

Imperial College of Science, Technology and Medicine
Department of Chemical Engineering

**Computer-Aided Molecular and System Design
of Diffusion Absorption Solar-Cooling Systems**

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Statement of Originality

To the best of my knowledge, I hereby certify that the enclosed thesis is all my work, and the results are original. Any work taken from another source and any assistance I received have been properly referenced and acknowledged.

Asmaa Aly Mohamed Hassan Harraz

October 2022

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Publications

To date, these are the publications that have been presented to the public domain concerning the works herein:

- A. A. Harraz, J. Freeman, K. Wang, N. Mac Dowell, and C. N. Markides, “Diffusion-absorption refrigeration cycle simulations in gPROMS using SAFT- γ Mie,” *Energy Procedia*, vol. 158, pp. 2360–2365, 2019
- A. Najjaran, A. A. Harraz, J. Freeman, R. Sacks, and C. N. Markides, “Experimental study of a diffusion absorption refrigeration unit at different charge-pressures,” in *ACEC 2019 Annual Clean Energy Conference*, pp. 1–8, Shiraz University, 2019
- A. Najjaran, A. A. Harraz, P. Sapin, K. Wang, and C. N. Markides, “Experimental investigation on the start-up time of a small-scale diffusion absorption refrigeration (DAR) unit,” in *14th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics*, (Wicklow, Ireland), 07 2019
- A. A. Harraz, A. Najjaran, R. Sacks, J. Freeman, A. V. Olympios, N. Mac Dowell, and C. N. Markides, “Experimentally validated simulations of a diffusion absorption refrigeration system,” in *ECOS 2019: Proceedings of the 32nd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems*, (Wroclaw, Poland), June 2019
- A. Najjaran, A. A. Harraz, J. Freeman, N. Mac Dowell, and C. N. Markides, “Numerical and experimental investigation of diffusion absorption refrigeration systems for Use with low-temperature heat sources,” in *ECOS 2018: Proceedings of the 31st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems* (J. C. Teixeira, ed.), (Guimarães, Portugal), p. 323, 6 2018

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Dedication

To my Late Father....

‘And my success is not but through Allah. Upon Him I have relied, and to Him I return.’

Holly Qur'an 11:88

Abstract

Diffusion absorption refrigeration (DAR) is an attractive thermally-powered refrigeration technology that can be powered using thermal solar collectors. DAR technology can address refrigeration security challenges, rising electricity costs and CO₂ emissions. Thus, adopting DAR technology and exploring alternative environmentally friendly working fluids for solar-cooling applications is interesting. Nevertheless, DAR systems usually have a lower coefficient of performance (COP) than conventional refrigeration technologies, and commercially available DAR units usually use NH₃–H₂O mixtures which require temperatures higher than 150 °C to initiate cooling. An integrated computer-aided molecular design (CAMD) and system optimisation framework using the group-contribution equation of state based on the statistical associating fluid theory (SAFT- γ Mie) was devised to select optimum working fluids and DAR-unit designs simultaneously, which has not been implemented before. The CAMD-DAR framework was implemented to identify optimum working-fluid mixtures considering different organic families, exploring non-polar simple hydrocarbons and complex polar hydrocarbons. Working fluids for maximising cooling rates are not necessarily the same for minimising the specific purchase cost. Thus, multi-objective optimisation was considered to obtain a set of non-dominated design alternatives. Due to the particular importance of the dynamic performance of solar-powered DAR systems under given climatic conditions, a quasi-transient DAR model is considered to simulate the performance of solar-powered DAR systems with a specific interest in the start-up and shut-down phases. The quasi-transient DAR model helps assess optimum DAR systems identified by the CAMD-DAR framework.

The CAMD-DAR framework identifies 2-C₄H₈–*n*-C₈H₁₈ as the optimum working fluid for maximum cooling. For ambient and cooling temperatures, respectively, $T_a = 20$ °C and $T_{co} = 4$ °C, A 250-W DAR unit charged with 2-C₄H₈–*n*-C₈H₁₈ can produce cooling up to 38 W corresponding to a specific purchase cost of cooling (*SPC*) of £ 15 per W. The CAMD-DAR framework suggests that non-polar organic working fluids enable higher cooling rates. Considering non-polar hydrocarbons, the CAMD-DAR framework identifies 2-C₄H₈–C₂H₅OH–He as the optimum working fluid for a wide range of cooling and ambient temperatures. This working fluid can produce maximum cooling rates up to 146 W for 440-W DAR system, corresponding to a *SPC* of £ 5.4 per W of cooling at ambient and cooling temperatures, respectively, of $T_a = 20$ °C and $T_{co} = 4$ °C. The CAMD-DAR framework suggests that olefins and branched refrigerants

can produce higher cooling rates than saturated straight chains. The current CAMD-DAR framework identifies working fluid mixtures that can compete with the standard $\text{NH}_3\text{--H}_2\text{O}$ system, thanks to the lower generator temperatures ($< 150^\circ\text{C}$) required by these organic working fluids to activate the DAR cycle. The solar-DAR simulations for climate data of Alexandria, Egypt, confirm that a DAR design based on $2\text{-C}_4\text{H}_8\text{--C}_2\text{H}_5\text{OH}$ and powered by evacuated tube collectors (ETCs) can produce more cooling than other organic working fluids. Given the climate data of Alexandria, Egypt, the ETC-powered organic-based DAR system could produce up to 1939 h of cooling per year ($68\text{ kWh}_{\text{co}}$ of cooling per year). However, low electricity prices cannot encourage households to use solar-powered DAR systems for their very long payback time and negative levelised cost of savings, with a levelised cost of cooling of $\pounds 1.93$ per kWh_{co} . The CAMD-DAR framework and dynamic DAR model results demonstrate the potential of this tool to introduce a new era of solar-powered cooling technologies for different applications.

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Nomenclature

Acronyms

AAD	Average absolute deviation	ECUK	Energy Consumption in the United Kingdom
AC	Alternating current	EE	Elementary effects
AIT	Auto ignition temperature	EoS	Equation of state
ASTM	American Society for Testing and Materials	EPCS	Environmental penalty cost saving
BDNLSOL	Block decomposition non-linear solver	ETC	Evacuated tube collector
CAGR	Global compound annual growth rate	FC	Fluorocarbons
CAMD	Computer-aided molecular design	FP	Flat plate
CAPMAS	The Central Agency for Public Mobilization and Statistics in Egypt	FP	Fully relaxed problem
CCHP	Combined cooling, heating and power	GA	Genetic Algorithm
CDD	Cooling degree-days	GC	Group contribution
CHP	Combined heating and power	GCC	Gulf Cooperation Council
CoMT	Continuous molecular targeting	GHI	Global horizontal irradiation
COP21	21 st Conference of the Parties to the United Nations Framework Convention on Climate Change	GRG	Generalised reduced-gradient
CPC	Compound parabolic concentrator	GWP	Global warming potential
CSP	Concentrated solar power	HFC	Hydrofluorocarbons
DAR	Diffusion absorption refrigeration	HP	Heat pipe
DC	Direct current	HTF	Heat-transfer fluid
DMAC	Dimethylacetamide	IAPWS	International Association of Pure Water and Steam
DNI	Direct normal irradiation	IEA	International Energy Agency
		IIR	International Institute of Refrigeration
		IRENA	International Renewable Energy Agency

KSA	Kingdom of Saudi Arabia	UB	Upper bound
LB	Lower bound	UK	United Kingdom of Great Britain and Northern Ireland
LC	Lethal concentration	US	United States of America
LCOC	Levelised level of cooling	VAT	Value-added tax
LCOE	Levelised cost of energy	VC	Vapour Compression
LPG	Liquefied petroleum gases	VCR	Vapour compression refrigeration
MBOE	Million barrels of oil equivalent	vdW	Van der Waal
MENA	Middle East and North Africa	VLE	Vapour–liquid equilibrium
MINLP	Mixed-integer nonlinear programming	VR	Variable range
MP	Master problem	WF	Working fluid
NLP	Nonlinear programming	WMO	World Meteorological Organisation
O&M	Operating and maintenance	XCPC	External compound parabolic concentrator
OA	Outer approximation	<i>Variables</i>	
OAERAP	Outer approximation–equality relaxation–augmented penalty	A	Helmholtz free energy
ODP	Ozone depletion potential	a_{0-4}	Constants in ideal-gas constant-pressure molar-specific heat capacity
ORC	Organic Rankin cycle	$\hat{c}_p$	Molar-specific heat capacity [J mol ⁻¹ K ⁻¹]
PBT	Payback time	C	Cost
PR	Primal problem	COP	Coefficient of performance
PTC	Parabolic trough concentrator	d	Diameter [m]
PV	Photovoltaic	E	Energy [kWh]
PVT	Photovoltaic-Thermal	EE	Elementary effects
QSPR	Quantitative structure property relationship	f	Function
RV	recreational vehicle	g	Gravity acceleration constant [9.81 m s ⁻²]
S-CCHP	Solar combined cooling, heating and power	$\hat{h}$	Molar-specific enthalpy [J mol ⁻¹]
SAFT	Statistical associating fluid theory	$\mathcal{H}$	Henry constant [atm m ³ mol ⁻¹]
SHC	Solar heating and cooling	i_d	Discount rate
SQP	Sequential quadratic programming	i_f	Inflation rate
UAE	United Arab of Emirate		

K^{HB}	Bonding volume due to cross-site association [$\text{\AA}^3$]	$\tilde{x}$	Liquid-phase molar composition [mol mol^{-1}]
K_{bs}	Base dissociation equilibrium constant	x	Liquid-phase mass composition [kg kg^{-1}]
k_{B}	Boltzmann's constant [$1.380\,649 \times 10^{-23} \text{ J K}^{-1}$]	$\tilde{y}$	Vapour-phase molar composition [mol mol^{-1}]
LT	Life time [years]	$\tilde{z}$	Two-phase molar composition [mol mol^{-1}]
MW	Molecular weight [g mol^{-1}]	$\dot{P}$	Power [W]
$\dot{n}$	Molar flowrate [mol s^{-1}]	<i>Number sets</i>	
N	Number of experimental points in Eq. 2.15 or number of molecules in Eq. 2.3	$\mathbb{R}$	Real numbers
		$\mathbb{Z}$	Natural numbers
n	Group or site multiplicity in a given molecular structure [mol]	<i>Greek symbols</i>	
		α	Void fraction
N^{ST}	Number or association-site types on a given species	β	Array of integer decision variable
		θ	Array of continuous decision variable
P	Parchor	Δ	Change
p	Pressure [MPa]	ϵ	Effectiveness
$\dot{Q}$	Rate of heat transfer [W]	Γ	Flammability number
q	Molar vapour quality [mol/mol]	γ	Surface tension [mN m s^{-1}]
q''	Heat flux [$\text{W/m}^2/\text{K}$]	λ	Exponent of the Mie intermolecular potential
R_{u}	Universal gas constant [$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$]	μ_{EE}	Mean value of elementary effects
R	Reflux ratio	μ_{EE}^*	Absolute mean value of elementary effects
S	Shape factor in SAFT of a given species	ν^*	Number of identical segments comprising a group
SPC	Specific cooling cost [$\text{\pounds W}^{-1}$]	ω	Acentric factor
T	Temperature [$^{\circ}\text{C}$ or K]	π	Ratio of a circle's circumference to its diameter [3.14]
t	Time [years]	ρ	Mass density [kg m^{-3}]
u	Linear velocity [m s^{-1}]	σ	Diameter of a given species [$\text{\AA}$]
U	Uncertainty [%]		
$\tilde{v}$	Molar-specific volume [$\text{cm}^3 \text{ mol}^{-1}$]		
w	Weight in Eq. 2.15		

σ_{EE}	Standard deviation of elementary effects	dew	Dew point
		elec	electricity
ε	Dispersion energy [J]	evap	Evaporator
ε^{HB}	Association energy [J]	exp	Expansion
$\Xi, \psi, \varpi, \varphi, \iota$	Constants in Sastri-Rao surface-tension model Eq. 2.10b	expt	Experimental
	<i>Subscripts and Superscripts</i>	g	Auxiliary gas
0	Initial	gen	Generator
1-11	State number	ig	Ideal gas
j	Compound index	L	Liquid
k, l	Group indices	max	Maximum
a	Attraction	min	Minimum
abs	Absorber	mono	Monomer
absr	Absorbent	O&M	Operating and maintenance
an	Annular	r	Repulsive or reduced
b	Normal boiling point	rect	Rectifier
bp	Bubble pump	refr	Refrigerant
bs	Bubble-to-slug transition	rs	Refrigerant-rich solution
bub	Bubble point	s	Savings
byps	Bypass	sat	Saturation
c	Critical	sys	System
calc	Calculated	T	Tension
co	Cooling, or cold	V	Vapour
cond	Condenser	ws	Refrigerant-weak solution

Chapter 1

Introduction

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1.1 Background and motivation

Heating and cooling consumed up to 52 % of global energy production worldwide in 2020; about a quarter of this consumption has been covered by electricity. [1] The demand for heating and cooling varies geographically depending on climates and economic growth levels. Cooling activities are necessary worldwide with particular importance in hot regions. Residential cooling applications range from food freezing (-18°C) to air-conditioning (18°C to 23°C). Although cooling is not a primary energy end-user compared to other domestic heating loads, cooling loads are – in most cases – covered solely by electricity, as can be observed in Figure 1.1. [1–3]

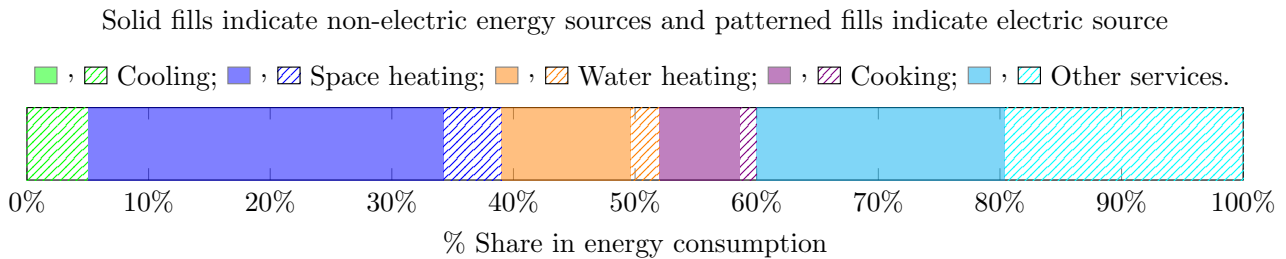


Figure 1.1: A breakdown of global energy consumption in households indicating shares of electricity. Notably, all household cooling needs are covered by only electricity. [1] Other services include computers and IT devices, water pumps, TVs..*etc.*

Cooling activities are essential for residential, commercial and industrial sectors as illustrated in Figure 1.2. In the United States of America (US), space cooling and refrigeration activities consumed about 20 % of the total electricity sales in 2020. Cooling and refrigeration consumed 16 % of total electricity sold to the industrial sector ($\sim 150 \times 10^3 \text{ GWh}_e$)¹, while consumed 23 % ($\sim 330 \times 10^3 \text{ GWh}_e$) of total electricity sold to the residential sector, and consumed 27 % ($\sim 300 \times 10^3 \text{ GWh}_e$) of total electricity sold to the commercial sector [2, 4]. In the United Kingdom (UK), Cooling activities in the residential sector consumed only 10 % of total electricity consumption as reported in “The Energy Consumption in the UK (ECUK)” [3] reports for 2020.

As it can be noticed in Figure 1.3, cooling activities in the UK share more of the overall electricity consumed by a given sector than in the US. In the residential sector, refrigeration consumed 10 % of overall electrical load in the UK, while it consumed slightly less (7 %) in the US. No detailed data was reported in ECUK reports [3] for residential space cooling in the UK. In the

¹Available consumption data for industrial sector in USA is for 2018.

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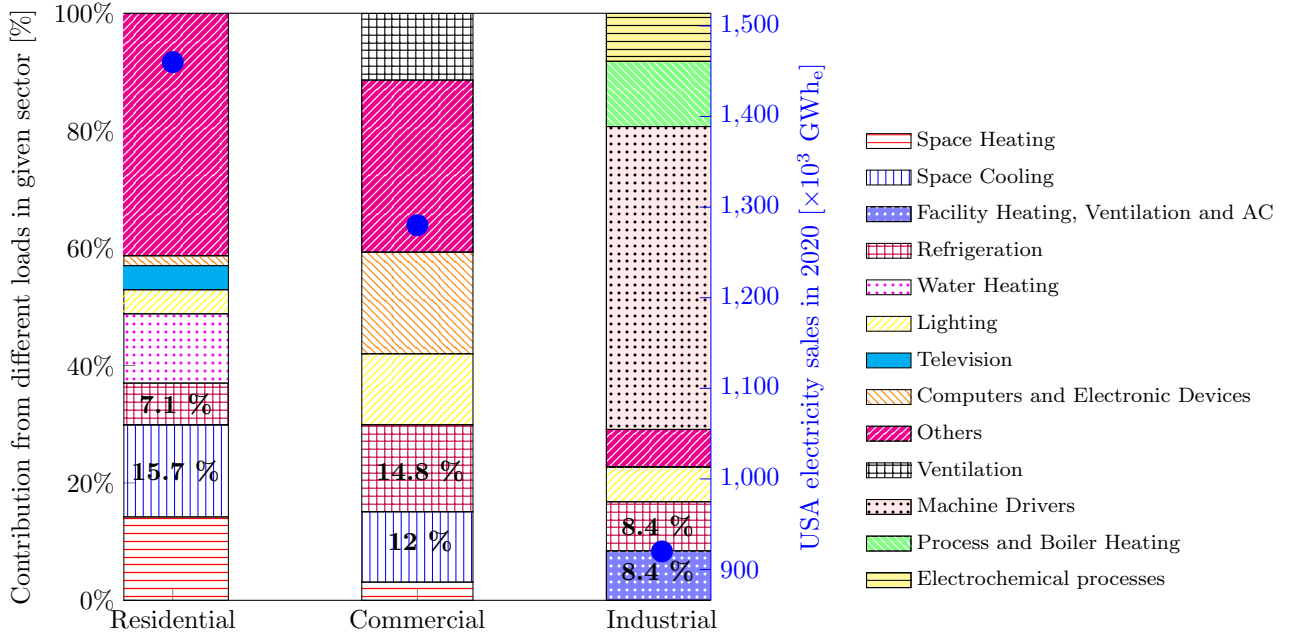


Figure 1.2: A breakdown of electricity consumption in the US for residential (2020), commercial (2020) and industrial (2018) sectors with a focus on cooling and refrigeration activities. [4]

commercial sector, space cooling shares were similar in both UK and US. It can also be noticed that industrial refrigeration and cold processes in the UK relied more heavily on electricity, which consumed 24 % of the overall industrial electricity demand compared to only 8.4 % in the US. It can also be seen that in the UK, cooling activities in the industrial sector consume more electricity per year than in the residential and commercial sectors. On the other hand, in the US, cooling activities in the industrial sector consume the least electricity compared to the other two sectors. In comparison, cooling activities in the commercial sector consume more electricity than the other two sectors.

Worldwide, refrigeration primarily relies on electricity in the residential sector. [1,3] According to the energy consumption in the UK report [3], household refrigeration electricity load has dropped since 1990 at an average rate of 3 % as can be observed in Figure 1.4, thanks to the advances and in energy efficiency and applying energy efficiency policies. It can also be noticed in Figure 1.4 that, in the UK, the fraction of electricity consumed to cover refrigeration demand has declined faster than refrigeration electricity consumption. [3]

On the other world bank, the International Institute of Refrigeration (IIR) [5] has reported over 821 million undernourished people around the globe in 2018, most of whom live in warm developing countries. Whereas about a 789 million people lack access to electricity, most of them live in remote rural areas where they face difficulties accessing cooling appliances, whether

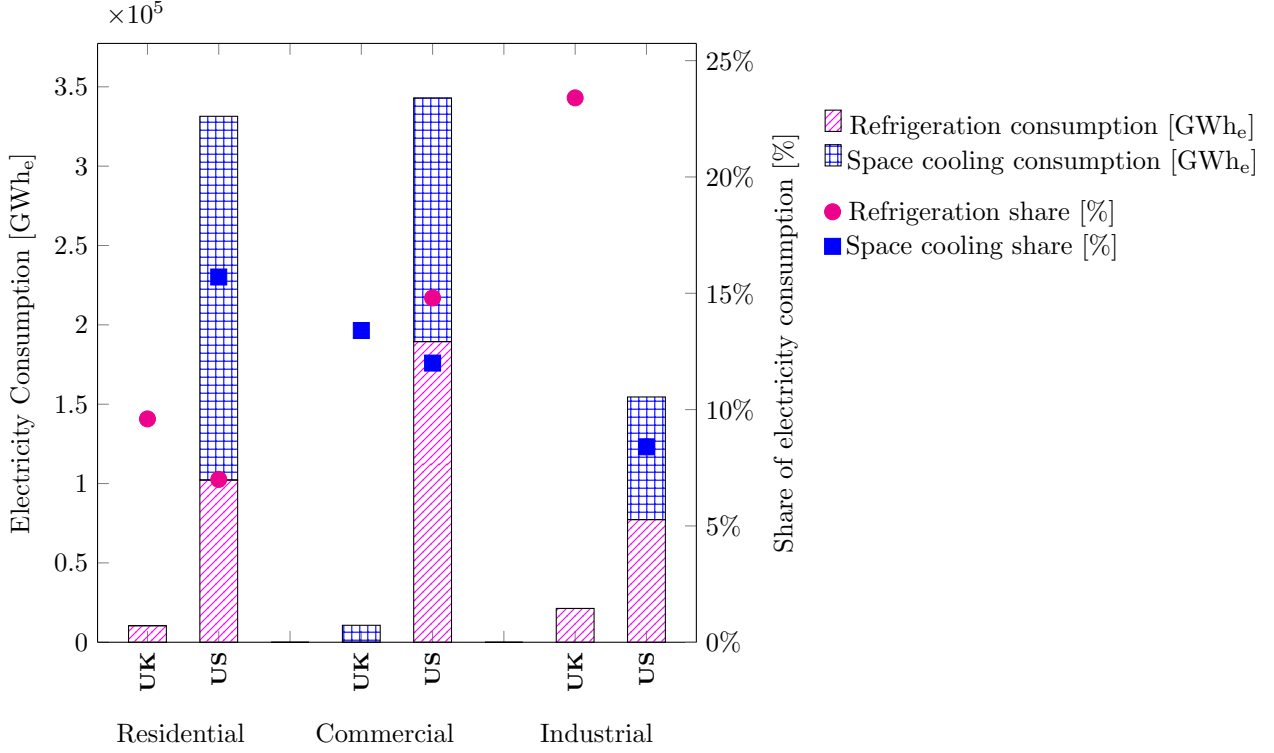


Figure 1.3: A comparison between the UK [3] and US [4] electricity consumption to cover cooling and refrigeration needs for 2020¹. Electricity consumption for cooling and refrigeration in UK and US are bar-plotted and can be read using the left axis. Shares of electricity consumption that cover cooling and refrigeration to total electricity consumption in a given sector are scattered and can be read using the right axis.

because they are not affordable or yet unavailable. [1]

The need for cooling is crucial for humankind, whether in combating famines or for better welfare. The absence of refrigeration can lead to illness due to contaminated food, waste of vaccines or heat-sensitive medicines. Biardeau *et al.* [2] argue that poor space cooling risks better well-being, productivity and facing the extreme heat waves we suffer nowadays. The spread of air conditioners in the USA reduced the heat-related mortality rate by more than 70 %.

The World Meteorological Organisation (WMO) [6] expects a continuous rise in global ambient temperature. Some studies suggest heating demands are coming down by the end of the century, but cooling demand will escalate due to these climate changes [2, 7]. Energy demand for cooling is proportional to what is called cooling degrees-days. Cooling degree-days (CDD) is the cumulative sum of the positive differences between daily-average outer door temperature and a base temperature (normally 18 °C). Cooling demands will increase with the continuous rise in ambient temperatures (and subsequently CDD). Hence, refrigeration electric loads are expected to increase since energy consumption for cooling purposes has been markedly increasing, as

1.1. BACKGROUND AND MOTIVATION

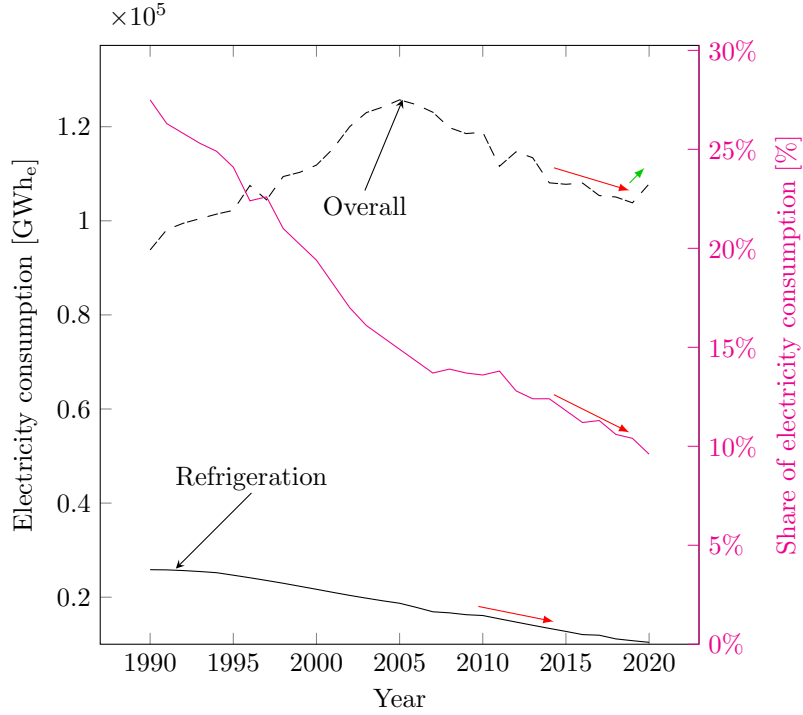


Figure 1.4: Historical data for annual household refrigeration electric loads in the UK between 1990 and 2020 [3].

suggested by IEA [2,8] which still primarily depends on electricity.

This anticipated increase in cooling demands and associating electricity loads increase direct and indirect greenhouse gas emissions. The International Energy Agency (IEA) [1] estimated that by 2020 heating and cooling have already contributed to global CO₂ emissions by almost 40 %.

Global ambient temperature is rising, the global population is booming too, and heating and cooling demands are looming, especially in warm climates. The world population is expected to increase by a 2 billion between 2020 and 2050 to reach 9.7 billion [9], 75 % of whom shall be living in developing countries as reported by IIR [5]. However, as highlighted earlier, cooling for air conditioning or food refrigeration is relatively absent in developing countries due to low per capita income and how expensive refrigeration devices are to install and operate.

In developing and emerging-economy countries, the need for cooling increased almost three-fold between 1990 and 2016. [1,8] This increase accompanies economic growth, climate changes and a change in lifestyles due to globalisation. [2] Unlike space cooling, there is not enough data about the change in household refrigeration needs over time in developing countries. Thus, the change in space cooling needs is taken as a guide to emphasise the importance of cooling.

In 2019, space cooling using air-conditioners has been estimated to account for about 8.5 % of

total final electricity consumption as IEA estimates [1]. Installed Air conditioners (AC) in USA and China can use up to 2×10^3 TWh_e/year, which is 2.5 as large as the total electricity use in Africa. [8] Some countries like those in the Middle East consume more than 70 % of the peak household electricity for space cooling, especially on sweltering days. At the same time, the global average in 2016 was only 14 % of the peak demand. [8]

For the household refrigeration and freezer market, a market study anticipated that the global compound annual growth rate (CAGR) of the household refrigerators and freezers market shall increase by 6.5 % between 2019 and 2024. [10] The global market of solar freezers is to jump from US\$ 8.0 billion in 2020 to reach US\$ 15.5 billion by 2030. This jump corresponds to a CAGR growth of 6.9 % from 2021 to 2030. [11] However, according to a later study [11], Asia-Pacific currently accounts for the largest share of the solar-freezer market, followed by North America and Europe, where there is still capacity for market growth in MENA. The refrigerant market is expected to grow at a CAGR of around 3 % between 2019 and 2026. As the cold chain market globally expands, this expansion is the primary driver of the refrigerant market. Stringent environmental regulations against fluorocarbon refrigerants usually restrain this expansion from meeting COP21 Paris Agreement on Climate Change and Kiabil agreement. [12]

The transition to cleaner cooling systems is attractive to investments creating many job opportunities and avoiding food spoilage. 4 % of households in rural African communities possess refrigerators; however, around one-third of household food is spoiled. [1]. Securing refrigeration in Africa can prevent the loss of 23 % foodstuff, [13] which can annually worth US\$ 4 billion food. [1] Unfortunately, providing refrigeration in rural areas like in sub-Saharan Africa is challenged by the high installation cost of refrigerating systems in the market, which are also inefficient. The intermittent power supply also challenges refrigeration systems in rural areas, such as sub-Saharan Africa. [1]. This challenge can be met and overcome by supplying off-grid refrigeration systems, particularly solar-powered ones. Thus, there is a growing interest in developing alternative sustainable cooling technologies. In Africa, solar-driven cooling technologies show great potential to meet this escalating demand for cooling. [14, 15]

With the devastating energy crisis, there is a great necessity to move towards solar cooling to decarbonise cooling demand, especially in the world's warmest spots. There is a great potential for solar cooling that coincides with the highest temperature, solar potential, and carbon emissions. Over the last decade, the global capacity of solar thermal collectors in

1.1. BACKGROUND AND MOTIVATION

operation has steadily increased almost three folds . [1] Although there are no clear statistics about solar-refrigeration market expansion, solar space-cooling remains a niche market with less than an estimated 2000 solar thermal cooling systems deployed worldwide in 2019. most projects are for demonstrating space cooling (*i.e.*, Arizona–US, Johannesburg–South Africa, and Singapore). The uptake of solar cooling is still limited by high cost, technical limitations, and a relatively expensive application-specific and immature supply chain. [1, 8, 15] Noting that a better cold chain shall reduce CO₂ by 50 % and food losses by 55 %. [16] Thus, the need to expand the solar-refrigeration market to address the arguments mentioned above led to a great motivation to study solar-powered cooling technologies to provide sustainable and affordable cooling to tackle different global issues (*i.e.*, famine, climate change, energy crisis).

1.1.1 Solar refrigeration perspective and opportunities in MENA region

Residential sector in MENA is primarily driven by electricity mainly produced using non-renewable energy sources. In Saudi Arabia, fossil fuels cover their electricity demands, contributing 16.39 tons of CO₂ per capita in 2013. [17] In 2014, Saudi Arabia was the top-third country globally in household energy consumption, where 72 % of this energy goes towards thermal uses, including cooling. In 2013, Radhi and Sharples [18] concluded that electricity consumption for cooling in Saudi Arabia had been estimated as 80 kWh/m².

A Breakdown of household electric loads in MENA is presented in Figure 1.5. Based on available data, refrigeration and freezing account for 1 % to 47 % of total household electric load in the MENA region. Tunisia is the most electricity consumer for residential refrigeration. Up to 47 % of household electricity consumption covers refrigeration loads. [19] Unlike their country neighbour, Algerian households do not use much electricity out of their total load to cover refrigeration activities; they use only 1 % of electricity consumption to cover their refrigeration needs. [19] In Egypt, about 20 % of residential electric load covers household refrigeration needs. [19, 20] This share is nearly double the share of refrigeration of household electricity consumption as demonstrated in Figure 1.3. As it can be noticed in Figure 1.5, the most household electric loads in the gulf cooperate council region (UAE, Saudi Arabia, Qatar, and Kuwait) are consumed by air conditioners and chillers due to their climates, [24, 26–28] around 10 % of total final energy

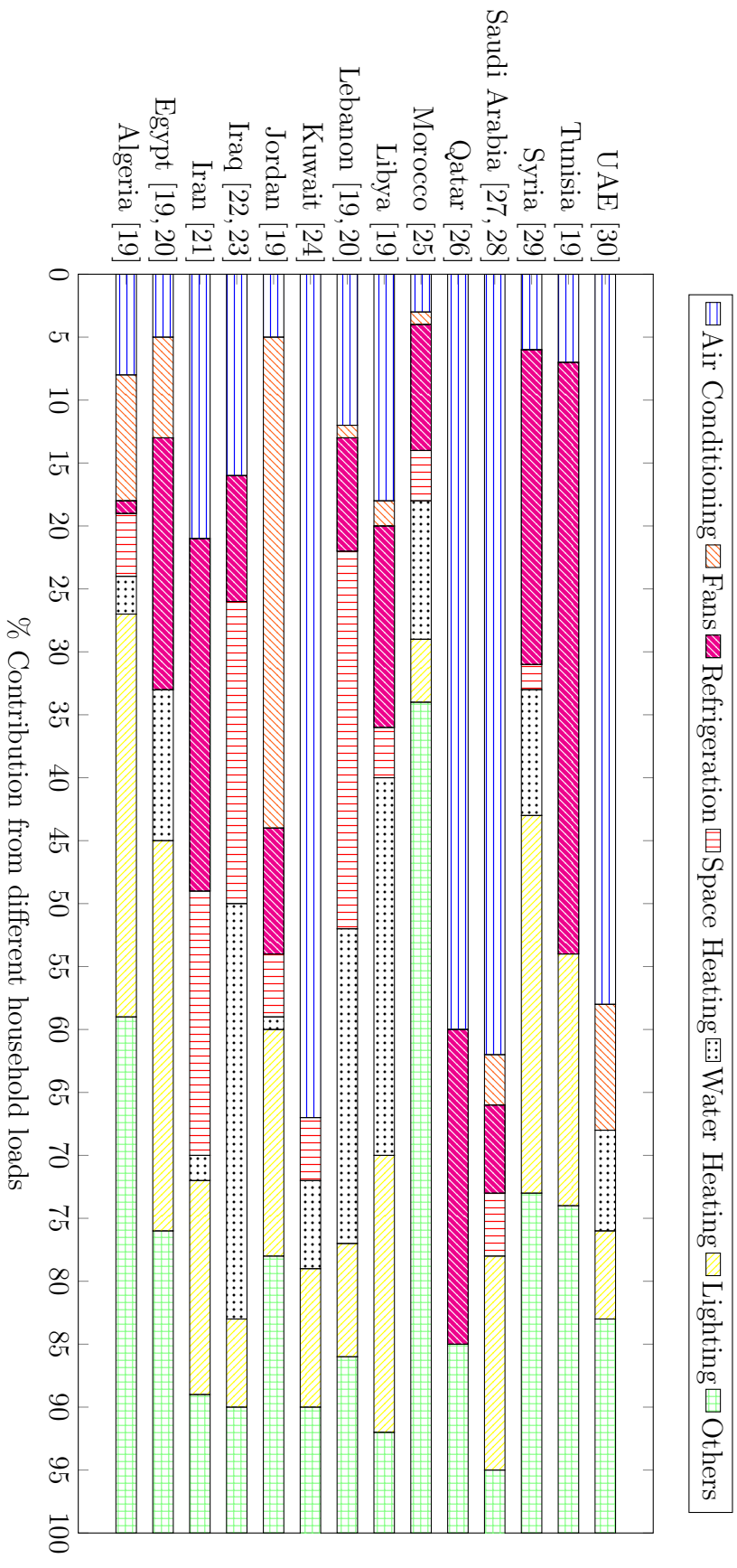
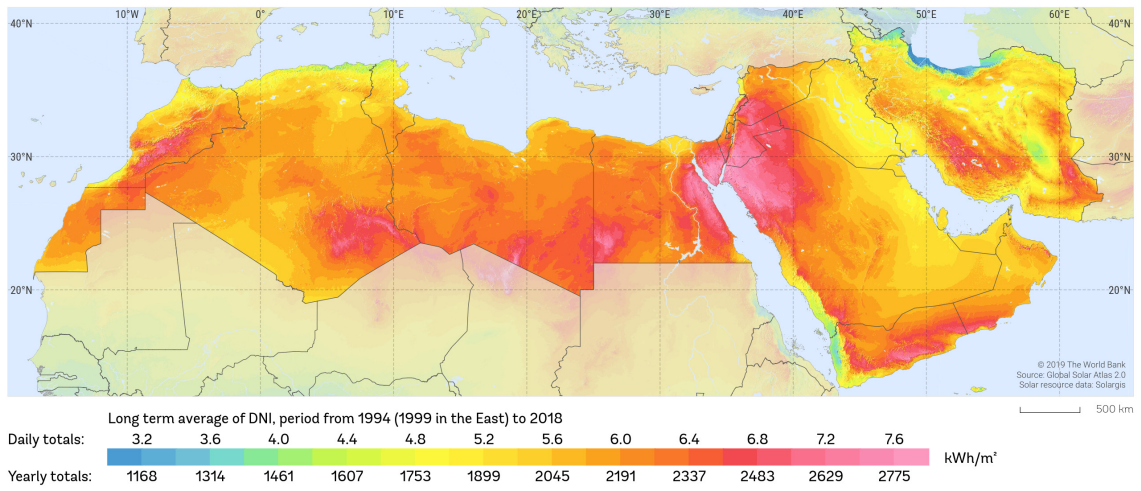


Figure 1.5: A breakdown of household energy consumption in MENA region [19–30]. Others include cooking, computers and IT devices, water pumps, TVs... Due to data availability limitations, loads for Algeria, Egypt, Iran, Jordan, Lebanon, Libya, Saudi Arabia, Syria, Tunisia and UAE date to 2010, while loads for Morocco date to 2015. Loads for Saudi Arabia are predicted in [27] for 2010 adjusted with ratings from [28]. Kuwait loads are predicted in [24] for 2017, while loads for Iraq are predicted by [22]. Qatar loads are measured in [26]. To the author's knowledge, the breakdown of household energy loads for Bahrain, Palestine authority and Yemen are unavailable.

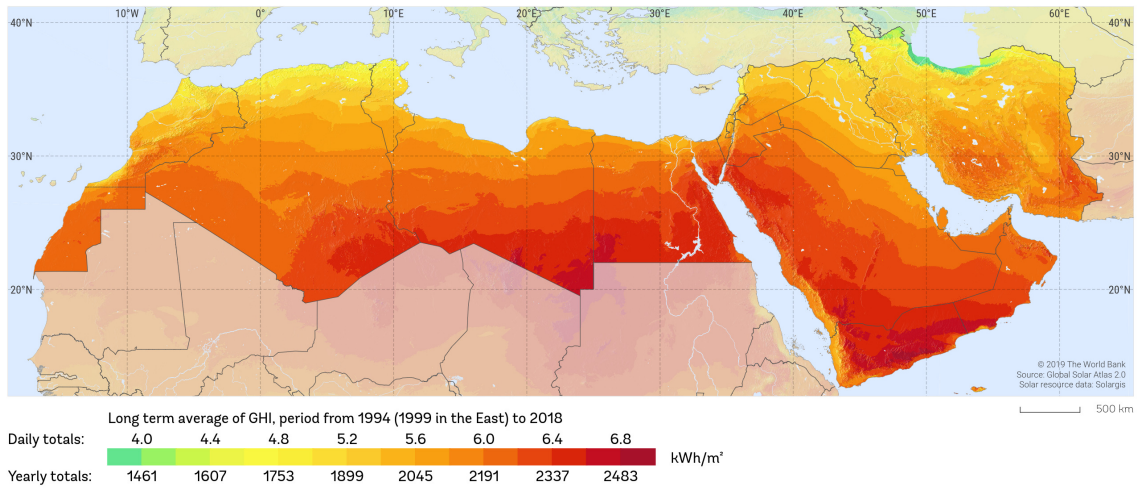
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consumption is taken by the residential sector. [30] For instance, in Abu Dhabi (UAE), chillers consumed 58 % of total electricity consumption in the residential sector in 2010.

Most MENA countries lie on the solar belt having high average annual solar irradiation as it can be seen in Figure 1.6 [31]. MENA countries are responsible for increased global warming gas emissions. [19] Thus, there is a great potential in the MENA region to decarbonise energy and heat sectors by making use of the abundant solar insolation, both direct normal irradiation (DNI) and global horizontal irradiation (GHI).



(a) Direct normal irradiation (DNI).



(b) Global horizontal irradiation (GHI).

Figure 1.6: Average daily and annual solar irradiation in MENA region. (a) Direct normal irradiation (DNI), (b) global horizontal irradiation (GHI) [31].

