leq 0, \\
 & \mathbf{x} \in [\mathbf{x}^{\text{lo}}, \mathbf{x}^{\text{up}}] \subseteq \mathbb{R}^n.
 \end{aligned} \tag{5.2}$$

In this formulation, there are no integer variables as the working-fluid groups are selected from Table 5.2 and the optimisation is carried out with a fixed number of $>\text{CH}_2$ groups. The equality constraints ($\mathbf{h}(\mathbf{x}, \mathbf{z}^m) = 0$) are those related to the ORC system model presented in Chapter 2 (Section 2.1) while the inequality constraints ($\mathbf{g}(\mathbf{x}, \mathbf{z}^m) \leq 0$) are the same as presented in Equation (2.33) in Section 2.1.4. The optimal cycles, sizing and system costs are presented in this section.

5.3.1 Thermodynamic performance and optimal cycles

The maximum power from the cycles are plotted in Figure 5.6; here C_n refers to the number of carbon atoms in the molecule (n -alkane, methyl alkane, 1-alkene or 2-alkene). The optimal working fluids for the three heat sources at temperatures of 150, 250 and 350 °C are n -propane (n -alkane, $C_n = 3$), 2-pentene (2-alkene, $C_n = 5$) and 2-hexene (2-alkene, $C_n = 6$), corresponding to maximum power outputs of 35.2, 136.7 and 219.0 kW respectively. The corresponding thermal cycle efficiencies are 9.7%, 16.9% and 17.8% respectively. The optimal cycles that correspond to the maximum power are explored in Figure 5.7, in which are displayed three of the cycles ($C_n = 4, 5$ and 6) for the n -alkane, 250 °C case-study on a T - s (temperature-entropy) diagram.

When $C_n = 4$, the evaporation temperature, and therefore evaporation pressure, is constrained by the critical temperature since subcritical cycles are considered. This results in an optimal cycle with a high reduced pressure and a large amount of superheating, since the high-temperature heat can only be absorbed by the cycle by increasing the working-fluid temperature whilst maintaining the same pressure. This introduces the need for an additional heat exchanger, namely the superheater, in addition to increasing the irreversibilities within the heat-addition process, owing to the increased temperature difference between the heat source and working fluid in the evaporation and superheating regions, resulting in a 16% reduction in the power output compared to the optimal cycle. It is also noted that the minimum allowable evaporator pinch point is observed at the preheater inlet in addition to the evaporator inlet. This corresponds to the the lowest heat-source outlet temperature, indicating that the ORC absorbs the maximum amount of heat from the available heat source. Arguably, the thermodynamic performance of the $C_n = 4$ cycle could be improved by increasing the evaporation pressure above the critical pressure, and thus operate a transcritical cycle. However, it is worth noting that higher evaporation pressures lead to more expensive system components, and this can make subcritical cycles more attractive from an economic perspective [242]. Nonetheless, future efforts should extend the existing CAMPD-ORC model to transcritical cycles.

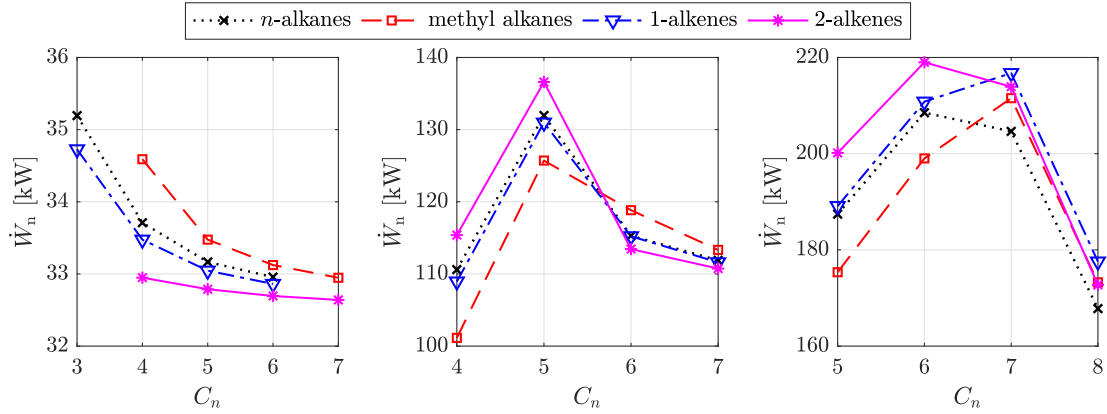


Figure 5.6: Optimal net power output from an ORC system operating with different hydrocarbon working fluids. Results are plotted against the number of carbon atoms C_n in the molecule (n -alkane, methyl alkane, 1-alkene or 2-alkene, as indicated). From left to right: $T_{hi} = 150, 250, 350$ °C.

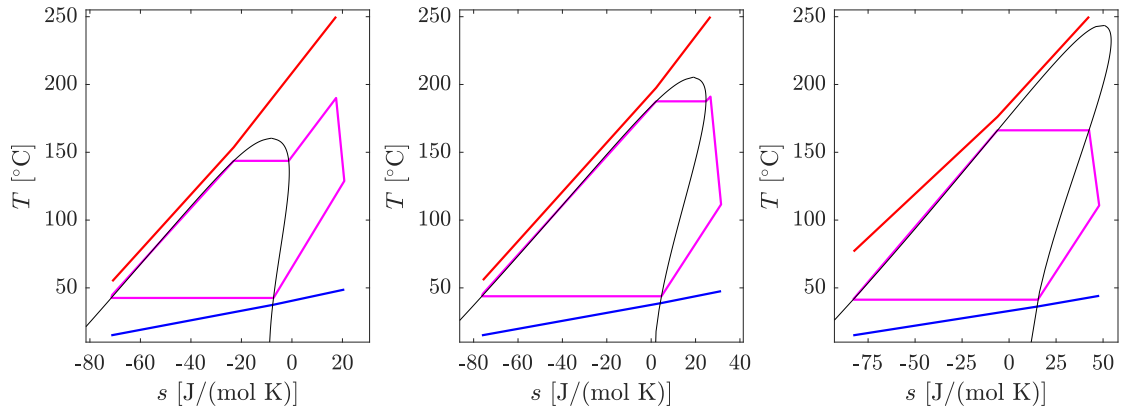


Figure 5.7: T - s plots for three cycles from the n -alkane, 250 °C case-study. From left to right: $C_n = 4$ (n -butane), 5 (n -pentane) and 6 (n -hexane). The red and blue lines are the heat-source and heat-sink streams, the magenta lines are the ORC and the black is the working-fluid saturation dome.

In comparison, when $C_n = 6$, the critical temperature of the working fluid is increased, which means the the evaporation temperature is no longer constrained by the critical temperature. Instead, the evaporation temperature, and therefore evaporation pressure, is constrained by the heat-source temperature profile, and the imposed pinch point at the evaporator inlet. This results in no superheating and a lower reduced evaporator pressure. Whilst the former means a superheater is no longer required, the latter results in a larger latent-heat of evaporation, which impacts the cycle in two ways. Firstly, the larger latent-heat means that a larger proportion of the heat-addition process occurs at a constant temperature, which increases the average temperature difference between the heat source and working fluid, resulting in more irreversibility. Secondly, the larger latent-heat also means that the preheater inlet is no longer pinched, which means this cycle absorbs less heat from the heat source. These combined effects result in a 13% reduction in power output compared to the optimal cycle.

Finally, where $C_n = 5$, the maximum power is obtained. This cycle has a high-reduced pressure, minimal superheating, and the minimum allowable pinch point is once again observed at both the preheater inlet and the evaporation inlet. Overall, this means that the ORC absorbs the maximum amount of heat possible, whilst a low latent heat of vaporisation, and minimal superheating results in the majority of heat-transfer occurring during in the preheating region. This minimises irreversibilities within the heat-addition process, and results in the maximum power output.

5.3.2 Heat exchanger thermal load

The effect of the working fluid, in terms of the number of carbon atoms, on the evaporator and condenser thermal load has been reported in Figures 5.8 and 5.9 respectively. For the evaporator, $\dot{Q}_{ph}$, $\dot{Q}_{ev}$ and $\dot{Q}_{sh}$ refer to the preheating, two-phase evaporation, and superheating loads respectively, and for the condenser $\dot{Q}_{ds}$ and $\dot{Q}_{co}$ refer to the desuperheating and two-phase condensation loads respectively. In Figures 5.8 and 5.9, only the results for one particular working-fluid family have been presented for each heat-source temperature, and this corresponds to *n*-alkane family for the 150 °C heat source, and the 2-alkene family for both the 250 and 350 °C heat sources. Since there was no significantly large difference observed in the heat-exchanger load breakdown as the working-fluid family is changed, the discussion in the following paragraphs is relevant to all of the families considered.

In terms of the evaporator load a number of observations can be made. Firstly, for the 150 and 250 °C heat-source temperatures there is a clear link between maximising

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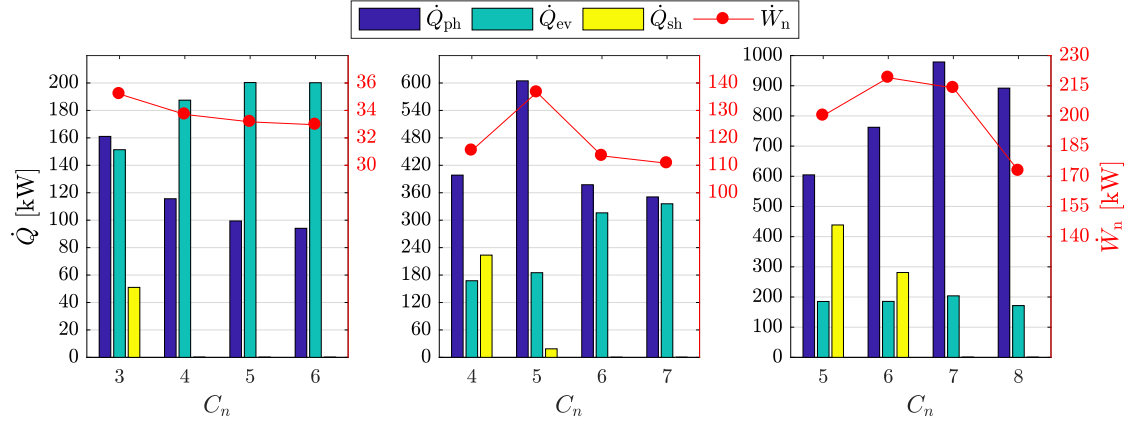


Figure 5.8: Breakdown of evaporator load for an optimal ORC system operating with different hydrocarbon working fluids. From left to right: $T_{hi} = 150^\circ\text{C}$ (n -alkane family); $T_{hi} = 250^\circ\text{C}$ (2-alkene family); $T_{hi} = 350^\circ\text{C}$ (2-alkene family).