There are many motivations for thermally-powered refrigeration systems to take-over electrically-driven refrigeration systems. The increase in energy demands and non-renewable energy prices,

as well as the depletion of fossil fuels and environmental concerns, all promote the use of alternative refrigeration systems powered by renewable energy, with a particular interest in thermally-driven refrigeration systems that can be powered using solar systems. Also, the expansion of renewable – particularly solar-energy systems – in MENA motivates using solar-powered refrigeration for residential applications. Many MENA governments have set ambitious goals to go renewable by 2030. [32, 33]

In Egypt, renewables' share in electricity production was only 9 % in 2016, and 1 % of electricity production was using solar plants. The Egyptian government has planned [34] to have 20 % of electricity production in Egypt from renewable sources by 2020. [35] Nevertheless, renewable energy sources (including hydropower) shared 12 % of total electricity production, 18 % of these renewables as solar, as reported by the Egyptian Electricity holding company [36]. Egypt's ambitious target for a renewable share in electricity production is to reach at least 32 % by 2030, and 16 % of electricity production should be covered by concentrated solar power (CSP) and photovoltaic (PV) farms. [34, 35] The targeted share of renewable energy in electricity production is predicted to lower greenhouse gas emissions by about 10 % by 2030.

The Gulf Cooperation Council (GCC) region is globally the most important oil-producing region. For instance, Saudi Arabia is the world's second-largest oil reserves in the world, as well as the sixth largest natural gas reserves. As highlighted earlier, the GCC region also enjoys abundant renewable energy, particularly for solar PV generation. [30] the UAE has about 80 % of installed PV plants in the GCC. In 2018, the installed capacity of renewable energy in the GCC reached 589 MW corresponding to 0.6 % of total electricity capacity. UAE had the largest installed capacities among other GCC nations. Solar PV is the most used solar technology in the GCC region, followed by CSP. In Saudi Arabia, about 354 MBOE and 136 MtCO₂ can be saved by achieving 2030 renewable-energy targets by 2030. [30] For instance, Saudi Arabia aims to increase the share 30 % of energy generation from renewable and nuclear resources by 2030.

The ambitious renewable-energy goals in the MENA region encourage the adoption of refrigeration technologies that cheap solar collectors can readily power. Solar-powered refrigeration can play an important role in a better standard of living in rural areas (such as those in north Africa and sub-Saharan Africa) where proper access to electricity is a problem.

1.1.2 Solar-powered refrigeration technologies

Following the discussion above, solar cooling is an attractive alternative to replace conventional means of refrigeration to match cooling loads and solar availability, especially in the world’s warmest regions. As highlighted earlier, many of the world’s fastest-growing cities are in the warm climates of south Asia, Africa and the GCC. It has been argued in Section 1.1 that many rural regions like Africa are deprived of proper refrigeration due to lack of electricity access and high upfront installation costs. [1] Thus, it is vital to provide low-cost, efficient off-grid refrigeration technologies taking advantage of the low cost of solar energy systems.

Solar-powered refrigeration can be either electrically driven or thermally driven. Some refrigeration technologies that solar energy can drive are reviewed by Zeyghami *et al.* [37]. The basic idea is to harvest solar energy using thermal collectors (*i.e.*, flat plates “FP”, evacuated-tube collectors “ETC”, parabolic trough concentrators “PTC”) or PV cells. Harvested solar energy is converted to thermal or electric energy that can either be stored or directly used to drive a refrigeration system. Some examples of how different solar-energy systems can be coupled with a refrigeration system are presented in Figure 1.7. As seen in Figure 1.7, solar-cooling systems comprise three main components: a solar collector, a heat-driven refrigeration cycle that converts energy harnessed by the solar collector into cooling, and a cooling medium that rejects its heat to the refrigeration cycle. Solar thermal cooling systems may additionally use thermal storage (hot-water tanks, phase-change material or ice storage).

Thermal cooling systems do not require shaft work to drive a compressor. [38,39] Single-effect absorption refrigeration machines are widely available at cooling outputs >10 kW, while more efficient double- and triple-effect systems tend to be better suited to applications >100 kW. [40]

Countries like China and Germany have offered incentives using solar thermal cooling systems [15]. The IEA [15] reports that, mostly in Europe, 1800 small solar thermal air conditioning units were installed in 2018. While in 2020, about 2000 small solar thermal air conditioners were installed. Although large-scale solar cooling systems are expanding, the number of installed projects is still limited to less than 25. Two large-scale solar spacing cooling plants were installed in 2020 for Graz, Austria (~ 3500 m²) and Dubai, UAE (710 m²). Nevertheless, the deep need for affordable refrigeration technologies powered by renewable energy for food storage evolves, especially in poor, remote areas. [1]

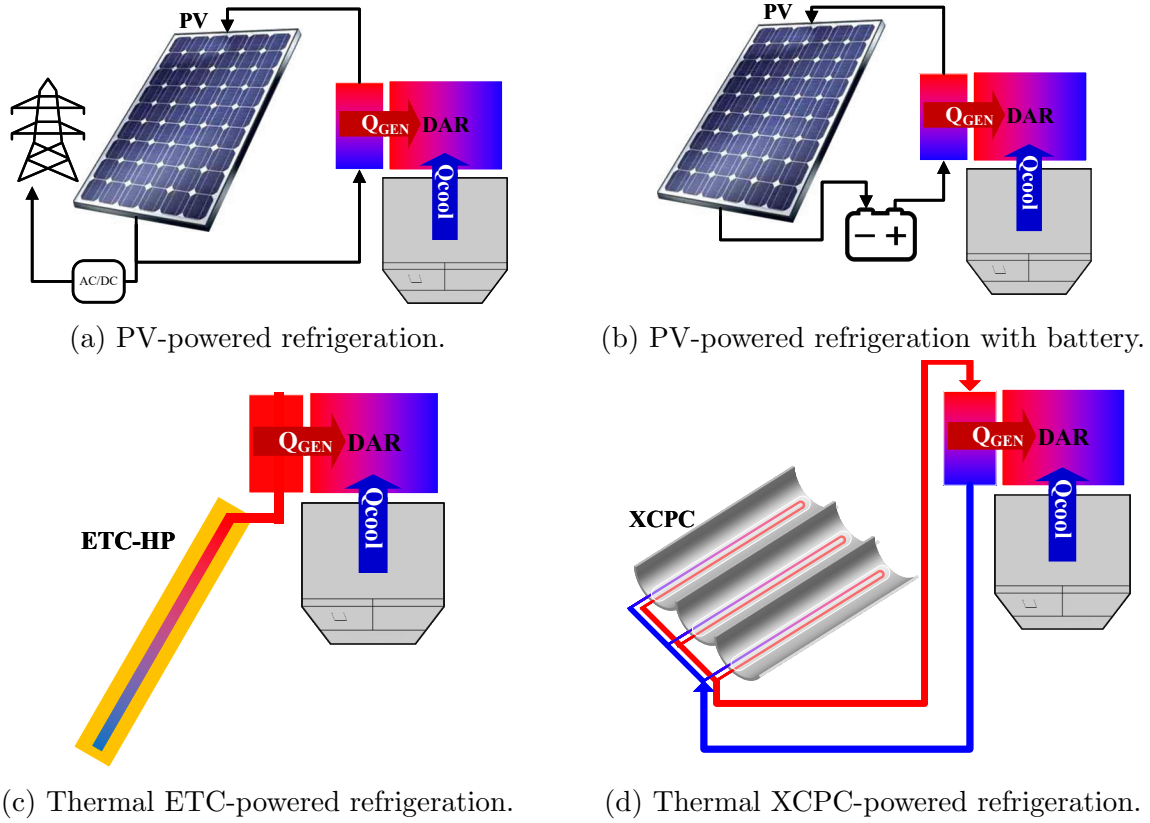


Figure 1.7: Some possible configurations of solar-powered DAR systems.

More focus is given here to absorption-based refrigeration systems. Thermally-driven cooling systems based on absorption refrigeration systems are mature and popular in certain countries (*i.e.*, Japan, Korea, USA), mostly in larger-scale space-cooling applications. Many authors [14, 41–44] have investigated solar-powered refrigeration technologies. Absorption refrigeration is among these environment-friendly technologies. [38, 40, 45, 46]

Best and Ortega [47], Kim and Ferreira [48], Ashraf *et al.* [49], Sarbu and Sebarchievici [50], Zeyghami *et al.* [37] reviewed state of the art and applications of solar-powered refrigeration systems. In 1998, Best and Ortega [47] discussed why solar refrigeration was not economically feasible, though technically feasible, due to their high system costs (by the time of this study), as discussed earlier in Section 1.1.1. Ten years later, Kim and Ferreira [48] presented a state-of-the-art review on different solar-powered refrigeration technologies. By 2008, solar-collector installed cost was still not competent with fossil-fuel power systems. The levelised cost of energy (LCOE) of PV systems ($> \text{US\$ } 0.381 \text{ kWh}^{-1}$) and CSP systems ($> \text{US\$ } 0.340 \text{ kWh}^{-1}$) were still high compared to fossil-fuel-fired power systems [30]. Kim and Ferreira [48] demonstrated that solar thermal-sorption refrigeration systems were more cost-effective than solar electric and thermo-mechanical refrigeration systems.

1.1. BACKGROUND AND MOTIVATION

The expansion in solar-energy utilisation helps to bring down energy costs. Globally, the LCOE of utility-scale PV plants declined from US\$ 0.381 kWh⁻¹ to US\$ 0.057 kWh⁻¹ between 2010 and 2020. [51] While LCOE of CSP declined from US\$ 0.34 kWh⁻¹ to US\$ 0.108 kWh⁻¹ over the same period. [52] This lower LCOE falls in the range of fuel-fired power generation. Thus, the merits of low LCOE of solar energy (both PV and CSP), low environmental impact, and the increasing market capacity for more thermal-powered refrigeration systems to be installed encourage investigating solar-powered refrigeration systems for household applications.

Recent research addresses expanding the use of solar-powered refrigeration systems. Amongst this research, Kitching [53] developed of compound parabolic concentrator (CPC) that can provide heat at 90 °C suitable for powering an NH₃–H₂O absorption-refrigeration system. Kitching recommended using electronically tracked CPC and highlighted the importance of controlling the flowrate through the collector. [53] Christopher *et al.* [54] used TRNSYS [55] to optimise a solar collector design with thermal storage to power an absorption refrigeration system, which can cover up to 65 % of the refrigeration unit power requirement. Baniasad Askari *et al.* [56] carried out a techno-economic assessment of large-scale solar-powered absorption refrigeration integrated with a humidification–dehumidification desalination system. They concluded that thermal energy storage can reduce the specific cost of cooling in the middle east but not in climates like that of Athens.

Solar-powered refrigeration systems can be easily integrated into solar-combined cooling, heating and power (S-CCHP) systems. Among many studies in this area, Ramos *et al.* [57] demonstrated the use of absorption refrigeration for space cooling in different European cities, driven by hybrid PV-thermal (PVT)-based S-CCHP. They reported cooling demand coverage of 100 % for all considered cities except Seville (Spain), where only 21 % could be covered.

In another relevant study, Herrando *et al.* [58] considered an S-CCHP system based on a hybrid PV thermal (PVT) solar collector. In their research, a single-effect absorption refrigeration system for space cooling in a university building in Bari (Italy), the PVT-base S-CCHP was compared to an ETC-based SHC system. Installed investment for the SHC system was lower than PVT system. Also, the heating and cooling demand covered by the ETC-SHC were higher than that covered by the PVT-based S-CCHP system. However, the payback time for the ETC-SHC system has been much higher than for PVT-based S-CCHP.

On a larger scale, Harraz *et al.* [59] focused on using different solar-powered refrigeration

scenarios to cover refrigeration needs for a dairy plant in Bari (Italy). They considered thermal, PV and PVT solar systems. The proposed systems showed that 29 % could cover cooling demand in case of thermal PTC, 36 % in case of PV collectors and 38 % in case of using PVT collectors. The proposed systems by Harraz *et al.* [59] can be integrated within the PVT-based CHP system investigated by Kai *et al.* [60]

Another important application is using off-grid refrigeration systems to deliver vaccines to remote poor regions. All commercially available solar vaccine refrigerators operate on photovoltaic panels using vapour compression refrigeration technology (PV-VC). [38, 61] The successful operation of such systems is often challenged by regular maintenance and the availability of spare parts, with high capital costs US\$ 2,350 to US\$ 7938 for small-capacity systems [61, 62]. Accordingly, finding ways to improve solar PVT-based refrigeration efficiencies at lower capital costs is vital. [63, 64]

Solar cooling systems based on absorption or adsorption cycles are still at a relatively early stage of uptake, with the majority of applications being for air conditioning, with cooling capacities >1 kW. [38] Chiller systems based on single-effect water–lithium bromide (H_2O –LiBr) absorption refrigeration systems are well suited to non-concentrating solar collectors, with heat source temperatures typically in the range of 60°C to 100°C . [38] (H_2O –LiBr) absorption refrigeration systems are suitable for space cooling as water (the refrigerant) freezes at 0°C . [65] Water is often used as the solar heat-transfer fluid (HTF). Solar-powered absorption refrigeration systems may also be combined with domestic water heating. Hot water storage tanks can provide buffering during intermittent solar availability.

A limitation that absorption refrigeration faces is that single-effect absorption refrigeration systems cannot meet small-scale cooling applications (<10 kW). [66] Diffusion absorption refrigeration is amongst other thermal-powered absorption-based refrigeration technologies that can be more suitable for small-scale refrigeration applications.

1.2 Diffusion absorption refrigeration

Diffusion absorption refrigeration (DAR) is a pumpless class of absorption refrigeration. DAR is a thermally driven cooling technology that can be solar driven. DAR technology can offer a

1.2. DIFFUSION ABSORPTION REFRIGERATION

great alternative to meet small-scale off-grid cooling demand [38,66]. Swedish engineers Von Platen and Munters [67–69] invented DAR and patented it by in 1928. Von Platen and Munters were motivated to propose this technology to meet the requirement for a low-cost domestic refrigeration system by modifying absorption refrigeration technology.

An absorption refrigeration cycle shown in Figure 1.8a uses a liquid pump to raise the working fluid from the evaporation to the condensation pressure. A DAR cycle shown in Figure 1.8b does not need a liquid pump. A DAR cycle is pressurised by a non-condensable auxiliary gas such as hydrogen or helium. In a DAR cycle, the evaporation step is driven by refrigerant diffusion into the auxiliary gas and evaporates due to changes in partial pressure while maintaining constant system total pressure. [65,66]

A typical DAR system is shown in Figure 1.9. DAR systems use three-component working fluids: refrigerant, absorbent and auxiliary gas. A refrigerant-rich solution (State 1) is heated in the generator. In principle, the generated vapour (at State 2) forms a train of Taylor plugs that lifts the rich-solution slugs through a bubble pump tube (as illustrated in Figure 1.10). When using a volatile absorbent, a bubble pump is not efficient enough to desorb all refrigerants. Thus, a rectifier takes vapour (State 4) and purifies it as partial condensation occurs. Stripped refrigerant-weak solution (State 5) mixes with liquid separated at the bubble-pump top (State 3). This weak solution spills down the bubble pump outer tube to the absorber through a solution heat exchanger. The vapour refrigerant leaving the rectifier at State 6 is admitted to a finned condenser and leaves as saturated or subcooled liquid (State 7). Sometimes, vapour (State 7') may leave the condenser and bypass the evaporator.

Condensed refrigerant and auxiliary gas are subcooled in a gas heat exchanger. The subcooled streams (State 9') mix adiabatically (as demonstrated in Figure 1.11). According to Dalton's law, the adiabatic mixing is accompanied by refrigerant expansion due to the drop in temperature and refrigerant partial pressure (State 9). [65] As the refrigerant-gas mixture flows down the evaporator tube, the refrigerant expands, removing heat from the gas heat exchanger and the cold space. The emerging mixture (State 10) leaves the evaporator, merging with any refrigerant bypass (State 7, V) in the reservoir. The combined gas rises to the absorber and meets the pre-cooled weak solution (State 8), and almost all the refrigerant is absorbed. Pure auxiliary gas (State 8,g) leaves the absorber coil towards the gas heat exchanger. Meanwhile, refrigerant-rich solution (State 11) flows to the solution heat exchanger. In the solution heat exchanger, the rich

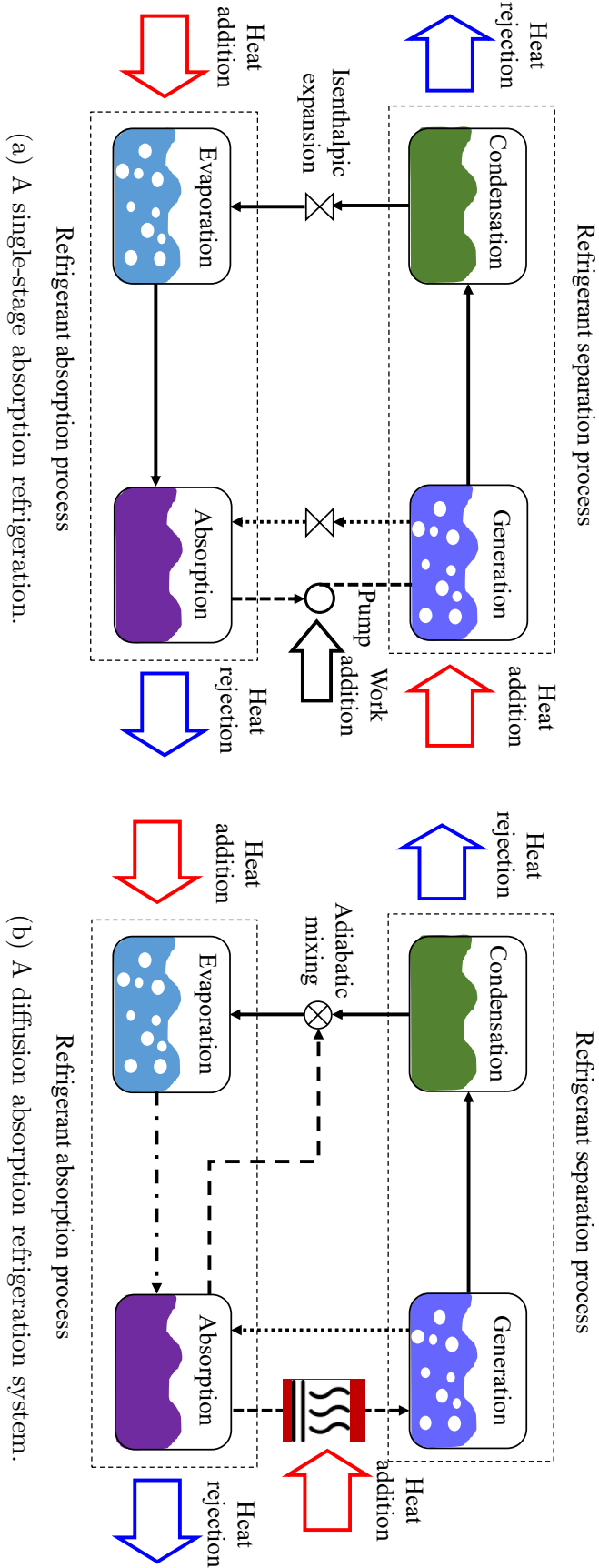


Figure 1.8: Basic operations in two absorption-based refrigeration cycles: (a) a single-stage absorption refrigeration cycle [46]; and (b) a diffusion absorption refrigeration cycle. Various streams are identified: refrigerant-rich solution (---); refrigerant-weak solution (.....); auxiliary gas (- - -); and “pure” refrigerant (—).

1.2. DIFFUSION ABSORPTION REFRIGERATION

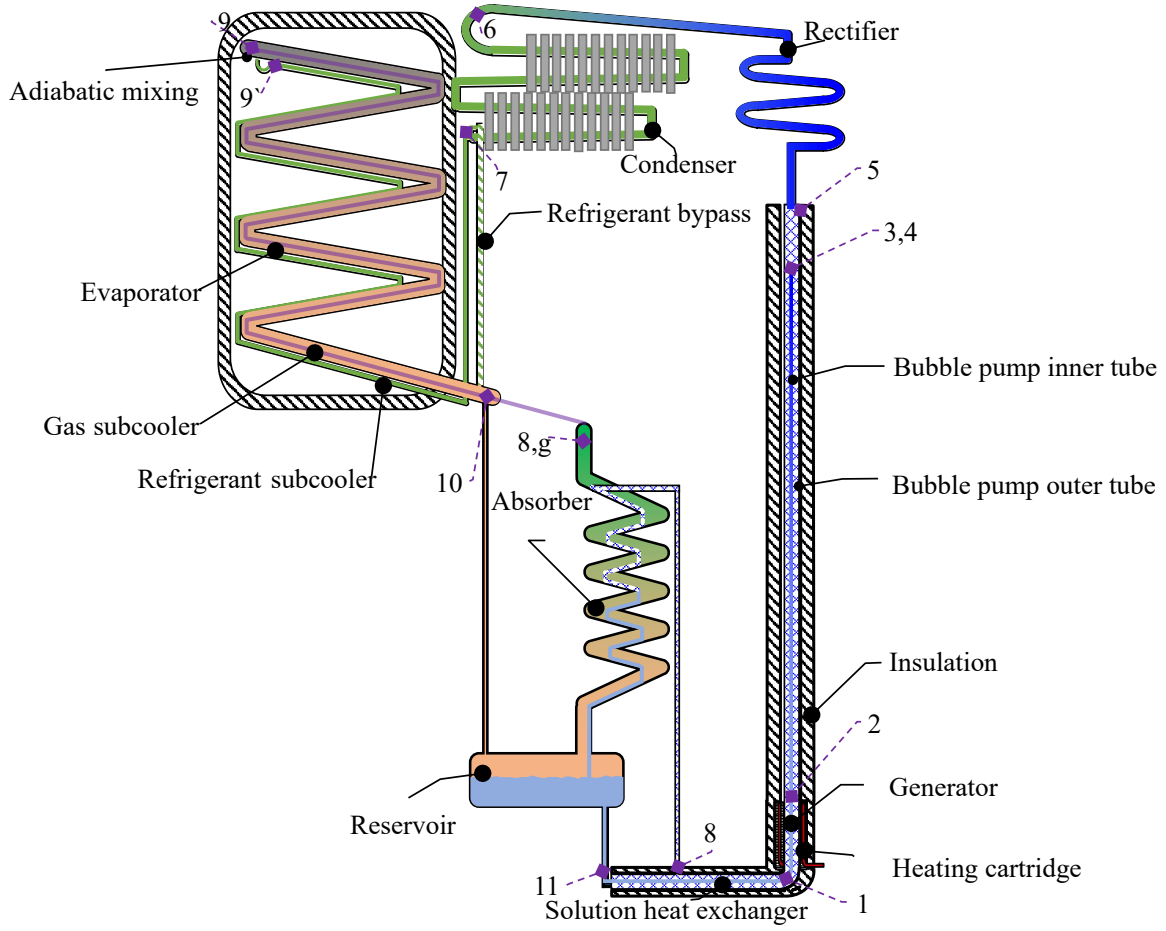


Figure 1.9: A schematic diagram for a typical DAR system.

solution is preheated by the pre-cooled weak solution before flowing into the generator again.

DAR is suitable for electricity-free operation. DAR systems do not have moving parts, leading to quiet operation, long lifetimes, minimal running (maintenance/operation) costs, and the ability to be manufactured as a single unit, resulting in low capital costs. [38, 65, 66] However, the auxiliary gas circulating in DAR imposes additional thermodynamic irreversibility. Accordingly, DAR systems have lower COP compared to other cooling technologies.² DAR systems sold in the market use $\text{NH}_3\text{-H}_2\text{O}$ with H_2 or helium as the auxiliary gas. DAR cooling system costs range between £ 300 and £ 1800 depending on system size and capabilities. [71, 72] DAR fridges are usually sold as recreational-vehicle (RV) or motor-home fridges. RV absorption units in the market are either two-way (operating on an AC electrical supply or using liquified petroleum gas (LPG)) or three-way (operating on AC, DC or LPG).

Another challenge facing DAR technology spread is the heat-source temperature requirement.

²Low COP for DAR should not be strictly compared to other electrically-driven systems should we consider the thermal quality of the heat source.

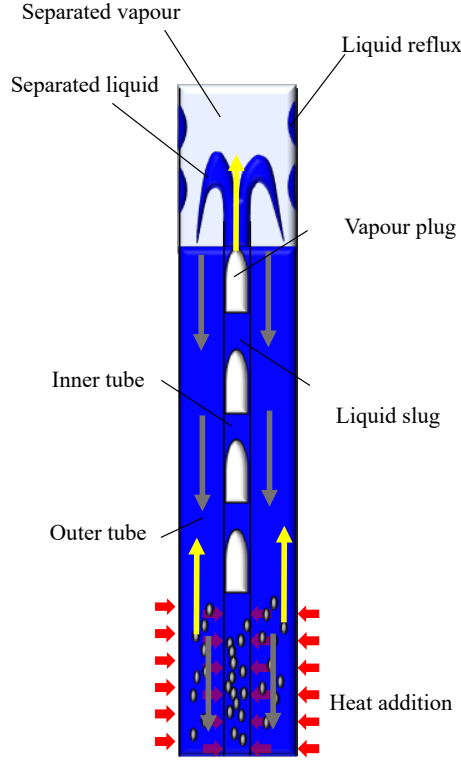


Figure 1.10: Basic bubble pump operation (adapted from Zohar *et al.* [70]).

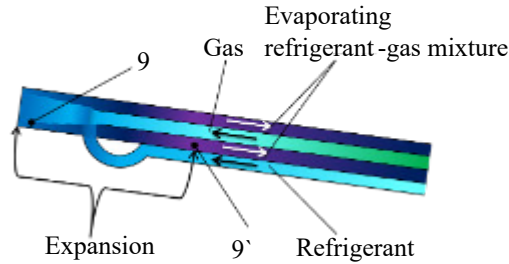


Figure 1.11: Illustration of adiabatic mixing and evaporation steps in a typical DAR system.

DAR cooling capacity is limited by the performance of the bubble pump [73], and thus DAR still has a niche market. [66] Heat-source temperatures in the range of 140°C to 200°C are required to drive DAR systems with $\text{NH}_3\text{--H}_2\text{O--H}_2$ as the working-fluid mixture, due to the system pressures and temperatures required for the operation of the bubble-pump and condenser. This latter challenge considers more working fluid mixtures to lower temperature and pressure requirements for easier and more efficient operation to match low-to-medium heat source availability. [38, 63, 64] This supports the effort (mentioned in Section. 1.1.2) paid to propose solar-powered DAR systems [42, 74–78] to adapt DAR systems to operate at lower temperatures using cheap solar collectors [46, 79]. One of the important considerations is the temperature difference for the heat flow to the generator. Narayankhedkar and Maiya [80] have suggested

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that this difference can range between 8 °C and 12 °C; they also added that an increase of 1 °C in generator temperature can lead to a 10 % reduction in refrigeration capacity.

Earlier, many investigators sought to alter the configuration of DAR systems for minimum losses and better performance [41, 81–84]. Srikhirin and Aphornratana [83] numerically and experimentally studied the performance of $\text{NH}_3\text{--H}_2\text{O--He}$ DAR system for air conditioning duties. They designed and built an experimental refrigerator, where they replaced air-cooled components (rectifier, condenser, and absorber) with water-cooled components [83, *see* Fig. 2]. Rattner and Garimella [84] developed a $\text{NH}_3\text{--NaSCN--He}$ DAR system suitable for with low-temperature heat-source operation. They used a non-volatile absorbent, NaSCN (sodium thiocyanate), which allowed them to alter the DAR system layout, taking off the rectifier and liquid solution heat exchanger. Rattner and Garimella [84] also proposed using a finned vertical-tube absorber (instead of the conventional serpentine arrangement) to increase the external heat transfer rates and the insertion of helical wires to ensure wetting on the inner walls of the tubes, giving a predicted COP of 0.26 at a cold delivery temperature of 15 °C.

A key component for DAR operation is the bubble pump which has been extensively considered in the literature. A DAR receives heat in the generator (at the bottom of the bubble pump) through heat cartridges. The heat cartridges can be electrical resistances as investigated by Najjaran *et al.* [38, 85] and Chaouchi *et al.* [86], or attached to thermal solar collectors as experimented by Schmid *et al.* [74] and studied by Pais [87] and simulated by Freeman *et al.* [42], or coupled with a waste-heat recovery system as studied by Aly *et al.* [88], and experimented by Farzadi *et al.* [89] and Kumar and Das [90]. DAR requires high-temperature heat sources; $\text{NH}_3\text{--H}_2\text{O}$ -based DAR systems need heat-source temperatures between 150 °C and 200 °C. [38, 42] Refrigerant circulation in DAR systems is entirely passive and governed by gravity and buoyancy.

Thus, DAR operation is sensitive to heat power input. Heat power input should be sufficient to activate the circulation of the refrigerant. For a bubble pump to operate efficiently, the heat input at the generator should generate a two-phase mixture at State 2 characterised by a slug-to-churn flow pattern. [66, 77, 82, 84, 91, 92] In two-phase upward slug flow, large enough vapour plugs lift the liquid slugs up the bubble pump as illustrated in Figure 1.10. The boundaries of the slug-to-churn flow operating range can be mapped as presented by Taitel *et al.* [93] for upward isothermal two-phase flows shown in Figure 1.12. Although this map was developed for steady-state upward gas-liquid flow, it can still be used as the efficient operation of the bubble

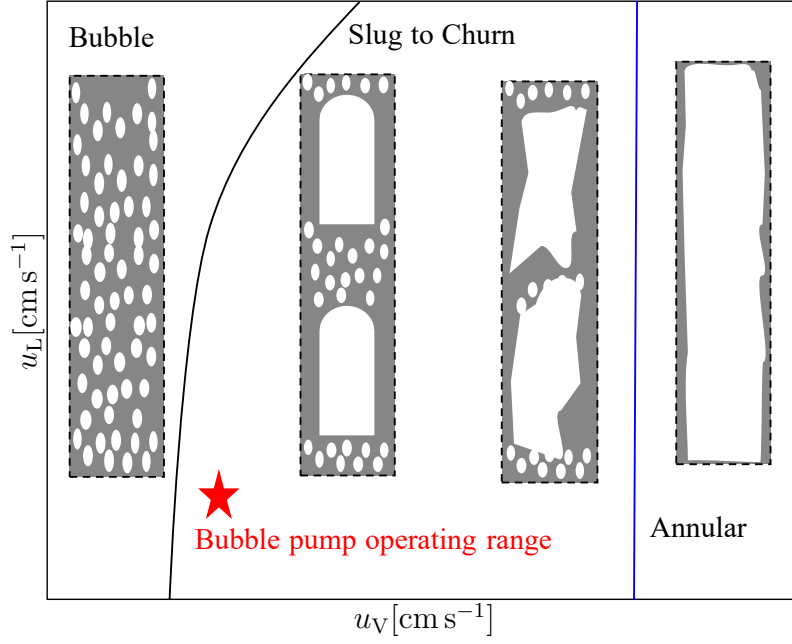


Figure 1.12: Flow pattern map for two-phase flow in bubble pump (adopted from Taitel *et al.* [93]).

pump is attributed to the presence of slug flow. [94, 95]

Bourseau and Bugarel [96, 97] assumed vapour and liquid leaving the bubble pump to be in vapour-liquid equilibrium. In contrast, Zohar *et al.* [98] assumed the liquid and vapour leaving the bubble pump are 5°C colder than the mixture at the bubble pump inlet (yet, they did not mention whether it was based on experimental observation or just an arbitrary assumption). Zohar *et al.* [98] also did not assume any vapour-liquid equilibrium and assumed the vapour mixtures to behave ideally. A Few years later, Zohar *et al.* [70] considered how modifying the generator/bubble-pump configuration shown in Figure 1.13 affected DAR performance. For the fully-attached bubble pump (shown in Figure 1.13a), heat supplied from the heating source is transferred to the down-flowing weak solution in the outer tube before heating the rich solution in the inner tube. By supplying heat directly to the rich solution through partial separation of the inner and outer tubes at the point of heat addition (shown in Figure 1.13b), Zohar *et al.* [70] demonstrated a COP improvement of up to 30 %. Though, it should be considered that heat recovery from the down-flowing solution helps prevent higher temperatures in the absorber and evaporator. Thus, full separation of the bubble pump tubes (shown in Figure 1.13c) was found to be undesirable and to lead to a deterioration in the system performance.

Rodríguez-Muñoz and Belman-Flores [66] and Benhamdiene *et al.* [99], reviewed different

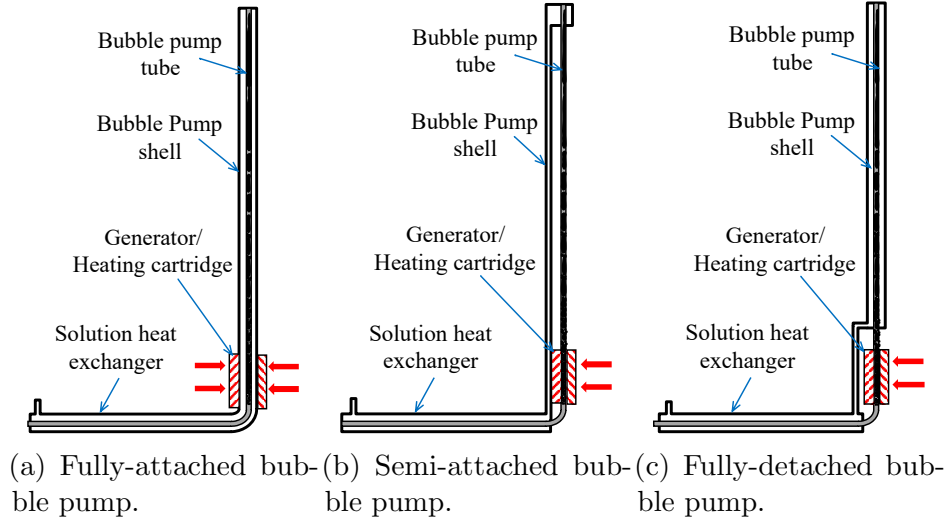


Figure 1.13: Different bubble pump configurations (adopted from Zohar *et al.* [70]).

bubble pump configurations. Several works [94, 99] suggested heating all the bubble lengths to allow the use of low-grade heat sources. Rattner and Garimella [94] argued that spot heated generator/bubble pump necessities a high-grade heat source and may not be adequate for low-grade heating sources like waste heat recovery and cheap solar collectors. [100] On another front, Shelton *et al.* [101], Jakob *et al.* [41], Vicatos and Bennett [73], and [102] noted that a single-tube bubble pump could potentially control cooling capacity as the mass flowrate of the working fluid is limited. They recommended multiple-tube-bubble pump DAR systems fitting the available heat source. Their experiments [41, 73, 102] showed a linear correlation between the number of tubes and mass flowrate without a significant reduction in COP of the system up to 3 parallel bubble-pump tubes.

Srihirin and Aphornratana [83] modelled vapour and liquid flowrates leaving a DAR bubble pump using a bubble-pump characteristic correlation given by the same authors. This bubble-pump characteristic correlation overestimated the liquid solution flowrate (125 % to 143 % of the actual values). [83] Srihirin and Aphornratana attributed this overestimation to unaccounted heat losses that might have been dissipated from the generator or the bubble pump (where their model assumed a perfectly insulated generator/bubble pump)—although their argument is realistic, yet limited by the use of a design-specific characteristic correlation.

Rattner and Garimella [103], Taieb *et al.* [104], Starace and De Pascalis [105], Sathe [82] and Jakob *et al.* [41] followed a similar approach. Chaouachi and Gabsi [86] developed a mathematical model based on material and energy balances to help them to design a single-pressure solar

DAR system for household applications. They determined liquid and vapour flowrates leaving the bubble pump through a bubble-pump model based on results by Koyfman *et al.* [91] and Shelton and Stewart [101]. Chaouachi and Gabsi [86] examined the effect of generator power up to 8 kW, producing cooling up to 900 W with COP limited below 0.15.

There is a growing body of literature providing DAR models, most of which are lumped, thermodynamic models. The model proposed by Bourseau and Bugarel [96] is one of the oldest DAR thermodynamic models. This model showed that the optimum generator outlet temperature (for maximum COP) was in the range of 90 °C to 140 °C for NH₃–H₂O–H₂ DAR systems, and in the range of 85 °C to 140 °C for NH₃–NaSCN–H₂ DAR systems.

Other authors like Freeman *et al.* [42], Jelinek *et al.* [106], Long *et al.* [107], and Ziapour and Tavakoli [108] developed steady-state thermodynamic models based on the models proposed by Starace and De Pascalis [97] or Zohar *et al.* [98,109,110]. In contrast to all the simple thermodynamic models, Taieb *et al.* [104] and Taieb *et al.* [111] presented two detailed models for the DAR system. Rattner and Garimella [84,103] used simultaneous momentum, mass and enthalpy balances to present a discretised model for each system component. [38] Ben Jemaa *et al.* [112], Mansouri *et al.* [113] developed a simple black box dynamic model for a dynamic DAR system based on first-order response function with lag time. Whereas, Adjibade *et al.* [114] presented a parametrised dynamic model for a simple DAR system based on a system of algebraic differential equations.

Zohar *et al.* [98], Bourseau and Bugarel [96], and Starace and De Pascalis [97] assumed saturated liquid leaving the condenser, where the system pressure has been a function of the condenser's temperature. This assumption may underestimate the condensation temperature, as the presence of traces of water would increase the saturation temperatures beyond that of pure refrigerant. [97] Furthermore, operating pressure is a crucial consideration for DAR design and operation because reducing the system pressure to lower the heat source temperature results in a poorer condenser performance under high ambient temperature conditions (with uncondensed refrigerant vapour bypassing the evaporator). [38].

The steady-state DAR model proposed by Starace and De Pascalis [97] is one of the most common models used in literature for its simplicity. In their 2012 model, Starace and De Pascalis assumed saturated liquid and vapour leaving the bubble pump. In a later article [105], they used the model by Shelton and Stewart [101] to estimate the liquid and vapour flow leaving the bubble pump. In both models [97,105], Starace and De Pascalis proposed a simple equation to

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account for the heat losses in the bubble pump. They also calculated the amount of auxiliary gas in the evaporator according to Dalton's gas law.

Unlike Zohar *et al.* [98] who accounted for refrigerant partial pressure variation across the evaporator, Starace and De Pascalis [97] did not account for the development of the partial refrigerant pressure in the evaporator in their models. A few thermodynamic models accounted for the system pressure during operation. Freeman *et al.* [42] introduced a parameterised equation that accounts for the system pressure as a function of the charge pressure and the generator temperature.

There are various approaches to numerically solving process flowsheets, such as those encountered in simulating DAR systems. For instance, Mansouri *et al.* [115] simulated a steady-state operating DAR system using Aspen Plus[®] [116], while Sayadi *et al.* [44] and Elsayed *et al.* [117] used Aspen HYSYS[®] [118] to simulate a steady-state operating DAR system. Mansouri *et al.* [115] and Sayadi *et al.* [44] solved their simulation cases using a sequential modular approach whereas Elsayed *et al.* [117] used equation-oriented approach introduced in recent versions of Aspen HYSYS[®] [118]. Chaves *et al.* [119] and Pérez-García *et al.* [120] presented a DAR process model that incorporates heat transfer resistance between air and various heat-dissipating components like rectifier, condenser and absorber, validating their model against a small mini-bar unit of heat input of 70 W. Authors like Zohar *et al.* [70, 98, 109, 110] and Starace and De Pascalis [97, 105] used routines on Engineering Equations Solver (EES) [121], MATLAB [122], or FORTRAN [123] to solve the thermodynamic model using an equation-oriented approach. Yet the sequential modular approach is robust and efficient and needs special consideration when simulating any DAR system's components. Apart from Aspen HYSYS[®] [118], most sequential modelling flowsheeting software packages can hardly do backward calculations. [124, 125].

Apart from work published by Harraz *et al.* [63, 64], no DAR model has been presented that can be easily deployed to assess DAR running using different classes of working fluids. These authors presented a DAR process modelling framework based on the first law of thermodynamics that incorporates a transferable EoS (SAFT- γ Mie) discussed in Section 1.4). Their modelling framework is built in gPROMS [126] and solved using equation-oriented approaches. Mejbri *et al.* [127] also presented an NH₃-H₂O-based DAR model build in Aspen Plus[®] [116] that uses PC-SAFT EoS. Unlike other authors, who use empirical EoS (mainly Pátek and Klomfar [128] to model NH₃-H₂O mixture), Harraz *et al.* [63, 64] and Mejbri *et al.* [127], presented a DAR modelling

framework that can be easily modified to assess any working-fluid system.