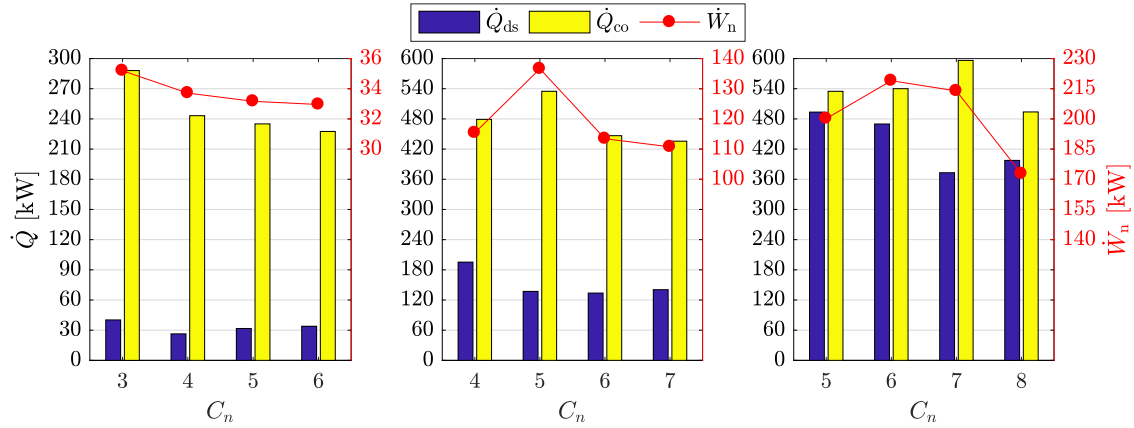


Figure 5.9: Breakdown of condenser load for an optimal ORC system operating with different hydrocarbon working fluids. From left to right: $T_{hi} = 150^\circ\text{C}$ (n -alkane family); $T_{hi} = 250^\circ\text{C}$ (2-alkene family); $T_{hi} = 350^\circ\text{C}$ (2-alkene family).

the power output and increasing the preheater load, with both parameters showing the same trend as C_n is increased. Moreover, for molecules that are less complex than the optimal fluid, it is always necessary to have superheating, whilst for molecules that are more complex than the optimal fluid the evaporation load increases. Furthermore, it is observed that as the heat-source temperature increases the proportion of heat-addition that occurs within the preheater increases. More specifically, for the 150 °C heat-source temperature the preheater accounts for between 32.0% and 44.3% of the total evaporator load, whilst for the 350 °C heat-source temperature, the preheater accounts for between 49.2% and 83.8% of the total evaporator load, depending on the fluid.

From Figure 5.9, it is observed that maximising the power output also corresponds to the largest condensation load for the 150 and 250 °C heat-source temperatures. It is also observed that in general the less complex (lower C_n) molecules result in the highest desuperheater loads. This was to be expected as these systems included superheaters, therefore the working-fluid at the outlet of the expander has a considerable degree of superheat. In terms of the effect of the heat-source temperature on the distribution of the condenser load, it is observed that increasing the heat-source temperature results in a larger proportion of the heat rejection occurring during the desuperheater stage. For example, for the 150 °C the desuperheater accounts for between 9.8% and 13.0% of the total condenser load, whilst for the 350 °C heat-source temperature this increases to between 38.5% and 48%. This effect can be explained by considering the behaviour of the saturation dome of hydrocarbon working fluids as the critical temperature is increased. In general, the saturation dome of a working fluid with a higher critical temperature (higher C_n) will have a larger overhang (*i.e.*, drier) when viewed on a T - s diagram. Therefore, expansion will result in a larger amount of superheat at the expander outlet. Moreover, this effect becomes more pronounced as the pressure ratio is increased, as is the case as the heat-source temperature increases.

5.3.3 Component sizing performance

Following from the thermodynamic analysis, the required heat-transfer areas for the evaporator and condenser can be obtained using the heat-exchanger sizing model based on the group-contribution transport properties. In Figures 5.10 and 5.11 the breakdown of the evaporator and condenser heat-transfer area requirements are plotted for the same working fluids and cycles considered in Figures 5.8 and 5.9. For the evaporator, A_{ph} , A_{ev} and A_{sh} refer to the preheating, two-phase evaporation, and superheating areas re-

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spectively, and for the condenser A_{ds} and A_{co} refer to the desuperheating and two-phase condensation areas respectively.

Unsurprisingly, for each heat-source temperature, the cycle with the highest power output results in the highest heat-transfer area requirements for the evaporator, corresponding to 78.8, 264.1 and 313.6 m² for the *n*-propane, 2-pentene and 2-hexene cases respectively. However, it is observed that whilst selecting a different working fluid will cause a reduction in the power output, the reduction in the heat-transfer area can be significant. For example, for the three heat-source temperatures, if C_n is increased by one, the power output is reduced by 4.2%, 16.9% and 2.3%, but this corresponds to a reduction in the total evaporator area by 35.6%, 66.1% and 48.1% respectively. Therefore, it is clear that a trade-off exists that must be considered when selecting the most suitable working fluid for a particular application.

Considering the breakdown of the evaporator heat-transfer area, it is observed that in general the preheater section accounts for the largest percentage of the required area. This was to be expected from considering the evaporator load breakdown (Figure 5.8), but is further exaggerated since the overall heat-transfer coefficient for the single-phase heat transfer section is generally lower than it is for the two-phase evaporation, meaning a larger area is required to transfer the same amount of heat across similar temperature differences ($\dot{Q} = UA\Delta T_{lm}$). For all the fluids evaluated, the preheating overall heat-transfer coefficient ranged between 0.176 and 0.305 kW/(m² K), whilst the two-phase evaporation overall heat-transfer coefficient ranged between 0.268 and 0.591 kW/(m² K). In addition, the minimum pinch point is recorded in the preheater section, significantly reducing the log-mean temperature difference between the two working fluids. This results in an increase of the area requirements of the preheater in comparison to the two-phase evaporating section, even for very similar heat-transfer loads.

A case in point is given by the propane working fluid (with $C_n = 3$) at the 150 °C heat-source temperature that have similar preheater and evaporator loads (Figure 5.8), but the preheater area required is more than double the respective one for the evaporator section (Figure 5.10). Similar findings are observed for the 2-heptene working fluid (with $C_n = 7$) at 250 °C heat-source temperature. Referring to the results in Figure 5.10, for the 150 °C heat-source temperature the preheater accounts for between 43.2% and 66.4% of the total evaporator area, whilst for the 350 °C heat-source temperature, the preheater accounts for between 89.5% and 96.4% of the total evaporator area, depending on the fluid.

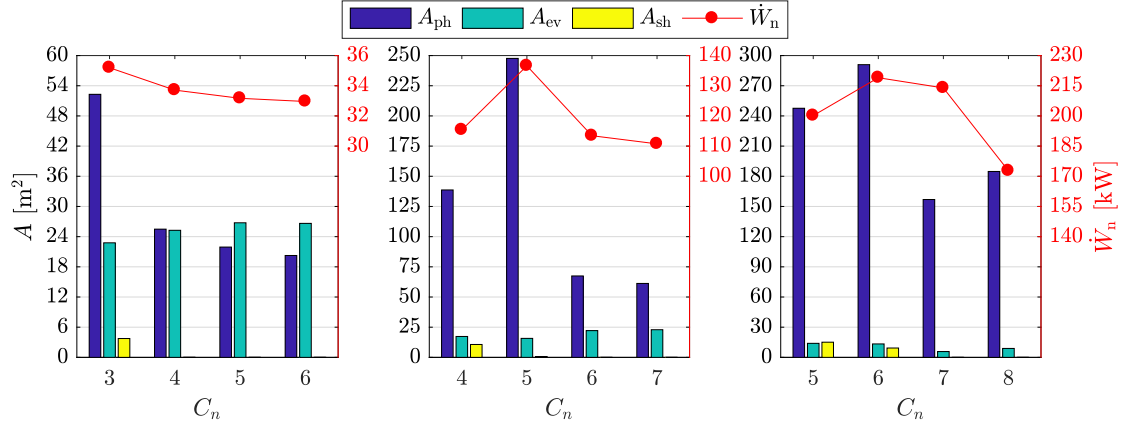


Figure 5.10: Breakdown of evaporator heat-transfer area requirements for an optimal ORC system operating with different hydrocarbon working fluids. From left to right: $T_{hi} = 150^\circ\text{C}$ (n -alkane family); $T_{hi} = 250^\circ\text{C}$ (2-alkene family); $T_{hi} = 350^\circ\text{C}$ (2-alkene family).

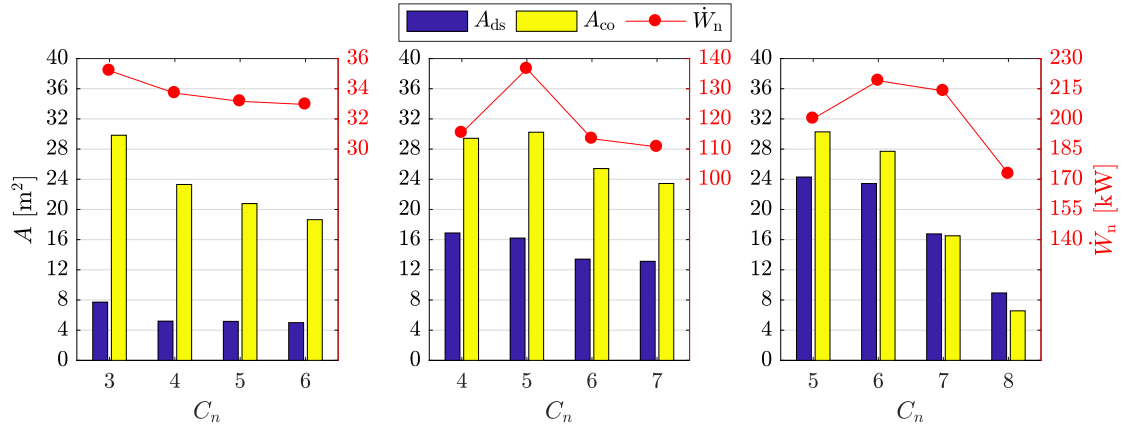


Figure 5.11: Breakdown of condenser heat-transfer area requirements for an optimal ORC system operating with different hydrocarbon working fluids. From left to right: $T_{hi} = 150^\circ\text{C}$ (n -alkane family); $T_{hi} = 250^\circ\text{C}$ (2-alkene family); $T_{hi} = 350^\circ\text{C}$ (2-alkene family).

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For the condenser heat-transfer area requirements, similar observations to those made when evaluating the evaporator load are found; the thermodynamic optimal cycles result in systems with the largest heat exchangers, with the exception of the 350 °C case study where 2-pentene ($C_n = 5$, instead of 2-hexene, $C_n = 6$). More specifically, for the n -propane, 2-pentene and 2-hexene cases, the total condenser areas are 37.6, 46.4 and 51.1 m² respectively.

However, the required condenser areas do not increase significantly as the heat-source temperature increases. This is attributed to the higher temperature differences between the expander outlet temperature and the condensation temperature, and the heat sink as the heat-source temperature increases. For example, for the cycles reported in Figure 5.11, the condensation temperatures range between 30.8 and 33.7 °C for the 150 °C heat source, 40.7 and 45.5 °C for the 250 °C heat source and 45.5 and 81.5 °C for the 350 °C heat source. Thus, although the condenser load increases with the heat source temperature (see Figure 5.9, the significant increase in the condensation temperature increases the average log-mean temperature difference in the condenser, resulting in similar heat-transfer area requirements between the condensers for the high temperature and lower temperature heat sources. It is also worth noting that the significant increase in the condensation temperature for the $C_n = 8$, 350 °C case, is because a minimum condensation pressure constraint is applied (0.25 bar) during the optimisation. In fact, for both the $C_n = 7$ and $C_n = 8$ cases for this heat-source temperature the condensation pressure is actually equal to the minimum allowable condensation pressure. Therefore, a lower condensation temperature cannot be achieved without violating this constraint.

Comparing the breakdown of the condenser heat-transfer area requirements, and the breakdown of the condenser load, it is observed that the breakdown of the load and area are fairly similar. The desuperheater area accounts for a slightly larger proportion of the total condenser area, compared to the desuperheating load, and this can again be attributed to the higher overall heat-transfer coefficients for two-phase heat transfer compared to the single-phase heat transfer. For all the fluids evaluated, the desuperheating overall heat-transfer coefficients ranged between 0.385 and 0.518 kW/(m² K), whilst for two-phase condensation it ranged between 0.926 and 1.45 kW/(m² K).

To conclude this section, the total heat-transfer area requirements (*i.e.*, total evaporator area A_h , and total condenser area A_c) for each heat-source temperature and each working fluid considered within this study are plotted in Figure 5.12. Considering this figure, and referring back to Figure 5.6, it is clear that the optimal thermodynamic cycles always result in the largest heat exchangers, and this is particularly true for the 150 and

250 °C heat-source temperature cases. The reason can also be explained by reconsidering Figure 5.7, and the accompanying discussion. That is to say that the optimal thermodynamic cycle results in a large preheating load, which means a large proportion of the available heat is absorbed by the cycle which increases power output. However, this heat transfer occurs under a small temperature difference, resulting in large heat-transfer area requirements.