As earlier discussed, diffusion absorption refrigeration is a promising thermally-powered refrigeration technology. However, running solar-powered DAR systems can be challenging due to high generator-temperature requirements. [75, 129, 130] Thus, one way to address this challenge is to seek alternative working fluids to $\text{NH}_3\text{--H}_2\text{O}$ mixture to allow bubble pump activation at lower temperatures provided by simple cheap solar collectors (*i.e.*, ETC-HP). To that end, in the following Section, different working fluids previously investigated in literature are considered, comparing how generator-temperature requirements can be altered by changing the working-fluid mixture and how these working fluids compare to the commercially common $\text{NH}_3\text{--H}_2\text{O}$ mixture.

Diffusion absorption refrigeration (DAR) is a thermal absorption refrigeration variant thoroughly discussed in Section 1.2. Some studies considered adapting DAR systems for optimal performance in solar applications. DAR can provide off-grid cooling with zero electrical input at a relatively low cost, provided it is coupled with low-cost solar collectors. The types of solar collectors most suitable are non-tracking collectors that use natural (or thermally-driven) fluid circulation to deliver heat to the generator. [38, 42]. Dammak *et al.* [131] Jakob [41] and Schmid *et al.* [74] studied how solar collector and bubble pump can be integrated into a single component to heat the working fluid with solar radiation directly.

Jakob *et al.* [41] developed a large-scale DAR machine for air-conditioning purposes that runs using ammonia–water–helium ($\text{NH}_3\text{--H}_2\text{O--He}$) as a working fluid. Jakob’s DAR has a cooling capacity of up to 3 kW. Jakob *et al.* [41] proposed the use of a multi-tube bubble pump. These authors reported that their DAR could be activated at temperatures as low as 110–125 °C reaching a coefficient of performance (COP, ratio of cooling output to thermal input) of up to 0.38. No further details about the design or rating of the used solar collector have been mentioned.

Schmid *et al.* [74] also developed a solar-driven DAR machine that runs using $\text{NH}_3\text{--H}_2\text{O}$. They proposed using a flat-plate solar collector with the DAR working fluid ($\text{NH}_3\text{--H}_2\text{O}$) instead of the collector heat-transfer fluid. However, this design showed low solar-collector efficiency. Thus, they also tried using a plate heat exchanger to transfer heat from commercial solar collectors to the generator working fluid. Schmid’s DAR system can produce a cooling capacity of up to 228 W with 11.4 % solar irradiance converted to cooling power. They achieved even better performance using the plate heat exchanger and commercial solar collectors.

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Acuña *et al.* [43, 132] also investigated the use of other solar collectors to power diffusion-absorption refrigeration and match generator temperature. They considered compound parabolic concentrators and evacuated tube collectors, comparing them to flat-plate solar collectors. Freeman [42] tested evacuated-tube heat pipe collectors (ETC-HP) in a solar-DAR system targeting off-grid cold-chain applications in rural developing economies. This study was extended to some regions in India, including the north-western area of Ahmedabad, during the October harvest season, when there is a high demand for cooling to store crops within its supply chain. [38]

It can be concluded that diffusion absorption refrigeration (DAR), thermally-driven absorption refrigeration, is an attractive refrigeration technology to consider. Being thermally driven, DAR is attractive for standalone and off-grid refrigeration. However, coupling commercially available DAR units with low-to-medium-heat cheap solar collectors may be challenging. It is interesting to present a DAR system that simple solar collectors can readily power.

1.3 Working fluids for diffusion absorption refrigeration

A suitable working fluid for a solar-powered DAR should be made-up of a refrigerant-absorbent pair that can be generated at relatively low solar-collector temperatures to promote the use of simple solar collectors as discussed in Section 1.1.2; the refrigerant should be readily soluble in the absorbent at absorber operating conditions. The refrigerant saturation temperature at system pressure should be higher than the ambient temperature of the working environment to ensure complete recovery of the refrigerant. A favourable inert gas should have very low density, viscosity, thermal conductivity, and heat capacity. In addition, it must not be soluble in the working solution and should be inert towards absorbent, refrigerant and construction materials. [66, 80]

Ammonia–water with hydrogen or helium are the most common working-fluid mixtures for running DAR systems. NH_3 – H_2O mixture is favoured due to its chemical stability within a large range of operating pressures and temperatures. [65] In addition, ammonia offers a high latent evaporation heat and a low freezing point ($-77\text{ }^\circ\text{C}$) allowing for more sub-zero cooling applications.

Average generator temperatures for DAR-system operation were surveyed and are compared as shown in Figure 1.14. The required generator temperatures to activate the bubble pump for NH_3 – H_2O DAR systems reported by Bourseau and Bugarel [96] and Chaouachi and Gabsi [86] are

much lower than temperatures reported later in literature [46,97,133] and far lower temperatures observed experimentally which can exceed 140°C (*see* Figure 1.14). [42, 98, 130, 134]. As pointed earlier (*see* Figure 1.14), high generation temperatures ($> 140^{\circ}\text{C}$) are needed to activate DAR systems running $\text{NH}_3\text{--H}_2\text{O}$, fluorocarbons–dimethylacetamide (FC–DMAC) or hydrofluorocarbons–dimethylacetamide (HFC – DMAC “ $\text{CH}_3\text{C}=\text{ON}[\text{CH}_3]_2$ ”). It can also be observed in Figure 1.14 that using hydrocarbon pairs like butane-nonane ($n\text{-C}_4\text{H}_{10}\text{--}n\text{-C}_9\text{H}_{20}$) or using inorganic absorbents like LiNO_3 or NaSCN can bring down generator temperatures without trading off the coefficient of performance. The choice of auxiliary gas does not significantly affect generator temperature. However, the auxiliary-gas choice affects COP. Narayankhedkar and Maiya [80] found that although the evaporator head required when using helium is higher than that required when using hydrogen, the refrigeration effect of a DAR system charged with hydrogen is slightly higher than that of a similar DAR charged with helium [80].

Bringing down the required temperature for generator activation has motivated investigating more working-fluid alternatives to $\text{NH}_3\text{--H}_2\text{O}$. [43, 132]. Organic working fluids can lower generation temperature requirements for DAR units, as seen in Figure 1.14. [38, 63] Many authors [44, 77, 92, 107, 110, 135, 137–145] discussed the potential use organic working fluids for DAR systems. Lee *et al.* [145] and Kim *et al.* [92] replaced $\text{NH}_3\text{--H}_2\text{O}$ in a small-size DAR unit with a mixture of $i\text{-C}_4\text{H}_{10}\text{--}n\text{-C}_8\text{H}_{18}$ mixture over a range of generator temperature (T_2) from 114°C to 168°C , using input data taken from Refs. [92, 145]. Tiwari *et al.* [146] and Rodríguez-Muñoz and Belman-Flore [66] reviewed some different working-fluid mixtures used for operating DAR systems.

Zohar *et al.* [110] assessed a couple of organic-fluid pairs (shown in Figure 1.15) with helium as an auxiliary gas for running DAR systems, and their simulations limited the condensation temperatures below 40°C which might not be the best option in high-temperature environments. On the other hand, Long *et al.* [107] investigated the 2,2,2-trifluoroethanol–tetraethylene glycol dimethyl ether ($\text{C}_2\text{H}_2\text{F}_3\text{OH--C}_{10}\text{H}_{22}\text{O}_5$) pair for its favourable thermophysical properties. Long *et al.* demonstrated that an air-cooled DAR system running with this working fluid could yield a high COP that can reach 0.35 at a higher condensation temperature than those considered by Zohar *et al.* [110] as can be noticed in Figure 1.15. However, the system proposed by Long *et al.* [107] required an elevated charge pressure (≥ 39 bar).

Stegou-Sagia [138] considered a numerical assessment of organic-aqueous pair ($\text{CH}_3\text{NH}_2\text{--H}_2\text{O}$)

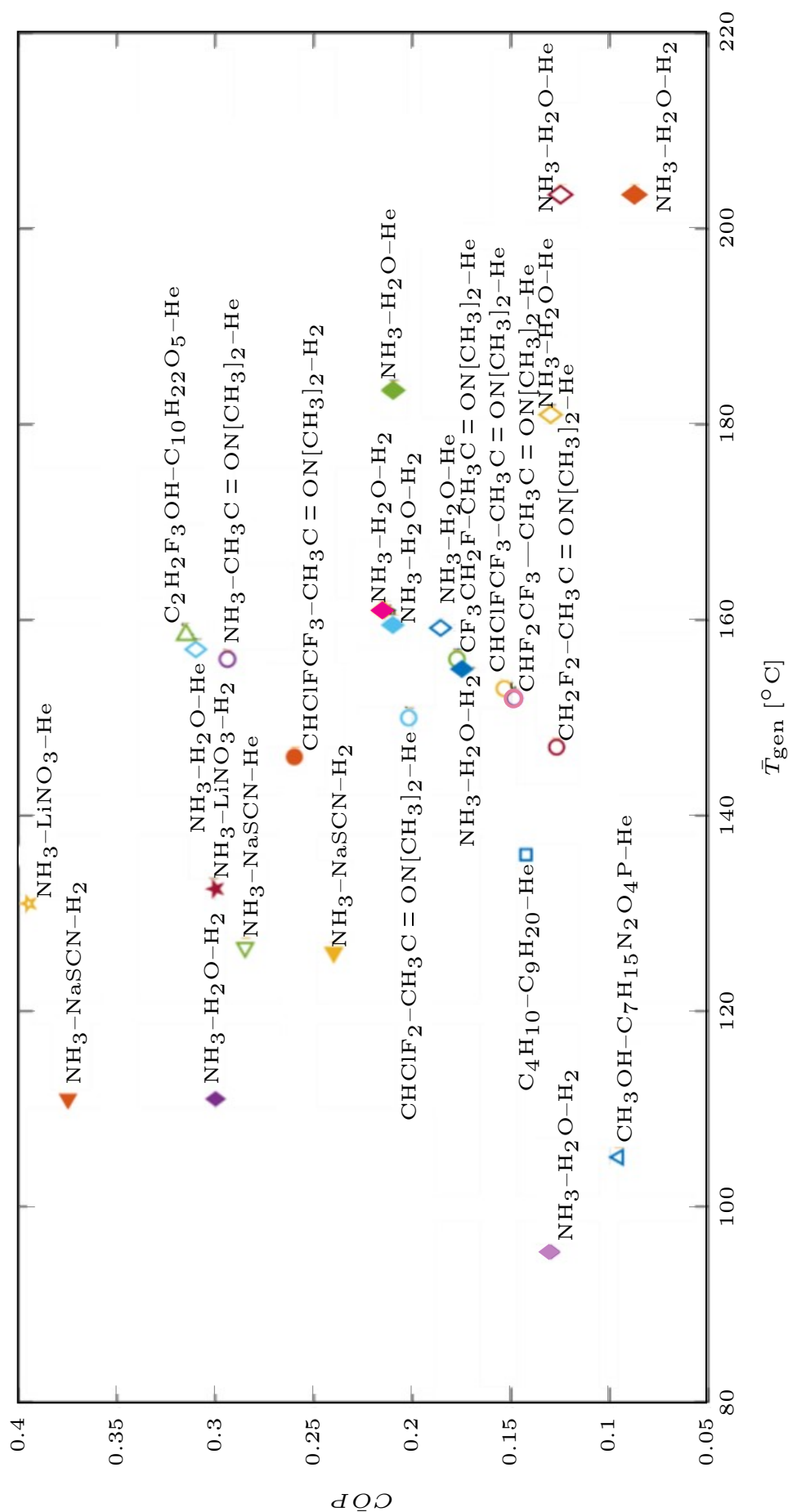


Figure 1.14: A map for average COP against average generator temperature, $\bar{T}_{\text{gen}}$ as reported in literature for some investigated DAR working-fluid systems: (●) Ben Ezzine *et al.* [77]; (◆) Chen *et al.* [81]; (◇) Sriksirin and Aphornratana [83]; (◆) Chaouachi and Gabai [86]; (▲) Bourseau and Bugarel [96]; (◆) Starace and De Pascalis [97]; (◇) Zohar *et al.* [98]; (○, ●, ○, ●) Zohar *et al.* [110]; (★, ▼, ◆, ★, ◆) Acuña *et al.* [133]; (△) Long *et al.* [107]; (◆) Freeman *et al.* [42] and Najjarian *et al.* [130, 134]; (□) Ben Ezzine *et al.* [135]; (◇) Yıldız and Ersöz [136]; and (△) Zhang *et al.* [137].

for H_2 as the auxiliary gas for absorption refrigeration purposes. Others attempted some experiments to demonstrate the validity of using organic-based working fluids to produce refrigeration using DAR systems [92, 143–145, 147]. Some of these studies showed promising performance of organic-based DAR systems in comparison with NH_3 – H_2O -based systems (*i.e.*, Ben Ezzine *et al.* [77]), though Zohar *et al.* [110] demonstrated lower performance of DAR systems operating using organic-based working fluids in favour of NH_3 – H_2O DAR systems. Unlike Jakob *et al.* [41] and Schmid *et al.* [74] who used NH_3 – H_2O in their experiments, Acuña *et al.* [43, 132] considered different working fluids, namely ammonia–lithium nitrate–helium (NH_3 – $LiNO_3$ – He) and ammonia–sodium thiocyanate–helium (NH_3 – $NaSCN$ – He), motivated by their lower activation temperatures compared to those of NH_3 – H_2O systems.

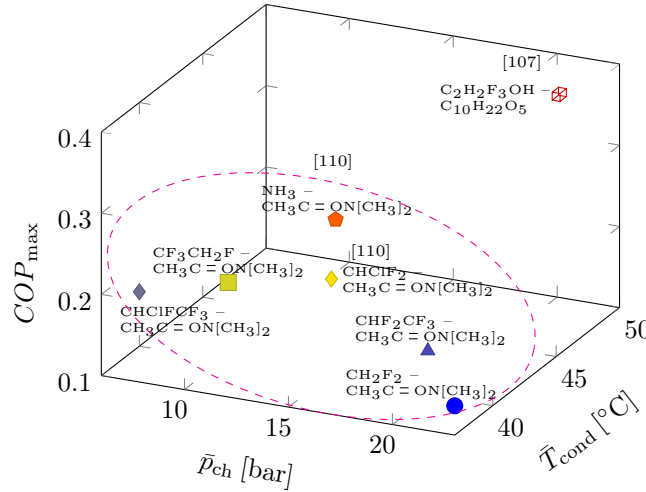


Figure 1.15: Maximum COP for some organic working fluids. Temperatures labelled are projected condensation temperatures at corresponding charge pressure. [63]

In Figure 1.16, maximum reported COP for some working-fluids are listed [77, 96, 107, 110, 133, 135, 137]. As mentioned earlier, ammonia is widely accepted as a refrigerant in DAR working-fluid systems, partly due to the high heat of vaporisation of ammonia. However, the thermodynamics of mixture composition also plays a role. Ammonia and methanol have approximately the same heat of vaporisation. Still, all the working pairs that use methanol as a refrigerant show a lower COP than those that use ammonia. Our analysis has also been shown later to demonstrate that using methanol as a refrigerant is infeasible, as shall be discussed in Chapter 4. COP for most commercial DAR systems is usually limited to lower than 0.3.

It is also crucial to consider safe and environment-friendly working fluids. Several environmental metrics should be considered while selecting refrigerant and absorbent. Gebreslassie *et al.* [148]

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presented a systematic method based on mathematical programming that allows the design of an environmentally conscious large-scale absorption cooling system driven by electricity and steam. Schilling *et al.* [149] considered some safety and environmental properties to constraint refrigerant selection for an ORC system.

Common environmental properties include global warming potential (GWP) and ozone depletion potential (ODP). GWP is the heat absorbed by any greenhouse gas relative to the heat absorbed by the same mass of carbon dioxide (CO_2). ODP of a given substance is the degradation of ozone caused by this substance relative to the ozone depletion values caused by trichlorofluoromethane (CFCl_3). [150] Other safety-related properties which Shilling *et al.* [149] recommended to consider while selecting refrigerants are: Flammability (considering flammability number, Γ); auto-ignition

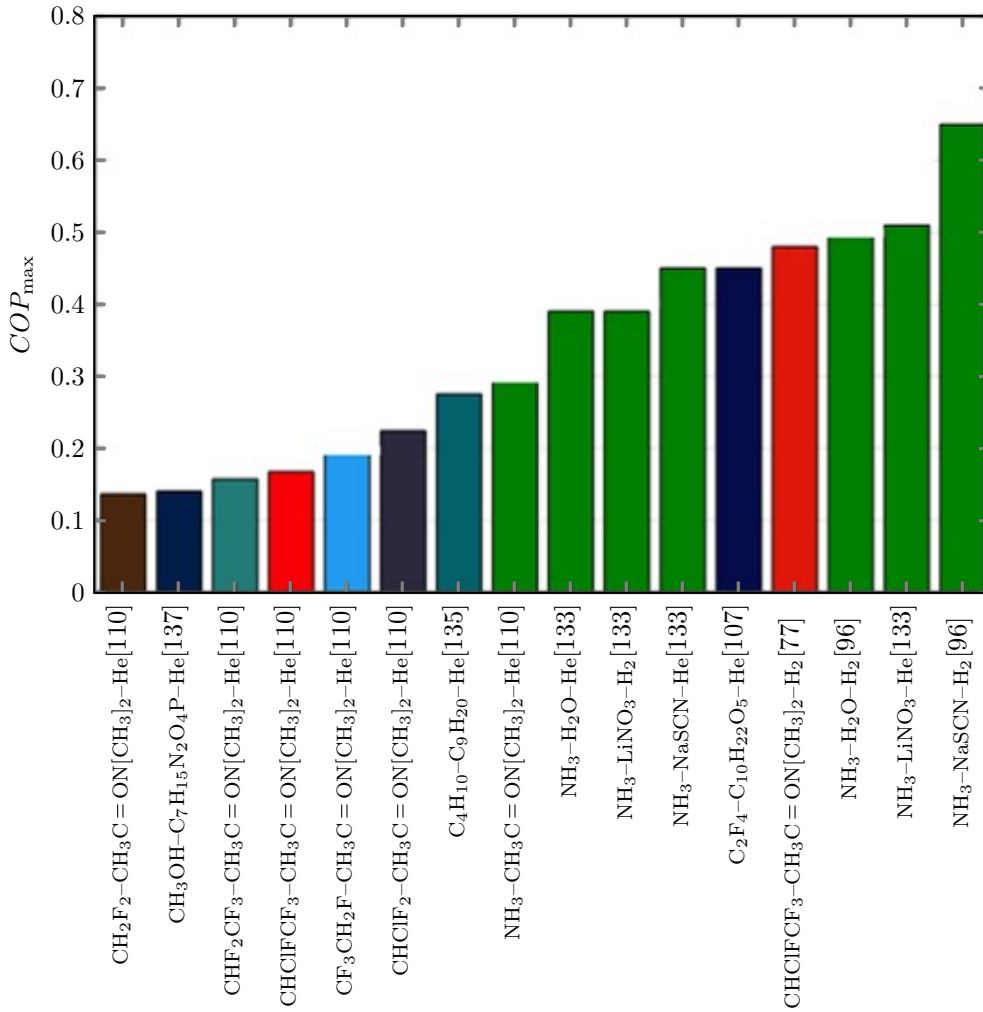


Figure 1.16: Maximum cooling COP reported in the literature for commonly-evaluated working pairs for DAR systems. [77, 96, 107, 110, 133, 135, 137] Bars are coloured according to refrigerant identity.

temperature (T_{AIT}); and toxicity (represented by the fathead minnow lethal concentration, LC_{50}). It is important to ensure that refrigerant-absorbent pairs are not hazardous and will not burn or explode at risk of leakage.

The flammability number is an index for representing the flammability characteristics of gases and vapours, considering the lower and upper flammability limits of a given gas or vapour. As lower and upper flammability limits become closer, the substance is less hazardous and smaller is the flammability number. [151]

Auto ignition temperature (T_{AIT}) defined by ASTM standard test method E659-78 as the lowest temperature at which a substance will produce hot-flame ignition in the air at atmospheric pressure without the aid of an external energy source such as spark or flame. [152] It is important to ensure that if a leak takes place from the generator (hottest spot in any operating DAR unit), the highest temperature at the generator is safely lower than T_{AIT} . For safe operation, Schilling *et al.* [149] recommended that highest temperature in the system is 30 K lower than T_{AIT} .

Also, at risk of leakage, it is important to ensure leakage is not toxic. For this purpose, the fathead minnow lethal concentration (LC_{50}) can be used to limit the choice of working-fluid pair components to be in-toxic. The fathead minnow lethal concentration (LC_{50}) is the concentration in water which kills half of the fathead minnow (*Pimephales promelas*) in 4 days (96 h). [150]. Schilling [149] recommended to constraint LC_{50} to be greater than 10 mg L^{-1} [153]. Values for the parameters mentioned above for common refrigerants and absorbents, assessed for operating DAR, are listed in Table 1.1. Thus, some studies considered optimising the performance of absorption refrigeration systems considering their environmental properties. Gebreslassie *et al.* [148, 154–156], and Chávez-Islas and Heard [157, 158] optimised the performance of absorption refrigeration systems.

The design of alternative working fluids for DAR operation in the literature has been majorly heuristic. Thus, a systematic approach to select working fluids is required to optimise DAR operation under variable operating conditions (*i.e.*, variant ambient conditions and variable heat available). [38, 63, 64] In addition, it is important to consider the thermo-economic performance to expand the DAR market. [38, 160, 161] Yıldız [162] presented a thermo-economic analysis for a DAR unit using exergic costing method [163]. He compared the exergic cost of the DAR system when driven by LPG to that driven by electricity. Based on the energy prices he adopted in his study (where LPG unit cost was twice as electricity price in T urkiye by the time of

Table 1.1: Some environmental properties of common refrigerants relevant to DAR in literature. [159]

Compound	Molecular formula	Common name	GWP	ODP	T_{AIR} °C	Γ	LC_{50} mg L ⁻¹
Ammonia	NH ₃	Ammonia	0	0	651	0.25	2,000
Methylamine	CH ₃ NH ₂	R630	0	0	430	0.51	1,850
Water	H ₂ O	Water	0	0	∞	0	∞
Propene	C ₃ H ₆	R1270	1.8	0	455	0.51	>570,000/15min
Methanol	CH ₃ OH	MeOH	2.8	0	440	0.45	81
Propane	C ₃ H ₈	R290	3.3	0	450	0.53	> 800,000/15min
Butane	C ₄ H ₁₀	R600	4	0	287	0.53	658
2,2,2-trifluoroethanol	C ₂ H ₂ F ₃ OH	TFE	18.3	0	450	n/a	470/6h
1-Chloro-1,2,2,2-tetrafluoroethane	C ₂ HClF ₄	R124	620	0.02	n/a	0	> 360,000/6H
Difluoromethane	CH ₂ F ₂	R32	650	0	530	0.372	1810
1,1,1,2-Tetrafluoroethane	C ₂ H ₂ F ₄	R134a	1430	0	n/a	0	500,000/4H
Chlorodifluoromethane	CHClF ₂	R22	1810	0.05	632	0	> 350,000
Pentafluoroethane	C ₂ HF ₅	R125	3400	0	n/a	0	2,910/4h

the study), he concluded that the LPG-driven DAR system was 64 % more expensive than the electrically-driven DAR system. This difference may be overweight in favour of the LPG-driven DAR system, where electricity is more expensive than LPG.

1.4 Working-fluid and DAR design using computer-aided molecular and system design

Following the discussion above in Section 1.3, the general approach has been to investigate different working-fluid systems for operating DAR systems heuristically, provided the availability of thermo-physical properties for candidate working fluids. Alternatively, computer-aided computer and system design can be deployed to design new working fluid mixtures. CAMD refers to the reverse problem of property prediction. CAMD involves the design of new molecules from their fragments under some process limitations and molecular feasibility constraints. Integrating computer and system design is also possible, where more information about the system and molecular structure are well captured by incorporating the system model.

For property predictions, some quantitative structure-property relationship (QSPR) should be used. QSPR establishes the connectivity rules and relates them to the thermo-physical properties of the molecule in terms of its fragments. Among different classes of QSPR, there are three standard classes; the group-contribution (GC) methods, the topological indices, and the signature descriptors. As of particular interest, the GC is only considered in our discussion, and more details about other QSPRs can be found in Austin *et al.* [164] and Ng *et al.* [165].

In GC methods, molecules are modelled as a set of fragments several molecular groups are defined (*i.e.*, $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $>\text{C}<$, $=\text{CH}_2$, $=\text{CH}-$, $-\text{NH}_2$...*etc.*) and each fragment contributes proportionally according to some indicator. This approach has been extended to consider mixtures in addition to pure components. GC methods are straightforward, making them user-friendly because of their shortcomings, like their inability to distinguish isomers and the lack of consistency between different approaches in fragment definitions. Gani *et al.* [166] developed GC+ methods that can consider second-order contributions due to isomer formation. It is also possible to consider matching different databases. [167]

The tractability of GC methods encourages using this QSPR within an acceptable margin of

accuracy. To ensure that the formed molecules are chemically feasible, additional molecular feasibility constraints are needed, such as those proposed by Odele and Macchietto [168], and Churi and Achenie [169]. A GC equation of state (EoS) is needed to predict the thermodynamic properties of pure components and mixtures and evaluate phase equilibria as required. Either a screening methodology, [170–172] or an optimisation method [149, 160, 161, 169, 173–179] is needed in order to design the pure-component molecule or mixture of interest.

Early implementations of GC-EoS include the use of Joback and Reid group-contribution method [180] and the UNIFAC model [181–183], and its variants. These methods are empirical; hence, they perform well only within the training range and target liquid-phase (rather than vapour-phase) properties. [184]. Alternatively, molecular-based equations of state based on statistical associating fluid theory (SAFT) [185, 186].

Statistical associating fluid theory (SAFT) is a molecular-based theory with a firm foundation in statistical mechanics. The incorporation of the thermodynamic perturbation theory (TPT1) of Wertheim [187–190] allows the accounting not only of molecular shape but, crucially, in this study, of intermolecular association (such as hydrogen bonding) that is often a feature of polar molecules that would be attractive for DAR. Moreover, its molecular basis makes SAFT predictive; it can be used for reliable predictions of a wider variety of thermodynamic properties across broader ranges of temperatures and pressures than, for example, traditional cubic EoS; more GC EoS based on SAFT are available in literature. [191–197].

Solvent design used to be one of the early applications of CAMD. [168, 198–200] CAMD was initially applied to identify molecules with specific solvent properties [201]. Hence after, CAMD has been implemented to address solvent and separation problems. [202, 203] CAMD has been deployed in other various problems. For instance, Schilling *et al.* [149, 177] proposed two-stage, and one-stage continuous-molecular targeting (CoMT) approaches for designing working fluids for ORC systems. van Kleef *et al.* [178], Oyewunmi *et al.* [161], White *et al.* [160, 204] considered integrated computer-aided molecular and system design using GC methods to design environment friendly refrigerant for ORC systems.

Computer-aided molecular design (CAMD) has also been applied for refrigerant selection. Churi and Achenie [169, 173, 205]. Duvedi and Achenie [206] introduced mixed-integer nonlinear programming (MINLP) model for single-component refrigerant design. They employed the outer approximation–equality relaxation–augmented penalty (OAERAP) [207, 208]. Churi and Ache-

nie [169, 173, 205], and Duvedi and Achenie [206] are among the authors who early used group contribution methods for molecular refrigerant design. Kernen *et al.* [170], Lararkeche *et al.* [209], and Khetib *et al.* [171, 172] carried out screening for various HFC absorbents using GC for water-based absorption refrigeration cycles, which are summarised in Table 1.2. In their work, the authors relied mainly on the UNIFAC model to predict the thermodynamic properties of considered working-fluid systems. Louaer *et al.* [175] performed thermodynamic analysis for four working-fluid pairs using the UNIFAC model and examined the effect of working fluid pairs on a newly configured COP.

Nevertheless, limited literature is found on deploying systematic computer-aided molecular and system design to design alternative working-fluid mixtures for absorption refrigeration systems. Tora [176] and considered developing refrigerant-absorbent pair for absorption refrigeration systems using a modular computer-aided molecular and system design approach. The first step in Tora's approach is identifying the refrigerant using pure-component target properties. Later, absorbents are identified according to their solubility with the pre-identified refrigerant. The last step entitles assessing the promoted refrigerant-absorbent. Absorption refrigeration simulations are carried out to identify COP for each pair. This approach is systematic, though it is not holistic; it does not enclose the process model while forming the working fluid. Thus, her approach does not allow predicting mixture properties at actual process conditions. [179] Separating the selection of refrigerant and absorbent also overlooks molecular interactions between the pair, particularly at actual process conditions, potentially excluding some working-fluid pairs leading to sub-optimal solutions. [160]

Recently, Papadopoulos *et al.* [179] proposed a two-stage integrated computer-aided molecular and system design approach for refrigerant-absorbent pair design that is intended to run absorption-refrigeration systems. They included a conceptual absorption-refrigeration process model within the first stage of their CAMD framework to overcome the limitations of Tora's [176] approach. Their CAMD approach can simultaneously design refrigerant and absorbent, relying on absorption-refrigeration performance rather than just target physical properties. In the second stage of the proposed CAMD approach, Papadopoulos *et al.* [179] use a more detailed absorption-refrigeration process model to optimise the absorption-refrigeration system design for each of the working-fluid pairs generated from the first step. They included safety and environment criteria to post-assess working-fluid pairs resulting from second-stage optimisations.

With a few exceptions, previous models in the literature are limited to models which considered pre-selected working fluids for thermodynamic and thermo-economic assessment of DAR systems. Thus, reliably integrated models are needed to assess DAR units operated by different heat sources using variant working fluid systems. There have been few contributions towards presenting a validated DAR model that can be used to explore various working fluids for DAR operation. In addition, apart from work presented by Harraz *et al.* [63,64] modelling working fluids for a DAR system using a group-contribution (GC) equation of state (EoS) such as SAFT- γ Mie has not been considered before.

1.5 MINLP optimisation for computer-aided molecular and system design problems

As mentioned earlier, it is common to use the UNIFAC model [181–183] and its variants to model liquid phases in molecular design problems. These methods are empirical; hence, they perform well only within the training range. Moreover, the UNIFAC model variants target liquid-phase (rather than vapour-phase) properties. [184] Alternatively, molecular-based equations of state based on statistical associating fluid theory (SAFT) [185,186] outstand UNIFAC model variants. SAFT-based equations of states can consistently model liquid and vapour phases accurately over wide ranges of temperatures and pressures. [212] For the integrated computer-aided molecular and system design for CO₂ capture via gas absorption, Burger *et al.* [202] used SAFT- γ Mie, while Stavrou *et al.* [213] used PC-SAFT. Another common computer-aided molecular and system design problem is the integrated CAMD-ORC framework for organic Rankine cycle (ORC) systems. For this latter computer-aided molecular and system design problem, Lampe *et al.* [214,215], and Schilling *et al.* [149,177,216] used PC-SAFT for the integrated computer-aided molecular and system design for ORC systems, while White *et al.* [160,204], van Kleef *et al.* [178], Oyewunmi [161], Bowskill *et al.* [217] and Papadopoulos *et al.* [218] considered using SAFT- γ Mie. SAFT- γ Mie has not been applied to such a thermal-powered domestic refrigeration system framework.

Thermodynamic and thermophysical models (*e.g.*, PC-SAFT, SAFT- γ Mie, UNIFAC) that relate the molecular structure to the properties become challenging for computer-aided molecular and system design problems as they are non-convex, which makes it challenging for the local

Table 1.2: Summary of some literature on computer-aided molecular and system design for absorption refrigeration systems using UNIFAC [183].

Refrigeration technology	CAMD approach	Refrigerant	Absorbent	GC EoS	Ref.
Absorption refrigeration	Three-staged integrated CAMD:				
	• Refrigerant-absorbent mixture screening incorporating a conceptual absorption refrigeration model; • optimise absorption refrigeration design for each mixture generated from Stage 1; and • Environmental and safety assessment for working pairs selected from Stage 2.	Variable	Variable	Soave-Redlich-Kwong (SRK), Redlich-Kwong (RK) EoS with UNIFAC	[179]
Absorption refrigeration	Generate and test	Variable	N ₂ N ₂ Dimethyl-formamide	UNIFAC	[172]
Ejector-compression absorption refrigeration using phase separation	Generate and test	H ₂ O	Variable HFC	UNIFAC	[171]
Absorption refrigeration system	Three stages:				
	• sequential CAMD using Pro-CAMD [210]; • Dühring curve; and • simulation using Aspen HYSYS® [118].	Variable	Variable	UNIFAC	[176]

Continued on next page

Table 1.2: (*Continued*)

Refrigeration technology	CAMD approach	Refrigerant	Absorbent	GC EoS	Ref.
Hybrid compression-absorption re- frigeration cycle	Generate and test	variant	Ionic liquid	UNIFAC	[211]
Absorption refrigeration with partial miscible working fluid	Generate and test	H ₂ O	Variable HFC	UNIFAC	[209]
Absorption refrigeration	Generate and test	Variable HFC	Dimethylac	UNIFAC	[175]
Phase-separation absorption refriger- ation	generate and test	Water	Variable	UNIFAC	[170]

solvers to reach a global optimum or even a good solution. computer-aided molecular and system design problems are more challenging than their counterpart process design problems with predefined working fluids, thanks to their combinatorial nature being solved as MINLP optimisation problems. [219] In addition, most, if not all, computer-aided molecular and system design problems for thermodynamic systems and systems with chemical processes are nonlinear non-convex being mixed-integer nonlinear problems, making it more tricky to reach global optima. [202, 217, 219, 220] Usually, in the absence of a good initial guess, identifying a feasible process point for a given set of design variables can be challenging. Thus, it is crucial to adopt a robust and reliable computer-aided molecular and system design framework for the integrated design of working fluids and processes. [217]

Several authors addressed the challenges of solving MINLP CAMD problems for chemical processes. Gopinath *et al.* [220] listed some examples of these challenges, such as in solvent design for absorption processes: if a solvent, defined using discrete variables, is vapour at its inlet conditions, this shall return an infeasible process; also, considering the vapour-liquid equilibrium coexistence, which is encountered quite frequent in a DAR process, is numerically challenging, considering the wrong phase may lead to numerical failure or a physically meaningless solution. The latter challenge is usually addressed by explicitly considering these phase-behaviour discontinuities.

Several methodologies have been found in the literature to tackle the aforementioned CAMD challenges. These methodologies range from transforming the MINLP problem into nonlinear programming (NLP) problem to decomposing the CAMD problem into a two-stage problem to reduce the combinatorial space. Different approaches are available while breaking down the CAMD problem, either a top-down or a bottom-up approach. [220]

In the top-down approach, normally, a continuous NLP problem is considered in the first step to seek some optimal process performance in the decision-variable space of molecular properties (which are continuous). In a second step, optimum working fluid is sought to match molecular properties optimised in the first step. For example, Schilling *et al.* [149, 177, 216] developed and used a continuous molecular targeting (CoMT) approach, through which they identified the optimal (hypothetical) solvent by continuous descriptors. Then they solve a CAMD problem to match these descriptors to the closest molecular structures in their database using PC-SAFT EoS.

On the other hand, in the bottom-up approach, the computer-aided molecular and system design starts from a molecular perspective and builds up to an optimal process. The main challenge

is to overcome the combinatorial complexity of the molecular design space by screening the molecules from a wide design space, often using relatively simple property models or user-defined property targets. However, a limitation to this approach is that the attempt to use predefined heuristic property targets may overlook or eliminate some optimal solutions. [179, 202, 217]

Apart from the bottom-up and top-down approaches, Gopinath *et al.* [220] noted that using multi-objective optimisation (MOO) can increase the chance of identifying a globally optimal solution. They also concluded that both top-down and bottom-up approaches might not guarantee the same solution to the fully integrated computer-aided molecular and system design problem. Thus, to overcome these limitations, Gopinath *et al.* [220] modified an outer approximation optimisation algorithm, in which each integer variable combination is subjected to tests before solving the primal problem to facilitate the solution by removing infeasible points from the search space and hence provide good initial values for the decision variables. It should be noted that Gopinath *et al.* [220] designed their tests to overestimate the feasible region to avoid eliminating potential solutions. They found this method to reduce the search space and enhance the solver convergence during primal problem solutions without eliminating possible solutions. Bowskill *et al.* [217] applied the algorithm presented by Gopinath *et al.* [220] to design working fluids for ORC.

Both Burger *et al.* [202] and Papadopoulos and Linke [221, 222] proposed two different multi-step hierarchical optimisation approaches to address the complexities of computer-aided molecular and system design problems which are mentioned above. Their proposed approaches rely on reducing or simplifying the process model in the first step, in which they carry out MOO. One of the differences between Burger’s and Papadopoulos’s approach is the technique used for the MOO. Burger *et al.* [202] used a modified sandwiching algorithm to solve the MOO problems. The sandwiching algorithm was initially developed for continuous convex problems and uses weighted sum scalarisation for the objective functions, making the sandwiching algorithms more likely to overlook non-convex regions of the problem. However, Burger *et al.* [202] have justified that sandwiching algorithms can still be sufficient for the Pareto-optimal set generated as initial guesses for the main problem. Each solution was then used as a starting point to solve the full mixed-integer nonlinear programming (MINLP) problem for the main process in the second stage. The same authors have used the hierarchical optimisation approach for solvent design in the context of CO₂ capture using

gas absorption.

Similar to Burger’s [202] hierarchical method, Papadopoulos and Linke [221] proposed a technique that uses the weighted-average method for solving MOO in the first step to simultaneously consider the interactions among all the thermo-physical and properties concerning the process of interest. To expand this approach for mixture design, Papadopoulos *et al.* [222] introduced the two-stage MOO method. The first component in the mixture is designed in the first stage, while the second component and mixture composition are optimised in the second stage. The latter approach developed by Papadopoulos *et al.* [222] has been applied to design working-fluid mixtures for ORC [222] and, more recently, the integrated process and working-fluid design for an absorption refrigeration system [179].

Liu *et al.* [223] developed a CAMD toolbox for pure and mixture design based on a three-step optimisation framework for molecular and mixture design, starting with gathering information about the end product need and translating these needs into a physicochemical target. Afterwards, an MINLP CAMD problem should be solved to design the pure-component/mixture that meets the predefined targets. Finally, the designed working fluid is validated for properties not covered in the solved CAMD problem. A limitation to this approach lies in the risk of eliminating or overlooking potential optimal solutions due to separating CAMD and process optimisation steps. [204, 220]

As mentioned earlier, MINLP computer-aided molecular and system design problems are non-convex; thus, choosing a good initial guess shapes the convergence of the problem towards a good high-quality local optimal solution. Further, reaching a globally optimal solution is not guaranteed using most deterministic gradient-based MINLP optimisation algorithms like Branch and bound methods and their variants. [202, 220] Global optima are only guaranteed to apply expensive global optima algorithms due to the curse of dimensionality. [224] Increasing the number of initial guesses and solving the optimisation problem for each initial guess increase the probability of reaching global optima. [202] Another way to limit the curse of dimensionality of computer-aided molecular and system design problems is using heuristic stochastic MINLP optimisation algorithms, like the Genetic Algorithm (GA) method and its variants. [178] Heuristic stochastic MINLP optimisation algorithms are more likely to find or approach global optima than gradient-based optimisation algorithms with randomly generated initial guesses. [225, 226] However, compared to deterministic gradient-based methods, stochastic optimisation methods are susceptible to premature termination. [225]

Zhou *et al.* [226] presented a hybrid stochastic-deterministic MINLP optimisation algorithm to solve the integrated MINLP computer-aided molecular and system design solvent and process design for CO₂ absorption. Zhou *et al.* [226] combined a GA algorithm developed by [227] with the generalised reduced-gradient (GRG) nonlinear program (CONOPT) [228]. In their algorithm, the GA is responsible for generating offspring molecules via genetic operations and the algorithm is terminated as a preset number of generations is reached.

Apart from work done by Papadopoulos [179], previous CAMD studies are limited by decoupling the working-fluid design and absorption-refrigeration cycle optimisation; almost no computer-aided molecular and system design study considers DAR systems and how working-fluid selection can matter with their thermo-economic performance and safety consideration. In addition, Integrated computer-aided computer and system design using MINLP optimisation has not been applied to diffusion absorption refrigeration before. Thus, this thesis aims to fill this gap by introducing a widely-validated process model and group-contribution methods to account for thermo-physical properties needed to model DAR systems. Little attention in the literature has been devoted to the thermo-economic assessment of DAR systems under variant operating conditions.