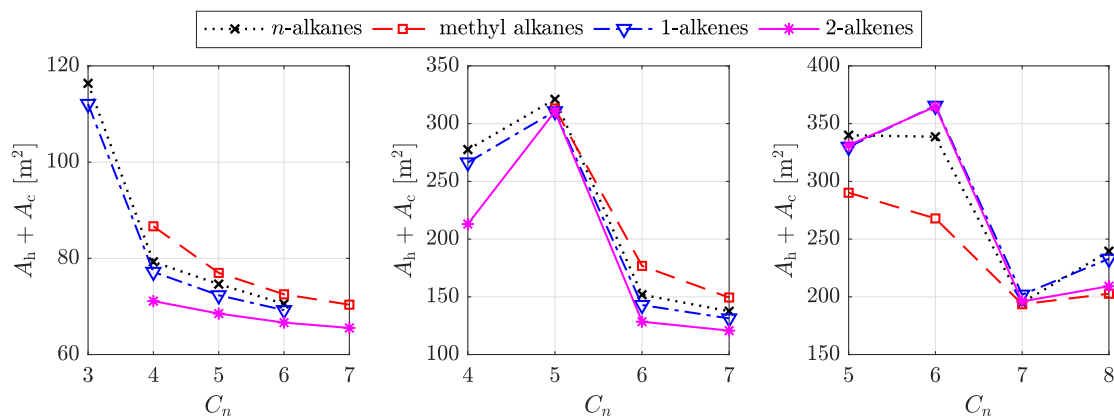


Figure 5.12: Total heat-transfer area requirements for each cycle previously identified in Figure 5.6. From left to right: $T_{hi} = 150, 250, 350$ °C.

5.3.4 Economic considerations

Clearly, there is a trade-off between thermodynamic performance and the size of the system components. Using the known heat-transfer areas, the pump work and expander work for each cycle, the cost correlations described in Chapter 2 (Section 2.1.3) can be used to obtain the the system investment costs and the corresponding specific purchased equipment cost (SPEC, Figure 5.13). As one would expect, the lowest temperature/rated systems (150 °C) correspond to highest SPEC whilst the highest temperature/rated systems (350 °C) correspond to the lowest SPEC. This is partly attributable to the higher relative costs associated with manufacturing smaller components, and partly attributable to the inherent lower efficiencies as the heat-source temperature reduces.

From Figure 5.13, it is clear that for each heat-source temperature and hydrocarbon family, there appears to be a particular working fluid that will result in systems with the lowest SIC/SPEC¹. For the 150, 250 and 350 °C heat-source temperatures the lowest

¹This is not the absolute minimum specific investment costs as the optimisation objective in Equation (5.2) is that of maximising the power output. Systems and optimisation problems with the minimum SIC as the objective are presented in Section 5.4

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SPECs are £5620, £2760 and £2070 per kW respectively, and these are found for $C_n = 7$ (isoheptane), $C_n = 5$ (2-pentene) and $C_n = 7$ (2-heptene) respectively. It should be noted that within the CAMPD-ORC model there is no consideration of the order of the functional groups within the molecule. Therefore, isoheptane can refer to either 2-methyl hexane or 3-methyl hexane, depending on the location of the $>\text{CH}-$ group.

For the 250 °C heat source 2-pentene is found to both maximise the power output and minimise the SPEC/SIC, and could therefore be identified as the optimal working fluid. However, for the other two heat sources, different working fluids are identified based on whether a thermodynamic or technoeconomic performance metric is used. In particular, for the 350 °C heat source, the results suggest that in terms of minimising the SIC/SPEC, it could be beneficial to use a working fluid with a relatively high condensation temperature, as this increases the temperature difference within the evaporator and reduces the heat-transfer area requirement. Alongside considering the SPEC values obtained for the systems, it is also interesting to consider the breakdown in the total system cost, and this is reported in Figure 5.14 for the same working fluids previously evaluated in terms of the heat-exchanger load and heat-transfer area requirements for the evaporator and condenser. Again, it is noted that the results reported in this figure are representative of the results obtained for each working-fluid family.

Firstly, it is noted that for all the cases considered the pump only accounts for a very small percentage ($< 2.3\%$) of the total system cost. Furthermore, the evaporator and condenser both account for a similar percentage of the overall costs, corresponding to approximately 35%, 20% and 13% for the 150, 250 and 350 °C heat-source temperatures respectively. However, the most obvious observation from Figure 5.14 is the significant percentage of the total cost that the expander accounts for as the heat-source temperature increases. This behaviour can, in part, be explained since a higher heat-source temperature will lead to a higher cycle efficiency. Therefore, a greater percentage of the heat that is input into the system can be converted into power, which therefore requires an expander with a higher power output, and a larger generator, for the same rating of heat exchanger.

Another possible reason for such a large cost estimate for the expander could relate to the suitability of the expander cost correlation for ORC systems. Arguably, within an ORC system, the cost of the expander is the largest unknown, particular for small-scale systems rated at hundreds of kilowatt, as the commercialisation of these systems is still in its infancy. For this study, the material factor F for the expander, which accounts for component manufacturing, was set to 3.5 based on recommendations within the literature.

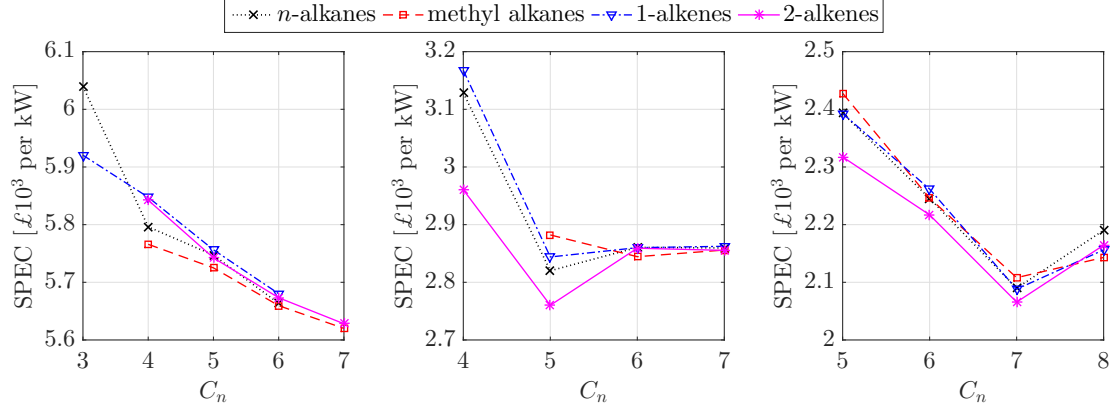


Figure 5.13: Specific purchased equipment cost (SPEC) in £ per kW for each optimal cycle previously identified in Figure 5.6. From left to right: $T_{hi} = 150, 250, 350^\circ\text{C}$.

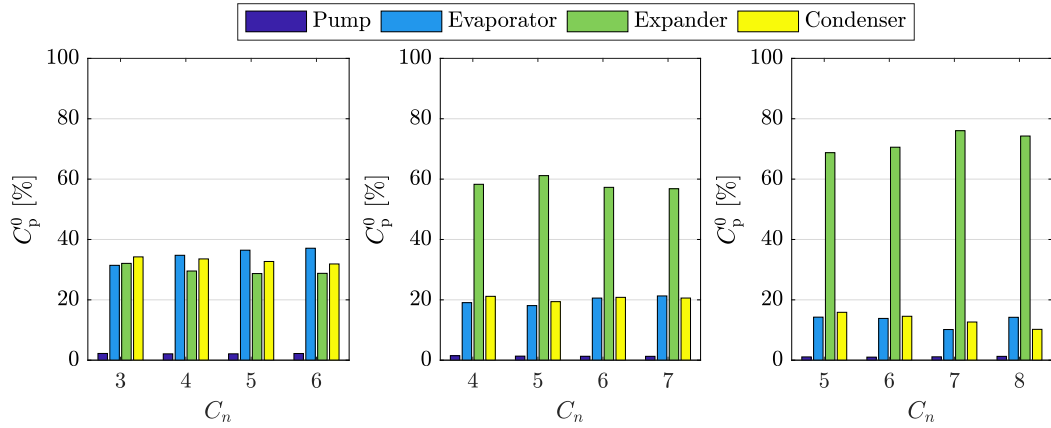


Figure 5.14: Component cost breakdown of the costs of ORC systems with different hydrocarbon working fluids and heat-source temperatures. From left to right: $T_{hi} = 150^\circ\text{C}$ (n -alkane family); $T_{hi} = 250^\circ\text{C}$ (2-alkene family); $T_{hi} = 350^\circ\text{C}$ (2-alkene family).

However, it should be noted that these correlations were not developed specifically for ORC expanders but they originate from the chemical industry, and should be used for comparing alternative system configurations and working fluids performance, where the relative results are more important than the absolute cost figures.

Despite possible uncertainties with the cost correlations, referring back to Figures 4.16 and 4.17 in Chapter 4, it has been shown that the SPEC (and thus, the SIC) values predicted by the CAMPD-ORC are in good agreement with values reported within the literature. Moreover, it should be stated the primary aim of in this research effort has been to develop a CAMPD-ORC framework that can be used to identify novel ORC architectures from a thermoeconomic perspective. Therefore, the cost correlations applied within this framework can be easily adapted as the ORC market continues to grow, and more cost information on the system components becomes available; the concerned cost correlations will only need to be updated as more information becomes available.

5.4 Minimum SIC designs via NLP formulations

The trade off between the performance of an ORC system and its equipment sizes and (total) costs was highlighted in Sections 5.3.3 and 5.3.4 where the objective was to maximise the power output from the ORC engine. In a bid to address this trade off, a set of NLP optimisations is performed for the three case studies specified in Table 5.1, with the objective of minimising the specific investment costs (SIC):

$$\begin{aligned} \min_{\mathbf{x}} \quad & \mathbf{f}(\mathbf{x}, \mathbf{z}^m) = \text{SIC}(\mathbf{x}, \mathbf{z}^m), \\ \text{subject to:} \quad & \mathbf{h}(\mathbf{x}, \mathbf{z}^m) = 0, \\ & \mathbf{g}(\mathbf{x}, \mathbf{z}^m) \leq 0, \\ & \mathbf{x} \in [\mathbf{x}^{\text{lo}}, \mathbf{x}^{\text{up}}] \subseteq \mathbb{R}^n. \end{aligned} \tag{5.3}$$

The working fluid is chosen *a priori*, from the four common hydrocarbon families in Table 5.2: *n*-alkanes, 2-methylalkanes (isoalkanes), 1-alkenes and 2-alkenes, by varying the number of >CH₂ groups in the working fluid molecule. Thus, as with Equation (5.2), there are no integer variables and the optimisation is carried out with a fixed number of >CH₂ groups. Similarly, the equality constraints ($\mathbf{h}(\mathbf{x}, \mathbf{z}^m) = 0$) are those related to the ORC system model presented in Chapter 2 (Section 2.1) while the inequality constraints ($\mathbf{g}(\mathbf{x}, \mathbf{z}^m) \leq 0$) are the same as presented in Equation (2.33), Section 2.1.4. However, the minimum pinch-point temperature difference in the heat exchangers ($\Delta T_{\text{pinch, min}}$) is

Minimum SIC designs via NLP formulations

relaxed from the value of 10 °C used in Section 5.3, to 0 °C here. In the MINLP problems presented in Section 5.5, assessment of more complex molecules is possible with the use of integer amounts of various molecular groups.

The optimisations are carried out using a Matlab implementation of the stochastic ‘non-dominating genetic algorithm II’ (NSGA-II) solver [243] which is capable of solving problems with either a single objective or multiple objectives. This solver is particularly preferred over deterministic solvers (such as the NLPSQP and the OAERAP solvers) due to the numerous discontinuities present in the model; these discontinuities arise from the correlations used in predicting heat transfer coefficients for different working fluid phases and from the equipment cost correlations. An important aspect of stochastic solvers are the parameters of the solver, such as the number of generations, the population size, the cross-over fraction of variables and mutation-fraction of variables. More information on these parameters and their effects can be found in the work by Srinivas and Deb [244]. This algorithm is used in subsequent optimisation problems in this chapter; the parameters that are used in this study for different optimisation problems are presented in Table 5.5.