Previously, Harraz *et al.* [63, 212] introduced a CAMD-DAR modelling framework that can be used to identify optimal working-fluid mixtures considering thermo-economic and environmental limitations. Thermodynamic properties of working-fluids mixtures are estimated using SAFT- γ Mie EoS, while some other needed properties like surface tension and critical properties are calculated using appropriate GC methods. The CAMD-DAR model has been validated against experiments performed at Imperial College London and other data from the literature.

1.6 Thesis structure, aims and objectives

Developing and promoting refrigeration technologies that rely less on conventional energy resources is necessary as the energy bills are soaring. Securing sustainable refrigeration is essential to cut-off food waste and improve the quality of life. Taking advantage of solar energy abundance in the MENA region, it is attractive to promote a low-carbon and sustainable refrigeration technology, such as diffusion absorption refrigeration (DAR). One of the research interests within the Clean Energy Processes (CEP) Laboratory is to optimise DAR systems to run with low-temperature heat sources ($< 150^{\circ}\text{C}$) and using intermittent heat sources such as

solar energy. After reviewing the literature on DAR, various research gaps have been identified. This includes the challenges facing the spread of DAR technologies and how new working-fluid mixture designs can activate DAR systems using low-temperature heat sources such as cheap solar collectors. Computer-aided molecular design using the group-contribution SAFT- γ Mie equation of state has not been applied to design working-fluid mixtures for thermal-powered refrigeration systems, such as diffusion absorption refrigeration. To this end, the coming chapters of this thesis are intended to address these challenges.

1.6.1 Aims and objectives

It has been highlighted that organic working fluids can lower generation temperature requirements for DAR units. Thus, this thesis aims to identify and assess alternative organic working-fluid mixtures that can replace the commercially used $\text{NH}_3\text{-H}_2\text{O}$ mixture, considering the thermo-economic performance, heat-source temperature requirements, and environmental and safety limitations. To achieve this aim, the following objectives can be identified:

- to adapt mathematical models that are experimentally validated and can simulate diffusion absorption refrigeration system performance;
- to develop cost correlations for DAR units to enable the economic assessment;
- to develop an integrated CAMD-DAR optimisation framework using group-contribution methods that can simultaneously evaluate optimum DAR operation parameters and working fluid (refrigerant-absorbent-gas) based on evaluating the thermo-economic performance;
- to apply a hybrid stochastic-deterministic MINLP optimisations that have not been applied to absorption refrigeration before and validate the approach;
- to deploy the validated CAMD-DAR framework to some case studies, carrying out single objective NLP, MINLP and multi-objective MINLP optimisations for alternative optimal working-fluid design;
- last but not least, to explore dynamic DAR performance with optimum organic working fluids.

1.6.2 Thesis structure

In Chapter 2, The GC SAFT- γ Mie EoS and other group-contribution methods used to model working-fluid mixtures are described. Additionally, a model is adapted for the ammonia–water cross-interaction for use with SAFT- γ Mie. Further in Chapter 2, a validated DAR thermodynamic model is presented for some predefined working-fluids mixtures, including $\text{NH}_3\text{--H}_2\text{O}$ and some low-GWP organic working fluids are considered. Some organic working-fluid pairs, based on six pre-selected refrigerants and four absorbents of normal and branched alkanes, are explored and compared to $\text{NH}_3\text{--H}_2\text{O}$ in terms of cooling output, charging pressure and generator temperature requirements. The influence of working fluid on DAR performance and heat requirements is investigated.

In Chapter 3, a DAR-cost correlation is developed based on DAR market prices. This cost correlation is coupled with the validated DAR thermodynamic model presented in Chapter 2. An integrated computer-aided computer and system design framework for diffusion absorption refrigeration (DAR) is presented. The CAMD-DAR framework consists of DAR thermodynamic model, DAR-cost correlation, molecular feasibility constraints, process constraints, and environment-related and safety-related constraints. Furthermore, in Chapter 3, a mixed-integer nonlinear programming (MINLP) model is described. The MINLP model is used to solve the CAMD-DAR using a hybrid stochastic-deterministic optimisation algorithm. The CAMD-DAR framework is applied to some cases with a limited number of decision variables for organic-based DAR systems.

The CAMD-DAR framework is carried forward to Chapter 4 and is applied to the problem of the simultaneous design of optimal working-fluid mixtures. A series of case studies are investigated on DAR process design operating at different ambient temperatures to mimic different climates. The CAMD-DAR framework is applied to single-objective and multi-objective MINLP optimisations to consider the trade-off between maximising cooling rate and minimising expenses.

Due to the particular importance of the dynamic performance of DAR systems, particularly solar-powered DAR, a dynamic model for solar-powered DAR systems is presented in Chapter 5, which can be used to assess different working-fluid mixtures under various operating conditions. Further, A thermo-economic assessment is also considered to shed light on the suitability of DAR in the Egyptian climate.

Chapter 6 concludes all thesis outcomes and offers future research directions that can be considered in the future.

Chapter 2

DAR Thermodynamic Modelling Based on Group-Contribution Methods

Contents

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2.1 Introduction

Diffusion absorption refrigeration (DAR) is a thermally-driven refrigeration technology that operates without mechanical shaft drivers. DAR technology is suitable for small-scale off-grid cooling demand [38, 66].

Diffusion absorption refrigeration (DAR) was introduced in Chapter 1. It has been established in Section 1.2 that a DAR system uses a three-component working-fluid mixture of a refrigerant which produces cooling; an absorbent which recovers the refrigerant eliminating the need for refrigerant compression; and an auxiliary gas which pressurise the system and eliminate the need for shaft machinery.

Modelling DAR performance is important for designing and analysing DAR systems. The model proposed by Bourseau and Bugarel (1986) is one of the earliest DAR thermodynamic models presented in the literature, Thout this model underestimated the required generator temperature to activate NH_3 -based DAR systems. This model showed that the optimum generator outlet temperature (for maximum COP) was in the range of 90°C to 140°C for $\text{NH}_3\text{--H}_2\text{O--H}_2$ DAR systems, and in the range of 85°C to 140°C for $\text{NH}_3\text{--NaSCN--H}_2$ DAR systems.

Other authors developed steady-state thermodynamic models based on the models proposed by Starace and De Pascalis [97] [42, 98, 106–110]. In contrast to all these simple thermodynamic models, Taieb *et al.* [104] and Taieb *et al.* [111] presented two more-detailed DAR models. Rattner and Garimella [84, 103] used simultaneous momentum, mass and enthalpy balances to present a discretised model for each system component. [38] Ben Jemaa *et al.* [112], Mansouri *et al.* [113] developed a simple black box dynamic model for a dynamic DAR system based on first-order response function with lag time which is limited to describe small-scale $\text{NH}_3\text{--H}_2\text{O}$ DAR units. Whereas, Adjibade *et al.* [114] presented a parametrised dynamic model for a simple DAR system based on a system of algebraic differential equations, which is also limited to describe small-scale $\text{NH}_3\text{--H}_2\text{O}$ DAR units.

The steady-state DAR model proposed by Starace and De Pascalis [97] is one of the most common models used in literature for its simplicity. In their 2012 model, Starace and De Pascalis assumed saturated liquid and vapour leaving the bubble pump. In a later article [105], they used the model by Shelton and Stewart [101] to estimate the liquid and vapour flow leaving the bubble pump. In both models [97, 105], Starace and De Pascalis proposed a simple equation to

account for the heat losses in the bubble pump. They also calculated the amount of auxiliary gas in the evaporator according to Dalton’s gas law.

Apart from work published by Harraz *et al.* [63,64], no DAR model has been presented that uses group contribution approaches to assess DAR running using different classes of working fluids. These authors presented a DAR system modelling framework based on the first law of thermodynamics that incorporates a transferable EoS (SAFT- γ Mie, which has not been applied before in this context) discussed in Section 1.4). Their modelling framework is built in gPROMS [126] and solved using equation-oriented approaches. Mejbri *et al.* [127] also presented an NH₃–H₂O-based DAR model build in Aspen Plus[®] [116] that uses PC-SAFT EoS. Unlike other authors, who use empirical EoS (mainly Pátek and Klomfar [128] to model NH₃-H₂O mixture), Harraz *et al.* [63,64] and Mejbri *et al.* [127], presented a DAR modelling framework that can be easily modified to assess any working-fluid system.

In this chapter, thermodynamic models describing both refrigerant-absorbent pairs and diffusion absorption refrigeration cycle are presented. First, different thermodynamic models adopted to describe the behaviour of working fluids are discussed, including the group-contribution (GC) equation of state (EoS) founded in statistical associating fluid theory (SAFT) for fluids with Mie-potential interactions (SAFT- γ Mie). It has been found to follow the assumption of ideal gas behaviour for auxiliary gas.

Furthermore, surface tension is crucial for DAR modelling, but surface tension calculations could not be implemented in the current SAFT tool used in this thesis. Thus, appropriate GC methods for estimating surface tension are listed. Later, the thermodynamic model describing the DAR thermodynamic cycle is presented and justified. Sensitivity analysis for some pre-selected organic working fluid pairs deemed potential for DAR activation using low-temperature heat sources is conducted using the validated model.

2.2 Working-fluid thermodynamic models

In this section, the discussion of working-fluid thermodynamic models is carried forward. As mentioned earlier, DAR systems run using a three-component working fluid: the refrigerant, the absorbent and the auxiliary gas. The auxiliary gas has to be non-reactive with both the

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refrigerant and absorbent with low heat capacity and viscosity. Under typical DAR operating conditions, Assuming the ideal-gas behaviour for modelling the auxiliary gas is convenient. This thesis considers two typical gases (hydrogen and helium) for pressuring DAR systems and is listed in Table 2.1. To carry forward with the conservation of energy, ideal-gas heat

Table 2.1: Primary properties and isobaric heat-capacity parameters in Equations (2.1) and (2.2) for auxiliary gases considered in this thesis [229].

Gas	MW [g · mol ⁻¹]	T_{fp} [K]	T_b [K]	T_c [K]	p_c [kPa]	ρ_c [kg m ⁻³]
Hydrogen	2.016	13.83	20.57	32.98	129.3	31.200
Helium	4.003	2.150	4.300	5.190	22.70	72.529

Gas	T range	a_0	$a_1 \times 10^3$	$a_2 \times 10^5$	$a_3 \times 10^8$	$a_4 \times 10^{11}$
Hydrogen	50-1000	2.883	3.681	-0.772	0.692	-0.213
Helium	-	2.500	0.000	0.000	0.000	0.000

molar-specific heat capacity is used for auxiliary gases according to the equation below: [229]

$$\hat{c}_p^{\text{ig}} = R_u \cdot (a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4), \quad (2.1)$$

where R_u is the universal gas constant (8.314 462 1 J mol⁻¹ K⁻¹), and T is the absolute temperature in Kelvin; isobaric heat-capacity parameters in Equation (2.1) are presented in Table 2.1. Thus, the change in enthalpy expression becomes

$$\Delta \hat{h}^{\text{ig}} = R_u \cdot \left(a_0 T + \frac{a_1}{2} T^2 + \frac{a_2}{3} T^3 + \frac{a_3}{4} T^4 + \frac{a_4}{5} T^5 \right) \Big|_{T_0}^T. \quad (2.2)$$

In the subsequent section, the adopted GC SAFT- γ Mie EoS and other relevant GC methods are presented. In addition, different functional groups that are interesting for working-fluid design are studied.

2.2.1 SAFT- γ Mie for refrigerant-absorbent pairs

To ensure the transferability of the DAR model, GC methods are used to predict the thermodynamic and thermo-physical properties of a given compound or mixture of compounds based on the molecular groups that formulate the molecule(s). [166] In this thesis, thermodynamic properties are evaluated using a GC equation of state based on the statistical associating fluid theory (SAFT) for fluids interacting with Mie potentials [195–197, 230].

SAFT is a molecular-based theory with a firm foundation in statistical mechanics. The incorporation of the thermodynamic perturbation theory (TPT1) of Wertheim [187–190] allows the accounting not only of molecular shape but, crucially in our current study, of intermolecular association (such as hydrogen bonding) that is often a feature of polar molecules that would be attractive for DAR. Moreover, its molecular basis makes SAFT predictive; it can be used for reliable predictions of a wider variety of thermodynamic properties across broader ranges of temperatures and pressures than, for example, traditional cubic EoS. Other empirical GC approaches (like the universal functional activity coefficient (UNIFAC) model [181–183], and its variants) perform well only within the training range and. Moreover, UNIFAC models are essentially developed for liquid-phase (rather than vapour-phase) properties. [184] In the context of DAR modelling, Mejbri *et al.* [127] used an alternative version of SAFT, namely the perturbed chain PC-SAFT, to model the thermodynamic functions for $\text{NH}_3\text{-H}_2\text{O-H}_2$ mixture; however, this particular version of SAFT is not a GC EoS. [63,64]

Table 2.2: Like group parameters for use with SAFT- γ Mie in this thesis [231].

Group k	ν_k^*	S_k	σ_{kk} [Å]	λ_{kk}^r	λ_{kk}^a	(ε_{kk}/k_B) [K]	$N_{\text{ST},k}$	$n_{k,\text{H}}$	$n_{k,\text{e}}$	Ref.
H ₂ O	1	1.00000	3.0063	17.020	6.0000	266.68	2	2	2	[230]
NH ₃	1	1.60000	2.8100	24.146	6.0000	265.28	2	1	3	[232]
-CH ₃	1	0.57255	4.0772	15.050	6.0000	256.77	-	-	-	[230]
>CH ₂	1	0.22932	4.8801	19.871	6.0000	473.39	-	-	-	[230]
>CH-	1	0.07210	5.2950	8.0000	6.0000	95.621	-	-	-	[230]
=CH ₂	1	0.44890	4.3175	20.271	6.0000	300.9	-	-	-	[230]
=CH-	1	0.20037	4.7488	15.974	6.0000	952.54	-	-	-	[230]
-OH	1	0.96340	2.7990	20.702	6.0000	410.31	2	1	2	[231]
-CH ₂ OH	2	0.58538	3.4054	22.699	6.0000	407.22	2	1	2	[231]
-NH ₂	1	0.79675	3.2477	10.254	6.0000	284.78	2	2	1	[231]
>NH	1	0.36589	3.2568	19.999	6.0000	100	2	1	1	[231]

The SAFT- γ Mie theory has been described in detail elsewhere [196] and is summarised in a recent comprehensive review [231] of the current status of the SAFT- γ Mie modelling. Here, only a summary of SAFT- γ Mie is provided. In SAFT- γ Mie, a molecule is modelled as a chain of different molecular-group segments that can associate. The Helmholtz free energy, A of the fluid is broken down into various contributions according to

$$\frac{A(\nu^*, S, \sigma, \lambda, \varepsilon, \varepsilon^{\text{HB}}, K^{\text{HB}})}{Nk_B T} = \frac{A^{\text{ideal}}}{Nk_B T} + \frac{A^{\text{mono}}}{Nk_B T} + \frac{A^{\text{chain}}}{Nk_B T} + \frac{A^{\text{assoc}}}{Nk_B T}, \quad (2.3)$$

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where N refers to the number of molecules in the system, k_B is the Boltzmann constant, and T refers to the system temperature. Here, A^{ideal} is the ideal (or kinetic) contribution; A^{mono} is the monomer contribution (comprising dispersive and repulsive interactions of the fluid of monomeric segments); A^{chain} is the contribution due to chain formation (the aggregation of different segments); and A^{assoc} is the contribution due to the intermolecular association of these chains (whenever association sites are present, *e.g.*, to represent hydrogen bonding).

The interaction between two molecular groups is described using a Mie (generalised Lennard-Jones) potential. Accordingly, six like-interaction parameters are usually needed to identify a functional group: the number of identical spherical segments forming the group, ν_k^* ; the shape factor of the segment, S_k ; the diameter of the segment, σ_k ; the segment energy of interaction, ε_{kk} ; and the exponents of the Mie potentials, λ_{kk}^r and λ_{kk}^a . For associating groups, additional parameters are required: the number of different association site types, $N_{\text{ST},k}$; the number of sites of each site type, $n_{k,a}$; the bonding energy, $\varepsilon_{kk,ab}^{\text{HB}}$; and the bonding volume, $K_{kk,ab}^{\text{HB}}$. More parameters are needed to model the cross interaction between two unlike groups, k and l : σ_{kl} , ε_{kl} , λ_{kl}^r , λ_{kl}^a and (for associating groups) $\varepsilon_{kl,ab}^{\text{HB}}$, and $K_{kl,ab}^{\text{HB}}$. In the absence of previously characterised (*i.e.*, specified) values, these unlike interaction parameters are estimated using standard combining rules like those in Equations (2.4) to (2.6). [196,231]

In this thesis, nine groups in addition to ammonia and water are considered: H_2O ; NH_3 ; $-\text{CH}_3$; $>\text{CH}_2$; $>\text{CH}-$; $=\text{CH}_2$; $=\text{CH}-$; $-\text{CH}_2\text{OH}$; $-\text{OH}$; $-\text{NH}_2$; and $>\text{NH}$. For the considered groups, like-group parameters which are listed in Table 2.2, unlike-group parameters which are listed in Table 2.3 and unlike-group association parameters which are listed in Table 2.4) are taken from the literature (as indicated in the tables). To accurately model any associating working pair, cross-interaction parameters are required, as mentioned earlier. In the absence of explicit values for unlike-group cross-interaction parameters, the unlike-group diameter is estimated using the Lorentz arithmetic-mean combining rule: [230,236]

$$\sigma_{kl} = \frac{\sigma_{kk} + \sigma_{ll}}{2}. \quad (2.4)$$

In SAFT- γ Mie it is also common to estimate the unlike dispersion energy, ε_{kl} , between groups k and l using an augmented geometric-mean rule [230,231],

$$\varepsilon_{kl} = \frac{\sqrt{\sigma_{kk}^3 \sigma_{ll}^3}}{\sigma_{kl}^3} \sqrt{\varepsilon_{kk} \varepsilon_{ll}}, \quad (2.5)$$

Table 2.3: Unlike group parameters for use with SAFT- γ Mie in the current work [231]. CR denotes combining rule (*i.e.*, using either of Equations. (2.5) or (2.6)).

Group k	Group l	(ε_{kl}/k_B) [K]	λ_{kl}^r	λ_{kl}^a	Ref.
-CH ₃	>CH ₂	350.77	CR	CR	196
-CH ₃	>CH-	387.48	CR	CR	230
-CH ₃	H ₂ O	358.18	100	CR	233
-CH ₃	NH ₃	CR	CR	CR	231
-CH ₃	=CH ₂	333.48	CR	CR	230
-CH ₃	=CH-	252.41	CR	CR	230
-CH ₃	OH	314.67	CR	CR	231
-CH ₃	-CH ₂ OH	333.2	CR	CR	231
-CH ₃	-NH ₂	244.15	CR	CR	231
-CH ₃	>NH	530.87	CR	CR	231
>CH ₂	>CH-	506.21	CR	CR	196
>CH ₂	H ₂ O	423.63	100	CR	233
>CH ₂	NH ₃	CR	CR	CR	231
>CH ₂	=CH ₂	386.8	CR	CR	230
>CH ₂	=CH-	459.4	CR	CR	230
>CH ₂	-CH ₃ OH	341.41	17.050	CR	230
>CH ₂	-OH	396.27	CR	CR	234
>CH ₂	-CH ₂ OH	423.17	CR	CR	233
>CH ₂	-NH ₂	348.39	CR	CR	231
>CH ₂	>NH	394.58	CR	CR	231
>CH-	H ₂ O	275.75	CR	CR	234
>CH-	NH ₃	CR	CR	CR	231
>CH-	=CH ₂	426.76	CR	CR	230
>CH-	=CH-	502.99	CR	CR	230
>CH-	-OH	198.08	CR	CR	234
>CH-	-CH ₂ OH	329.22	CR	CR	234
>CH-	-NH ₂	CR	CR	CR	231
>CH-	>NH	CR	CR	CR	231
=CH ₂	H ₂ O	387.25	94.463	CR	235
=CH-	H ₂ O	332.21	17.309	CR	235
=CH-	-OH	625.17	CR	CR	234
=CH ₂	=CH-	275.75	CR	CR	230
=CH ₂	-OH	CR	CR	CR	231
=CH ₂	-CH ₂ OH	375.51	CR	CR	235
=CH ₂	-NH ₂	CR	CR	CR	231
=CH ₂	>NH	CR	CR	CR	231
=CH-	-CH ₂ OH	414.91	CR	CR	235
=CH-	-NH ₂	CR	CR	CR	231
=CH-	NH	CR	CR	CR	231
H ₂ O	-CH ₂ OH	353.37	CR	CR	233
H ₂ O	-NH ₂	358.55	CR	CR	231
H ₂ O	>NH	646.1	13.195	CR	231
H ₂ O	NH ₃	338.92	CR	CR	see Table 2.10
H ₂ O	-OH	375.92	CR	CR	
-OH	-CH ₂ OH	CR	CR	CR	231
-OH	-NH ₂	241.94	CR	CR	231
-OH	>NH	188.61	CR	CR	231
-CH ₂ OH	-NH ₂	528.21	52.305	CR	231
-CH ₂ OH	>NH	313.25	CR	CR	231
-NH ₂	>NH	381.98	CR	CR	231

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The values of the Mie-potential repulsive and attractive exponents are estimated using the combining rule [196, 230]:

$$\lambda_{kl} = 3 + \sqrt{(\lambda_{kk} - 3) \cdot (\lambda_{ll} - 3)}. \quad (2.6)$$

The ideal-gas contributions to the heat capacity, enthalpy of formation and entropy of formation

Table 2.4: Group association parameters for use with SAFT- γ Mie in this thesis [231].

Group k	Site a on k	Group l	Site b on l	$(\varepsilon_{kl,ab}^{\text{HB}}/k_B)$ [K]	$K_{kl,ab}$ [$\text{\AA}^3$]	Ref.
H ₂ O	e	–OH	H	500	1383.1	[231]
H ₂ O	H	–OH	e	2225.6	114.53	[231]
H ₂ O	e	–CH ₂ OH	H	621.68	425	[233]
H ₂ O	H	–CH ₂ OH	e	2153.2	147.4	[233]
H ₂ O	H	–NH ₂	e	1460	179.6	[231]
H ₂ O	e	–NH ₂	H	1988.3	55.824	[231]
H ₂ O	e	>NH	H	1064.5	400.82	[231]
H ₂ O	H	>NH	e	3890.4	928	[231]
H ₂ O	H	H ₂ O	e	1985.4	101.69	[230]
H ₂ O	H	NH ₃	e	1735.43	13.14	*
–CH ₂ OH	H	–CH ₂ OH	e	2097.9	62.309	[233]
–CH ₂ OH	e	–NH ₂	H	629.88	346.08	[231]
–CH ₂ OH	H	–NH ₂	e	2403.8	26.192	[231]
–CH ₂ OH	e	>NH	H	341.13	1499.8	[231]
–CH ₂ OH	H	>NH	e	1390.1	947.93	[231]
–NH ₂	e	–NH ₂	H	1070.8	95.225	[231]
–NH ₂	H	>NH	e1	1639.86	37.9	[231]
–NH ₂	e	>NH	H	1682.08	0.582	[231]
>NH	e	>NH	H	1370.3	10.062	[231]
H ₂ O	e	NH ₃	H	1558.16	559.6	*
NH ₃	e	NH ₃	H	823.580	35	[232]

* Evaluated in the current work, see Table 2.10

are evaluated using the correlations of Joback and Reid [180]

$$\hat{c}_{p,k}^{\text{ig}} = a_0 - 37.93 + [a_1 + 0.210] T \quad (2.7)$$

$$+ [a_2 - 3.9 \times 10^{-4}] T^2 + [a_3 + 2.06 \times 10^{-7}] T^3,$$

$$\Delta \hat{h}_{f,298}^{\text{ig}} = 68.29 + \hat{h}_{f,298}^{\text{ig}}, \quad (2.8)$$

$$\Delta \hat{s}_{f,298}^{\text{ig}} = 48.36 + \hat{s}_{f,298}^{\text{ig}}, \quad (2.9)$$

where $a_{0,\dots,3,\hat{c}_{p,k}^{\text{ig}}}$ are the ideal-gas heat capacity group contribution parameters for groups k , while $\hat{h}_{f,298}^{\text{ig}}$ and $\hat{h}_{f,298}^{\text{ig}}$ are, respectively, the ideal-gas enthalpy and entropy contribution parameters for groups k . The values for the aforementioned parameters for the considered groups are listed in Table 2.5 (see also Ref. [229]).

The adopted implementation of SAFT- γ Mie in gPROMs does not support the estimation of

Table 2.5: Group-contribution heat capacity parameters using Joback and Reid [180] correlations.

Group k	m_k^{Wk} [g mol ⁻¹]	a_0 [J mol ⁻¹ K ⁻¹]	a_1 [J mol ⁻¹ K ⁻²]	a_2 [J mol ⁻¹ K ⁻³]	a_3 [J mol ⁻¹ K ⁻⁴]	$\hat{h}_{f,298}^{ig}$ [J mol ⁻¹]	$\hat{s}_{f,298}^{ig}$ [J mol ⁻¹ K ⁻¹]
-CH ₃	15.0345	19.5	-0.0081	0.000153	-9.70 × 10 ⁻⁸	-76450	-109.027
>CH ₂	14.02658	-0.909	0.095	-5.40 × 10 ⁻⁵	1.19 × 10 ⁻⁸	-20640	-97.5168
>CH-	13.01864	-23	0.204	-0.00027	1.20 × 10 ⁻⁷	29890	-95.5369
=CH ₂	14.02658	23.6	-0.0381	0.000172	-1.00 × 10 ⁻⁷	-9630	-44.9664
=CH-	13.01864	-8	0.105	-9.60 × 10 ⁻⁵	3.56 × 10 ⁻⁸	37970	-35.4362
-OH	17.0073	25.7	-0.0691	0.000177	-9.90 × 10 ⁻⁸	-208040	-63.215
-CH ₂ OH	31.0339	24.791	0.0259	0.000123	-8.70 × 10 ⁻⁸	-228680	-160.738
-NH ₂	16.02258	26.9	-0.0412	0.000164	-9.80 × 10 ⁻⁸	-22020	-121.107
>NH	15.01464	-1.21	0.0762	-4.90 × 10 ⁻⁵	1.05 × 10 ⁻⁸	53470	-120.537
H ₂ O	18.01528	32.9388	-0.00032	1.23 × 10 ⁻⁵	-3.70 × 10 ⁻⁹	-241818	-44.4497
NH ₃	17.031	35.236	-0.03504	0.0001697	-17.68 × 10 ⁻⁸	-45940	192.77

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surface tension for variable-structure molecular compounds. Thus, other methods from the literature are adopted. In the case of ammonia–water mixture, these are predicted as suggested in Ref. [237] assuming a quasi-ideal mixture. For other organic compounds, either the method of Sugden [229] which is expressed in Equation (2.10a) or Sastri and Rao [238] method expressed in Equation (2.10b) is adopted. The IAPWS method [239] expressed in Equation (2.10c) is used for calculating pure-component surface tensions of water:

$$\gamma_T = [P \cdot (\rho_L - \rho_V)]^4, \quad (2.10a)$$

$$\gamma_T = \Xi \cdot p_c^\psi \cdot T_b^\varpi \cdot T_c^\varphi \cdot \left(\frac{1 - T_r}{1 - T_{br}} \right)^\iota, \quad (2.10b)$$

$$\gamma_{T,H_2O} = 235.8 \cdot (1 - T_r)^{1.256} \cdot [1 - 0.625 \cdot (1 - T_r)], \quad (2.10c)$$

and ideal-mixing rules are adopted for mixtures according to

$$\gamma_{T,mix} = \sum_{j=1}^{NC} \tilde{x}_j \cdot \gamma_{T,j}. \quad (2.11)$$

In the Sugden [240] model (Equation (2.10a)), the Parchor, $P = 0.324 \cdot T_c^{0.25} \cdot \tilde{v}_c^{7/8}$, [229] where T_c and $\tilde{v}_c$ are the critical temperature and specific volume, while ρ_L and ρ_V are, respectively, saturated liquid and vapour mass densities. In Equation (2.10b), the reduced temperature is $T_r = T/T_c$ and the reduced normal boiling temperature is $T_{br} = T_b/T_c$, while $\Xi, \psi, \varpi, \varphi$ and ι are constants in the Sastri-Rao method [238], listed in Table 2.6, that account for the effect of hydrogen-bonding (whenever present). In this thesis, any thermodynamic property (*e.g.*, ρ, T_b) needed for a surface-tension calculation is evaluated using SAFT- γ Mie, while critical properties for organic compounds are calculated using GC methods developed by Joback and Reid [180]:

$$T_c = T_b \left[0.584 + 0.965 \sum_{k=1}^{N_G} (n_k C_{T_c,k}) - \sum_{k=1}^{N_G} (n_k C_{T_c,k})^2 \right]^{-1}, \quad (2.12)$$

$$p_c = \left[0.113 + 0.0032 \sum_{k=1}^{N_G} n_{atom,k} - \sum_{k=1}^{N_G} (n_k C_{p_c,k}) \right]^{-2}, \quad (2.13)$$

$$\tilde{v}_c = 17.5 + \sum_{k=1}^{N_G} (n_k C_{\tilde{v}_c,k}), \quad (2.14)$$

where $C_{T_c,k}$, $C_{p_c,k}$, and $C_{\tilde{v}_c,k}$ are the Joback and Reid [180] group contributions listed in Table 2.7, respectively, for critical temperature, pressure, and volume.

Table 2.6: Parameters used with Sastri and Rao surface tension method in Equation (2.10b) [229, 238]

Family	Ξ	ψ	ϖ	φ	ι
Alcohols	2.28	0.25	0.175	0	0.8
Acidic	0.125	0.5	-1.5	1.85	11/9
Others	0.158				

Table 2.7: Group-contribution critical properties using Joback and Reid [180] correlations.

Group k	$C_{T_i,k}$	$C_{T_c,k}$	$C_{pc,k}$	$C_{\tilde{v}_c,k}$
-CH ₃	-5.10	0.0141	-0.0012	65
>CH ₂	11.27	0.0189	0	56
>CH-	12.64	0.0164	0.002	41
=CH ₂	-4.32	0.0113	-0.0028	56
=CH-	8.73	0.0129	-0.0006	46
-OH	44.45	0.0741	0.0112	28
-CH ₂ OH	55.72	0.093	0.0112	84
-NH ₂	66.89	0.0243	0.0109	38
>NH	52.66	0.0295	0.0077	35
H ₂ O	150.7	0.9726	0.0553	38
NH ₃	72.92	0.008	0.0319	58

The reliability of refrigerant-absorbent-pair thermodynamic models is supported by Figures 2.1 and 2.4, and Table 2.8. For demonstration, only two aliphatic organic families are considered in this chapter, normal alkanes and 2-methylalkanes that can be formed using the organic functional groups (-CH₃, >CH₂, and >CH-) in addition to NH₃ and H₂O. In Figure 2.1 a comparison is provided of calculated values of thermodynamic properties to pseudo-experimental values from NIST [241] for pure normal alkanes (CH₃ - [CH₂]_{*n*} - CH₃), where *n* varies from 1 to 8. It can be noticed in Figure 2.1a that using SAFT- γ Mie tends to marginally over-predict the critical point for pure components. At the same time, liquid-vapour coexistence densities are calculated with a %AAD of 8.29 %.

In Figure 2.2, a comparison is presented of calculated values and pseudo-experimental values (from NIST [241]) of thermodynamic properties of pure 2-methylalkanes ([CH₃]₂ > CH- [CH₂]_{*n*} - CH₃), where *n* varies from 0 to 7. It can be noticed in Figure 2.2a that for carbon chains with $n \leq 3$, SAFT- γ Mie tends to accurately predict the critical point. For pure components, while for longer chains $3 < n \leq 8$, SAFT- γ Mie slightly over-predicts the critical point. Overall, the absolute average deviation for predicting phase-coexistence densities for the branched alkanes (2-methylalkanes) is ± 7.80 %. This slight over-prediction is not a concern since the design is kept well below the critical region to ensure sub-critical operation. Saturation temperatures

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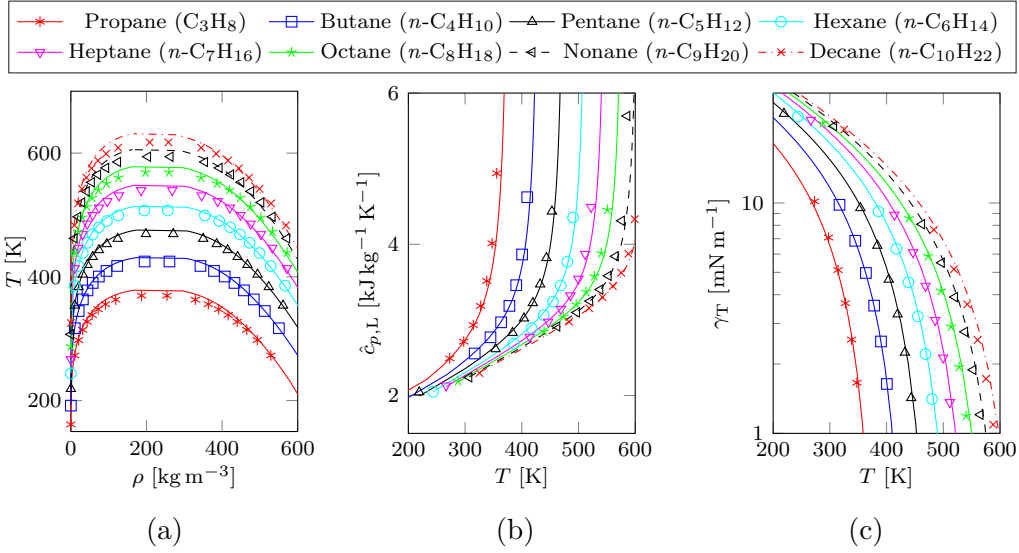


Figure 2.1: A Comparison of calculated thermodynamic properties (curves) to NIST [241] pseudo-experimental values (symbols) for n -alkanes ($CH_3 - [CH_2]_n - CH_3$), where n varies from 1 to 8: (a) liquid–vapour coexistence densities; (b) saturated-liquid isobaric heat capacities; and (c) surface tensions.

calculated with SAFT- γ Mie have a %AAD of 1.66 % from the pseudo-experimental values. In contrast, the %AAD value for mass density is 7.72 %, that for single-phase heat capacity is 5.06 % and that for the latent heat of vaporisation is 4.81 %.

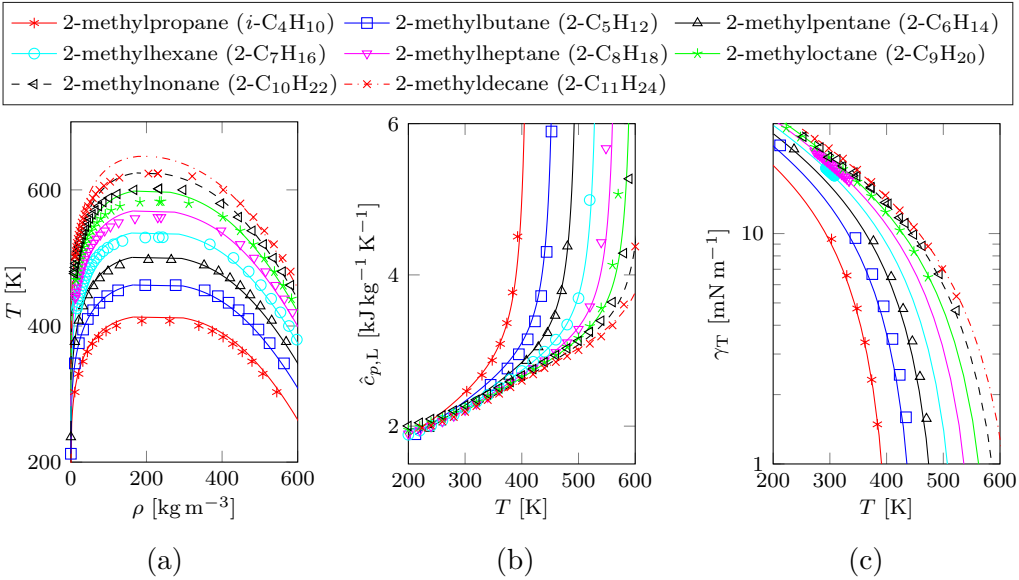


Figure 2.2: A Comparison of calculated thermodynamic properties (curves) to NIST [241] pseudo-experimental values (symbols) for 2-methylalkanes ($[CH_3]_2 > CH - [CH_2]_n - CH_3$), where n varies from 0 to 7: (a) vapour–liquid coexistence densities; (b) saturated-liquid isobaric heat capacities; and (c) surface tensions (surface tension experimental data for 2-methyloctane and 2-methyldecane are taken from [242], while those for 2-methylnonane are from [242, 243]).

Both Figures 2.1b and 2.2b demonstrate the success of deploying SAFT- γ Mie to estimate

single-phase heat-capacity, whereas estimating thermodynamic second-derivative properties commonly challenge equations of state. [232] The validity of using SAFT- γ Mie for predicting thermodynamic functions of other organic families of concern are presented in Table 2.8. It can be observed in Table 2.8 that the Sugden model, Equation (2.10a), provides acceptable accuracy for estimating the surface tension of pure aliphatic compounds ($\leq 5.05\%$), as can also be seen in Figures 2.1c and 2.2c, while for other polar compounds like 1-alcohols and 1-amines, it is recommended to use the Sastri and Rao approach, Equation (2.10b). The Sastri and Rao method also provides acceptable accuracy for pure ammonia surface tension, as seen in Figure 2.4f. Water remains a special case, for which the specific method documented by IAPWS (Equation (2.10c)) is recommended, whereas other models fail to predict its surface tension within acceptable limits.

Many operations in a DAR unit involve a mixture of refrigerant and absorbent rather than dealing with pure components. Thus, it is crucial to demonstrate the adequacy of the presented methods to model the behaviour of any working-fluid mixture of interest. As mentioned earlier, one of the attractive aspects of using a SAFT-based EoS is its transferability and ability to describe working fluids over a wide range of molecular structures and operating conditions. [230] A challenge that one faces when modelling mixtures is the availability of experimental data against which to compare calculated data. Dufal *et al.* [230], and Haslam *et al.* [231] have shown how accurate is SAFT- γ Mie in modelling different working-fluid mixtures. In this chapter, to demonstrate the convenience of using the methods mentioned above, available data from literature are used for comparison as far as possible. In addition, SAFT- γ Mie predictions are also compared to REFPROP [244] estimations to extend the comparison whenever possible.

Some comparisons for some organic mixtures are presented in Figure 2.3. Thermodynamic functions calculated using the methods described in Section 2.2.1 are compared to values generated by REFPROP [244] and available experimental data. In Figure 2.3a, the binary-mixture pressure-composition (p - x,y) diagrams generated using SAFT- γ Mie for three pairs are plotted. The abscissa represents the molar composition of liquid and vapour phases of three different branched alkanes in normal-octane (n -C₈H₁₈). The three considered 2-methylalkanes are 2-methylpropane (i -C₄H₁₀), 2-methylbutane (2-C₅H₁₂), and 2-methylpentane (2-C₆H₁₄). For the 2-methylalkanes+ n -octane mixtures considered, experimental data are available only for the binary pair (i -C₄H₁₀+ n -C₈H₁₈) [246]; in this case, the bubble-point curve predicted using

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SAFT- γ Mie lies closer to the experimental data than that generated using REFPROP. On the other hand, predictions using SAFT- γ Mie are very comparable to those by REFPROP for 2-C₅H₁₂+ n -C₈H₁₈ and 2-C₆H₁₄+ n -C₈H₁₈ mixtures.

In this thesis, the surface tension of a given organic pair is calculated using the molar-based mixing rule in Equation (2.11), where the pure-component surface tension is computed using Equation (2.10a) expressing the Sugden method. In Figure 2.3b a comparison is presented of surface-tensions calculated for C₃H₈+ i -C₄H₁₀ mixture using this method and using REFPROP against experimental data measured by Tanaka and Higashi [247].

It can be noticed that both the described method and REFPROP can reproduce the experimental surface tension within acceptable deviation. Using the Sugden method combined with the molar-based mixing rule, one can predict surface tension for this system with % AAD of 4.7 %. Tanaka and Higashi [247] concluded that the molar-based mixing rule is adequate for this pair. Propane (C₃H₈) and 2-methylpropane (*aka* iso-butane, i -C₄H₈) are similar in shape and size with minimal special secondary bonding that affects the inter-molecular volume of the pair. Although

Table 2.8: Absolute average deviations, %AAD between calculated thermodynamic properties and NIST pseudo-experimental values [241] for some selected organic families and inorganic compounds relevant to DAR. Evaluated thermodynamic functions, ϕ are: T_{sat} ; ρ ; $\hat{c}_{p,L}$; $\Delta_{LV}\hat{h}$ and γ_T . T_{sat} ; ρ ; $\hat{c}_{p,L}$ and $\Delta_{LV}\hat{h}$ are evaluated using SAFT- γ Mie with the parameters listed in Tables 2.2 to 2.5. Surface tensions, γ_T are calculated using Equation (2.10), together with SAFT- γ Mie for any other required thermodynamic properties.

Family	%AAD = $\frac{100}{N} \sum_{i=1}^N \left \frac{\phi_{\text{calc},i} - \phi_{\text{expt},i}}{\phi_{\text{expt},i}} \right *$				
	T_{sat}	ρ	$\hat{c}_{p,L}$	$\Delta_{LV}\hat{h}$	γ_T
N-alkanes	0.35	8.29	1.65	4.20	5.05 [†]
2-methylalkanes	1.89	7.80	1.49	4.35	4.40 [†]
1-alkenes	0.70	7.01	2.97	5.67	3.34 [†]
1-alkanols	2.12	4.57	3.91	4.00	8.48 [‡]
2-alkanols	3.21	12.23	10.10	10.90	3.38 [‡]
1-amines	2.59	9.02	2.64	4.19	3.59 [‡]
2-methylamines	2.86	8.86	4.50	4.29	25.42 [‡]
2°-amines	2.60	8.01	1.27	6.17	8.33 ^{‡§}
Ammonia	0.20	4.17	9.67	0.69	<1 [¶]
Water	0.12	7.23	12.40	3.60	<1
<i>Average</i>	1.66	7.72	5.06	4.81	7.9

* N is the number of data points taken for comparison.

[†] Calculated using Sugden model (Eq. 2.10a) [229].

[‡] Calculated using Sastri and Rao model (Eq. 2.10b) [238].

[§] Pseudoexperimental data are available in Yaw's [245]

[¶] Calculated using method listed in Ref. [237].

^{||} Calculated using IAPWS model (Eq. 2.10c) [239].

this simple rule might not be adequate for more-complicated binary component systems [229], for simplicity, this method is used henceforth within the current analysis, excepting the particular case of the ammonia+water mixture for which, following [95], the surface tension has been estimated using the methods described in Ref. [237].

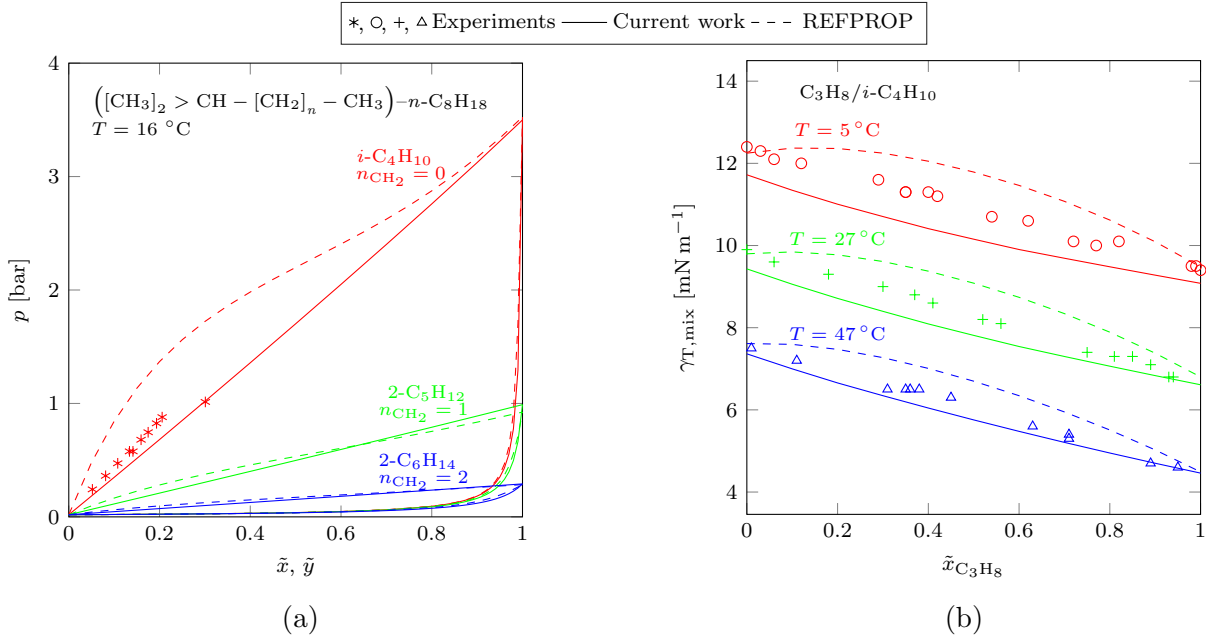


Figure 2.3: A Comparison for some organic-mixture thermodynamic properties between experimental values, REFPROP estimations and values calculated using the suggested methods based on SAFT- γ Mie. (a) Pressure–composition (p – x, y) isotherms at 25°C , generated using SAFT- γ Mie (solid lines) and REFPROP (dashed curves), for three 2-methylalkane + n -octane binary mixtures. The experimental data (symbols) for $i\text{-C}_4\text{H}_{10} + n\text{-C}_8\text{H}_{18}$ were reported by Siesy and Krafczyk [246]. (b) Surface tension for $\text{C}_3\text{H}_8 + i\text{-C}_4\text{H}_{10}$ calculated using the Sugden method in Equation (2.10a) for pure components, combined with a molar-based mixing rule in Equation (2.11) (solid curves), and REFPROP estimations (dashed curves). The experimental data (symbols) are from Tanaka *et al.* [247].

2.2.2 Ammonia-water cross-interaction model

As mentioned earlier in Section 1.2, all DAR units in the market run using the ammonia–water working-fluid pair. An accurate $\text{NH}_3 + \text{H}_2\text{O}$ model is important to be used as a benchmark for selecting alternative working fluids. The parameters for the $\text{NH}_3 + \text{H}_2\text{O}$, unlike (cross) interaction parameters, are developed as part of this thesis. Bagga and Teoh [232] already carried out

The development of a SAFT- γ Mie model for pure ammonia; the water model adopted is that of Dufal *et al.* [230]. It is worth mentioning that there is a more recent non-spherical model

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developed by Graham *et al.* [248] for water; however, the spherical water model developed by Dufal *et al.* [230] is found to be convenient for this study, provided the availability of cross-interaction parameters against other considered functional groups. To accurately model this associating working pair, cross-interaction parameters are required, as mentioned earlier. Bagga and Teoh [232] developed a cross-interaction model for $\text{NH}_3+\text{H}_2\text{O}$ mixture considering the non-spherical H_2O model developed by Graham *et al.* [248]. Thus, there is a need to develop cross-interaction parameters for $\text{NH}_3+\text{H}_2\text{O}$ mixture considering the spherical H_2O model developed by Dufal *et al.* [230].

The unlike group diameter for $\text{NH}_3+\text{H}_2\text{O}$ pair is estimated using the Lorentz arithmetic-mean combining rule in Equation (2.4). [230, 236] The values of the Mie-potential repulsive and attractive exponents are estimated using the combining rule expressed by Equation (2.6). [196, 230] The remaining parameters (ε_{kl} , $\varepsilon_{kl,ab}^{\text{HB}}$, and $K_{kl,ab}^{\text{HB}}$) are estimated using a Levenberg-Marquardt algorithm [249, 250] to minimise the difference between the experimental and calculated property values. The Levenberg-Marquardt method also referred to as the damped least-squares method, is a local gradient-based minimisation technique. As applied in the current context, the least-squares objective function can be expressed as

$$\begin{aligned}
 & \min_{\varepsilon_{\text{NH}_3-\text{H}_2\text{O}}, \varepsilon_{\text{NH}_3\text{e}-\text{H}_2\text{O:H}}^{\text{HB}}, K_{\text{NH}_3:\text{e}-\text{H}_2\text{O:H}}^{\text{HB}}} F_{\text{obj}} \left(\varepsilon_{\text{NH}_3-\text{H}_2\text{O}}, \varepsilon_{\text{NH}_3\text{e}-\text{H}_2\text{O:H}}^{\text{HB}}, K_{\text{NH}_3:\text{e}-\text{H}_2\text{O:H}}^{\text{HB}} \right) \quad (2.15) \\
 & = \frac{w_{p_{\text{dew}}}}{N_{p_{\text{dew}}}} \left[\sum_{i=1}^{N_{p_{\text{dew}}}} \left(\frac{p_{\text{dew,clac},i} - p_{\text{dew,expt},i}}{p_{\text{dew,expt},i}} \right)^2 \right] \\
 & + \frac{w_{p_{\text{bub}}}}{N_{p_{\text{bub}}}} \left[\sum_{i=1}^{N_{p_{\text{bub}}}} \left(\frac{p_{\text{bub,clac},i} - p_{\text{bub,expt},i}}{p_{\text{bub,expt},i}} \right)^2 \right] \\
 & + \frac{w_{\hat{c}_p}}{N_{\hat{c}_p}} \left[\sum_{i=1}^{N_{\hat{c}_p}} \left(\frac{\hat{c}_{p,\text{clac},i} - \hat{c}_{p,\text{expt},i}}{\hat{c}_{p,\text{expt},i}} \right)^2 \right],
 \end{aligned}$$

where w is the weight assigned to each property. The data used in the current study are indicated in Table 2.9 along with ranges of temperatures and pressures, uncertainties, and the number of data points. The equal weights for dew and bubble pressures are set to 10, and the weight for single-phase heat capacity is set to 20; as calorific properties are relevant to this study, more weight is assigned to heat-capacity data, thereby providing higher accuracy in predicting the excess-enthalpy of the mixture.

The optimisations are carried out using the gSAFT material modeller provided in the commercial software package gPROMS[®] [126] with five Sobol points which guarantee to reach a global optimum. Later, model predictions are compared to experimental data, assessing the absolute average deviation (%AAD) between calculated and experimental values.

Table 2.9: Experimental data for ammonia-water SAFT- γ Mie model-parameter estimation.

Thermodynamic property	ΔU [%]	Range	No. of data	Ref.
Dew pressure (p_{dew})	1	$20 \leq T$ [°C] ≤ 110	125	[251, 252]
Bubble pressure (p_{bub})	3	$40 \leq T$ [°C] ≤ 121	107	[251]
Liquid-phase molar-specific heat capacity ($\hat{c}_p$)	1.8	$47 \leq T$ [°C] ≤ 87 $10 \leq p$ [bar] ≤ 100	43	[253]

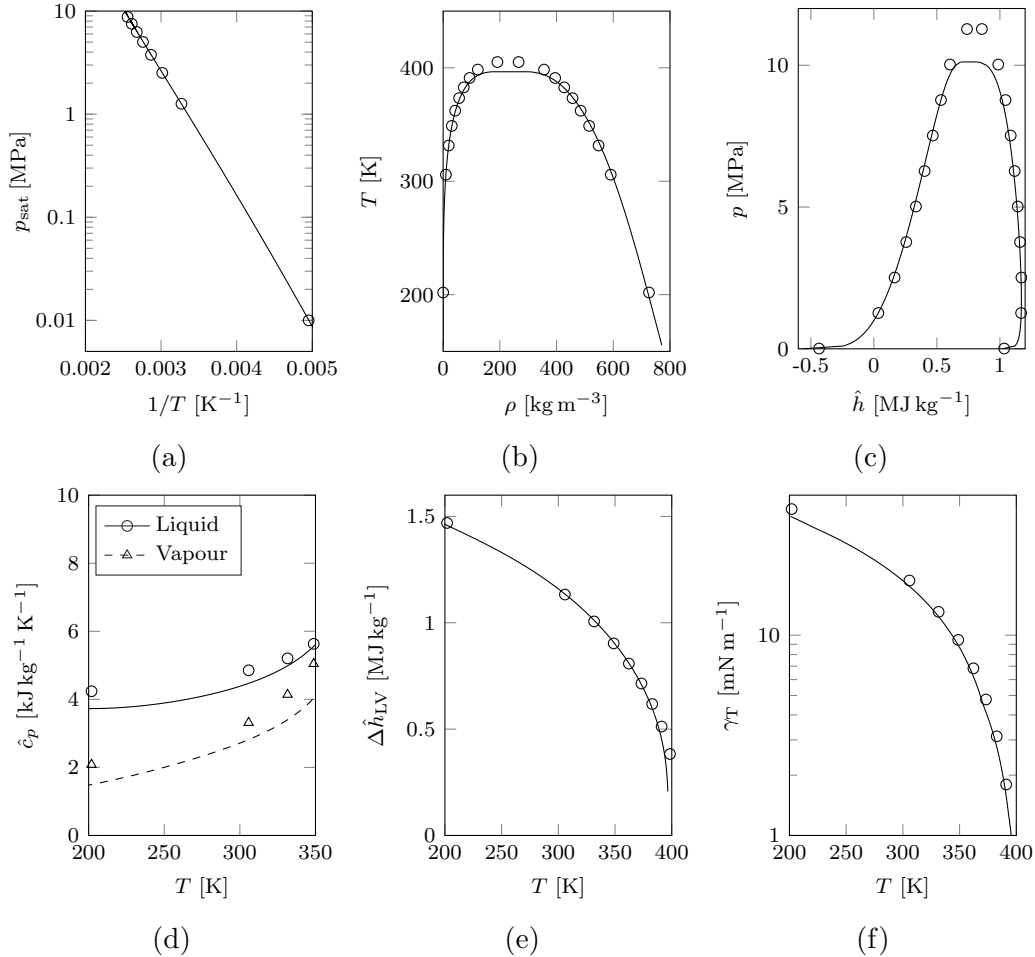


Figure 2.4: A Comparison between calculated thermodynamic properties (as modelled by Bagga and Teoh [232]) and NIST [241] pseudo-experimental data of ammonia (symbols).

As mentioned earlier, the SAFT- γ Mie EoS parameters of the molecular group, NH_3 listed in

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Table 2.2 were estimated by Bagga and Teoh [232] using SAFT-VR Mie¹. In Figure 2.4, the NH₃ SAFT-VR Mie model from Bagga and Teoh [232] is compared against NIST [241] pseudo-experimental data. The model accuracy can be observed in Figure 2.4. Unlike the case for normal alkanes and high-carbon 2-methylalkanes, SAFT- γ Mie slightly under-predicts the critical point as observed in Figures 2.4b and 2.4c. This under-prediction does not represent an issue since, within the scope of this thesis, a DAR system should always operate well inside the sub-critical region. Studying Figure 2.4f, it can be observed that the Sastri and Rao [238] model is acceptable for predicting pure-ammonia surface tension, with an %AAD from experimental data of 8.61 %.

Ammonia is a base that dissociates partially in water into NH₄⁺ and OH⁻ ions. The base dissociation constant for ammonia in water is small ($K_{bs} = 1.8 \times 10^{-5}$). Thus, a relatively large number of ammonia molecules can be found in an aqueous ammonia solution compared to the ionic species. This implies that, although considering speciation effects is very important for VLE prediction, it is fair to neglect explicit speciation for aqueous ammonia solution. [232, 254]

Beyond hydrogen bonds that occur between pure-component molecules, two distinct hydrogen bonds form between associating ammonia and water molecules: NH₃:e-H₂O:H and NH₃:H-H₂O:e. These hydrogen bonds have been modelled symmetrically by many authors. This means that association energies and bonding volumes of the hydrogen bonds mentioned above are treated as equivalent so that three parameters characterise the symmetric model: $\epsilon_{\text{NH}_3-\text{H}_2\text{O}}$, $\epsilon_{\text{NH}_3\text{e}-\text{H}_2\text{O:H}}^{\text{HB}}$, and $K_{\text{NH}_3\text{:e}-\text{H}_2\text{O:H}}^{\text{HB}}$ [232, 254].

However, published hydrogen-bond energies in the literature differ, suggesting that hydrogen bonds in the ammonia-water mixture are asymmetric; [255] an asymmetric model is characterised by five optimisable parameters: $\epsilon_{\text{NH}_3-\text{H}_2\text{O}}$, $\epsilon_{\text{NH}_3\text{e}-\text{H}_2\text{O:H}}^{\text{HB}}$, $K_{\text{NH}_3\text{:e}-\text{H}_2\text{O:H}}^{\text{HB}}$, $\epsilon_{\text{NH}_3\text{H}-\text{H}_2\text{O:e}}^{\text{HB}}$, and $K_{\text{NH}_3\text{:H}-\text{H}_2\text{O:e}}^{\text{HB}}$ [232, 255], so the objective function becomes

¹Note that SAFT- γ Mie and SAFT-VR Mie are equivalent for the case of molecules (*i.e.*, H₂O and NH₃).

$$\begin{aligned}
 & \min_{\substack{\epsilon_{\text{NH}_3-\text{H}_2\text{O}}, \epsilon_{\text{NH}_3\text{e}-\text{H}_2\text{O:H}}^{\text{HB}}, K_{\text{NH}_3\text{:e}-\text{H}_2\text{O:H}}^{\text{HB}}, \\ \epsilon_{\text{NH}_3\text{H}-\text{H}_2\text{O:e}}^{\text{HB}}, K_{\text{NH}_3\text{:H}-\text{H}_2\text{O:e}}^{\text{HB}}}} F_{\text{obj}} \quad (2.15 \text{ revisited}) \\
 &= \frac{w_{p_{\text{dew}}}}{N_{p_{\text{dew}}}} \left[\sum_{i=1}^{N_{p_{\text{dew}}}} \left(\frac{p_{\text{dew,clac},i} - p_{\text{dew,expt},i}}{p_{\text{dew,expt},i}} \right)^2 \right] \\
 &+ \frac{w_{p_{\text{bub}}}}{N_{p_{\text{bub}}}} \left[\sum_{i=1}^{N_{p_{\text{bub}}}} \left(\frac{p_{\text{bub,clac},i} - p_{\text{bub,expt},i}}{p_{\text{bub,expt},i}} \right)^2 \right] \\
 &+ \frac{w_{\hat{c}_p}}{N_{\hat{c}_p}} \left[\sum_{i=1}^{N_{\hat{c}_p}} \left(\frac{\hat{c}_{p,\text{clac},i} - \hat{c}_{p,\text{expt},i}}{\hat{c}_{p,\text{expt},i}} \right)^2 \right].
 \end{aligned}$$

Commonly, VLE data are used for estimating cross-interaction parameters. However, considering additional second-order thermodynamic functions (such as the single-phase constant-pressure heat capacity, $\hat{c}_p$) in parameter estimation leads to parameters that provide for better predictions of the excess-enthalpy of the mixture. This can be obviously seen in Figure 2.5. Considering $\hat{c}_p$ does not significantly affect the quality of VLE predictions (as noticed in Figure 2.5a). Nevertheless, considering $\hat{c}_p$ significantly improves the accuracy of the model in predicting the excess enthalpy of mixing as demonstrated by Figure 2.5b.²

Table 2.10: A Comparison between symmetric and asymmetric hydrogen-bond models for the $\text{NH}_3+\text{H}_2\text{O}$ system in terms $\% \text{AAD} = \frac{100}{N} \sum_{i=1}^N \left| \frac{\phi_{\text{calc},i} - \phi_{\text{expt},i}}{\phi_{\text{expt},i}} \right|$, where ϕ is the property studied, and N is the number of experiments involved in the assessment.

Model	$\epsilon_{\text{NH}_3-\text{H}_2\text{O}}/\text{k}_\text{B}$ [K]	$\epsilon_{\text{NH}_3\text{:e}-\text{H}_2\text{O:H}}^{\text{HB}}/\text{k}_\text{B}$ [K]	$K_{\text{NH}_3\text{:e}-\text{H}_2\text{O:H}}^{\text{HB}}$ [Å ³]	$\epsilon_{\text{NH}_3\text{:H}-\text{H}_2\text{O:e}}^{\text{HB}}/\text{k}_\text{B}$ [K]	$K_{\text{NH}_3\text{:H}-\text{H}_2\text{O:e}}^{\text{HB}}$ [Å ³]
Symmetric	300.41	1951.98	41.7	1951.98	41.7
Asymmetric	338.92	1735.43	13.14	1558.16	559.6
%AAD					
Model	p_{bub}	p_{dew}	$\hat{c}_p$	$\Delta_{\text{mix}} \hat{h}$	
Symmetric	6.02	4.10	5.12	16.08	
Asymmetric	4.00	3.30	3.32	10.07	

We consider two models for the ammonia + water unlike interaction, which differ in how the hydrogen bond between NH_3 and H_2O is treated; one is symmetric (*i.e.*, solving Equation (2.15)), while the other is asymmetric (*i.e.*, solving Equation (2.15 revisited)). Calculated bubble and dew pressures, heat capacities and excess enthalpies are compared to compare the two models.

²The model that does not consider second-order functions in optimisation is obtained from gPROMS gSAFT built-in databank.

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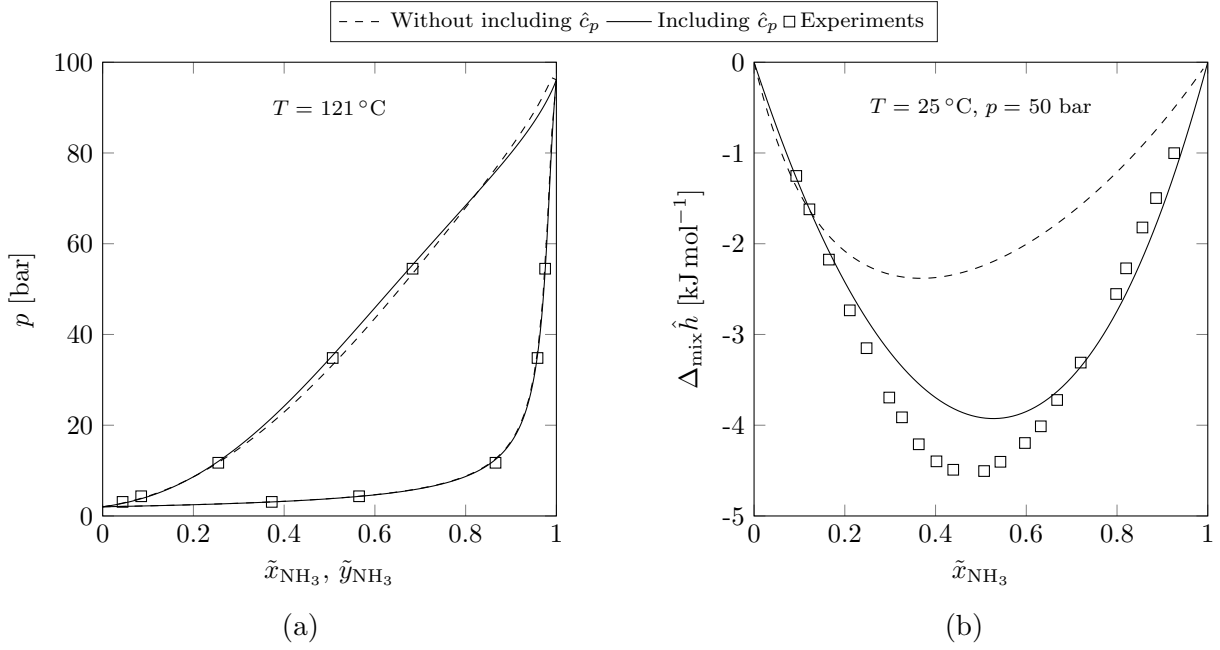


Figure 2.5: Effect of including second order thermodynamic functions, here the iso-baric heat capacity on the accuracy of $\text{NH}_3+\text{H}_2\text{O}$ system.

In Table 2.10, optimal association parameters are presented for the symmetric and asymmetric models, as well as %AAD for the calculated properties. It is reassuring that the asymmetric hydrogen-bond model features hydrogen-bond energy for $\text{NH}_3:\text{e}-\text{H}_2\text{O}:\text{H}$ that is larger than that for $\text{NH}_3:\text{H}-\text{H}_2\text{O}:\text{e}$; this qualitatively agrees with the findings of Kitaura and Morokuma [255], obtained using quantum-mechanical calculations, as was also highlighted by Bagga and Teoh [232] for their $\text{NH}_3+\text{H}_2\text{O}$ model.

Compared to the model with symmetric hydrogen bonding, considering asymmetric hydrogen bonding leads to higher accuracy in the calculated bubble and dew pressures, as seen in Figure 2.6a, as well as heat capacity, as can be seen in Figure 2.6c, and excess heat of mixing, as seen in Figure 2.6b. These are reflected in the lower %AAD (as observed in Table 2.10). Therefore, the model with asymmetric hydrogen bonds is chosen for use in subsequent simulations, where an accurate determination of VLE and enthalpy changes is crucial for absorption refrigeration system analysis.

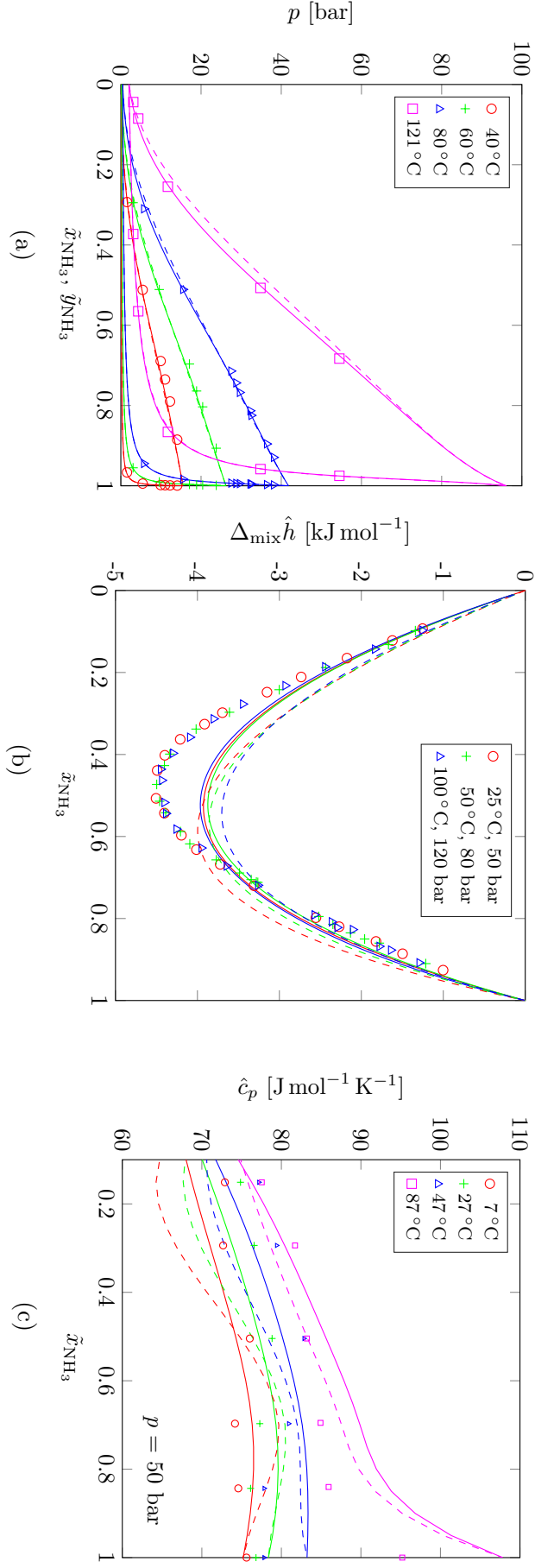


Figure 2.6: Thermodynamic properties of $\text{NH}_3+\text{H}_2\text{O}$ system obtained using the different hydrogen-bonding models: Asymmetric (solid curves); and Symmetric (dashed curves). (a) Calculated pressure-composition (p - x, y) isotherms, symbols denote experimental data of Gillespie *et al.* [251] and Smolen *et al.* [252]; (b) Calculated excess heats of mixing, symbols denote experimental data of Fujita *et al.* [253]. (c) single-phase isobaric heat capacity, symbols denote experimental data of Staudt [256].

2.3 DAR thermodynamic mathematical description

Having presented in the previous section GC SAFT- γ Mie EoS and other methods for surface tension calculation. The adequacy of the presented methods in relevance to diffusion absorption refrigeration and working-fluid design has been demonstrated. In this section, the mathematical description of the DAR system is discussed. The main operations involved in a DAR cycle have been detailed in Section 1.2. A block diagram describing the main processes involved in a typical DAR system is depicted in Figure 2.7.

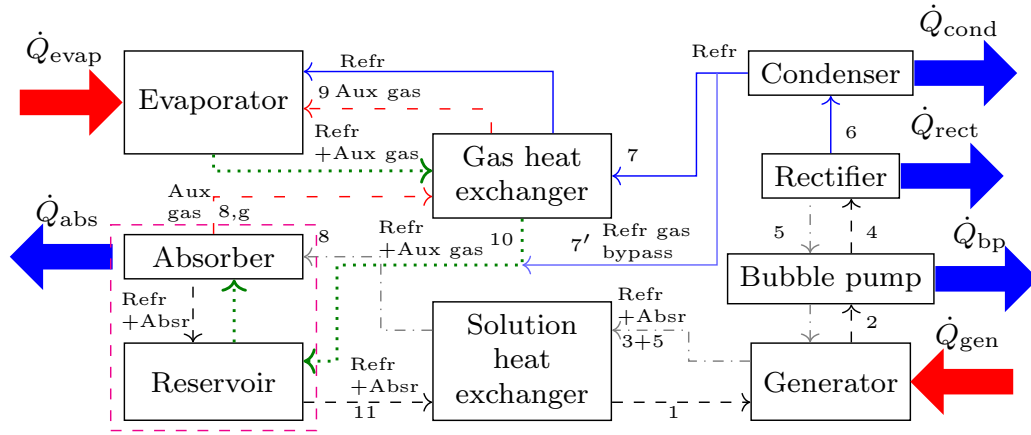


Figure 2.7: A schematic block diagram showing typical operations in diffusion absorption refrigeration (DAR) systems. DAR state points are already defined in Figure 1.9 in Chapter 1: refrigerant-rich mixture (---); refrigerant-weak solution (-.-.); “pure” refrigerant (—); auxiliary gas (- -); and refrigerant–auxiliary gas mixture (-.-.-.).

Many authors considered modelling DAR systems as it has been reviewed in Chapter 1. Mansouri *et al.* [115] simulated a steady-state operating DAR system using Aspen Plus[®] [116], while Sayadi *et al.* [44] and Elsayed *et al.* [117] used Aspen HYSYS[®] [118] to simulate a steady-state operating DAR system. Chaves *et al.* [119] and Pérez-García *et al.* [120] presented a DAR system model that incorporates heat transfer resistance between air and various heat-dissipating components. Zohar *et al.* [70, 98, 109, 110] and Starace and De Pascalis [97, 105] presented DAR thermodynamic models. As mentioned earlier, Mejbri *et al.* [127] presented an NH₃–H₂O-based DAR model that uses PC-SAFT EoS. Apart from work published by Harraz *et al.* [63, 64] that shall be discussed in this section, no DAR model has been presented that can be easily deployed to assess DAR performance using different classes of working fluids. Unlike other authors, who mostly use empirical EoS (mainly Pátek and Klomfar [128] to model NH₃–H₂O mixture), Harraz *et al.* [63, 64] introduced the use of the GC SAFT- γ Mie EoS in their DAR modelling

framework which allows the assessment of any working-fluid system given its molecular structure.

2.3.1 Early DAR model development

Earlier, Harraz *et al.* [63,64] proposed the concept for a CAMD-DAR framework illustrated in Figure 2.8. Further, these authors introduced using SAFT- γ Mie EoS for DAR modelling. Unlike the rest of the thesis, Harraz *et al.* [63] used the SAFT- γ Mie equation of state and adopted the NH_3 and $\text{NH}_3+\text{H}_2\text{O}$ mixture models provided by Bagga and Teoh [232]. In contrast, they used the H_2O model developed by Graham *et al.* [248]. Further, they modelled hydrogen through the gSAFT tool using the encrypted gSAFT databank in the gPROMS environment [126].

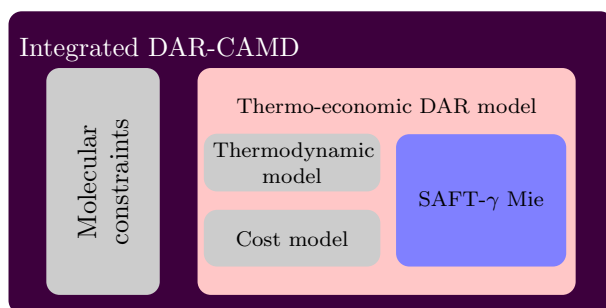


Figure 2.8: A schematic representation of the integrated CAMD-DAR framework concept proposed by Harraz *et al.* [63].

In their work, Harraz *et al.* [63] considered the DAR thermodynamic model presented by Starace and De Pascalis [97] that used Pátek and Klomfar [128] equations for the $\text{NH}_3+\text{H}_2\text{O}$ thermodynamic properties. Harraz *et al.* [63], replaced SAFT- γ Mie EoS for the empirical (fluid-specific) Pátek and Klomfar correlation (with hydrogen properties evaluated using SAFT- γ Mie in all cases). As mentioned earlier, SAFT- γ Mie EoS allows exploring more organic working fluids made-up of different functional groups. The simulations carried out by Harraz *et al.* [63] using SAFT- γ Mie show acceptable agreement with those DAR simulations which involved Pátek and Klomfar as it can be observed in Figure 2.9. DAR simulations using SAFT- γ Mie were also verified against experimental data. It can also be noticed in Figure 2.9 that these simulations show good agreement with the experimental measurements (within $\pm 7\%$) for generator heat input ranging between 150 and 500 W, charge pressure of 17 bar and cooling delivery temperature (cold space temperature) of 5 °C. [63] In this study, the maximum COP was reported as 0.24 at a generator heat input of about 300 W, beyond which various components' effectiveness limits the COP (*e.g.*, the rectifier, the condenser and the evaporator).

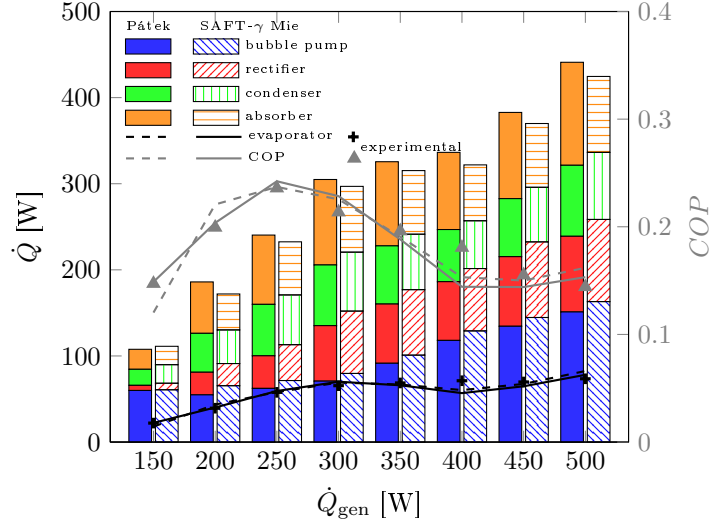


Figure 2.9: A comparison between SAFT- γ Mie EoS and Pátek and Klomfar equations [128], both applied to Starace and De Pascalis [97] model for $150 \leq \dot{Q}_{\text{gen}} \leq 500$. Both set of simulations are also compared against experimental data for an $\text{NH}_3\text{-H}_2\text{O-H}_2$ DAR system operating at 17 bar charge pressure and cooling delivery at 5°C .

Harraz *et al.* [64] extended their earlier work [63] and carried out simulations based on the DAR-model developed by Starace and De Pascalis [97] to investigate the Effect of charge pressure on the performance of $\text{NH}_3\text{-H}_2\text{O-H}_2$ DAR systems. Harraz *et al.* [63,64] pointed out that the input variables they used in their simulations depend on the generator heat input. For this reason, Freeman *et al.* [42,95] presented some correlations based on experimental data to relate these dependent variables and limit the degrees of freedom in the model to the experimentally-controllable parameters and the climatic conditions. Unlike their earlier work [63], Harraz *et al.* [64] evaluated the input variables to the model using the relationships proposed by Freeman *et al.* [42]. This approach has shown good predictability; however, it is limited to $\text{NH}_3\text{-H}_2\text{O}$ based DAR systems. It may not be convenient to describe DAR systems that run using alternative working fluids.

Figure 2.10 shows three DAR operating zones for different charge pressures and cooling applications, initially proposed by Najjarian *et al.* [129]. The three zones are low powered, design range, and high powered. In Zone 1 (low powered), the cooling capacity is proportional to the generator power; in Zone 2 (design range), the change in cooling is insignificant compared to any additional generator power. In Zone 3 (high powered), The cooling capacity declines adding more power to the system. [64,129]

Using these operating zones, Harraz *et al.* [64] tried to account for the rectifier part-load operation

(below the nominal design point), in which the temperature of State 6 might fall below the refrigerant saturation temperature. Leaving below the saturation temperature means that more absorbent is likely carried out with Stream 6, resulting in less purity going into the condenser and more refrigerant draining back to the absorber. To account for this behaviour, Harraz *et al.* [64] slightly modified Starace and De Pascalis [97] by replacing a reflux ratio expression for the assumption of equilibrium state between States 5 and 6. The reflux ratio, R is defined as

$$R = \frac{\dot{m}_5}{\dot{m}_6}, \quad (2.16)$$

where the reflux ratio can be defined as a ratio of a minimum reflux ration, $R_{\min} = \frac{1-y_4}{y_4-x_3}$ which corresponds complete condensation of the pure refrigerant at State 6 and reflux at State 5 in equilibrium with State 4. They also introduced a rectifier temperature effectiveness, ϵ_{rec} which they set as 85 %, so that the temperature of the rectifier outlet at State 6, T_6 can be calculated by

$$T_6 = T_a + \epsilon_{\text{rec}}(T_4 - T_a), \quad (2.17)$$

where T_a is the ambient temperature, and T_4 is the vapour temperature at state 4. It should be stressed that $R = R_{\min}$ corresponds to Starace and De Pascalis's original DAR model.

To validate their results, Harraz *et al.* [64] compared their predictions varying the ratio between R and $R_{\min}$, which are listed in Table 2.11, to experimental data collected for a laboratory-scale $\text{NH}_3\text{--H}_2\text{O--H}_2$ DAR unit over a wide range of generator heat input. Generally speaking, their simulations, as seen in Figure 2.10 are comparable to the experimental evaluations in Zones 1 and 2. Nonetheless, the simulations in Zone 3 highly overestimate the cooling capacity. The deviation between simulations and experimental measurements over operating Zones 1 and 2 are quantified using the absolute average deviation, %AAD and listed in Table 2.11. It can be noticed that %AAD up to the design point varied between 4 % to 19 % depending on the operating conditions and the assumed reflux ratio.