Table 5.5: Algorithm parameters for the NSGA-II solver as used for optimisation problems in this and subsequent sections.

Parameter	NLP	MINLP	Multi-objective
Max. generations	60	150	200
Population size	150	400	500
Mutation fraction	0.3	0.6	0.7
Cross-over fraction	0.7	0.4	0.3
Mutation scale	0.5	0.5	0.5
Shrink factor	0.25	0.25	0.25
Cross-over ratio	1.5	1.5	1.5

5.4.1 Minimum investment costs and power output

The results of minimising the specific investment costs (SIC) for each heat source and hydrocarbon family are presented in Figure 5.15. Here, the SIC and the corresponding

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net power output ($\dot{W}_n$), are plotted against the number of carbon atoms that are present in the working fluid (C_n).

As can be seen in Figure 5.15, a substantial increase in $\dot{W}_n$ is observed with increasing $T_{h,in}$. The highest $\dot{W}_n$ values are 27.7 kW, 94.3 kW and 157.0 kW, in order of ascending $T_{h,in}$. From Figure 5.15, it follows that, for each hydrocarbon family, the molecular size of the optimal working fluid (leading to the lowest SIC) increases with $T_{h,in}$. More specifically, the optimal molecular sizes are C_3/C_4 for $T_{h,in} = 150$ °C, C_4/C_5 for $T_{h,in} = 250$ °C and C_7 for $T_{h,in} = 350$ °C. Thus, light working fluids are favoured for the low-temperature heat source, while increasingly larger working fluids are chosen at higher temperatures. The best performing systems have propane, 2-butene and 2-heptene as working fluids in increasing order of $T_{h,in}$. The corresponding (minimum) SIC values are £10,120 per kW, £4,040 per kW and £2,910 per kW. Thus, a decrease of the SIC values is observed as the heat-source temperature (and consequently the system size) increases.

In Section 5.3, optimisations on similar case studies were carried out, but with the objective of maximising $\dot{W}_n$. While an increase in $\dot{W}_n$ with $T_{h,in}$ was also reported, the $\dot{W}_n$ values reported in Figure 5.6 are, on average, 37% higher than the values in Figure 5.15. This is not surprising as the objective in Section 5.3 was to maximise the $\dot{W}_n$, and the effect of pressure drops on the performance was not accounted for, resulting in the higher $\dot{W}_n$. The working fluids that resulted in the maximum $\dot{W}_n$ were propane, 2-pentene and 2-hexene, for the 150 °C, 250 °C and 350 °C heat sources, respectively, while the highest $\dot{W}_n$ values reported in Figure 5.15 are achieved with *n*-butane, 2-pentene and 2-hexene. Thus, using the SIC as objective function leads to a reduction in $\dot{W}_n$ (in comparison with maximising $\dot{W}_n$), and in the low temperature case, a different working fluid that achieves the highest $\dot{W}_n$.

In addition, the SPEC values corresponding to the maximum power systems from Section 5.3 are determined and presented in Figure 5.13 (Section 5.3.4). On average, the reported SPEC values are 49% higher than those obtained in this section, and the lowest SPEC values were achieved by iso-heptane, 2-pentene and 2-heptene for the 150 °C, 250 °C and 350 °C heat source, respectively. Thus, for both the 150 °C and 250 °C case, different working fluids (propane and 2-butene respectively) are identified as having the lowest SPEC in this section when the SIC/SPEC is minimised. Since multiplying the SPEC with a multiplication factor results in the SIC, minimising the SIC is expected to lead to similar optimal systems to optimising the SPEC. From this comparison, it is clear that minimising the SIC indeed results in less costly systems, but also in lower capacities. The SIC/SPEC and $\dot{W}_n$ are roughly inversely related, as higher values for $\dot{W}_n$ generally

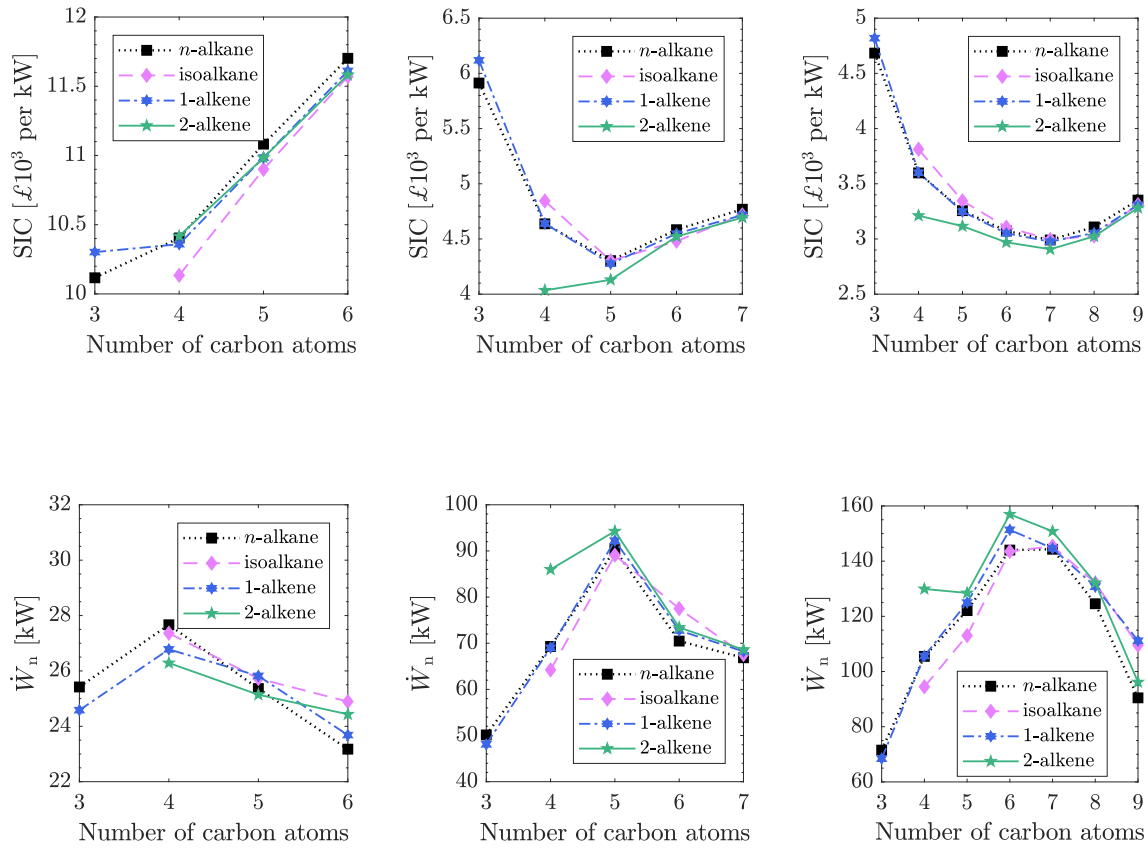


Figure 5.15: TOP ROW: Optimal specific investment costs determined by NLP optimisations for waste heat recovery ORC systems with different heat source temperatures of 150 °C (LEFT), 250 °C (MIDDLE) and 350 °C (RIGHT), and working fluids from different working-fluid families. BOTTOM ROW: The corresponding net power generated by the ORC systems for which the SIC is minimised with different heat source temperatures.

correspond to lower values of SIC and it is clear that both objectives (*i.e.*, minimising the SIC/SPEC *vs.* maximising the power output) do not result in the same optimal systems.

5.4.2 Total costs and equipment cost distribution

The total investments costs for the optimised system are shown in Figure 5.16. In case of the 250 °C and 350 °C heat sources, the highest TIC is required for systems with C₅ and C₆ working fluids, respectively. For a $T_{h,in}$ of 150 °C, the molecular size that achieves the highest TIC varies between the hydrocarbon families. Between the lowest and highest heat source temperature, an increase in the maximum TIC from £288,000 to £466,100 is observed. Thus, both the TIC and $\dot{W}_n$ increase with heat source temperature. However, the highest TIC increases by a factor of roughly 1.6, whereas the highest $\dot{W}_n$ increases by a factor of ~ 6 (see Figure 5.15). This illustrates how the total costs of an ORC engine increase with the capacity of the system, while the costs per kW (the SIC and/or SPEC) decreases.

Thus, it is clear that the SIC represent a trade-off between performance and costs. For example, with the 150 °C heat source temperature, systems with 1-propene or propane (both C₃) as a working fluid require a lower SIC than their respective C₄ alternatives 1-butene and *n*-butane. However, systems with 1-butene and *n*-butane achieve higher $\dot{W}_n$ than those with 1-propene and propane. This is a direct illustration of how minimising the SIC represents choosing a working fluid that can achieve a fairly high $\dot{W}_n$ at the lowest possible costs. Merely choosing a system that maximises $\dot{W}_n$ has the potential to lead to a suboptimal SIC, resulting in higher investment costs.

To compare the composition of the total investment costs (TIC) between different working fluids and heat sources, the bare module costs are shown in Figure 5.16. For each heat source, these costs are only shown for the hydrocarbon family containing the optimal working fluid. Thus, the *n*-alkanes are shown for the 150 °C heat source and 2-alkenes are shown for both the 250 °C and 350 °C heat sources. For the 150 °C heat source, an increase in the TIC is observed between systems with propane and *n*-butane. It follows that this rise in the TIC can solely be attributed to an increase in the evaporator costs. Furthermore, a slight decrease in TIC is observed between systems with *n*-butane and *n*-hexane for the same heat source temperature of 150 °C. Between these fluids, $\dot{W}_n$ decreases, and this translates directly to a decrease in turbine costs, as seen in Figure 5.16 (LHS).

On average, the two heat exchangers account for 73.5% of total bare module costs for the 150 °C heat source, but this percentage decreases to 50.3% and 38.5% for the 250 °C