It can be concluded from the discussion above that DAR system modelling is challenging due to the complexity of the physical processes that govern the operation of these systems. [64] There is a scarcity of experimentally validated models that offer a detailed understanding of the DAR system performance over a broader range of operating conditions. Harraz *et al.* [63, 64] has considered combined experimental observations on a laboratory-scale $\text{NH}_3\text{--H}_2\text{O--H}_2$ DAR system,

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Table 2.11: A Comparison between modified Starace and De Pascalis model and experimental data for cooling temperature, $T_{co} = 5^\circ\text{C}$, considering various reflux ratios. The comparisons are quantified using average absolute deviation, $\%AAD = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| \frac{\dot{Q}_{\text{evap,expt},i} - \dot{Q}_{\text{evap,pred},i}}{\dot{Q}_{\text{evap,expt},i}} \right|$, where $\dot{Q}_{\text{evap,expt},i}$ and $\dot{Q}_{\text{evap,pred},i}$ are the experimental and predicted $\dot{Q}_{\text{evap}}$ respectively, and N_p is the number of experimental measurements. [64]

$R/R_{\min}$	%AAD in $\dot{Q}_{\text{evap}}$		Average
	p_{ch} [bar]		
1	18	19	11.5
1.2	3	13	8
1.3	4	10	7
1.4	6	8	7
1.5	8	8	8

with simulations using a modified Starace and De Pascalis model. Their significant modification involves the integration of SAFT- γ Mie EoS to the model for modelling the working-fluid mixture

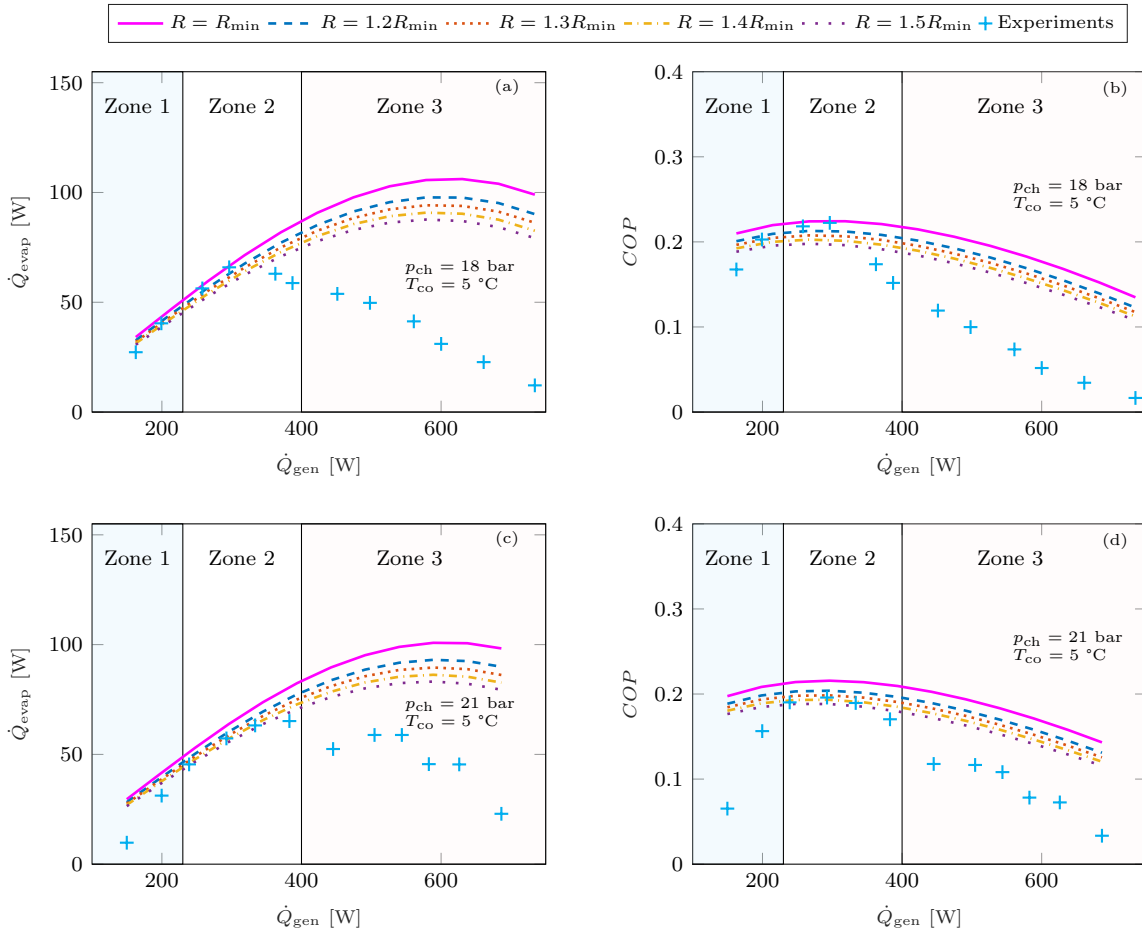


Figure 2.10: An evaluation of the modified Starace and De Pascalis model which is modified by Harraz *et al.* [64] showing the effect of different reflux ratios on predicting DAR cooling output, $\dot{Q}_{\text{evap}}$ and coefficient of performance, COP under various operating conditions: $150 \leq \dot{Q}_{\text{gen}} \leq 500$; $p_{\text{ch}} \in [18; 21]$ bar; and cooling application temperature, T_{co} of 5°C

to allow a more flexible approach to exploring more working fluids. The simulation results in Figure 2.10 show good agreement with experimental measurements unless the DAR is overpowered. The earlier simulations overestimated the cooling capacity of overpowered DAR systems. In the following discussion, the model is taken a step further, where more modifications are applied, and validation of the final model is presented for a broader range of operating conditions.

2.3.2 DAR mathematical model formulation

Throughout the rest of this thesis, to ensure transferability to different DAR systems and working fluids, a fundamental thermodynamic model for DAR systems is adopted based on the conservation of energy and mass, avoiding – whenever possible – the use of system-specific correlations. The presented model is summarised in Table 2.12.

Referring to Figure 2.7, the DAR thermodynamic cycle analysis starts from State 1, at which the refrigerant-rich working fluid enters the generator. The conservation of material across the generator is expressed in Equation (2.18a), where $\dot{n}$ is the molar flowrate. Considering that States 1 and 2 are each well defined by their temperature, composition and pressure, the steady-state generator energy balance can be used to evaluate the rich-solution flowrate, $\dot{n}_{rs}$ generated when $\dot{Q}_{gen}$ is received by the DAR system, where the molar-specific enthalpies at States 1 and 2 are, respectively, $\hat{h}_1 = f(T_1, p_{sys}, \tilde{x}_{rs})$ and $\hat{h}_2 = f(T_2, p_{sys}, \tilde{x}_{rs})$. For fully-attached bubble pumps, Equation (2.18b) is used, while Equation (2.18c) is used to describe the energy balance for a semi-detached bubble pump as illustrated by Fig 1.13. It is assumed that the rich solution enters the generator as saturated liquid (*i.e.*, $q_1 = 0$), and vapour quality of the mixture leaving the generator is $q_2 = (\tilde{x}_{rs} - \tilde{x}_2) / (\tilde{y}_2 - \tilde{x}_2)$.

The bubble pump takes the generated rich solution at State 2; this flows up the inner tube and separates into liquid (State 3, *i.e.*, $q_3 = 0$) and vapour (State 4, *i.e.*, $q_4 = 1$) at equilibrium. The bubble pump also receives liquid returning from the rectifier (State 5). The liquid at State 5 combines with that at State 3, flowing down the bubble-pump outer tube. The total material balance on the bubble pump tube is described by Equation (2.19a), while the refrigerant material balance for the bubble pump tube is described by Equation (2.19b). Molar compositions of leaving streams at the top of the bubble pump are evaluated by solving vapour–liquid equilibrium relations; the liquid and vapour mole fractions, $\tilde{x}_3$ and $\tilde{y}_4$, are thereby evaluated as functions of

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temperature, pressure and (overall) mixture composition, $\tilde{x}_{rs}$. From Equation (2.19d), the rate of heat dissipated from the bubble pump, $\dot{Q}_{bp}$ can be estimated applying the energy balance on the bubble pump tube control volume, where the molar-specific enthalpies at States 3 and 4 are, respectively, $\hat{h}_{L,3} = f(T_3, p_{sys}, \tilde{x}_3)$ and $\hat{h}_{V,4} = f(T_4, p_{sys}, \tilde{y}_4)$.

The rectifier receives the vapour leaving the bubble pump at State 4 and partially condenses

Table 2.12: Fundamental DAR-thermodynamic mathematical model equations founded in first-law of thermodynamics as used in this thesis.

Generator	$\dot{n}_1 = \dot{n}_2 = \dot{n}_{rs},$	(Total material balance) (2.18a)
	$\dot{n}_1 \cdot \hat{h}_1 + \dot{n}_5 \cdot \hat{h}_5 + \dot{Q}_{gen}$ $= \dot{n}_4 \cdot \hat{h}_4 + \dot{n}_{ws,in} \cdot \hat{h}_{ws,in} + \dot{Q}_{bp}$	(Energy balance – fully attached bubble pump) (2.18b)
	or	
	$\dot{n}_1 \cdot \hat{h}_1 + \dot{Q}_{gen} = \dot{n}_2 \cdot \hat{h}_2.$	(Energy balance – semi-attached bubble pump) (2.18c)
Bubble pump	$\dot{n}_2 = \dot{n}_3 + \dot{n}_4$	(Total material balance) (2.19a)
	$\tilde{x}_{rs} \cdot \dot{n}_2 = \tilde{x}_3 \cdot \dot{n}_3 + \tilde{y}_4 \cdot \dot{n}_4$	(Refrigerant material balance) (2.19b)
	$\{\tilde{x}_3, \tilde{y}_4\} = f(T_4, p_4, \tilde{x}_{rs})$	(VLE) (2.19c)
	$\dot{Q}_{bp} = \dot{n}_2 \cdot \hat{h}_2 - \dot{n}_3 \cdot \hat{h}_{L,3} - \dot{n}_4 \cdot \hat{h}_{V,4}$	(Energy balance) (2.19d)
Rectifier	$\dot{n}_4 = \dot{n}_5 + \dot{n}_6$	(Total material balance) (2.20a)
	$\tilde{y}_4 \cdot \dot{n}_4 = \tilde{x}_5 \cdot \dot{n}_5 + \tilde{y}_6 \cdot \dot{n}_6$	(Refrigerant material balance) (2.20b)
	$\tilde{y}_6 = \begin{cases} 1 & , \text{ if } T_6 \leq T_{sat,refr}(p_{sys}) \\ f_{dew}(T_6, p_{sys}) & , \text{ otherwise.} \end{cases}$	(Refrigerant purity) (2.20c)
	$\dot{n}_4 \cdot \hat{h}_{V,4} = \dot{n}_5 \cdot \hat{h}_{L,5} + \dot{n}_6 \cdot \hat{h}_{V,6} + \dot{Q}_{rect}$	(Energy balance) (2.20d)
Condenser	$\dot{n}_6 = \dot{n}_{L,7} + \dot{n}_{V,7}$	(Total material balance) (2.21a)
	$\tilde{y}_6 \cdot \dot{n}_6 = \tilde{x}_7 \cdot \dot{n}_{L,7} + \tilde{y}_7 \cdot \dot{n}_{V,7}$	(Refrigerant material balance) (2.21b)
	$\{\tilde{x}_7, \tilde{y}_7\} = f(T_7, p_{sys}, \tilde{y}_6)$	(VLE) (2.21c)
	$\dot{n}_6 \cdot \hat{h}_{V,6} = \dot{n}_{L,7} \cdot \hat{h}_{L,7} + \dot{n}_{V,7} \cdot \hat{h}_{V,7} + \dot{Q}_{cond}$	(Energy balance) (2.21d)
Expansion	$\dot{n}_g = \dot{n}_{V,9} \cdot \left(\frac{p_{sys} - p_9}{p_9} \right)$	(Dalton's law) (2.22a)
	$p_9 = \begin{cases} p_{refr}^{sat}(T_9) & , \text{ if } \tilde{y}_6 = 1 \\ p_{bub}(T_9, \tilde{x}_9) & , \text{ otherwise} \end{cases}$	(Expansion pressure) (2.22b)
	$\dot{n}_{L,7} = \dot{n}_{L,9} + \dot{n}_{V,9}$	(Total material balance) (2.22c)
	$\tilde{x}_7 \cdot \dot{n}_{L,7} = \tilde{x}_9 \cdot \dot{n}_{L,9} + \tilde{y}_9 \cdot \dot{n}_{V,9}$	(Refrigerant material balance) (2.22d)
	$\dot{n}_{L,7} \cdot \hat{h}_{9'} + \dot{n}_g \cdot \int_{T_9}^{T_{9'}} \hat{c}_{p,g}^{ig}(T) dT$ $= \dot{n}_{L,9} \cdot \hat{h}_{L,9} + \dot{n}_{V,9} \cdot \hat{h}_{V,9}$	(Energy balance) (2.22e)
Evaporator	$p_{10} = \begin{cases} p_{10,max} & , \text{ if } p_{10} \geq p_{10,max} \\ \frac{\dot{n}_{V,10}}{\dot{n}_{V,10} + \dot{n}_g} \cdot p_{sys} & , \text{ otherwise} \end{cases}$	(Evaporator pressure) (2.23a)
	$\dot{n}_{L,7} \cdot \hat{h}_{L,7} + \dot{Q}_{evap}$ $= \dot{n}_{V,10} \cdot \hat{h}_{V,10} + \dot{n}_{L,10} \cdot \hat{h}_{L,10} + \dot{n}_g \cdot \int_{T_{8,g}}^{T_{10}} \hat{c}_{p,g}^{ig}(T) dT$	(Energy balance) (2.23b)
	$\dot{n}_{L,7} = \dot{n}_{L,10} + \dot{n}_{V,10}$	(Total material balance) (2.23c)
	$\tilde{x}_7 \cdot \dot{n}_{L,7} = \tilde{x}_{10} \cdot \dot{n}_{L,10} + \tilde{y}_{10} \cdot \dot{n}_{V,10}$	(Refrigerant material balance) (2.23d)

Continued on next page

Table 2.12: (*Continued*)

Absorber	$\dot{n}_{V,10} \cdot \hat{h}_{V,10} + \dot{n}_{V,7} \cdot \hat{h}_{V,7} + \dot{n}_8 \cdot \hat{h}_{L,8} + \dot{n}_g \cdot \int_{T_{8,g}}^{T_{10}} \hat{c}_{p,g}^{\text{ig}}(T) dT$ $= \dot{n}_{11} \cdot \hat{h}_{L,11} + \dot{Q}_{\text{abs}}$	(Energy balance) (2.24)
Solution heat exchanger	$\dot{n}_{\text{rs}} \cdot (\hat{h}_{L,11} - \hat{h}_1) + \dot{n}_8 \cdot [\hat{h}(T_{\text{ws,in}}, p_{\text{sys}}, \tilde{x}_8) - \hat{h}_{L,8}] = 0$	(Energy balance) (2.25a)
	$\tilde{x}_8 = \tilde{x}_{\text{ws}} = (\tilde{x}_3 \cdot \dot{n}_3 + \tilde{x}_5 \cdot \dot{n}_5) / (\dot{n}_3 + \dot{n}_5)$	(Refrigerant material balance) (2.25b)
	$\dot{n}_8 = (\dot{n}_3 + \dot{n}_5), \dot{n}_{11} = \dot{n}_1$	(Total material balance) (2.25c)

the mixtures into refrigerant-rich vapour that leaves the rectifier at State 6 (*i.e.*, $q_6 = 1$) and the saturated liquid at State 5 (*i.e.*, $q_5 = 0$) where $T_5 = T_3 - \Delta T_{\text{rec}}$. The total and refrigerant material balances expressed in Equations (2.20a) and (2.20b) are written for the rectifier.

Suppose the refrigerant vapour (State 6) leaves the rectifier with a temperature lower than (or equal to) the pure-refrigerant saturation temperature, $T_{\text{sat,refr}}$ evaluated at system pressure. In that case, the vapour leaving the rectifier is of pure refrigerant. Alternatively, suppose the temperature at State 6 is higher than the pure-refrigerant saturation temperature at system pressure. In that case, some absorbent is carried away with refrigerant at State 6 (*i.e.*, impure refrigerant vapour leaves the condenser). Mathematically, this is expressed by Equation (2.20c).

The liquid at State 5 is saturated liquid with mass fraction $\tilde{x}_5 = f_{\text{bub}}(T_5, p_{\text{sys}})$. Thus, the rate of heat dissipated from the rectifier to the heat sink (which is usually ambient), $\dot{Q}_{\text{rect}}$ is evaluated by writing a steady-state energy balance around the rectifier according to Equation (2.20d), where the molar-specific enthalpies at States 5 and 6 are, respectively, $\hat{h}_{L,5} = f(T_5, p_{\text{sys}}, \tilde{x}_5)$ and $\hat{h}_{V,6} = f(T_6, p_{\text{sys}}, \tilde{y}_6)$.

The condenser receives the vapour, which leaves the rectifier (State 6) and rejects the condensation heat to a heat sink. The condensed solution leaves the condenser at State 7. If the pure refrigerant is condensing at a temperature lower than refrigerant saturation temperature, $T_{\text{sat,refr}}$, only liquid refrigerant leaves the condenser (*i.e.*, $\dot{n}_{V,7} = 0$); otherwise, if pure refrigerant partially condenses at $T_{\text{sat,refr}}$, a portion of vapour refrigerant bypasses the evaporator and moves to reservoir. For impure refrigerant, the idea is similar, though instead of $T_{\text{sat,refr}}$, no vapour leaves the condenser only if $T_6 \leq T_{\text{bub}}(p_{\text{sys}}, \tilde{y}_6)$. The rate at which liquid and vapour refrigerant streams leave the condenser can be worked out by solving total and refrigerant material balances, according to Equations (2.21a) and (2.21b). Here respective molar compositions of liquid and vapour phases leaving the condenser are evaluated carrying out vapour-liquid calculations at State 7, such that Equation (2.21c) applies. The rate of heat rejected from the condenser, $\dot{Q}_{\text{cond}}$ can be calculated from the steady-state energy balance described by Equation (2.21d), where the molar-specific

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enthalpies are $\hat{h}_{L,7} = f(T_7, p_{\text{sys}}, \tilde{x}_7)$, and $\hat{h}_{V,7} = f(T_7, p_{\text{sys}}, \tilde{y}_7)$.

The liquid leaving the condenser undergoes further subcooling in the gas-heat exchanger to State 9'. The subcooled refrigerant mixes with pre-cooled auxiliary gas adiabatically. The mixing results in a drop in the mixture temperature, $T_9 = T_{9'} - \Delta T_{\text{exp}}$, and a reduction in partial refrigerant pressure. The adiabatic mixing is accompanied by refrigerant expansion, where a part of the refrigerant is evaporated. According to Dalton's law expressed by Equation (2.22a), where p_9 is refrigerant equilibrium pressure at State 9 is expressed by Equation (2.22b). [95] The composition of vapour generated following the adiabatic mixing is $\tilde{y}_9 = f(T_9, p_9, \tilde{x}_9)$, the total material balance described by Equation (2.22c), the refrigerant-material balance in Equation (2.22d), and the adiabatic energy balance which is expressed by Equation (2.22e) complement Equations (2.22a) and (2.22b) to solve for $\tilde{x}_9$, $\tilde{n}_{L,9}$ and $\tilde{n}_{V,9}$.

The evaporator removes heat from a low-temperature heat source (cooling application). The heat removed by the evaporator results in more refrigerant evaporation from State 9 to State 10 and a corresponding increase in partial refrigerant pressure is expressed by Equation (2.23a), [95] where the maximum partial pressure that the refrigerant can reach, corresponds to complete vaporisation of the refrigerant so that $p_{10,\text{max}} = p_{\text{sys}} \cdot \tilde{n}_{L,7} / (\tilde{n}_{L,7} + \tilde{n}_g)$. Corresponding to $p_{10,\text{max}}$, the equilibrium temperature is $T_{10,\text{max}} = T_{\text{dew}}(p_{10,\text{max}}, \tilde{x}_{L,7})$. The net rate of cooling, $\dot{Q}_{\text{evap}}$ corresponds to the net change of flow enthalpies crossing the evaporator/gas-heat-exchanger control volume expressed by Equation (2.23b) (see Figure 1.11), where molar specific enthalpies of liquid and vapour phases at State 10 are $\hat{h}_{L,10} = f(T_{10}, p_{10}, \tilde{x}_{10})$, and $\hat{h}_{V,10} = f(T_{10}, p_{10}, \tilde{y}_{10})$. Liquid and vapour molar flowrates, $\tilde{n}_{L,10}$, and $\tilde{n}_{V,10}$ can be evaluated solving total and refrigerant material balances in Equations (2.23c) and (2.23d). Molar compositions of respective phases leaving the evaporator are evaluated by solving vapour-liquid equilibrium relations; the liquid and vapour mole fractions, $\tilde{x}_{10}$ and $\tilde{y}_{10}$, are thereby evaluated as functions of temperature, pressure and (overall) mixture composition.

The refrigerant-gas mixture that leaves the evaporator at State 10 mixes with any bypass refrigerant, $\tilde{n}_{V,7}$ and enters the absorber/reservoir control volume where the refrigerant is absorbed into the weak solution. The rate of heat rejected from the absorber, $\dot{Q}_{\text{abs}}$ is described by Equation (2.24).

The weak-solution temperature, $T_{\text{ws,in}}$, is evaluated by solving the solution-heat-exchanger energy balance in Equation (2.25a), assuming it is perfectly insulated. The composition of the weak solution can be expressed by Equation (2.25b), where $\dot{n}_8$ is the molar flowrate of

weak-solution, and $\dot{n}_{11}$ is the molar flowrate of rich-solution evaluated by Equation (2.25c). The molar-specific enthalpy of rich solution leaving the reservoir at State 11 is $\hat{h}_{L,11} = f(T_{11}, p_{11}, \tilde{x}_{rs})$, with $p_{11} = p_{\text{bub}}(T_{11}, \tilde{x}_{rs})$. The molar-specific enthalpy of weak solution leaving the solution heat exchanger at State 8 is $\hat{h}_{L,8} = f(T_8, p_8, \tilde{x}_8)$, with $p_8 = p_{\text{bub}} = (T_8, \tilde{x}_8)$.

As any refrigeration system, the thermodynamic performance of DAR is indicated by its coefficient of performance, COP , given by

$$COP = \frac{\dot{Q}_{\text{evap}}}{\dot{Q}_{\text{gen}}}. \quad (2.26)$$

Several assumptions are made following standard practice in the literature. these assumptions are listed in Table 2.13. To validate the current model, the inputs listed in Table 2.13 are provided to return cooling capacity, mass flowrates, and heat dissipated from different system sub-components.

Table 2.13: Basic DAR model assumptions and model inputs used for model validation.

Model assumptions are:

- the solution heat exchanger and generator are well-insulated;
- pressure drops across the cycle are neglected;
- the temperature difference between liquid condensate at bubble pump top and liquid reflux from the rectifier ($\Delta T_{\text{rec}} = T_3 - T_5$) is 5°C; [98]
- the temperature drop due to expansion is taken from experimental observation to be $\Delta T_{\text{exp}} = T_{9'} - T_9 = 18.5 - 0.15 \times p_{\text{ch}}$; [95]
- the mixture of auxiliary gas and vapour-refrigerant is an ideal-gas mixture, and the auxiliary gas is ideal under operating conditions;
- lastly, all the refrigerant vapour that enters the absorber is entirely absorbed, whereas the auxiliary gas is completely incondensable.

Input variables for validation are:

- system pressure, $p_{\text{ch}} = p_{\text{sys}}$;
- working fluid and auxiliary gas;
- rate of heat available at the generator, $\dot{Q}_{\text{gen}}$;
- refrigerant-rich solution composition, $\tilde{x}_{rs}$;
- temperatures: $T_1, T_2, T_3, T_6, T_7, T_8, T_{9'}, T_{8,g}, T_{10}$, and T_{11} .

After listing the equations involved in the adopted DAR model, a solution procedure is presented. In Figure 2.11, an algorithm adopted for solving the presented model is set out. To ensure model convergence, the model is initialised as illustrated in Figure 2.11. Even for a DAR with a fully-attached bubble pump, the model is initialised by: assuming values for vapour

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quality at the expansion and evaporator outlet refrigerant partial pressure, q_9 and p_{10} ; and for fully-attached DAR systems, the initialisation also includes assuming a semi-attached bubble pump (*i.e.*, using Equation (2.18c) instead of Equation (2.18b) for initialisation). The initialised model is solved to provide an initial guess for the model to be solved. Once solved, post-calculations are carried out to evaluate the coefficient of performance. The model is solved in gPROMS[®] ModelBuilder versions 6.0.4 and 7.0.7 [126]. The block decomposition non-linear solver (BDNLSOL) is employed; this rearranges a system of non-linear equations into smaller blocks of equations that take triangular form. The MA48 linear algebraic solver developed by Duff and Reid [257] is used by gPROMS, and the Newton-Raphson [124] method is deployed to solve non-linear blocks where Jacobians are evaluated analytically whenever possible. A solution convergence tolerance of 10^{-5} is used. Working-fluid thermodynamic functions are evaluated using the gSAFT/gPROPERTIES tool implemented in gPROMS[®] ModelBuilder, where the SAFT- γ Mie EoS is used and SAFT- γ Mie parameters listed in Tables 2.2 to 2.5 are provided to the modelling software.

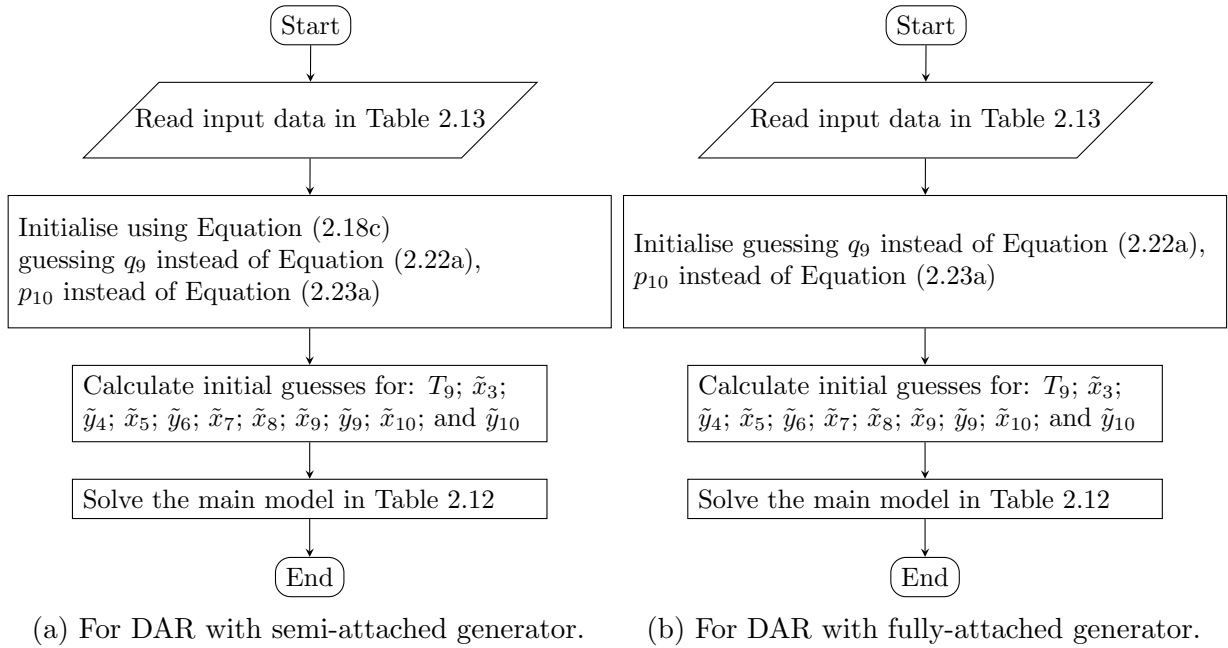


Figure 2.11: DAR thermodynamic-model solution procedure as implemented in gPROMS modelling environment.

The thesis is concerned with the use of DAR for household refrigeration and chilled food storage. Thus, all further validations, comparisons and simulations are carried out, taking the cooling temperature to be 8°C to -12°C . Two sets of data were considered to validate the proposed model. Most of the experimental data used in this thesis represent an $\text{NH}_3\text{--H}_2\text{O--H}_2$ system at

the CEP Laboratory, Imperial College London. A description of the experiment can be found in the work of Najjaran *et al.* [85] and is also described by Harraz *et al.* [63,64]. The resulting experimental data, obtained under various operating conditions (three pressure levels (15 bar, 18 bar and 21 bar), and three charging compositions (25 wt.%, 30 wt.% and 38 wt.% refrigerant)), have been detailed by Najjaran [258]. Validation of the present framework was carried out over a range of heat inputs from 150 W to 500 W.

The second set of data used for comparison represents an $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$ DAR system with heat input of 70 W, under charge pressures of 4 bar, 4.65 bar, 5.30 bar and 6 bar and a charge composition of 17 wt.% refrigerant. A comparison of the present framework against the work done by Lee *et al.* [145] is presented over generator temperatures, T_2 ranging from 114 °C to 168 °C. Input data for the $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$ system are available in Refs. [92,145]. It is important to mention that for $\text{NH}_3\text{-H}_2\text{O-H}_2$, Equation (2.18b) is used to describe the conservation of energy in the generator, and Equation (2.18c) is used to describe the conservation of energy in the generator for $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$ system.

2.3.3 Current DAR model validation

The quality of the proposed DAR thermodynamic model described in Section 2.3.2 is assessed. Experimental DAR data for $\text{NH}_3\text{-H}_2\text{O-H}_2$ obtained from Najjaran [258] are used as input to carry out calculations representing various operating conditions: three pressure levels 15 bar, 18 bar and 21 bar, and three charging compositions 25 wt.%, 30 wt.% and 38 wt.% refrigerant. Validation of the present framework is carried out over a heat-input range of 150 W to 500 W. In addition, a further validation of the present framework, for the $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$ system, is presented over a range of generator temperature, T_2 , from 114 °C to 168 °C, using input data taken from Refs. [92,145].

In Figure 2.12 parity plots of calculated and experimentally determined COP for the two sets of data mentioned above are presented to demonstrate the model’s applicability. For the $\text{NH}_3\text{-H}_2\text{O-H}_2$ data set, the model average deviation between the calculated and measured COP is ± 0.036 , which corresponds to an average deviation between calculated and measured cooling power of 10 W or %AAD of ± 26 %. One can discern from Figure 2.12a that most COP data for an $\text{NH}_3\text{-H}_2\text{O-H}_2$ fall between 0.1 and 0.2. The model performs better at the two lower pressure levels (15 bar and 18 bar), especially when the heat input is not low.

2.3. DAR THERMODYNAMIC MATHEMATICAL DESCRIPTION

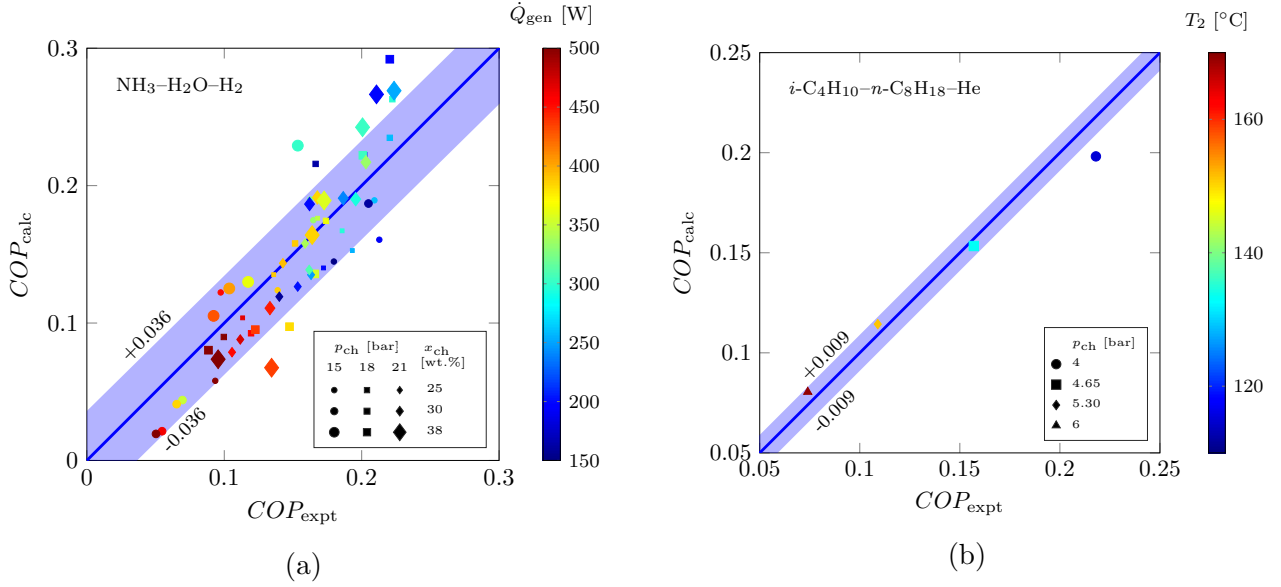


Figure 2.12: Validation of the presented DAR model in Table 2.12 against (a) $NH_3-H_2O-H_2$ DAR experiments performed by Najjaran [258], and (b) simulations by Lee *et al.* [145] on a commercial $i-C_4H_{10}-n-C_8H_{18}-He$ DAR unit. The $NH_3-H_2O-H_2$ system in (a) delivers cooling at 5 °C under three different charging pressures (15 bar, 18 bar and 21 bar), three different charging compositions (25 wt.%, 30 wt.% and 38 wt.%) and variable heat power inputs (150 W to 500 W); COP predictions made using this model lie within ± 26 %. The $i-C_4H_{10}-n-C_8H_{18}-He$ unit considered in (b) is powered by a generator delivering 70 W and charged with 17 wt.% refrigerant-rich solution, under four charging pressures (4 bar, 4.65 bar, 5.30 bar and 6 bar) and a variable generator temperature (114 °C to 168 °C); COP predictions made using the model lie within ± 6.4 % of the experimental estimates. Symbol sizes reflect the variation of charging compositions, symbol colours map generator heat input in (a) and generator temperature in (b), and symbol shapes represent different charging pressures.

The model predictions deviate less from the experimental data for the $i-C_4H_{10}-n-C_8H_{18}-He$ system. The model average deviation in this case is ± 0.009 (as seen in Figure 2.12b) corresponding a deviation of only 0.6 W or %AAD of ± 6 %. We note that further DAR data for the $i-C_4H_{10}-n-C_8H_{18}-He$ system have recently been published by Choi *et al.* [259]; these data were not available at the time of our calculations but could be used in future to extend the validation of the present model.

A key component in any DAR unit is the bubble pump; it is the heart of a DAR cycle. Some authors (*see* Refs. [83, 94, 100, 102, 260–264]) have investigated bubble-pump flow; they performed experiments on standalone bubble-pump systems with various working-fluid pairs to simulate conditions inside a DAR bubble pump. White [262] and Rattner and Garimella [94] have confirmed that, for a DAR to run efficiently, the flow should exhibit a slug-to-churn two-phase flow. With a few exceptions (*see* Ref. [74]), We note in passing that, to the best of our knowledge,

there is no other existing study in which flow rates were measured for an operational DAR unit.

For the design of a DAR unit, it is essential to decide the appropriate heat power input that is sufficient to activate the circulation of the refrigerant. For a bubble pump to operate efficiently, the heat input at the generator should generate a two-phase mixture at State 2 characterised by a slug-to-churn flow pattern. [66, 77, 82, 84, 91, 92] In two-phase upward slug flow, there are large enough vapour plugs to lift the liquid slugs up the bubble pump as illustrated in Figure 1.10. The boundaries of the slug-to-churn flow operating range, as suggested by Taitel *et al.* [93] for upward isothermal two-phase flows, are shown in Figure 1.12. In the current analysis, liquid-phase superficial velocity ($u_{L,2}$),

$$u_{L,2} = \frac{4 \cdot (1 - q_2) \cdot \dot{n}_{rs} \cdot \tilde{v}_{L,2}}{\pi \cdot d_{\text{gen,in}}^2}, \quad (2.27)$$

should be less than the bubble-slug transition velocity, $u_{L,BS}$ calculated according to

$$u_{L,BS} = u_{V,2} \cdot \frac{(1 - \alpha_{BS})}{\alpha_{BS}} - (1 - \alpha_{BS}) \cdot \left\{ 1.53 \cdot \left[\frac{g \cdot (\rho_{L,2} - \rho_{V,2}) \cdot \gamma_{T,2}}{\rho_{L,2}^2} \right]^{\frac{1}{4}} \right\}, \quad (2.28)$$

Taitel *et al.* recommended a value of 0.25 for the bubble-to-slug transition void fraction (α_{BS}) [93].

To avoid annular flow, the vapour-phase superficial velocity ($u_{V,2}$)

$$u_{V,2} = \frac{4 \cdot q_2 \cdot \dot{n}_{rs} \cdot \tilde{v}_{V,2}}{\pi \cdot d_{\text{gen,in}}^2}, \quad (2.29)$$

should be less than slug-annular transition velocity, $u_{V,an}$ calculated as

$$u_{V,an} = 3.1 \cdot \left[\frac{g \cdot (\rho_{L,2} - \rho_{V,2}) \cdot \gamma_{T,2}}{\rho_{V,2}^2} \right]^{1/4}. \quad (2.30)$$

In Figure 2.13 an analysis for all the experimental data for the $\text{NH}_3\text{--H}_2\text{O--H}_2$ DAR system is depicted in Figure 2.13a), while the data for $i\text{-C}_4\text{H}_{10}\text{--}n\text{-C}_8\text{H}_{18}\text{--He}$ is presented in Figure 2.13b).

One can see from these two flow maps that all simulations that correspond to data from Najjarian [258] and Lee *et al.* [145] fall within a bubble-pump operating range indicating a possible two-phase flow in slug-to-churn flow. According to Equation (2.30), the transition velocity to annular flow is independent of liquid-phase superficial velocity and is a function only of the difference in phase densities at generator outlet conditions (State 2). On the other hand,

2.3. DAR THERMODYNAMIC MATHEMATICAL DESCRIPTION

according to Equation (2.28), the bubble-to-slug transition velocity can be seen to correlate with vapour-phase superficial velocity linearly. Using such maps is important in defining the appropriate heat input to a given DAR unit. [95]

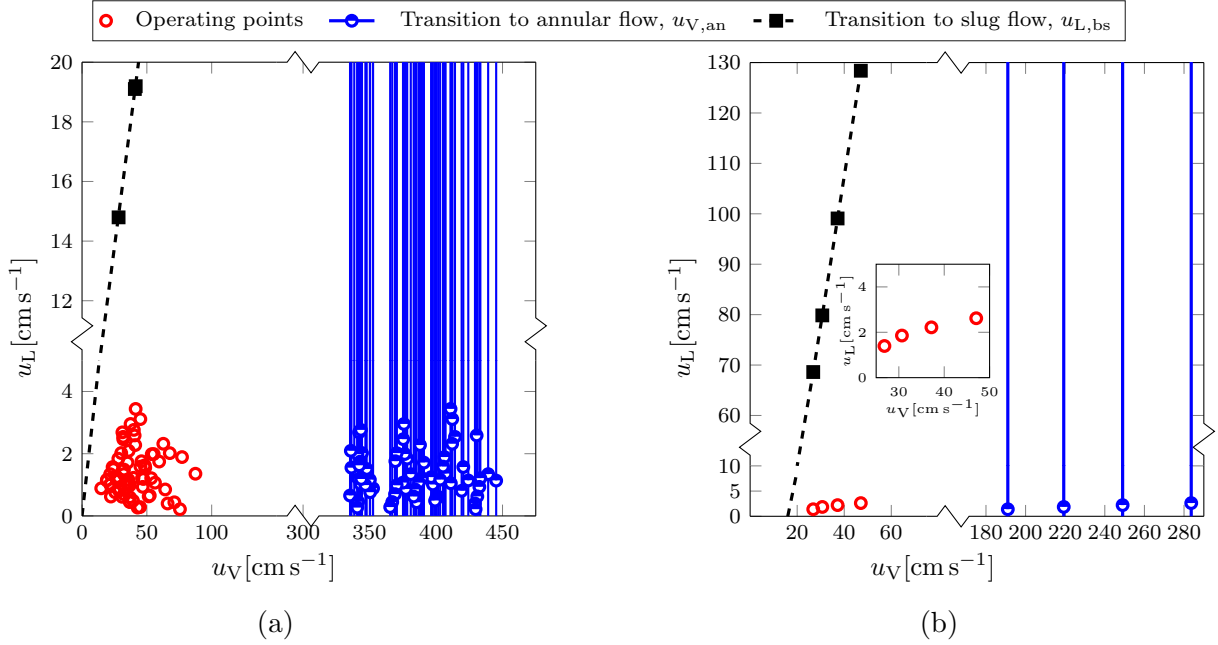


Figure 2.13: Bubble-pump two-phase flow maps for DAR using different working fluids, according to the model presented by Taitel *et al.* [93]. (a) The $\text{NH}_3\text{-H}_2\text{O-H}_2$ system with DAR experiments carried out by Najjaran [258]; (b) the $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$ system with data from work done by Lee *et al.* [145].