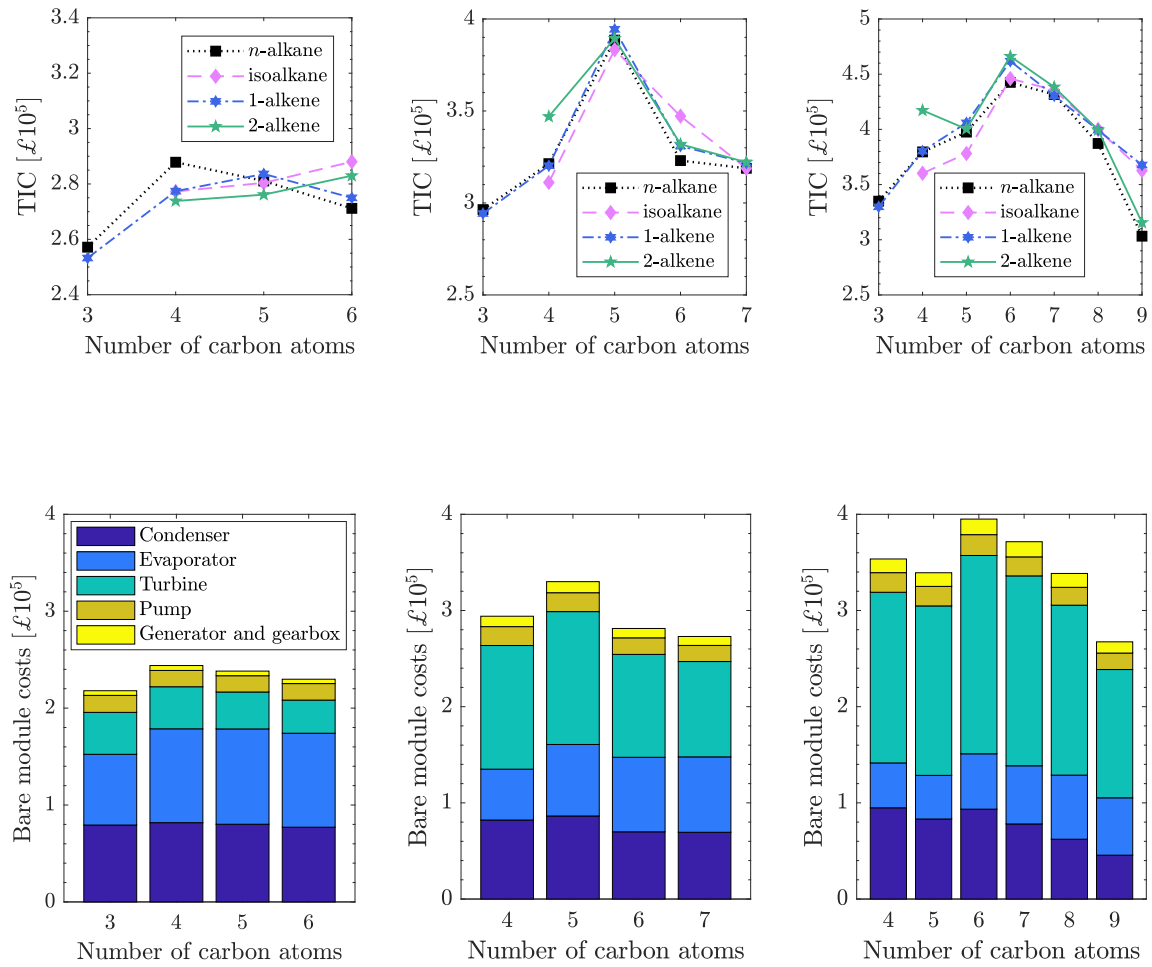


Figure 5.16: TOP ROW: Total investment costs (TIC) of waste heat recovery ORC systems for which the specific investment cost (SIC) is minimised with different heat source temperatures of 150 °C (LEFT), 250 °C (MIDDLE) and 350 °C (RIGHT), and working fluids from different working-fluid families. BOTTOM ROW: The corresponding bare module costs of the waste heat recovery ORC systems for each heat source temperature; the bare module costs of the hydrocarbon family containing the optimum (minimum SIC) working fluid is shown.

and 350 °C heat sources, respectively. Vice versa, the turbine makes up 17.1%, 40.0% and 51.6% of the costs, in order of increasing $T_{h,in}$, as the costs of the turbine are directly related to $\dot{W}_n$. Other general trends are an overall increase in evaporator costs and a decrease in condenser costs, when comparing the lightest and heaviest working fluids; these trend applies to all three heat sources. These component cost distributions are similar to those obtained in Section 5.3.4, where the system power output was maximised. Thus, the component cost distribution is not largely affected by the choice of the objective function.

5.4.3 Comparison of objective functions

In all the optimisations presented in this section, the objective was to minimise the SIC. To illustrate the significance of the choice of the objective function and in comparison with the results from Section 5.3, two additional optimisations were performed for an ORC engine with 2-heptene and a $T_{h,in}$ of 350 °C; this combination of heat source temperature and working fluid yielded the lowest SIC in Figure 5.15. The results for this working-fluid and heat source combination from Section 5.3 and this section where the SIC is minimised are retained. It should be noted that a minimum pinch point temperature difference of 10 °C was used in Section 5.3 (maximum power case) while that constraint was removed when the SIC was minimised.

With respect to the two additional optimisations, an objective of minimising the total investment costs (TIC) was applied in one case (*i.e.*, $\mathbf{f}$ in Equation (5.1) is the TIC). For the second problem, the objective was to maximise the net power output or alternatively, to minimise the negative of the power output (*i.e.*, $\mathbf{f}$ in Equation (5.1) is $-\dot{W}_n$). In both cases, the minimum pinch point temperature difference was not applied in the heat exchangers. This was expressed as $\Delta T_{pinch, min} = 0$ °C to ensure that the hot stream is always at a higher temperature than the cold stream through the length and across all sections of the heat exchangers. The results of the two retained simulations and the two additional simulations are presented in Table 5.6.

The choice of objective function has a significant effect on the optimal solution. When maximising $\dot{W}_n$ without a pinch-point constraint, the costs of the system are completely ignored and are only evaluated after the optimisation is completed. This has numerous effects on the optimal operating conditions. Since the costs of the heat exchangers are not evaluated as part of the objective, low fluid velocities are identified as optimal, leading to low pressure drops and large heat exchanger sizes. The heat exchanger size is further magnified by a low pinch-point temperature difference ($\Delta T_{pinch,ev}$) of 0.1 °C.

Table 5.6: Results of NLP optimisations with the objectives to minimise SIC, maximise $\dot{W}_n$ or minimise TIC. The working fluid is 2-heptene, $T_{h,in} = 350$ °C. The pinch point constraint in the heat exchangers is defined as $\Delta T_{pinch, \min} \leq \Delta T_{pinch}$, where $\Delta T_{pinch, \min} = 10$ °C.

Objective function	Pinch point constraint?	SIC [£/kW]	$\dot{W}_n$ [kW]	TIC [£]	$T_{h,out}$ [°C]	$A_{s,ev} + A_{s,co}$ [m ²]	$\Delta T_{pinch,ev}$ [°C]	$\Delta T_{pinch,co}$ [°C]
Min. SIC	No	£2,907	150.8	£438,369	115.8	40.1	41.8	33.6
Max. $\dot{W}_n$	Yes	£4,320	210.3	£908,377	70.0	541.2	10.1	15.3
Max. $\dot{W}_n$	No	£4,557	221.2	£1,008,016	58.3	1709.4	0.1	12.5
Min. TIC	No	£2,707,948	0.009	£25,475	344.2	0.2	86.1	184.3

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This is achieved at the inlet of the preheating section of the evaporator, where the exit temperature of the heat source at 58.3 °C is the lowest amongst the four cases. This makes intuitive sense, since this leads to the highest heat transfer rate between the heat source and the system, and therefore the possibility to generate more power. However, the low ΔT_{pinch} leads to heat exchangers with large areas (A_s).

When the power output is maximised, but with $\Delta T_{\text{pinch, min}} = 10$ °C, the total A_s decreases significantly by a factor of 3 in comparison with the case where there was no pinch-point constraint. Only the temperature of the working fluid in the evaporator is limited by the pinch point constraint. Clearly, such a constraint limits $\dot{W}_n$, with $\dot{W}_n$ reducing by about 5%; the constraint however substantially reduces the required A_s and therefore the corresponding investment costs with a TIC reduction of about 10%. Thus, applying the minimum pinch-point constraint in the heat exchangers when maximising the power output helps to significantly reduce the heat exchanger sizes and the overall investment costs.

If the objective is to minimise the TIC, large values of fluid velocities in the heat exchangers and ΔT_{pinch} are specified, leading to large heat exchanger pressure drops and small values of A_s respectively. In addition, as any power generation results in turbine and generator costs, $\dot{W}_n$ is effectively minimised to keep the TIC low. Minimising the TIC should ultimately result in a TIC of £0. However, the solver was not able to identify a set of decision variables that results in a working-fluid flowrate and/or power output of exactly zero while remaining feasible (*e.g.*, sometimes one of the A_s values would become slightly negative). Furthermore, if any equipment sizing parameter becomes zero, this results in a numerical error, since the cost correlations contain natural logarithms of these sizing parameters. Although minimising the TIC results in the lowest investment costs, its combination with the very low corresponding power output leads to the highest SIC, several orders of magnitude higher than that of any other objective function.

From these comparisons, it can be concluded that using the SIC as the objective function enables the solving algorithm to make multiple trade-offs between total costs and performance of the ORC system. This is evidenced in Table 5.6 where minimising the SIC results in intermediate values for ΔT_{pinch} , A_s , $T_{\text{h,out}}$, TIC and $\dot{W}_n$ to those of the maximum power and minimum TIC. Maximising $\dot{W}_n$ requires the introduction of additional pinch point constraints that can prevent the identification of excessive A_s and TIC values, while minimising the TIC requires the introduction of a minimum requirement on $\dot{W}_n$, to prevent identification of systems with very poor and unreasonable performance. However, such minimum pinch-point constraints and power requirements are not nec-

essary when using the SIC as the objective function, as a balance is inherently struck between maximising the power output and minimising the investment costs, leading to systems with fairly high performance and low investment costs.

5.5 Optimal working fluid designs via MINLP formulations

In the preceding sections, working fluid classes were specified manually prior to optimisation. Although this allows a systematic comparison of different hydrocarbons, it is not an effective strategy to screen many working fluids or find novel candidates. For example, the complete set of *n*-alkanes, isoalkanes, 1-alkenes and 2-alkenes considered in earlier sections contains only about 30 working fluids when a maximum of 10 carbon atoms are considered. Thus, only a small subset of all possible working fluids is assessed when merely common hydrocarbon families are considered. To overcome these limitations and prevent the use of heuristics-based pre-selection, working fluids are incorporated into the optimisation decision space as a collection of integer variables, indicating the quantity of each molecular group in the working fluid. Thus, more complex working-fluid formulations are possible in these MINLP problems.

This MINLP problem, presented in Section 5.1, is restated here with the objective of minimising the specific investment costs of the ORC system, and with the inclusion of the integer variables ($\mathbf{z}$) for the selection of working-fluid molecular groups:

$$\begin{aligned}
 \min_{\mathbf{x}, \mathbf{z}} \quad & \mathbf{f}(\mathbf{x}, \mathbf{z}) = \text{SIC}(\mathbf{x}, \mathbf{z}), \\
 \text{subject to: } \quad & \mathbf{h}(\mathbf{x}, \mathbf{z}) = 0, \\
 & \mathbf{g}(\mathbf{x}, \mathbf{z}) \leq 0, \\
 & \mathbf{x} \in [\mathbf{x}^{\text{lo}}, \mathbf{x}^{\text{up}}] \subseteq \mathbb{R}^n, \\
 & \mathbf{z} \in [\mathbf{z}^{\text{lo}}, \mathbf{z}^{\text{up}}] \subseteq \mathbb{N}^m.
 \end{aligned} \tag{5.1 revisited}$$

In this full MINLP optimisations, the molecular groups considered are $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $>\text{C}<$, $=\text{CH}_2$ and $=\text{CH}-$, where $-$ denotes a single bond, $=$ a double bond and $>$ or $<$ denotes two separate single bonds attached to the same carbon atom. As described in Section 5.1, the set of equalities $\mathbf{h}$ contains all equations relating to the ORC model: the thermodynamic cycle, the group contribution property prediction methods, heat exchanger sizing and costing methodology. Similarly, $\mathbf{x}$ is the set of process design variables and the set $\mathbf{g}$ contains the system constraints mentioned earlier.

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Not all the possible combinations of the above molecular groups are feasible molecules, thus additional constraints are needed in the problem to enforce the feasibility of proposed solutions. Without the molecular feasibility constraints, the six molecular groups mentioned earlier can be combined in over 1.8 million ways. However, only 128 combinations satisfy all valency and molecular feasibility constraints, and thus are feasible molecules. These constraints would ensure that all groups connect with another group through the correct number bonds, and that a molecular group with a single bond and that with a double bond cannot be directly combined to form (part of) a molecule. For example, a $=CH_2$ group and a $>CH_2$ do not form a feasible molecule as there is no configuration in which all single bonds are occupied, and there is only one double-bond group.

One of the additional constraint is the well-known ‘octet-rule’ [123], which for the non-cyclic molecules in this study is:

$$\sum_i n_i \times (2 - \nu_i) = 2, \quad (4.6 \text{ revisited})$$

where n_i denotes the integer amount of molecular group i present in the molecule while ν_i denotes its valency. This value of ν_i represents the number of bonds a molecular group type must form to obtain eight electrons in the valence shell of the carbon atom, ensuring that no bonds remain unused within a molecule.

Two other constraints (see Equation (4.7)) ensure that only an even number of groups containing a double bond can be present, and that the number of $=CH_2$ groups is equal to or less than the number of $=CH-$ groups. These rules prevent combinations between a single and double bond, and an infeasible number of $=CH_2$ end-groups. These are implemented as conditional statements (presented in pseudo-code):

$$\text{if } \cos(\pi \times (n_{=CH_2} + n_{=CH-})) > 0, \quad \text{then } \mathbf{f} = \text{SIC}, \quad \text{else, } \mathbf{f} = 10^6; \quad (5.4)$$

$$\text{if } n_{=CH_2} \leq n_{=CH-}, \quad \text{then } \mathbf{f} = \text{SIC}, \quad \text{else, } \mathbf{f} = 10^6. \quad (5.5)$$

Thus, when the number of $=CH$ and $=CH_2$ groups are uneven, leading to an infeasible molecule, Equation (5.4) ensures the vector of the objective function $\mathbf{f}$ takes on a large value of 10^6 , which makes this solution very poor and it is rejected by the solver. Similarly, Equation (5.5) ensures in that there can only be a feasible number of $=CH_2$ groups in the final solution¹.

¹Ethylene ($H_2C=CH_2$) is excluded by this constraint. Its critical temperature is 9.2 °C, which is lower than the inlet temperature of the cooling water as presented in Table 5.1. Thus, it is only present in the system as a vapour or supercritical fluid, making it unsuitable as a working fluid.

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Finally, an upper bound of 10 is introduced to the number of each molecular group, to prevent the assessment of excessively large molecules. In comparison with the NLP problem considered in Section 5.4 (and Sections 5.2 and 5.3) where working fluids are selected from the families in Table 5.2, the MINLP problem here does not have such a requirement. The functional molecular groups present in candidate working fluids are handled explicitly by the molecular constraints in Equations (4.6) – (5.5). Therefore, the family of the selected working fluid is not known *a priori* and more complex working-fluid formulations can thus be explored from the six molecular groups: $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $>\text{C}<$, $=\text{CH}_2$ and $=\text{CH}-$.

In this section, the results of a waste heat recovery case study with $T_{\text{h,in}}$ of 150 °C and 250 °C are presented. The other specifications are similar to those presented in Table 5.1. After each run, the working fluid that is identified as the optimal working fluid is excluded from the decision space of the next run by adding an additional constraint, called an integer cut that penalises future occurrence of that solution; this generates the next best fluid. The integer cut is manually implemented in Matlab as a conditional statement similar to those presented in Equation (5.4). If, for example, propane is to be excluded:

$$\begin{aligned} &\text{if } n_{-\text{CH}_3} = 2, n_{-\text{CH}_2-} = 1 \text{ and } \sum_j n_j = 0, j = \{>\text{CH}-, >\text{C}<, =\text{CH}_2, =\text{CH}-\}; \\ &\text{then } \mathbf{f} = 10^6, \text{ else } \mathbf{f} = \text{SIC}. \end{aligned}$$

This ensures that if propane is formed, $\mathbf{f}$ is given a large value of 10^6 . Since the objective is to minimise the SIC, propane is processed as a poor solution in the next run and will not be identified by the solver as optimal, preventing the solver from converging on the same working fluid twice.

The MINLP formulation is seen to result in more complex and novel working fluids; the results of eight consecutive MINLP optimisations are shown in Table 5.7 for the 150 °C heat source and Table 5.8 for the 250 °C heat source. For the 150 °C heat source, the best performing ORC system (with the minimum SIC) has 1,3-butadiene as its working fluid. For the seven next best systems, their working fluids are all members of the hydrocarbon families in Table 5.2 and assessed in the NLP formulations in Section 5.4. However, for the 250 °C heat source (Table 5.8), only 2-butene and 2-pentene (4th and 7th best respectively) are members of those hydrocarbon families; the remaining six formulations (including the best three) are new formulations. Thus, the MINLP solver was able to identify novel working fluids that have not been assessed previously by the traditional the NLP methods.

In Table 5.8, the ORC systems with the two best ranking working fluids require a substantially lower SIC. This can be attributed to the slight overestimation of the P_{cr}

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Table 5.7: Results of MINLP optimisations with $T_{h,in} = 150$ °C. Rank refers to a ranking based on the value of the objective function (the SIC), while finding order refers to the order in which the working fluids were identified as optimal solutions by the solver.

Rank	Finding order	Chemical structure	Systematic name	SIC [£/kW]	$\dot{W}_n$ [kW]
1	7	$H_2C=CH-CH=CH_2$	1,3-butadiene	£9,645	26.7
2	2	$H_3C-CH_2-CH_3$	propane	£10,106	25.3
3	3	$(H_3C)_2-CH-CH_3$	isobutane	£10,142	27.6
4	1	$H_3C-CH=CH_2$	propene	£10,277	24.6
5	6	$H_3C-CH_2-CH=CH_2$	1-butene	£10,369	27.9
6	5	$H_3C-(CH_2)_2-CH_3$	<i>n</i> -butane	£10,406	27.7
7	4	$H_3C-CH=CH-CH_3$	2-butene	£10,418	26.0
8	8	$H_3C-(CH_2)_3-CH_3$	<i>n</i> -pentane	£11,080	25.6

Table 5.8: Results of MINLP optimisations for the 250 °C heat source. Rank refers to a ranking based on the value of the objective function, while finding order refers to the order in which the working fluids were identified as optimal solutions by the solver.

Rank	Finding order	Chemical structure	Systematic name	SIC [£/kW]	$\dot{W}_n$ [kW]
1	1	$(H_3C)_3-C-CH=CH-CH_3$	4,4-dimethyl-2-pentene	£3,569	82.4
2	2	$(H_3C)_2-C-(CH=CH_2)_2$	3,3-dimethyl-1,4-pentadiene	£3,603	78.6
3	3	$(H_3C)_2-CH-CH=CH-CH_3$	4-methyl-2-pentene	£4,001	91.5
4	4	$H_3C-CH=CH-CH_3$	2-butene	£4,019	88.6
5	8	$(H_3C)_3-C-CH_2-CH_3$	2,2-dimethylbutane	£4,110	83.9
6	6	$H_3C-CH-(CH=CH_2)_2$	3-methyl-1,4-pentadiene	£4,121	90.8
7	5	$H_3C-CH=CH-CH_2-CH_3$	2-pentene	£4,124	96.0
8	7	$H_2C=CH-CH_2-CH=CH_2$	1,4-pentadiene	£4,223	95.0

ORC system design from multi-objective problem formulations

value predicted by the empirical group contribution method (see Section 4.3) compared to the value that is inherently determined through SAFT- γ Mie. Only subcritical ORC systems are examined in this study, and an upper bound on P_r of 0.85 is introduced to prevent critical or supercritical evaporation pressures. For these two working fluids, the value of P_{evap} , that is limited at $0.85 \times P_{\text{cr}}$, is very close to the P_{cr} that follows from SAFT- γ Mie. At such pressures, the enthalpy of vaporisation becomes negligible, since the saturated liquid and vapour lines are very close or even coincide and, therefore, the heat transfer areas of the two-phase sections (in the evaporator) becomes almost negligible, leading to low TIC and SIC values.

These tables of optimal ORC and working-fluid systems for different heat-sources/sinks and system sizes, derived from MINLP problem formulations and integer cuts, can serve as a very important tool for a design engineer. In the first instance, they offer (at a glance) the selection of a working fluid that will lead to the ORC system design with the minimum investment cost (in terms of the SIC, although the objective can be suitably modified). They also offer additional options for the engineer in a number of instances where the system with the best fluid may not be viable. For instance, the best fluid could have undesirable properties in terms of environmental, financial or safety considerations; these factors *e.g.*, environmental impact, GWP, ODP, price, corrosion *etc.*, were not captured in the optimisation problem¹. In addition, the manufacturing process for the optimal working fluid may not be available yet or perhaps very inefficient or costly which in turn makes the working fluid and solution much more expensive than anticipated. The next best working-fluids/systems can then be resorted to and so on and so forth.

5.6 ORC system design from multi-objective problem formulations

As discussed in Section 5.4, an inherent trade-off between the total investment costs (TIC) and net power output ($\dot{W}_n$) is made when performing optimisations with the minimum specific investment costs (SIC) as the objective function. However, as presented in Table 5.6, the minimum SIC design does not exactly correspond to a maximum power design, neither does it correspond to a minimum total cost design. Thus, while minimising the SIC partly addresses the trade-off between the minimum TIC and the maximum

¹There may be cases where capturing all of these factors and others could lead to empty design spaces such that there are no feasible molecules or solutions returned from the solver.

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$\dot{W}_n$, it does not exactly correspond to the preferred objective of maximising the power output while simultaneously minimising the investment costs. This combined objective is better approached via multi-objective optimisation.

Thus, a multi-objective optimisation can be performed to obtain more insight into the relationship between these two objectives of maximising the power output and minimising the investment costs. For these optimisations, the minimisation objective function vector $\mathbf{f}$ in Equation (5.1) contains both the TIC and the $-\dot{W}_n$ (*i.e.*, maximum $\dot{W}_n$) and the other aspects of the problem setup and applicable constraints are similar to those in Equation (5.1 revisited). By simultaneously optimising the TIC and $\dot{W}_n$, a set of solutions called the ‘non-dominated Pareto front’ can be obtained. For each of these solutions, it is not possible to obtain a better value for one of the objectives without degrading the other objective. The algorithm regards the set of solutions within a Pareto front as equally optimal, or ‘non-dominated’. From this set, a final solution can be chosen, while taking the relative importance of each objective into consideration.

To compare the results from the multi-objective optimisation with the MINLP results obtained in Section 5.5, the $T_{h,in} = 250^\circ\text{C}$ case study is used. Two distinct optimisations studies were performed. In the first instance, to demonstrate the suitability of the NSGA-II solver for multi-objective MINLP problems, only the 2-alkenes were considered during the optimisation. Thus the only integer decision variable was the number of $>\text{CH}_2$ groups present in the 2-alkene, with general formula $\text{H}_3\text{C}-(\text{CH}_2)_n-\text{CH}=\text{CH}-\text{CH}_3$. The results of this optimisation are presented in Figure 5.17. In the second optimisation, all molecular groups from Section 5.5 were considered as decision variables and thus a full multi-objective MINLP problem is solved; both 4,4-dimethyl-2-pentene and 3,3-dimethyl-1,4-pentadiene (from Table 5.8, where the critical pressure is slightly overestimated) are excluded from the search space. The results are presented in Figure 5.18.

Among the 2-alkene working fluids, the best SIC value is obtained by the system with 2-butene, which is in agreement with the results shown in Figure 5.15. From Figure 5.17, it follows that at system capacities of 85 kW or higher, 2-pentene is preferred over 2-butene. Thus, if an ORC system with a capacity exceeding 85 kW is required, 2-pentene might be a better working fluid than 2-butene since systems with 2-pentene require lower SICs at these capacities. This illustrates how a multi-objective optimisation can provide additional insight into the optimal solutions over a range of system characteristics. If only a single objective optimisation is applied, no information about the behaviour of sub-optimal systems is obtained.

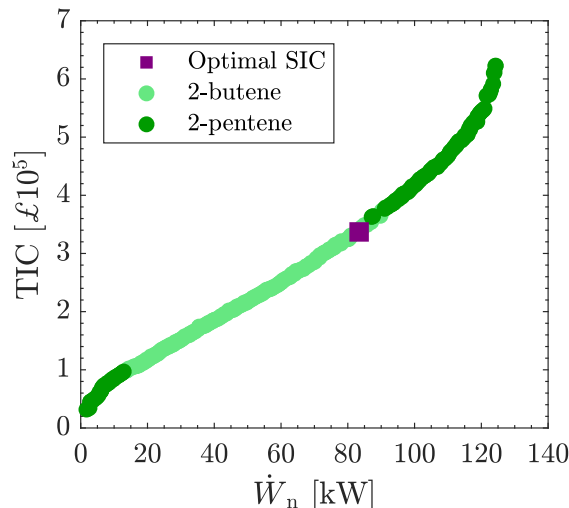


Figure 5.17: Results of multi-objective optimisations for 2-alkenes with 250 °C heat source. The objectives are the maximum power output ($\dot{W}_n$) and the minimum investment costs (TIC).