Another key operation in a DAR cycle is absorption. The vapour refrigerant leaving the evaporator is condensed by contacting the weak solution (which is rich in absorbent), so it is easily pumped. Without a detailed model that captures the absorption process, the absorption capacity of a given refrigerant-absorbent pair can be assessed thermodynamically using Henry's law or equilibrium solubility constants. According to Henry's law, the vapour pressure of a solute is proportional to the liquid-phase equilibrium concentration of solute in a given solvent; the constant of proportionality is called Henry's constant, $\mathcal{H}$. [265] Applying Henry's law to a DAR absorber:

$$\mathcal{H} = \frac{\tilde{y}(p_{\text{abs}}, \tilde{x}_{\text{ws}})}{\tilde{x}_{\text{ws}}} \cdot \frac{p_{\text{abs}}}{\tilde{\rho}_{\text{L},8}}, \quad (2.31)$$

where $p_{\text{abs}} = f(T_8, \tilde{x}_{\text{ws}})$. It is important to map the solubility of different refrigerant-absorbent pairs to assess the thermodynamic suitability of a given working-fluid pair for DAR operation. Following Figure 2.14, higher solubility is attained at lower Henry's constant. In Figure 2.14 Henry's constant as calculated using Equation (2.31) is mapped for the two working-fluid pairs

considered in our DAR-model validation. It is evident from Figure 2.14a that $\mathcal{H}_{\text{NH}_3-\text{H}_2\text{O}} \leq 5 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1}$ for all DAR experiments; this value is lower than the lowest value for the second working pair as read from Figure 2.14b ($\mathcal{H}_{i\text{-C}_4\text{H}_{10}-n\text{-C}_8\text{H}_{20}} \leq 5 \times 10^{-4}$ for $i\text{-C}_4\text{H}_{10}-n\text{-C}_8\text{H}_{18}$ -He DAR unit). Ammonia solubility in water should be considered a special case due to the basic nature of the solution, as mentioned earlier. Ammonia partially dissociates in water to form ammonium ions (NH_4^+) and hydroxide ions (OH^-).

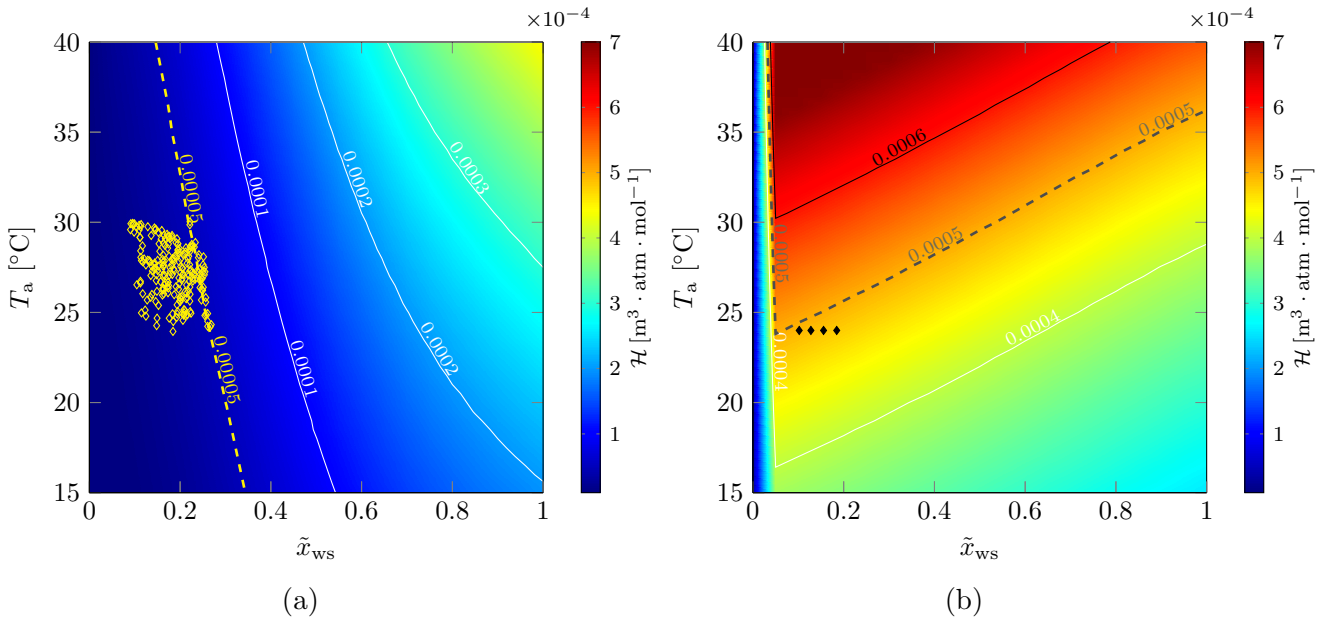


Figure 2.14: Henry's constant maps for two different working-fluid pairs: (a) the $\text{NH}_3\text{-H}_2\text{O}$ system with DAR experiments carried out by Najjaran [258]; (b) the $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}$ system with data from work performed by Lee *et al.* [145].

2.4 Parametric sensitivity analysis for some low-GWP alkane-based working fluids

2.4.1 Case study definition and input parameters

One of the uses of the presented framework is the assessment of any organic-based working-fluid alternatives. To demonstrate this, some working-fluid pairs are considered. The framework is used to evaluate steady-state cooling capacities and coefficients of performance for a DAR unit charged with 20 mol.% refrigerant-rich solution, pressurised with helium and cooled to operate under variant ambient temperatures and heat power inputs. Cooling is received at 5 $^{\circ}\text{C}$,

resembling the operation of a domestic fridge. The working-fluid candidate list includes six different refrigerants with four different absorbents, forming 24 assessed pairs. Six refrigerants are considered. Three of these are 2-methylalkanes: iso-butane ($i\text{-C}_4\text{H}_{10}$); 2-methylbutane ($2\text{-C}_5\text{H}_{12}$); and 2-methylpentane ($2\text{-C}_6\text{H}_{14}$), while the other three are normal alkanes: n-butane ($n\text{-C}_4\text{H}_{10}$); n-pentane ($n\text{-C}_5\text{H}_{12}$); and n-hexane ($n\text{-C}_6\text{H}_{14}$). Four absorbents are considered including two 2-methylalkanes and two normal alkanes: 2-methylheptane ($2\text{-C}_8\text{H}_{18}$), 2-methyloctane ($2\text{-C}_9\text{H}_{20}$), n-octane ($n\text{-C}_8\text{H}_{18}$), and n-nonane ($n\text{-C}_9\text{H}_{20}$) respectively. From a design point of view, the charging pressure of a given DAR unit will rely primarily on the ambient pressure. Thus, a wide range of ambient temperatures is considered to represent a wide range of climate classes with a minimum of 2 bar as a design charging pressure (for those refrigerants which may have sub-atmospheric vapour pressures at ambient conditions). Mathematically this statement is equivalent to:

$$p_{\text{ch}} = \max [2 \text{ bar}, p_{\text{sat,ref}} (T_{\text{a}} + 5)]. \quad (2.32)$$

It is interesting to establish some expression that can allow relating generator temperature to the rate of heat received by the generator. A simple model used for predicting the mean generator-wall temperature needed to activate the system is:

$$T_{\text{gen,w}} = T_{\text{bub,rs}} + \frac{q''}{h_{\text{b,w}}}, \quad (2.33)$$

where q'' is the heat flux calculated at the inner wall of the generator $\left(\frac{\dot{Q}_{\text{gen}}}{\pi d_{\text{gen,in}} l_{\text{gen}}}\right)$ with $d_{\text{gen,in}}$ and l_{gen} are, respectively, the generator-tube inner diameter and length. $T_{\text{gen,w}}$ is the temperature at the generator wall and $T_{\text{bub,rs}}$ is the bubble temperature of rich-solution at DAR charge pressure. Cooper correlation [266] is adopted to calculate the boiling heat transfer coefficient at the generator wall, $h_{\text{b,w}}$. Rattner and Garimella [84], and Freeman [95] used Cooper correlation to estimate the heat transfer coefficient at the generator wall. Although being a simplification, Cooper's correlation for nucleate boiling heat transfer coefficient can be used to predict heat transfer coefficient in small tubes even for flow boiling heat transfer pretty well. [267, 268]

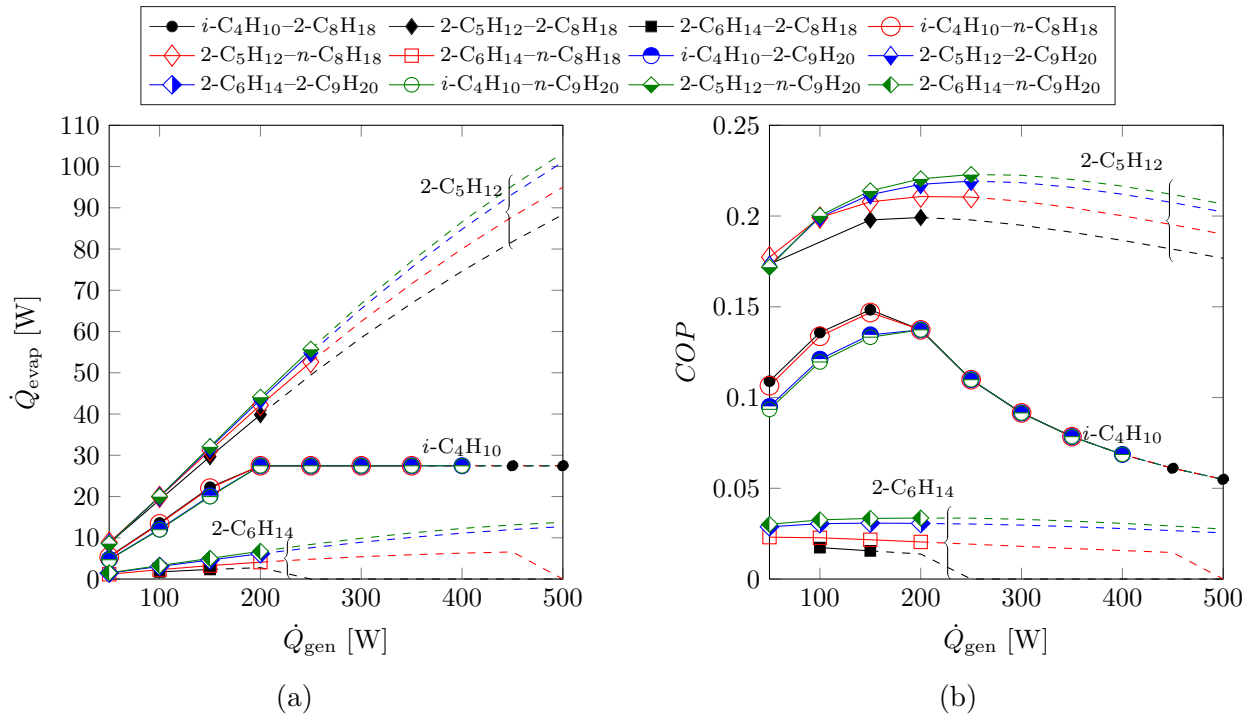


Figure 2.15: Parametric sensitivity analysis of 12 working-fluid pairs including three refrigerants and four absorbents for running a DAR unit charged with 20 mol.% refrigerant-rich solution, pressurised with helium and rejecting heat at ambient temperature (25 °C): (a) $\dot{Q}_{\text{evap}}$; (b) COP . Dashed curves indicate the thermodynamic cooling capacity or COP while the two-phase flow is annular (or bubbly, as in the case of using $2\text{-C}_6\text{H}_{14}$).

2.4.2 Selected sensitivity analysis results

As mentioned earlier, the presented framework can be used to assess organic-based working-fluid alternatives. More working-fluid pairs are considered. In Figures 2.15 and 2.16, steady-state cooling rates and coefficients of performance are presented for a DAR unit charged with 20 mol.% refrigerant-rich solution, pressurised with helium and rejects heat into the air with ambient temperature (25 °C). Cooling is received at 5 °C, which resembles the operation of a domestic fridge. The candidate list includes six different refrigerants with four different absorbents to form 24 assessed pairs. Being less volatile, pentanes produce about three-fold more cooling than butanes. Although hexanes are also much less volatile, being closer to octanes and nonanes in size, they cannot offer suitable pairs for cooling.

Four simple organic working-fluid pairs are further investigated. The variation of carbon-chain lengths in both refrigerants and absorbents are introduced in one-methylene-group ($>\text{CH}_2$) increments. The choice of helium as the auxiliary gas is consistent for each studied pair as it is inert toward all organic compounds under nearly all operating conditions. Our results

2.4. PARAMETRIC SENSITIVITY ANALYSIS FOR SOME LOW-GWP ALKANE-BASED WORKING FLUIDS

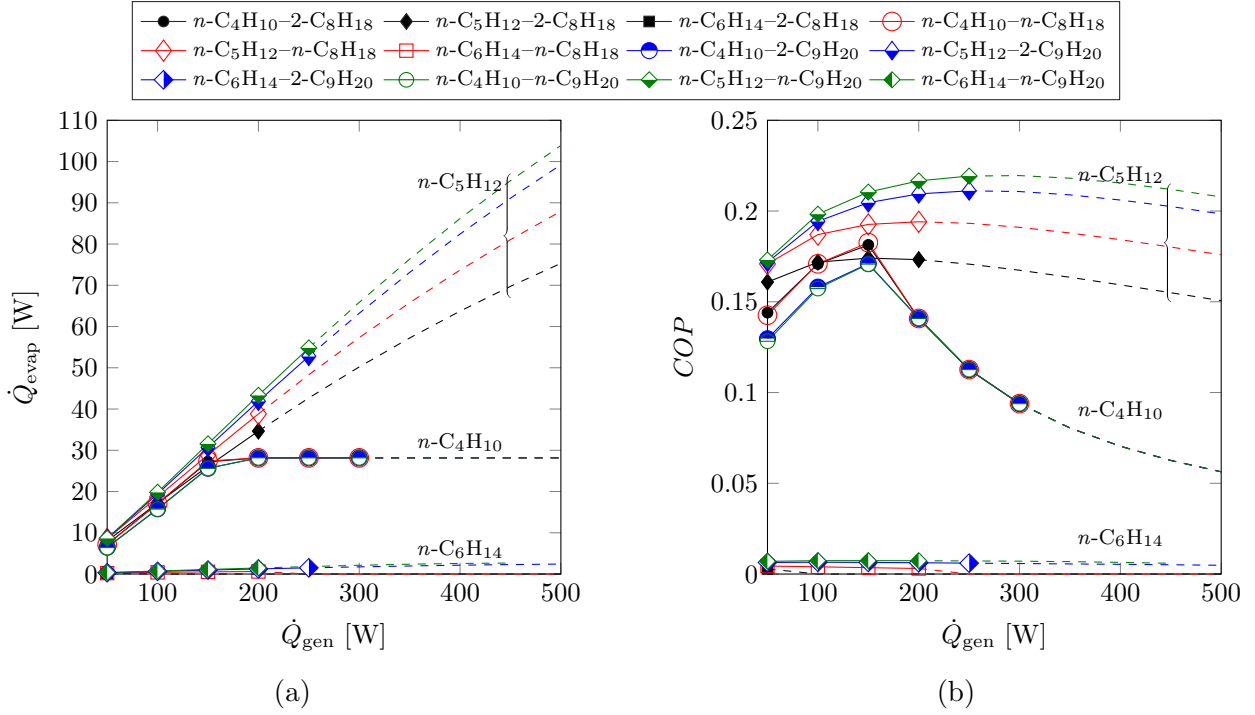


Figure 2.16: Parametric sensitivity analysis of 12 working-fluid pairs including three n-alkanes as refrigerants and four absorbents for running a DAR unit charged with 20 mol.% refrigerant-rich solution, pressurised with helium and rejecting heat at ambient temperature (25 °C): (a) $\dot{Q}_{\text{evap}}$; (b) COP. Dashed curves indicate the thermodynamic cooling capacity or COP while the two-phase flow is annular.

are presented in four sets of colour maps depicting DAR performance metrics. In the first of these, collected in Figure 2.17, the effect of the choice of working-fluid pair on cooling capacity is illustrated. Comparing Figure 2.17b to Figure 2.17a, and Figure 2.17d to Figure 2.17c, one can see that increasing the number of CH_2 groups in the absorbent chain (moving from $n\text{-C}_8\text{H}_{18}$ to $n\text{-C}_9\text{H}_{20}$), can widen the operating range, shifting forward the heat input ($\dot{Q}_{\text{gen}}$) limit at which the flow in the bubble pump is likely to turn annular (where $u_V \geq u_{V,\text{an}}$). On the other hand, comparing Figure 2.17c to Figure 2.17a, and Figure 2.17d to Figure 2.17b, it can be easily observed that the opposite is true of the refrigerant chain. Increasing the number of CH_2 groups in the refrigerant chain significantly increases cooling capacity. For the same refrigerant, a longer-chain absorbent does not substantially affect the cooling ability, provided that the rectifier is sufficiently well designed to recover 100% of the refrigerant.

However, as can be observed in Figure 2.18, pairing $i\text{-C}_4\text{H}_{10}$ with $n\text{-C}_9\text{H}_{20}$, instead of $n\text{-C}_8\text{H}_{18}$, can slightly lower the locus of COP and shift it towards slightly higher heat inputs, thanks to higher generation temperature needed (as noticed in Figure 2.19) and higher rich-solution circulation rates (see Figure 2.20). Higher rates of vapour generation limit the operation of

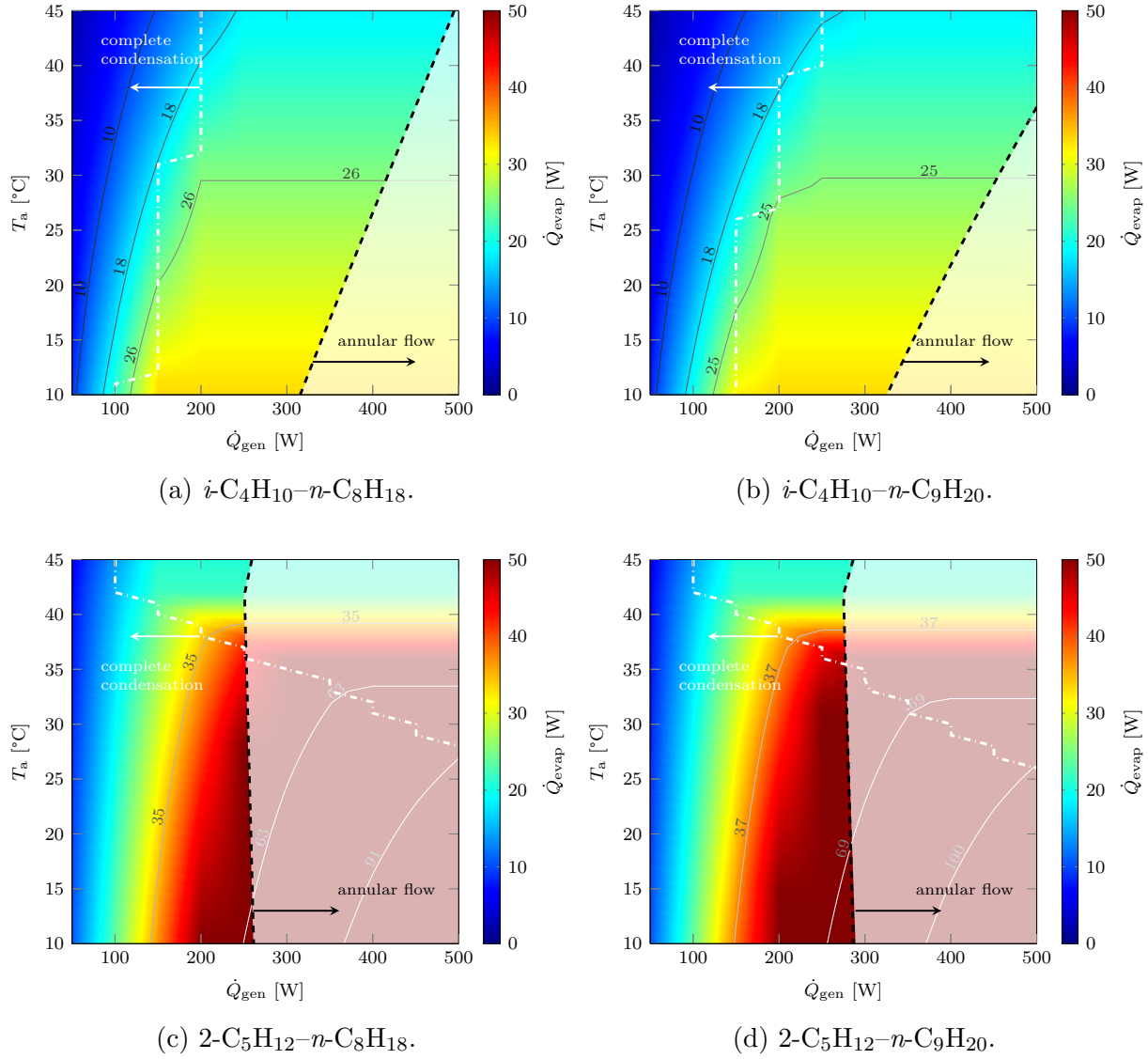


Figure 2.17: Variation of cooling capacity of a DAR unit charged with 20 mol.% for various working-fluid pairs: (a) $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$; (b) $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_9\text{H}_{20}\text{-He}$; (c) $2\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$; and (d) $2\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_9\text{H}_{20}\text{-He}$. In each panel, the area to the right of the dashed black curve represents the operating region, where the two-phase in the bubble pump is likely annular. In contrast, the area to the left of the white dash-dotted line represents the operating range where complete condensation is attained in the condenser.

the condenser. Thus, more vapour bypasses the evaporator, which limits the cooling capacity and decreases the coefficient of performance. The case of $2\text{-C}_5\text{H}_{12}$ differs, however. The vapour pressure of $2\text{-C}_5\text{H}_{12}$ is lower than atmospheric pressure for temperatures below 26°C , and reaches 2 bar at 47°C . Thus, charge pressures for simulated $2\text{-C}_5\text{H}_{12}$ DAR systems are bounded by 2 bar up to ambient temperatures of 42°C . Unlike the case with $i\text{-C}_4\text{H}_{10}$, pairing $n\text{-C}_9\text{H}_{20}$ with $2\text{-C}_5\text{H}_{12}$ offers a higher coefficient of performance compared to pairing with $n\text{-C}_8\text{H}_{18}$ at higher heat inputs, as can be observed in Figure 2.18. It can also be observed that, for the same

2.4. PARAMETRIC SENSITIVITY ANALYSIS FOR SOME LOW-GWP ALKANE-BASED WORKING FLUIDS

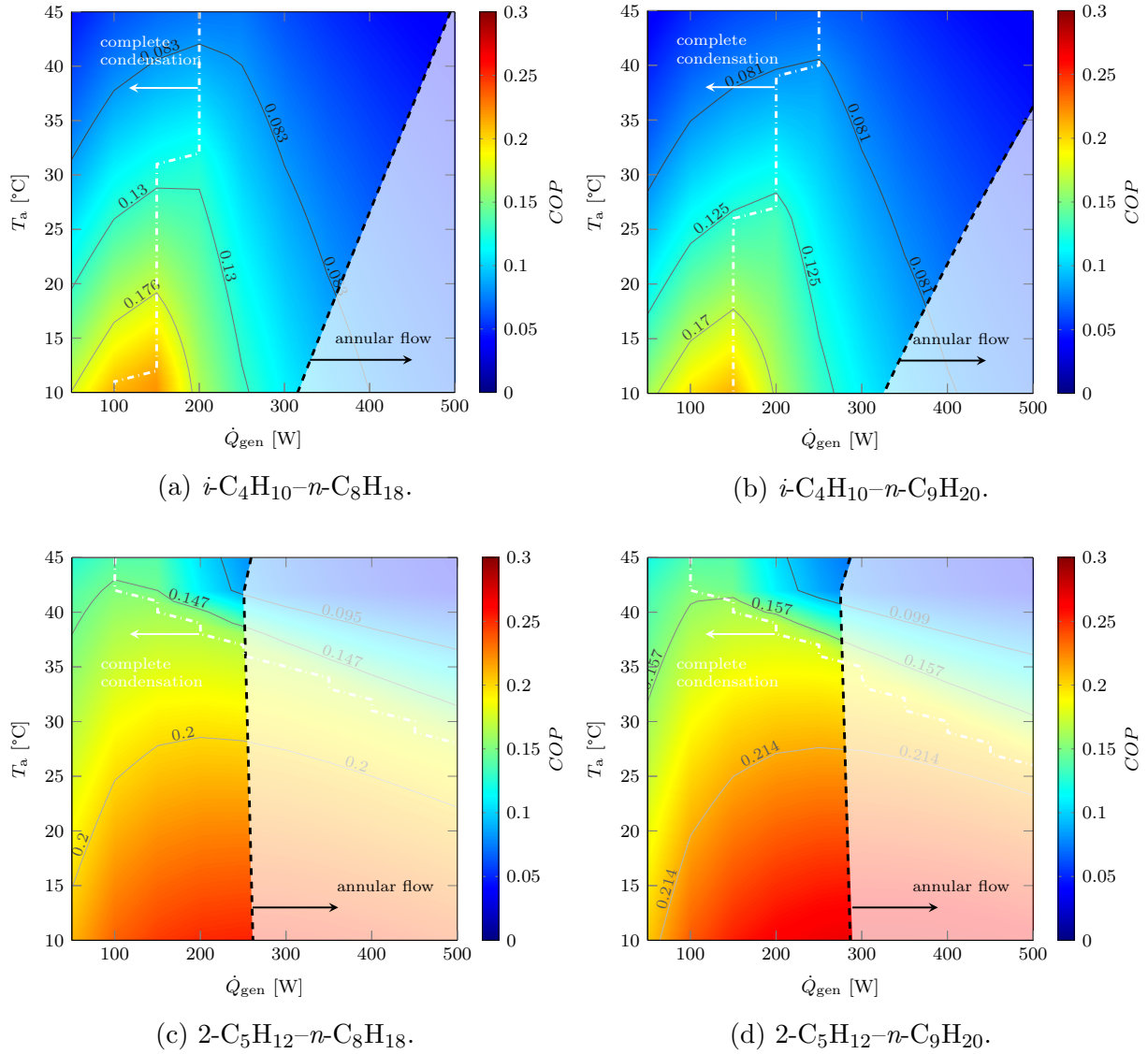


Figure 2.18: Variation of the coefficient of performance of a DAR unit charged with 20 mol.% for various working-fluid pairs: (a) $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$; (b) $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_9\text{H}_{20}\text{-He}$, (c) $2\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$; and (d) $2\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_9\text{H}_{20}\text{-He}$. In each panel, the area to the right of the dashed black curve represents the operating region where two-phase flow in the bubble pump is likely to be annular. In contrast, the area to the left of the white dash-dotted line represents the operating range where complete condensation is attained in the condenser.

absorbent with the same charging pressure and composition, the longer-chain refrigerant shifts up the coefficient of performance.

It can be demonstrated in Figure 2.19 that, for the same refrigerant and operating conditions, a higher generation temperature is required when the size of the absorbent carbon chain is increased. For DAR systems running using $2\text{-C}_5\text{H}_{12}$, the generator temperature becomes less sensitive to ambient temperature and the heat input, unlike the case of using $i\text{-C}_4\text{H}_{10}$, for which the generator temperature is more sensitive to ambient temperature (or charge pressure) than it

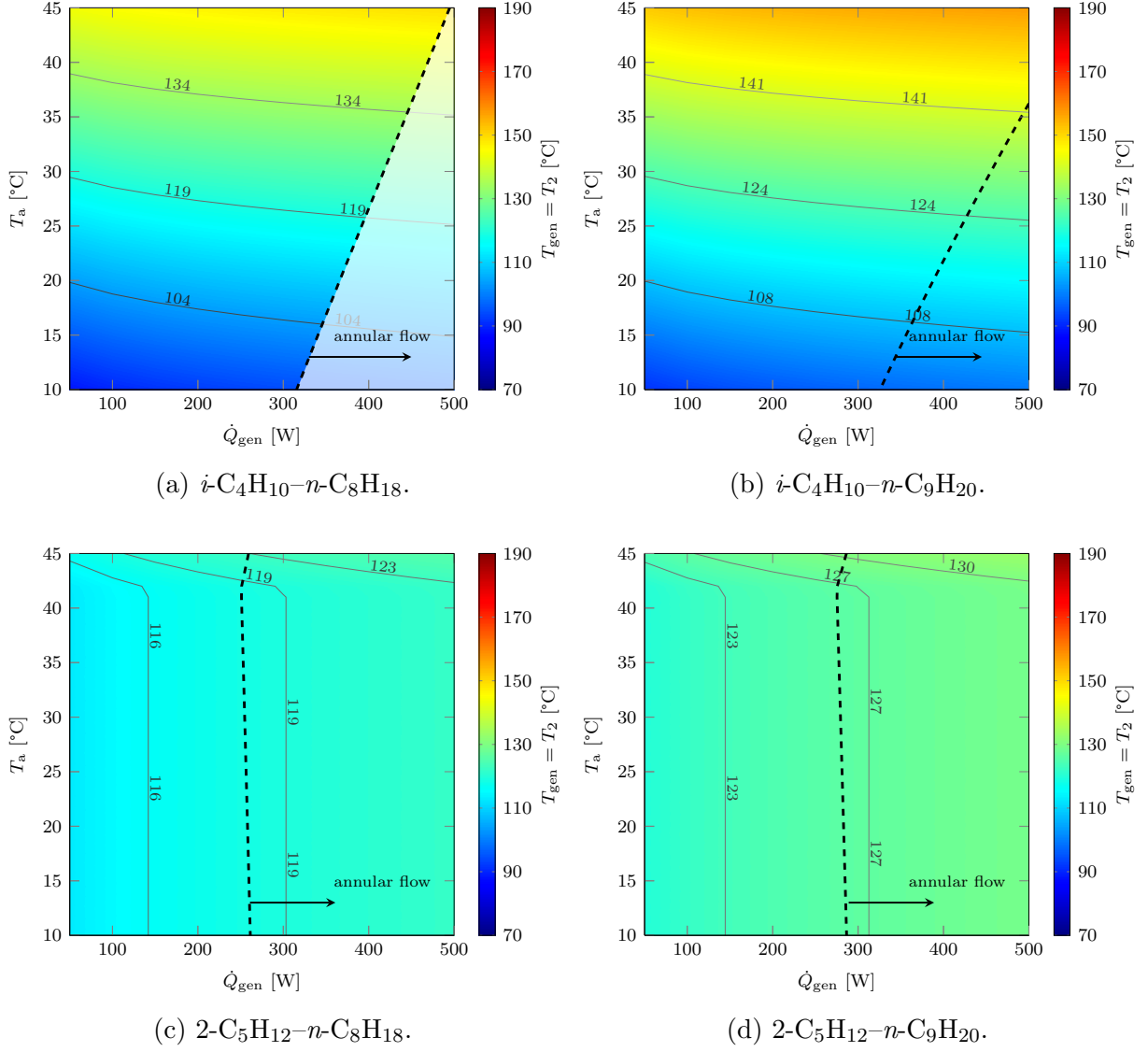


Figure 2.19: Variation of generator temperature in a DAR unit charged with 20 mol.% for various working-fluid pairs: (a) $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$; (b) $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_9\text{H}_{20}\text{-He}$; (c) $2\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$; and (d) $2\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_9\text{H}_{20}\text{-He}$. In each panel, the area to the right of the dashed black curve represents the operating region where two-phase flow in the bubble pump is likely to be annular.

is to the generator heat input. On the other hand, in Figure 2.20, the rich-solution circulation flowrate is shown to be more sensitive to heat input than it is to ambient temperature. For the same refrigerant, a longer-chain absorbent results in a higher rich-solution circulation rate, while for the same absorbent, longer-chain refrigerant results in a lower rich-solution circulation rate.

As highlighted in Figures 2.17 and 2.18, for a given system, cooling capacity and COP deteriorate as ambient temperature rises. As can be expected after examining Figures 2.15 and 2.16, pentanes can be recommended as refrigerants to provide cooling powered by a 250 W heat input with COP between 0.245 and 0.269. When the ambient temperature is low (below 18 °C), $2\text{-C}_5\text{H}_{12}$ is

2.4. PARAMETRIC SENSITIVITY ANALYSIS FOR SOME LOW-GWP ALKANE-BASED WORKING FLUIDS

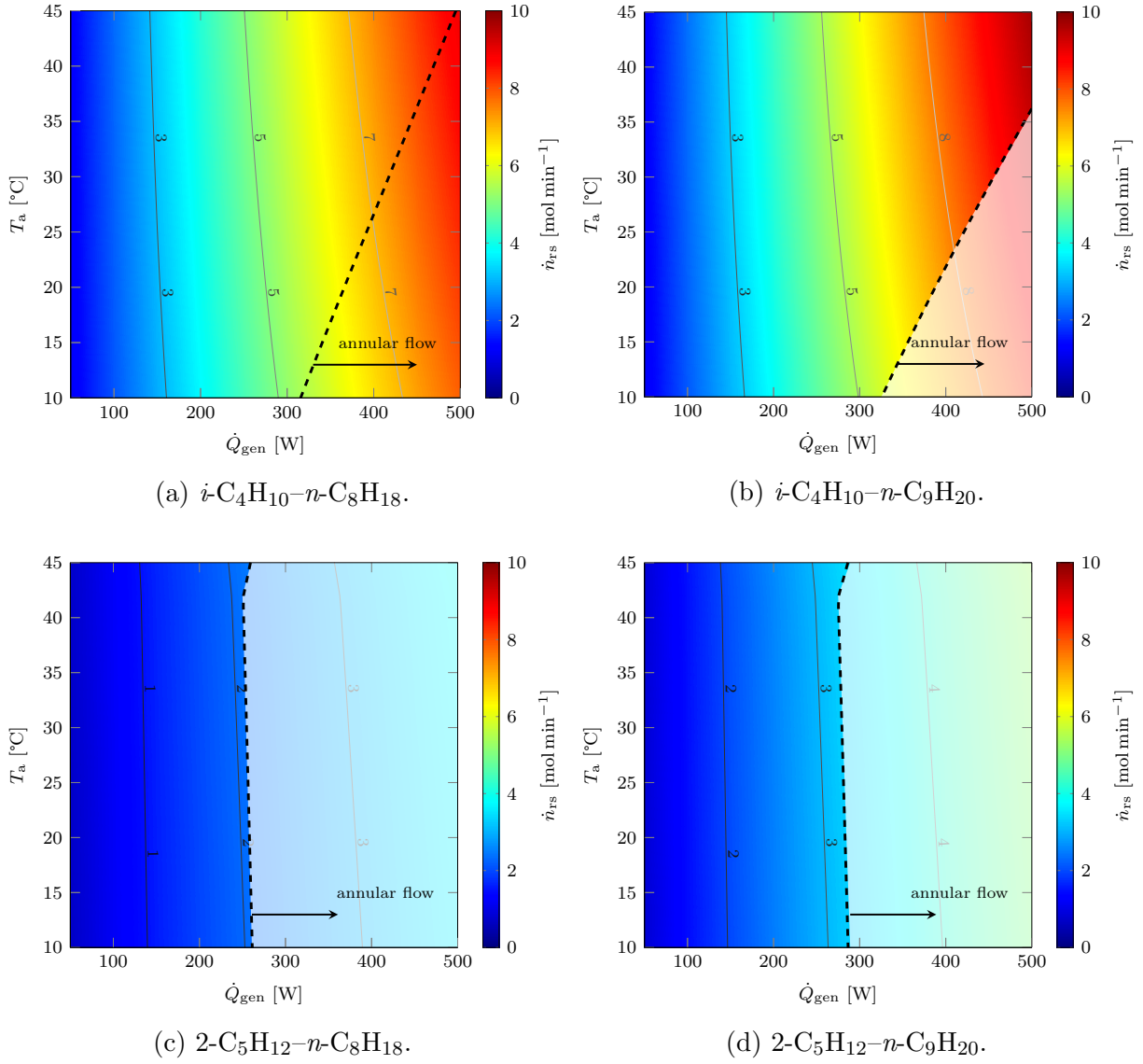


Figure 2.20: Variation of rich-solution circulation flowrate in a DAR unit charged with 20 mol.% for various working-fluid pairs: (a) $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$; (b) $i\text{-C}_4\text{H}_{10}\text{-}n\text{-C}_9\text{H}_{20}\text{-He}$; (c) $2\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$; and (d) $2\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_9\text{H}_{20}\text{-He}$. In each panel, the area to the right of the dashed black curve represents the operating region where two-phase flow in the bubble pump is likely to be annular.

favoured, while $n\text{-C}_5\text{H}_{12}$ is the sub-optimal choice for temperate locations (above 32°C). Based on the current analysis, $n\text{-C}_9\text{H}_{20}$ is favoured in terms of maximising cooling capacity or COP thanks also to its ability to widen the heat-input operating range away from annular flow in the bubble pump, but this comes at the price of a higher temperature requirement at the generator compared to other studied refrigerants, as shown in Figure 2.19. Any heat source that can provide heat at temperatures between 130°C to 150°C would be adequate to drive the system whereby, for example, it could be powered by any medium-heat range solar collector.

The use of pentanes should be considered with caution as the boundary towards two-phase flow shifting from churn-to-annular is very close, as demonstrated in Figure 2.17. Thus, butanes still show more flexible operation under variant heat inputs at the expense of lower cooling throughput, making them a better choice for solar applications. It can be observed that the assessed organic-based DAR systems can offer a comparable performance to $\text{NH}_3\text{--H}_2\text{O--H}_2$ systems, though organic-based DAR systems can be activated at lower charging pressures and heat-source temperatures compared to $\text{NH}_3\text{--H}_2\text{O--H}_2$ systems.

It should also be noted that the sensitivity analysis presented here and earlier considered in Refs. [44, 110, 132] offers, as highlighted, sub-optimal solutions and requires a tremendous number of calculations to introduce an optimal working fluid pair. However, the approach can be advantageous when assessing a limited list of working-fluid pairs.

2.5 Summary

Diffusion absorption refrigeration is a promising cooling technology that can entirely operate using a thermal heat source. A validated thermodynamic framework has been presented in which the GC SAFT- γ Mie is EoS is used to assess low-GWP organic working fluids that require low-temperature heat sources to run DAR systems, comparing these with the ammonia-water pair as a benchmark. A model for the ammonia-water cross interactions for use with SAFT- γ Mie has been established. The presented framework allows predictions of cooling capacity to within $\pm 16\%$, demonstrating the proposed model's validity and suitability to design alternative working fluids for thermal-powered DAR systems. As a case study, some simple low-GWP organic working-fluid pairs, based on six refrigerants and four absorbents chosen from a selection of normal alkanes and 2-methylalkanes, were assessed following a generate-and-test approach. Among the fluids considered, for a more-flexible operation, butanes are recommended as refrigerants for variant heat-input conditions. At the same time, pentanes are preferred for higher cooling capacities, as they can produce cooling with higher *COPs* (up to 0.27, depending on the prevailing ambient temperature). In the following chapters, the presented thermodynamic models are integrated into a computer-aided molecular and system design framework to incorporate optimisation approaches and explore optimal working-fluid pairs and charging conditions under different operating conditions.

Chapter 3

CAMD-DAR: A Computer-Aided Molecular and System Design Framework for Diffusion Absorption Refrigeration Systems

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3.1 Introduction

In Chapter 2, a DAR thermodynamic model has been validated and tested. The SAFT- γ Mie GC-EoS has been used to model these working fluid mixtures. Due to the importance of $\text{NH}_3+\text{H}_2\text{O}$ mixtures in studying DAR systems, an asymmetric cross-interaction model has been presented for ammonia and spherical water. Furthermore, the DAR thermodynamic model was used to assess some predefined working fluid mixtures in terms of their cooling output, required generator temperature, and operation flexibility under a wide range of heat inputs and ambient temperatures. As highlighted in Section 1.3, changing the working fluid can lower the required generator temperature to match medium-to-low temperature heat sources. Many authors (*e.g.*, Refs. [43, 44, 92, 110]) has considered testing pre-selected working-fluid mixtures depending on data and resource availability. This approach is useful, though it may overlook non-conventional working fluids. As suggested earlier in Section 1.4, integrated computer-aided molecular design (CAMD) and DAR system optimisation offers a systematic approach to design the working-fluid mixtures and DAR system simultaneously. Such a computer-aided molecular design and system optimisation problem entitles solving mixed-integer nonlinear programming (MINLP) optimisation problems.