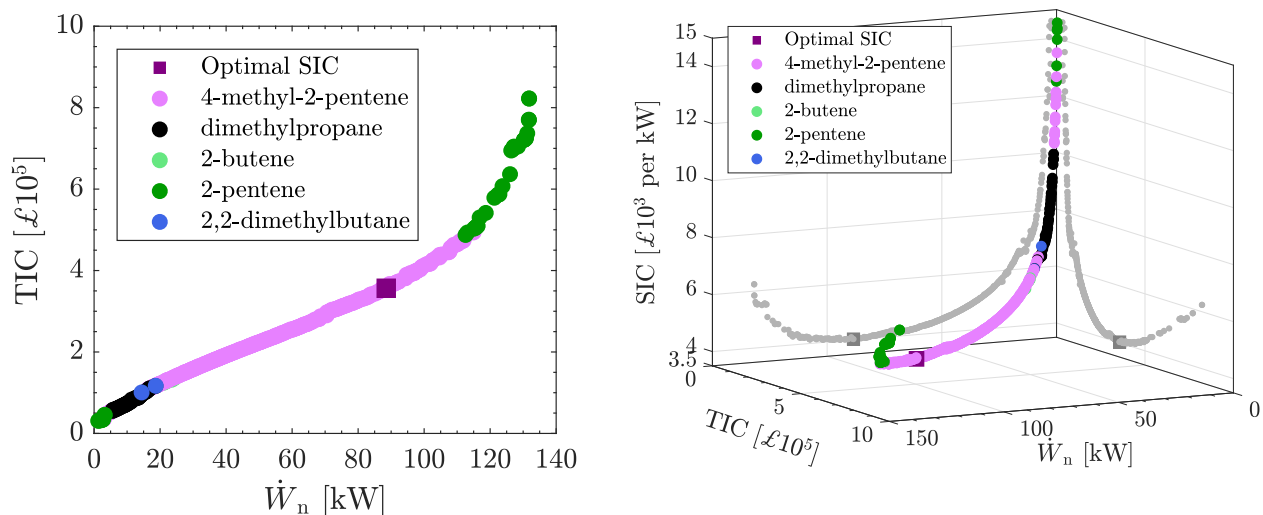


Figure 5.18: Results of the multi-objective MINLP optimisations with the 250 °C heat source. The objectives are the maximum power output ($\dot{W}_n$) and the minimum investment costs (TIC); molecules 4,4-dimethyl-2-pentene and 3,3-dimethyl-1,4-pentadiene are excluded from search space. LHS: TIC versus $\dot{W}_n$; RHS: Three-dimensional plot of TIC versus $\dot{W}_n$ versus SIC; the grey points are two-dimensional projections of the data points on each plane.

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The result of the full multi-objective MINLP problem is presented in Figure 5.18 and as expected, the excluded working fluids do not appear in the Pareto front. The working fluid that yields the best SIC is 4-dimethyl-2-pentene, which is also the best working fluid identified in the MINLP optimisation in Section 5.5, after the exclusion of 4,4-dimethyl-2-pentene and 3,3-dimethyl-1,4-pentadiene. The reported trade-off between the power output and investment costs can be seen in this figure, since systems which achieve a high power rating also lead to a high TIC. In the same vein, systems requiring very low investment costs also have a high SIC. Finally, within the power output range of 60 kW – 110 kW, SIC values between approximately £4,000 per kW and £4,200 per kW can be achieved. This can be observed in the two-dimensional projection of the Pareto front on the SIC– $\dot{W}_n$ plane. Within this capacity range, the SIC value is not sensitive to $\dot{W}_n$, and remains roughly constant. Thus, this multi-objective optimisation allows the designer to select a desired power output from a range of capacities and still achieve a SIC which is close to the optimum value.

The results presented here in Figures 5.17 and 5.18 represent an improvement on the typical multiobjective studies as a series of optimal working fluids is part of the solution, enabling designers and manufacturers to have more flexibility in cycle and system design and working fluid selection. In addition, optimal working fluids are suggested for the full range of possible power output (from 0 kW or 0% to 120 kW or 100% capacity), allowing designs of varying capacity to be attempted with the best possible working fluids. This sort of description of optimal working fluids for the full range of the possible design space is usually not provided in the typical studies of multiobjective optimisation of ORC systems, limiting the possibilities and flexibility of designing the engines to suit the requirements of particular (or bespoke) applications. A few of these studies are described briefly.

For example, in Yang *et al.* [245], a number of refrigerant and hydrocarbon working fluids (R600, R600a, R601a, R245fa, R1234yf and R1234ze) are employed in a multiobjective cost-power optimisation; the solutions provided did not include options for lower power output designs, as only designs within 50% of the maximum power output were explored. Similarly, in Lecompte *et al.* [63] where R245fa was selected as the working fluid, only designs within 30% – 60% of the maximum power were explored; thus 40% – 70% of the possible design range is not explored. While a larger proportion (> 80%) of the possible design space is explored in Noriega Sanchez *et al.* [246], only a few working fluids were considered. Thus, the solutions provided are local to the design space

Summary

for which the results are presented, or are only applicable to the working fluid that was preselected before the optimisation was carried out and hence not transferable.

In comparison with the aforementioned works where traditional multiobjective optimisations of ORC systems are attempted, the multiobjective MINLP formulations presented in this chapter provide a continuous spectrum of feasible design points spanning the full design range from the lowest power output to the maximum power output. This is made possible by incorporating the design of the optimal working fluid as part of the optimisation problem as formulated in Equation (5.1) and with the results presented in Figures 5.17 and 5.18. This demonstrates the power and potency of combining the working fluid and process system design in the problem formulation via CAMPD, aided by accurate group contribution methods; this would undoubtedly become more powerful and applicable to a wider range of waste-heat recovery engines as more molecular groups are included in the CAMPD framework.

5.7 Summary

Having developed the necessary framework for the CAMPD of waste-heat recovery systems in Chapter 4, case studies of CAMPD of ORC systems are considered in this chapter. For these case studies, the objective was to determine the optimal hydrocarbon working fluids for subcritical, non-recuperated ORC systems for waste-heat sources at 150, 250 and 350 °C, each with a heat capacity rate ($\dot{m}c_p$) of 4.2 kW/K. Various NLP optimisation problems were set up for this purpose, with different objective functions ranging from maximising the power output from the ORC engine to minimising the investment costs of the ORC systems for specific families of hydrocarbon working fluids. Integer variables were introduced later on to enable the working fluid design to be included in the optimisation problem via an MINLP formulation; multi-objective combinations of the maximum power output and the minimum costs were also explored.

The results suggest that a theoretical optimum fluid, which maximises the power output, should have thermodynamic properties such that the evaporation pressure is maximised and the amount of superheating is minimised. This reduces the latent heat of vapourisation, permitting a better thermal match between the working fluid and heat source. In terms of actual working fluids, simple molecules such as propane and propene are particularly suitable for low-grade (150 °C) heat sources, whilst more complex molecules containing a $-\text{CH}=\text{CH}-$ double bond are favoured for medium- and higher-grade heat sources at temperatures between 250 and 350 °C. Specifically, *n*-propane, 2-pentene and

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2-hexene are identified as the optimal working-fluids for the three heat-source temperatures, and result in optimal power outputs of 35.2, 136.7 and 219.0 kW, with thermal efficiencies of 9.7, 16.9 and 17.8% respectively.

The working fluids that maximise the power output from the system generally have the highest heat-exchanger area requirements. Therefore, working-fluid selection based on SIC minimisation can result in different optimal working fluids to those identified from an optimisation that considers power output or other common thermodynamic objective functions. For the three heat-source temperatures considered the ORC systems with the lowest SIC (not the minimum SIC) are those with isoheptane, 2-pentene and 2-heptene as working fluids, with SICs of £5,620, £2,760 and £2,070 per kW respectively. The corresponding power outputs for these systems are 32.9, 136.7 and 213.9 kW, and these power outputs are 6.38%, 0.0% and 2.32% lower than the power outputs obtained for working fluids that maximise the power output. This corresponds to a reduction in the SIC of 6.95%, 0.0% and 6.82%.

From the set of NLP problems (wherein the SIC is now minimised) with predefined working fluid classes and different heat source inlet temperatures, it follows that at 150 °C, propane is the optimal working fluid with an SIC of £10,120 per kW, while a corresponding $\dot{W}_n$ of 27.7 kW is achieved by the system with *n*-butane. For a heat source inlet temperature of 250 °C, the best performing working fluid is 2-butene with an SIC of £4,035 per kW, whereas the highest $\dot{W}_n$ of 94.3 kW is generated by the system with 2-pentene. Similarly, at 350 °C, the optimal fluid is 2-heptene with an SIC of £2,910 per kW, and the system with 2-hexene generates the highest $\dot{W}_n$ of 157.0 kW.

While there is a relation between high $\dot{W}_n$ and low SIC, minimising the SIC and maximising $\dot{W}_n$ are not equivalent objectives and therefore do not lead to the same results. Merely maximising the $\dot{W}_n$ and/or minimising the TIC result in costly or poor performing systems. Introducing a pinch point constraint is necessary when maximising $\dot{W}_n$, to prevent the identification of systems with excessive heat exchange surface areas and costs. However, when the SIC is minimised, such pinch point constraints are not necessary as the nature of the objective requires the solver to strike a balance between the ORC system performance (which is favoured by very low pinch point constraints) and the system costs that are minimised by large temperature differences between the heat source/sink and the working fluid in the heat exchangers.

The current framework is able to effectively identify novel working fluid candidates during an MINLP optimisation. Eight consecutive MINLP optimisations were performed for ORC systems with heat source temperatures of 150 °C and 250 °C. In both cases,

Summary

novel working fluids are identified that do not belong to the common hydrocarbon families assessed in the NLP optimisations. In addition, a multi-objective optimisation was performed for the same heat source, during which minimising the TIC and maximising $\dot{W}_n$ was done simultaneously. Of the five working fluids present in the Pareto front of optimal solutions, three are identified during the single-objective MINLP optimisations. The other two working fluids are only present at very low capacities, and SIC values above £6,000 per kW. These values are far removed from the optimum of approximately £4,000 per kW.

These sets of NLP, MINLP and multi-objective MINLP optimisations have shown that the current CAMPD framework is capable of optimising the operating conditions of waste-heat recovery systems with a variety of heat source temperatures and capacities, and also capable of deriving a series of suitable and optimal working fluid for each system. Trade-offs between costs and performance are made, and it is possible to make a selection of working fluids and/or operating conditions when multiple objectives are employed, with the capability of predicting optimal working fluids for a varying capacity of system designs ranging from low power output systems to those with the maximum power output possible.

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Chapter 6

Conclusions and Recommendations

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6.1 Motivation and summary of objectives

Increasing concerns over the depletion of fossil-fuel reserves and their detrimental effects on human health and the environment have led to a surge of interest in renewable and sustainable energy systems in recent years. The use of waste heat and of alternative sources of low- or medium-grade heat, such as geothermal or solar heat, can play a key role in decreasing the current dependence and consumption rates of fossil fuels, thereby increasing energy security and decreasing carbon emissions, as well as enhancing the overall efficiency and economic outlook of industrial and urban energy systems.

This is brought to the fore by the fact that (once the heat-recovery infrastructure is in place) no significant further costs are incurred in continuously generating the waste-heat stream that serves as energy input to a suitable heat recovery engine. Within this remit falls a number of technologies such as the organic Rankine cycle engine and the Up-THERM heat converter, that aim to recover waste heat from industrial processes. These heat engines usually have lower thermal efficiencies than those typically associated with large-scale, centralised fossil-fuelled power plants, due to the low temperature of the heat input involved. However, the waste-heat energy source (which serves as the energy input for these engines) is easily accessible, abundant and much cheaper than the fuels used in conventional power plants.

With these engines, low- and medium-grade heat can be recovered in space heating applications to provide heating for buildings, or in power generation by conversion into useful power such as electricity, or a combination of the two as in combined heating and power (CHP) applications. The optimal design of these heat engines as well as the accompanying working fluid is crucial to their uptake in industrial waste-heat recovery applications and has formed the basis of this research. In Section 1.6, the aims and objectives of the work presented in this thesis were introduced; in these concluding sections, the findings from the research herein are summarised.

6.2 Summary of thesis findings

6.2.1 Working-fluid mixtures in ORC systems

Working-fluid mixtures have been highlighted to provide performance improvements in organic Rankine cycle (ORC) systems, due to the possibility of providing a better thermal match to the heat source and/or heat sink due to the non-isothermal phase change

Summary of thesis findings

encountered with the mixtures. Thus, the thermodynamic, heat transfer and economic benefits of employing such working-fluid mixtures in ORC systems were investigated. Working-fluid mixtures proved desirable in waste-heat recovery applications with limited or constrained cooling resources as may be found in energy-intensive industries, in arid regions and in combined heat-and-power applications. Their cycles were found to produce higher power outputs and were more efficient than those of pure working fluids; improvements in power output of up to 30% were recorded. With such cooling streams, the condensation temperature glides of the working-fluid mixtures can be suitably optimised to provide an improved thermal match to the temperature profile of the cooling stream. Thus, unlike a pure fluid that would be limited by its isothermal condensation profile, fluid mixtures would be better suited for these applications from a thermodynamic perspective.

However, the working-fluid mixtures performed poorly from a heat transfer, equipment size and economic points of view. ORC systems featuring such mixtures required larger heat exchangers, with heat transfer areas up to 80% higher than those required for systems with pure working fluids. Due to the larger power output from the systems with mixtures, they also require larger expanders than the systems with pure fluids. These results imply that ORC systems with working-fluid mixtures would require larger plant sizes and layout areas, contributing significantly to their overall installation costs. When such costs are measured in terms of the specific investment costs (*i.e.*, total investment costs weighted by the plant's power output), the mixtures were found to lead to systems with the highest specific costs notwithstanding the fact that they had higher power outputs than those with pure working fluids; systems with pure fluids could be up to 14% cheaper than those with the working-fluid mixtures with the highest power output. The costs of these systems may be further reduced by avoiding vacuum expansion where possible. Thus, it is important to employ a combined thermodynamic, thermal and cost approach in the selection of optimal working-fluid (mixtures) for ORC (and waste heat recovery in general) systems.

6.2.2 The Up-THERM heat converter

The Up-THERM heat converter relies on the periodic phase-change of its working fluid and the oscillatory vertical motion of its single solid-piston, which are transformed to a unidirectional flow of the working fluid through a hydraulic motor to extract power. With its few moving parts, the resulting device requires low capital and maintenance costs making it suitable in low-power applications especially in remote or off-grid locations where

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low investment and maintenance costs are crucial for favourable returns, and economic viability. In its nominal configuration with water as the working fluid, the engine delivers 2.64 kW at an exergy efficiency of 11.2%. This performance can be considerably improved by employing organic working fluids such as R113 and isomers of hexane, delivering up to 8 kW of power.

Another aspect of the engine is its generator, characterised by an optimal resistance, which was found to be generally insensitive to the external conditions of heat-source and heat-sink temperatures, and the employed working fluid. In terms of the thermodynamic properties of working fluids, the performance of the engine is dictated to a large extent by the saturation pressure and the vapour-phase density; the phase-change entropy also has a marginal effect on the engine's performance. Higher values of saturation pressure and lower values of vapour density lead to higher power outputs, suggesting a compromise between both properties as that combination is not feasible for real working fluids.

Consequently, the engine's efficiency and power output were found to be inversely related. Testing the engine with a larger set of working fluids at various external (heat source) conditions revealed that the working fluids' critical properties have a profound effect on the engine's performance. High-power designs were generally favoured by working fluids with low critical temperatures and high reduced temperatures and pressures, such as light alkanes. Conversely, fluids with high critical temperatures and low reduced temperature/pressure, such as heavier alkanes, will favour high-efficiency engine designs. From the optimal working-fluid selection map, wet fluids perform best in the engine for maximal power at heat-source temperatures below 210 °C, and dry fluids were optimal at higher heat-source temperatures. Ammonia, R245ca, R32, propene and butane feature prominently as high performing fluids over large ranges of heat-source temperatures; this adaptability to variations in heat source and sink temperatures while the engine is in operation makes them good candidates for the Up-THERM heat engine.

6.2.3 Computer-aided molecular and process design

The discovery of new working-fluids that can improve system performance while meeting increasingly restrictive environmental legislation, and the identification of novel and optimal waste-heat recovery and conversion systems based on technoeconomic performance indicators are key steps to enable a more widespread uptake of such technology. Thus a computer-aided molecular and process design (CAMPD) framework, based on the SAFT- γ Mie equation of state, has been developed. In addition to the thermodynamic description of the heat engines, the technoeconomic criteria through system component

Prospective outlook and possible future works

sizing and suitable cost correlations has been incorporated into the CAMPD framework for the analysis of organic Rankine cycle (ORC) waste-heat conversion systems.

Organic Rankine cycle engines in particular can efficiently convert low-grade heat into electrical power. Traditionally, working fluid selection for such engines has been via heuristics and the (pre-)screening of known working fluids. However, CAMPD techniques allow the selection of an optimal working fluid during ORC system optimisation. This enables the design of working fluids that fit the particular characteristics of the heat source/sink and can lead to the identification of novel working fluids that would hitherto not be found using heuristics. Using representative industrial waste-heat sources at temperatures of 150, 250 and 350 °C, various NLP, MINLP and multi-objective optimisation studies were undertaken to determine the optimal working fluids and process design of ORC systems with objectives of maximising the power output and/or the total and specific investment costs.

With these studies, the framework is able to identify suitable optimal and novel working fluids for the ORC systems operating with each heat source. The identified working fluids in the MINLP and multi-objective optimisations were different from those obtained from the NLP optimisations with predefined working fluid families. More generally, the results presented in this study have demonstrated how conventional working-fluid selection studies can be replaced with a more holistic approach. Not only does this streamline the design process, but it also removes subjective and pre-emptive screening criteria and introduces the possibility of identifying the next generation of optimal working-fluids and ORC (and waste-heat recovery) systems in targeted waste-heat recovery and conversion applications in industrial settings, and beyond.

6.3 Prospective outlook and possible future works

A number of interesting areas of additional research could be highlighted from the work presented herein. While the use of working-fluid mixtures in ORC systems has been investigated from both thermodynamic and heat transfer points of view, the general heat-transfer characteristics of such mixtures are yet to be fully understood, especially with respect to the phase change processes. The current model assesses the heat transfer characteristics of the mixtures based on the available experimentally-derived heat transfer correlations. These correlations were derived from experiments with a few refrigerants and thus they cannot, in principle, be applied to any other system of working-fluid mixture. Thus, when other working-fluid mixtures are being considered for use in ORC systems,

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experimental studies on the variation of their heat transfer coefficients with respect to the pure fluid need to be commissioned.

The extent and effect of such variations on the size and cost of heat exchangers needs to be ascertained before ORC systems operating with the mixtures can be implemented on a large scale, with a recommendation for the close monitoring of the thermal performance in key sections of the engine. Another practical consideration to bear in mind is the possible fractionation of working-fluid mixtures in the components of the engine, due to the tendency of the heavier phase(s) to separate. Thus, the engine and its components should be designed to ensure a continuous mixed phase. The ORC engine performance can be further improved by considering additional cycle architectures such as transcritical cycles, multiple-evaporation cycles and cycles with internal regeneration/recuperation. The costing models also need to be routinely updated as more data on ORC systems and system components become available.

In comparison with ORC engines, the Up-THERM heat converter is a relatively new concept and thus requires further research before it can become truly competitive, especially with low-temperature heat sources [193]. This is because the ORC engine generally outperforms its Up-THERM counterpart purely in terms of power output, exergy efficiency and thermal efficiency. However, the capital costs are always lower for the Up-THERM heat converter and thus, the Up-THERM heat converter becomes the more affordable solution in terms of specific costs (relative to the equivalent ORC engine) at heat source temperatures higher than 300 °C. Aside from waste-heat recovery, the Up-THERM heat converter can also be deployed in other applications such as solar power generation and biomass plants. Such deployment would benefit from further laboratory testing and the building of a demonstrative prototype.

The performance of the the Up-THERM can be further improved by considering the deployment of working-fluid mixtures with respect to the relationship between the engine's performance and working fluids' critical pressures as detailed in Figures 3.13 and 3.14. It is well known that two fluids can be combined in such a way that the critical pressure of the resulting mixture is higher than those of its constituent fluids, for example, as evident from the constant-composition P - T phase boundaries of the alkane mixtures and the perfluoroalkane mixtures in Figure 4.4. The higher critical pressures of the suitably designed working-fluid mixtures, by the inferences from the above listed figures, should lead to improved performance for the Up-THERM converter. Such performance improvements should however be considered hand in hand with the possible heat transfer deterioration that the mixtures may suffer, especially as the Up-THERM is inherently a

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two-phase heat engine with most of the heat transfer from the heat source to the working fluid (and working fluid to the heat sink) occurring during working-fluid phase change (evaporation and condensation).

The models presented in the previous chapters could benefit from improvements in the accuracies associated with the correlations employed, especially those related to the heat transfer coefficients during phase change and those related to the costing methods. Another area of research that could be explored is the prediction of heat transfer coefficients via group contribution methods; this would fit in with the theme of the computer-aided molecular and process design of heat recovery engines. In addition, the transport property prediction, provided here by semi-empirical group contribution methods, could be incorporated into the SAFT- γ Mie equation of state such that both the thermodynamic and transport property component of the working fluid property prediction is derived from one tool. This would improve the performance of the framework (in terms of simulation time) as a lower number of function calls will be required since a single consistent function or equation of state will now provide both properties of interest. This can be accomplished as demonstrated with PC-SAFT [148, 247], using Rosenfeld’s residual-entropy scaling method [248, 249].

While the CAMPD framework has been applied to case studies involving organic Rankine cycle engines, it can easily be extended to other waste-heat recovery systems, heat pumps, refrigeration systems, as well as the Up-THERM heat converter, so long as the process models of the systems in question are available or can be developed. Furthermore, just as shown for the ORC engine, optimal working fluids and process settings can be obtained for these systems. However, the current framework can be improved further still by reducing the computational effort required to optimise the system. The computational effort required, measured in terms of the simulation time, is compounded by the finely discretised nature of heat exchanger sub-models. This can be circumvented by deploying surrogate models for the heat exchange processes, while ensuring that the accuracy and consistency of the framework is maintained.

The current CAMPD framework (and any CAMPD system in general) is limited by the number of molecular groups available and considered in the optimisation setup. Earlier, molecular groups relating to parafinic and olefinic hydrocarbons were explored; other interesting groups from which ORC working fluids could be derived include those relating to refrigerants such as fluoride and chloride groups. It is only natural that research efforts be directed into developing the thermodynamic and transport property group-contribution parameters for these groups. Thus, the outlook of CAMPD techniques

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for waste-heat recovery systems could include the incorporation of additional molecular groups and molecular constraints into the problem formulations. This would allow the assessment of a larger family of working fluids, such as aromatics, alcohols or ethers and refrigerants, expanding the possible optimal working fluid candidates.

In line with expanding the possible working-fluid database, decision variables for cycle architectures can also be directly incorporated in the decision space to enable the design of transcritical or recuperated cycles, or cycles with working-fluid mixtures *etc.* When evaluating these waste-heat recovery projects, it is also important to consider a variety of economic metrics such as the payback period, levelised cost of electricity or the operational costs and revenue, potentially forming a better basis for comparison between candidate systems and enabling a more informed decision on the economic prospects of waste-heat recovery systems in general.

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