As mentioned earlier in Chapter 1, MINLP CAMD problems are non-convex; thus, choosing a good initial guess shapes the convergence of the problem towards a good high-quality local optimal solution. Further, reaching a globally optimal solution is not guaranteed using most deterministic gradient-based MINLP optimisation algorithms like Branch and Bound (B&B) methods and their variants. [202, 220] Global optima are only guaranteed to apply expensive global optima algorithms due to the curse of dimensionality. [224] Increasing the number of initial guesses and solving the optimisation problem for each initial guess increase the probability of reaching global optima. [202] Another way to limit the curse of dimensionality of CAMD problems is using heuristic stochastic MINLP optimisation algorithms, like the Genetic Algorithm (GA) method and its variants. [178] Heuristic stochastic MINLP optimisation algorithms are more likely to find or approach global optima than gradient-based optimisation algorithms with randomly generated initial guesses. [225, 226] However, compared to deterministic gradient-based methods, stochastic optimisation methods are susceptible to premature termination. [225]

Following the discussion in Chapter 1, Zhou *et al.* [226] presented a hybrid stochastic-deterministic MINLP optimisation algorithm to solve the integrated MINLP computer-aided solvent and

3.1. INTRODUCTION

system design for CO₂ absorption. Zhou *et al.* [226] combined a GA algorithm developed by [227] with the generalised reduced-gradient (GRG) nonlinear program (CONOPT) [228]. In their algorithm, the GA is responsible for generating offspring molecules via genetic operations and the algorithm is terminated as a preset number of generations is reached.

In this chapter, a hybrid stochastic-deterministic method implemented in gPROMS [126] for solving global optimisation problems is adopted to combine the advantages of both approaches. The hybrid stochastic-deterministic approach levitates the limitation of how a single initial guess may affect the quality of the optimal solution. In addition, it allows more exploration of the decision-variable space. The decision-variable space is uniformly distributed, and multiple initial guesses are generated randomly using a quasi-random Sobol algorithm [269]. For each initial guess, a solution for the MINLP CAMD problem is attempted using an outer approximation–equality relaxation–augmented penalty (OAERAP) algorithm described by Viswanathan and Grossmann [207]. The OAERAP algorithm implements a sequential quadratic program (SQP) for NLP problems (*see* Ref. [225]) and a mixed-integer linear programming (MILP) solver based on the revised simplex and Branch-and-bound methods developed by Berkelaar *et al.* [270] for the integers. This hybrid stochastic-deterministic approach has been recently adopted by Santíuste [271] in the context of integrated computer-aided molecular design (CAMD) and organic Rankine cycle (ORC) system optimisation. Flevaris and Chatzidoukas [272] have recently used it to optimise the performance of a fed-batch bioreactor for microbial bioethanol production. To the author’s best knowledge, this hybrid stochastic-deterministic method has not been implemented before for working-fluid mixture design or cooling applications.

The objective of this chapter is to present a CAMD-DAR framework in the context of domestic refrigeration by extending the use of the DAR thermodynamic model presented in Chapter 2. The adapted MINLP CAMD-DAR framework is implemented to explore more organic-based working fluid mixtures suitable for DAR domestic use. The MINLP CAMD-DAR problem is solved using a hybrid stochastic-deterministic optimisation method.

A holistic overview of the CAMD-DAR framework is first presented in Section 3.2. The computer-aided molecular design and DAR system optimisation framework can be used to consider any refrigeration or heat pump in general; however, the DAR system is selected as discussed in Sections 1.2 and 2.3.2 for its suitability as a solar-powered refrigeration system. A costing method is also presented in Section 3.2.1 to assess the systems economically. Further, a set of

constraints are listed in Section 3.2.3 to ensure process, molecular feasibility, environmental and safety-related limitations are all met. The hybrid stochastic-deterministic optimisation method mentioned above is further described in Section 3.2.4. The adapted CAMD-DAR framework is then validated to ensure its conversion to global optima via carrying a series of NLP and MINLP optimisations for some predefined organic-based working-fluid families. Later the CAMD-DAR framework is implemented to a small-scale working-fluid and DAR design problem where the molecular-structure groups are limited to simple hydrocarbon groups (*i.e.* $-\text{CH}_3$, $>\text{CH}_2$, $=\text{CH}_2$ and $=\text{CH}-$).

3.2 The MINLP CAMD-DAR problem for domestic refrigeration

The CAMD-DAR framework structure shown in Figure 3.1 integrates the design of a working-fluid mixture: refrigerant, absorbent, and auxiliary gas, with the optimisation of other DAR operating conditions like charging pressure; refrigerant-rich solution charging composition and unit size. As it can be observed in Figure 3.1, the CAMD-DAR framework is built up of five main components: a DAR process model; a working-fluid model based on SAFT- γ Mie GC-EoS; costing method; process and molecular constraints; and finally, an optimisation method. The DAR process model and the SAFT- γ Mie GC-EoS have already been presented in Chapter 2.

3.2.1 Costing of commercial DAR systems

Estimating the DAR system’s cost is crucial in carrying out the thermo-economic assessment of DAR systems. One approach is to deal with the DAR unit cost in terms of the costs of its components, similar to what is conventionally done with other heat pumps [149,178]. However, it has been found challenging to use correlations from literature to size heat-exchange areas for a given DAR system (*e.g.*, condenser, absorber, evaporator). Most heat-exchanger sizing and costing correlations available in the literature (*see* Refs. [273,274]) are not intended to fit small-component sizes which are encountered in small-scale DAR systems and can hardly be validated, especially in the absence of detailed heat and mass transfer measurements for DAR systems. It is also noticed that DAR cooling units are sold and replaced as a single welded

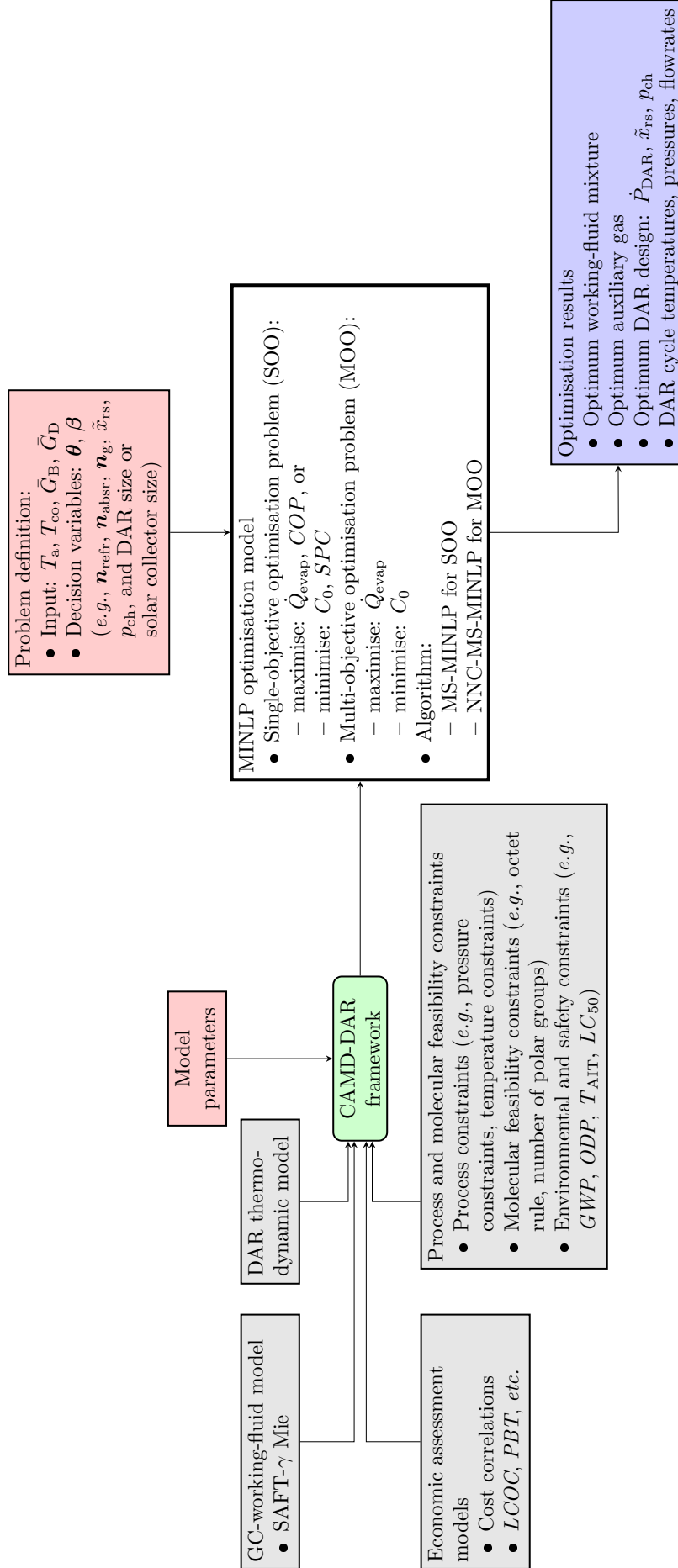


Figure 3.1: The proposed integrated computer-aided molecular and DAR-system design (CAMD-DAR) framework.

component, unlike conventional vapour compression refrigeration systems. In other words, an end-user cannot replace just one of the DAR components. Available DAR units in the market are rated using their cooling volume capacity in ft^3 and their AC power inputs ($\dot{P}_{\text{DAR}}$) in W. As seen in Figure 3.2a, there is a direct correlation between the capacity and the operating power. Operating power is proportional to DAR volume capacity

$$\dot{P}_{\text{DAR}} = 43.8 \times V_{\text{CU}}. \quad (3.1)$$

Following the discussion above, finding a costing method that can relate any DAR design parameters to its price is reasonable. The market for DAR has relatively expanded with time. DAR units are sold of 1- ft^3 capacity – perfect for camping – up to 18.3- ft^3 capacity suitable for households. Small-capacity DAR units can operate using as low as 50 W rate power input, while larger capacity units are rated to operate with 50 W. All DAR units sold in the market use $\text{NH}_3\text{--H}_2\text{O--H}_2$ as the working-fluid mixture.

It can be noticed in Figure 3.2b that for the same DAR rated power, $\dot{P}_{\text{DAR}}$ there is a large variance in the purchase price. The price variation can be partially due to model differences or being provided by different manufacturers. From the market survey, it is noticed that the price of a DAR fridge can be worth up to three-fold the price of a DAR cooling unit of the same capacity accounting for cabinet and other auxiliary costs included in the fridge. To correlate the DAR unit purchase price to its rated power, 237 data points were gathered from six suppliers for seven cooling-unit manufacturers for four fridge makes. Prices were collected from online suppliers in the American and British markets. Prices in US \$ were converted to GB£ using 2019-average exchange rate of £1=\$1.276 [275]. Nonlinear regression was carried out, and the data are fitted to $C_{\text{CU},0} = a\dot{P}_{\text{DAR}}^b$, where $C_{\text{CU},0}$ is the installed cost (including shipping expenses and VAT) of a DAR unit rated with power input, $\dot{P}_{\text{DAR}} \approx \dot{Q}_{\text{gen}}$. The fitted parameters, a and b , are estimated using a Levenberg-Marquardt algorithm [249, 250] to minimise the difference between the market and calculated prices. The least-squares objective function can be expressed as

$$\begin{aligned} \min_{a,b} \quad & \frac{1}{N} \sum_{i=1}^N \left[\frac{C_{\text{CU},0i}(a,b) - C_{\text{CU},i}^*}{C_{\text{CU},i}^*} \right]^2 \\ \text{s.t.} \quad & a, b \subseteq \mathbb{R}^+, \end{aligned} \quad (3.2)$$

3.2. THE MINLP CAMD-DAR PROBLEM FOR DOMESTIC REFRIGERATION

where N is the number of data points considered, C_{CU}^* are the market values including shipping expenses and VAT. The nonlinear regression resulted in the following cost correlation:

$$C_{CU,0} = 23 \times \dot{P}_{DAR}^{0.58}, \quad (3.3)$$

which is plotted in Figure 3.2b and can reproduce DAR purchase cost with % AAD of 18%. It should be stressed that this is a relatively high average deviation attributed to, as mentioned earlier, the large variance in some market data. However, it has been chosen not to exclude any of these prices to reflect the wide variation of the market as it is still relatively niche compared to other more stable technologies, which may suffer fewer price variations.

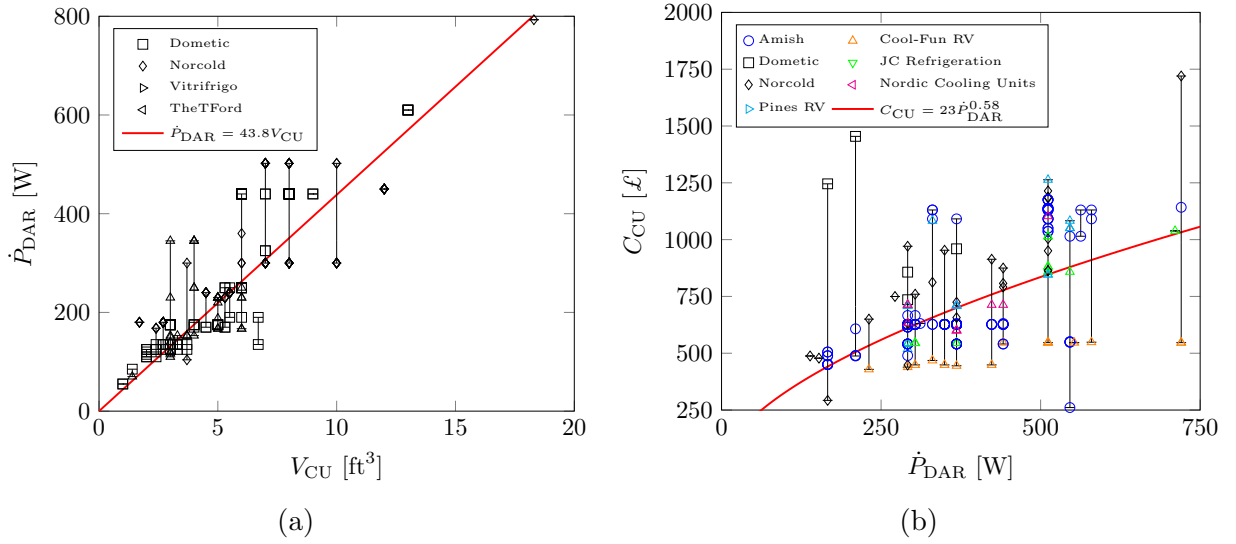


Figure 3.2: DAR cost data and models for the current CAMD-DAR framework. (a) DAR rating power. (b) Purchase prices of commercial DAR cooling units. All prices are presented in £, where prices available in US\$ are converted to GB£ using 2019-average exchange rate of £1=\$1.276 [275].

3.2.2 Problem definition

The considered DAR shown in Figure 3.3 is specified by having a semi-attached bubble pump configuration as it has been recommended by Zohar *et al.* [70] and tested by Kim *et al.* [92]. The DAR-model presented in Chapter 2 is used, and the input variables presented by Equations (3.4) to (3.12) in Table 3.1 are considered.

Equation (3.4) assumes the generation step to begin with a saturated-liquid refrigerant-rich working-fluid mixture. [84, 97, 98] Due to difficulties in measuring flow temperatures, DAR

temperature measurements are wall temperatures. For an operating DAR unit, the heat transfer rate is sufficiently high enough so that the working fluid temperature in the generator is reasonably assumed to approach the generator wall temperature as represented by Equation (3.5). Following validations presented in Chapter 2. [42,95] Following the model proposed by Zohar *et al.* [70,98], temperature drops across the bubble pump, and between rectifier liquid and vapour at the top of the bubble pump are assumed to be 2°C and 5°C, respectively as demonstrated by Equations (3.6) and (3.7).

For most organic pairs shall be presented later; the bubble-pump vapour effluent is purer than ammonia-water mixtures under similar operating conditions. In addition, it is reasonable to design DAR system charge pressure to ensure recovery of pure refrigerant, thus considering

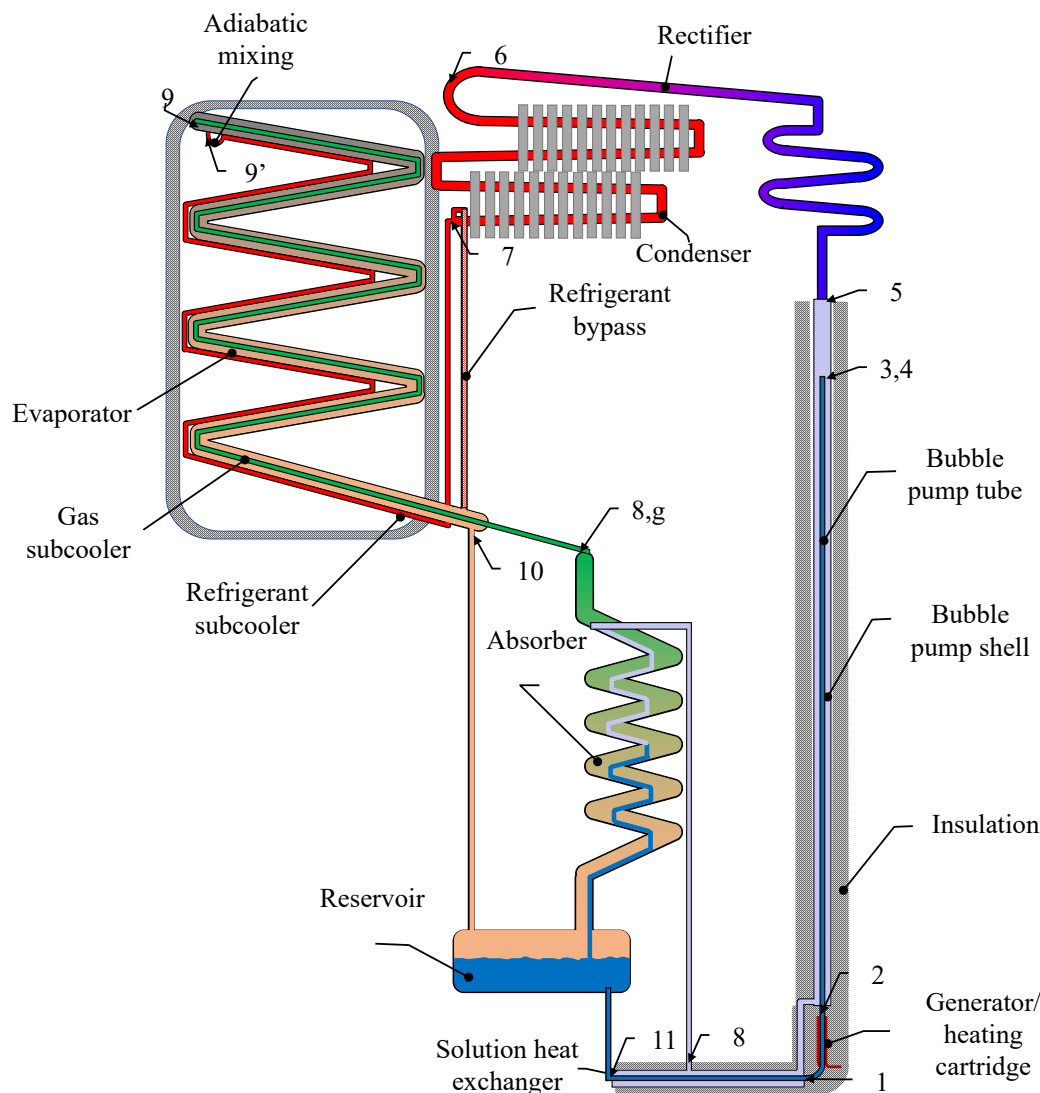


Figure 3.3: A schematic diagram for a typical DAR system with a semi-attached generator (Figure 1.9 revisited).

3.2. THE MINLP CAMD-DAR PROBLEM FOR DOMESTIC REFRIGERATION

Table 3.1: DAR-process model inputs for considered thermo-economic optimisation and analysis.

DAR model input	Description	
$T_1 = T_{\text{bub}}(p_{\text{ch}}, x_{\text{rs}})$	Generator inlet temperature	(3.4)
$\Delta T_{\text{gen,o}} = T_{\text{gen,w}} - T_2 = \Delta T_{\text{lo}}$	Generator outlet temperature	(3.5)
$T_3 = T_4 = T_2 - 2$	Bubble-pump outlet temperature	(3.6)
$T_5 = T_3 - 5$	Rectifier liquid temperature	(3.7)
$T_6 = T_{\text{sat,refr}}(p_{\text{ch}})$	Rectifier vapour temperature	(3.8)
$\Delta T_{\text{cond,o}} = T_7 - T_{\text{a}} = \Delta T_{\text{lo}}$	Condenser outlet temperature	(3.9)
$T_{8,\text{g}} = T_{\text{a}} + 0.1$	Desorbed gas temperature	(3.10)
$\Delta T_{\text{exp}} = T_{9'} - T_9 = (18.5 - 0.15 \times p_{\text{ch}})$	Expansion temperature drop	(3.11)
$T_{11} = T_7$	Reservoir temperature	(3.12)

Equation (3.8). Moreover, complete condensation should be sought in DAR design, such that subcooled refrigerant leaves the condenser approaching ambient temperature, which is considered by Equation (3.9). Equation (3.9) ensures that the DAR design has a large enough condenser. The auxiliary gas escaping the absorber is assumed to approach also ambient temperature as described by Equation (3.10), [95]. In contrast, the temperature difference across the gas-refrigerant mixing step is described by Equation (3.11) developed by Freeman [95]. Finally, for simplicity, many authors (*see* Refs. [65, 97, 98]) consider refrigerant-rich working fluid mixture leaves the absorber as temperate as the condenser effluent as presented by Equation (3.12).

As mentioned earlier, one of the arguments of this thesis is to design working fluids for running DAR using lower heat-source temperatures compared to ammonia–water systems. For this purpose, the following organic functional groups are used throughout the thesis for both refrigerant and absorbent design: $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $=\text{CH}_2$, $=\text{CH}-$, $-\text{CH}_2\text{OH}$, $-\text{OH}$, $-\text{NH}_2$ and $>\text{NH}$, while hydrogen and helium are considered alternatives for the choice of auxiliary gas. This functional group list is selected to represent low-GWP organic compounds and some polar organic compounds, such as those relevant to ammonia listed in Table 3.2. Although it is out of the scope of this thesis, it is worth mentioning that this functional group list can be extended to use other organic functional groups subject to the availability of relevant thermodynamic models.

In the current work, various optimisation objectives are sought. It is common to consider maximising the cooling rate, $\dot{Q}_{\text{evap}}$ as an objective function. In addition, maximising the coefficient of performance, COP is considered, provided that the rate of heat input to a given DAR unit affects the coefficient of performance as demonstrated in Figure 2.10 in Chapter 2. Considering the thermo-economic evaluation of DAR for domestic refrigeration, two other objective functions are considered: minimising

the total DAR fridge cost, $C_{CU,0}$ and minimising SPC ,

$$SPC = C_{CU,0}/\dot{Q}_{\text{evap}}. \quad (3.13)$$

The decision-variable space varies from considering only continuous DAR operating conditions for predefined working-fluid mixtures to integer and continuous decision variables for simultaneous working-fluid and system design. The general optimisation problem can be described as:

$$\begin{aligned} \min_{\boldsymbol{\theta}, \boldsymbol{\beta}} \quad & \mathbf{f}(\boldsymbol{\theta}, \boldsymbol{\beta}) \\ \text{s.t.} \quad & \mathbf{h}(\boldsymbol{\theta}, \boldsymbol{\beta}) = 0, \\ & \mathbf{g}(\boldsymbol{\theta}, \boldsymbol{\beta}) \leq 0, \\ & \boldsymbol{\theta} \in [\boldsymbol{\theta}^{\text{LB}}, \boldsymbol{\theta}^{\text{UB}}] \subseteq \mathbb{R}^n, \\ & \boldsymbol{\beta} \in [\boldsymbol{\beta}^{\text{LB}}, \boldsymbol{\beta}^{\text{UB}}] \subseteq \mathbb{Z}^m, \end{aligned} \quad (3.14)$$

where $\boldsymbol{\theta}$ is the set of continuous decision variables (*e.g.*, p_{ch} , $\tilde{x}_{\text{ch}}$), $\boldsymbol{\beta}$ is the set of integer decision variables (*e.g.*, $\mathbf{n}_{\text{refr}}$, $\mathbf{n}_{\text{abs}}$, $\mathbf{n}_{\text{g}}$), and $\mathbf{f}$ is the array of objective functions, which can be, for instance, $-\dot{Q}_{\text{evap}}$, $-COP$, $C_{CU,0}$ or SPC , or multiobjective combination of cooling rate and cost. The vectors of $\mathbf{h}(\boldsymbol{\theta}, \boldsymbol{\beta}) = 0$, and $\mathbf{g}(\boldsymbol{\theta}, \boldsymbol{\beta}) \leq 0$, respectively, represent the sets of equality and inequality constraints relevant to the DAR system. The vectors $\boldsymbol{\theta}^{\text{LB}}$, $\boldsymbol{\theta}^{\text{UB}}$, $\boldsymbol{\beta}^{\text{LB}}$, $\boldsymbol{\beta}^{\text{UB}}$ are lower bounds and upper bounds imposed on the continuous and integer decision variables. In addition to the integer decision variables that describe the working-fluid identity, four other continuous DAR process variables listed in Table 3.3 are needed to optimise the DAR system.

Table 3.2: Organic families, their structural formulae and constituent functional groups as considered in this study, where n represents the number of CH_2 groups in corresponding molecules. $-$ denotes one single bond, $>$ denotes two single bonds and $=$ denotes one double bond.

Hydrocarbon family	Structural formula	Functional groups
n -alkanes ($n\text{-C}_n\text{H}_{2n+2}$)	$\text{CH}_3\text{--}[\text{CH}_2]_n\text{--CH}_3$	--CH_3 and $>\text{CH}_2$
2-alkanes ($2\text{-C}_n\text{H}_{2n+2}$)	$[\text{CH}_3]_2>\text{CH--}[\text{CH}_2]_n\text{--CH}_3$	--CH_3 , $>\text{CH}_2$ and $>\text{CH--}$
n -alkenes ($1\text{-C}_n\text{H}_{2n}$)	$\text{CH}_2=\text{CH--}[\text{CH}_2]_n\text{--CH}_3$	--CH_3 , $>\text{CH}_2$, $=\text{CH}_2$ and $=\text{CH--}$
2-alkenes ($2\text{-C}_n\text{H}_{2n}$)	$\text{CH}_3\text{--CH=CH--}[\text{CH}_2]_n\text{--CH}_3$	--CH_3 , $>\text{CH}_2$ and $=\text{CH--}$
1-amines ($1\text{-C}_n\text{H}_{2n+1}\text{NH}_2$)	$\text{CH}_3\text{--}[\text{CH}_2]_n\text{--NH}_2$	--CH_3 , $>\text{CH}_2$ and --NH_2
2-amines ($2\text{-C}_n\text{H}_{2n+1}\text{NH}_2$)	$[\text{CH}_3]_2>\text{CH--}[\text{CH}_2]_n\text{--NH}_2$	--CH_3 , $>\text{CH}_2$, $>\text{CH--}$ and --NH_2
2°-amines ($2^\circ\text{-C}_n\text{H}_{2n+2}\text{NH}$)	$[\text{CH}_3]_2>\text{NH--}[\text{CH}_2]_n\text{--CH}_3$	--CH_3 , $>\text{CH}_2$ and $>\text{NH}$
1-alcohols ($1\text{-C}_n\text{H}_{2n+1}\text{OH}$)	$\text{CH}_3\text{--}[\text{CH}_2]_n\text{--OH}$	--CH_3 , $>\text{CH}_2$ and $\text{--OH}/\text{--CH}_2\text{OH}$

3.2. THE MINLP CAMD-DAR PROBLEM FOR DOMESTIC REFRIGERATION

Table 3.3: Continuous optimisation decision variable for DAR case studies with their lower and upper bounds definition and ranges for parametric NLP.

Variable	Description	Lower bound	Upper bound	Units
$\dot{P}_{\text{DAR}} = \dot{Q}_{\text{gen}}$	Generator heat rate	50	500	W
p_{ch}	Charging pressure	2	25	bar
$\tilde{x}_{\text{rs}}$	Rich solution molar composition	0.1	0.38	—
$\bar{p}_9$	Relative low evaporator pressure	0.02	0.2	—

3.2.3 Process and molecular feasibility considerations

To ensure the feasibility of proposed DAR designs, various constraints summarised in Table 3.4 are considered to complement the presented framework. These constraints are grouped into three classes: process constraints described by Equations (3.15) to (3.19); molecular-feasibility constraints described by Equations (3.20) to (3.22); and environmental and safety constraints described by Equations (3.24) to (3.26).

Process feasibility constraints

Equations 3.15a and 3.15b are employed to ensure that for a proposed working fluid, the two-phase mixture generated has enough slugs to push the working fluid up the bubble pump, as discussed earlier in Sections 1.2 and 2.3.3. As earlier mentioned, the bubble-to slug transition velocity, $u_{\text{L,bs}}$ in Chapter 2, is calculated by Equation (2.28), while the slug-to-annular transition velocity, $u_{\text{V,an}}$, is calculated by Equation (2.30) in Chapter 2.

Equation 3.16a considers partial refrigerant pressure at the beginning of evaporation should be suppressed by its partial pressure at the end of the evaporation step to ensure feasible cooling, where p_9 is refrigerant partial pressure after adiabatic mixing (at evaporator inlet) calculated by Equation (2.22b) in Chapter 2 and p_{10} is the refrigerant partial pressure at the evaporator outlet calculated by Equation (2.23a) in Chapter 2.

The constraints in Equations (3.16c) and (3.16d) impose limitation on DAR charging pressure. DAR charging pressure should not exceed an allowable maximum pressure, $p_{\text{max}} = \min(21 \text{ bar}, 0.85 \cdot p_{\text{c,min}})$. To ensure that the DAR unit operates above ambient pressure and allows complete refrigerant condensation, the charge pressure should be greater than or equal a minimum charging pressure, $p_{\text{min}} = \max[2 \text{ bar}, p_{\text{sat},1}(T_{\text{a}} + 5)]$.

Table 3.4: List of constraints involved in the CAMD-DAR framework representing the set of equality constraints, $\mathbf{h}(\boldsymbol{\theta}, \boldsymbol{\beta}) = 0$ and set inequality constraints, $\mathbf{g}(\boldsymbol{\theta}, \boldsymbol{\beta}) \leq 0$, which are relevant to the DAR system. The constraints are classified as process-related constraints, molecular-feasibility-related constraints or safety-and-environmental-related constraints.

Process constraints		
- Bubble pump		
$u_L \leq u_{L,bs}$	(No bubbly flow)	(3.15a)
$u_{V,an} \leq u_V$	(No annular flow)	(3.15b)
- Pressure constraints		
$p_9 \leq p_{10}$	(Evaporator pressure build up)	(3.16a)
$p_{10} \leq p_{evap,max}$	(Evaporator maximum pressure)	(3.16b)
$p_{ch} \leq p_{max}$	(Feasible charge pressure 1)	(3.16c)
$p_{min} \leq p_{ch}$	(Feasible charge pressure 2)	(3.16d)
- Temperature constraints		
$T_{sat,refr} < T_{bub,rs}$	(Positive temperature gradient across the rectifier)	(3.17a)
$T_{bub,rs} < T_{gen,w}$	(Positive driving force at generator wall)	(3.17b)
$T_{sat,refr} < T_{sat,absr}$	(Refrigerant-absorbent relative volatility)	(3.17c)
- Composition constraints		
$\tilde{x}_{ws} < \tilde{x}_{rs}$	(Feasible absorption)	(3.18a)
$\tilde{x}_{ws} < \tilde{x}_{ws,min}$	(High absorption affinity)	(3.18b)
- Heat flow		
$\dot{Q}_{evap,g} < \dot{Q}_{evap,refr}$	(Positive cooling capacity)	(3.19)
Molecular feasibility constraints		
- Octet rule		
$2m_j = \sum_{k=1}^{N_{G,j}} (2 - \nu_k) \cdot n_{k,j}$	$\forall j \in [\text{refr}, \text{absr}]$	(3.20)
- Olefin		
$0 \leq \cos [\pi (n_{=CH_2,j} + n_{=CH-,j})]$		(3.21a)
$n_{=CH_2,j} \leq n_{=CH-,j}$		(3.21b)
- Polar groups		
$n_{-NH_2,j} + n_{-CH_2OH,j} + n_{>NH,j} + n_{-OH,j} = 1$		(3.22)
- Auxiliary gas		
$n_{H_2,j} + n_{He,j} = 1$		(3.23)
Safety and environmental constraints		
- Safe operation		
$T_{gen,w} + 30 \leq T_{AIT,j}$	(Auto ignition temperature)	(3.24a)
$\Gamma_j \leq 0.8$	(Flammability)	(3.24b)
- Environmental		
$\log_{10}(GWP_j) \leq \log_{10}(150)$	(Global warming potential)	(3.25a)
$\log_{10}(ODP_j) \leq \log_{10}(0.2)$	(Ozone depletion potential)	(3.25b)
- Health		
$1 < \log_{10}(LC_{50,j})$	(Toxicity)	(3.26)

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Equation (3.17a) ensures a positive temperature gradient across the rectifier, while Equation (3.17b) limits DAR operation to when generator wall temperature suppresses refrigerant-rich solution bubble temperature. This limitation ensures robust calculation for the generator. The constraint represented by Equation (3.17c) imposes a check that refrigerant is more volatile than absorbent at DAR system pressure.

The constraint in Equation (3.18a) ensures the refrigerant-weak solution composition is lower than that of the refrigerant-rich solution to ensure a positive composition gradient across the absorber. While the constraint in Equation (3.18b) limits the weak solution composition to be lower than 10 mol %. As presented by Equation (2.31) in Chapter 2, weak-solution compositions below 10 mol % ensure a relatively low Henry coefficient (or thermodynamically favoured absorption).

The constraint in Equation (3.19) ensures a positive net $\dot{Q}_{\text{evap}}$ in the evaporator, where $\dot{Q}_{\text{evap,refr}}$ is the net enthalpy difference for the refrigerant across the evaporator and $\dot{Q}_{\text{evap,g}}$ is the net enthalpy difference for the auxiliary across the evaporator. This constraint is intended to prevent the optimiser from ending with some working-fluid mixtures, which under operating conditions result in a negative net $\dot{Q}_{\text{evap}}$.

Molecular feasibility constraints

It is important to ensure that the designed working-fluid mixture components are chemically feasible. For a given component, j in the working fluid mixture, available bonds, $\nu_{k,j}$ of functional group, k must suffice eight electrons in the outermost electron level of the central atoms (C, N, O) in the functional groups of interest. The well known “octet rule” [168] stated in Equation (3.20) ensures the chemical feasibility of designed working-fluid pair components, where $n_{k,j}$ is the number of multiplicity of functional group, k in molecule, j . Only acyclic molecules for both refrigerant and absorbent are considered in this study, $m_j = 1$.

Two other constraints in Equation (3.21) are important to ensure a feasible olefin compound is designed and to avoid mixing single and double bonds. The number of double-bond groups (*i.e.*, $=\text{CH}_2$ and $=\text{CH}-$) should be even as indicated in Equation (3.21a), and the number of occurrence of the terminal group ($=\text{CH}_2$) should be less than or equal that of the internal group ($=\text{CH}-$) as constrained by Equation (3.21b). [161, 178]

To compromise the robustness and the reliability of the presented CAMD-DAR framework, it is chosen to limit second-order interaction effects within a given molecule as much as possible, especially with the presence of polar groups, to ensure accurate representation of the adopted thermodynamic models in this study. Thus, the number of occurrence of polar groups (*i.e.*, $-\text{NH}_2$, $-\text{NH}$, $-\text{CH}_2\text{OH}$, $-\text{OH}$) in a given molecule, j is constrained to only single group per molecule as described by Equation (3.22). Only single auxiliary gas is to be selected, which is imposed to Equation (3.23).

Environmental and safety feasibility constraints

It is crucial to ensure that the selected working-fluid pair alongside its substances (refrigerant and absorbent) comply with environmental and safety regulations. Thus, some constraints are imposed for this purpose. The constraint in Equation (3.24a) implies that the highest temperature in the DAR system must be lower than the auto-ignition temperatures, $T_{\text{AIT},j}$ of both the refrigerant and absorbent. This constraint eliminates any risk of ignition at an incidence of leakage to the atmosphere during operation. [149,218] ASTM standard test method E659-78 defines the auto-ignition temperature, T_{AIT} as the lowest temperature at which a substance will ignite with a hot flame when it comes in contact with air at atmospheric pressure without the aid of any external energy source such as a spark or flame. It is one of the essential safety specifications used to characterise how hazardous is a chemical substance. The absolute auto-ignition temperatures for pure substances are estimated using the GC method suggested by Albahri *et al.* [152]:

$$T_{\text{AIT},j} = 729.7 + 24.9 \sum_{k=1}^{N_{\text{G},j}} n_{k,j} \cdot C_{\text{AIT}k} - 1.57 \left(\sum_{k=1}^{N_{\text{G},j}} n_{k,j} \cdot C_{\text{AIT}k} \right)^2 - 0.0773 \left(\sum_{k=1}^{N_{\text{G},j}} n_{k,j} \cdot C_{\text{AIT}k} \right)^3 + 0.0032 \left(\sum_{k=1}^{N_{\text{G},j}} n_{k,j} \cdot C_{\text{AIT}k} \right)^4 \quad \forall j \in [\text{refr}, \text{absr}] \quad (3.27)$$

where $n_{k,j}$ is the number of multiplicity of functional group, k in molecule, j and values of the group contributions, $C_{\text{AIT}k}$ are taken from Albahri *et al.* [152] and listed in Table 3.5.

The constraint in Equation (3.24b) ensures that Γ -number for pure refrigerant and absorbent is at most 0.8 as Schilling *et al.* has considered it [149], to ensure that the working-fluid pair is not

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hazardously flammable. The method proposed by Kondo *et al.* [151] is adopted to predict the Γ -number for pure refrigerant and absorbent:

$$\Gamma_j = C_{P1,j} \cdot \left(1 + C_{P2,j} C_{F,1,j} + C_{P6,j} C_{RNH,j} + C_{P9,j} C_{R=,j} \right) \cdot \left(1 + C_{P13,j} C_{ROH,j} + C_{P15,j} C_{RNH_2,j} \right) \quad \forall j \in [\text{refr}, \text{absr}]. \quad (3.28)$$

Parameters in Equation (3.28): $C_{F,1,j}$, $C_{P1,j}$, $C_{P2,j}$, $C_{P6,j}$, $C_{P9,j}$, $C_{P13,j}$, $C_{P15,j}$, $C_{R=,j}$, $C_{RNH,j}$, $C_{RNH_2,j}$, and $C_{ROH,j}$ are defined and listed in the work done by Kondo *et al.* [151].

Equations (3.25a) and (3.25b) ensure the design of environment-friendly refrigerant-absorbent pair, where the global warming potential, GWP is estimated using the first-order GC method adopted from work by Hukkerikar *et al.* [150]

$$\log_{10} (GWP_j) = \sum_{k=1}^{N_{G,j}} n_{k,j} \cdot C_{GWP_k} \quad \forall j \in [\text{refr}, \text{absr}], \quad (3.29)$$

while the ozone depletion potential, ODP is estimated using the first-order GC method adopted from work by Hukkerikar *et al.* [150]

$$\log_{10} (ODP_j) = \sum_{k=1}^{N_{G,j}} n_{k,j} \cdot C_{ODP_k} \quad \forall j \in [\text{refr}, \text{absr}], \quad (3.30)$$

In Equations (3.29) and (3.30), $n_{k,j}$ is the number of multiplicity of functional group, k in molecule, j , and C_{GWP_k} and C_{ODP_k} are the first-order group contributions accounting for GWP and ODP, respectively, which are developed by Hukkerikar *et al.* [150] and listed in Table 3.5.

At the risk of leakage or disposal in water, Equation (3.26) is implemented to ensure the design of a low-toxic working fluid. One way to express toxicity is the fathead minnow 96-h lethal concentration, $LC_{50}(\text{FM})$ endpoint, which represents the concentration in water which kills half of the fathead minnow (*Pimephales promelas*) in 4 days (96 h). [150] For less-toxic working-fluid pairs, 96-h LC_{50} should be greater than or equal $10 \text{ mg} \cdot \text{L}^{-1}$. [149] The fathead minnow 96-h, $LC_{50}(\text{FM})$ can be estimated using the first-order GC method proposed by Hukkerikar *et al.* [150]:

$$-\log_{10} [LC_{50}(\text{FM})_j \cdot MW_j \cdot 10^3] = \sum_{k=1}^{N_{G,j}} n_{k,j} \cdot C_{LC_{50}(\text{FM})_k} - FM_0 \quad \forall j \in [\text{refr}, \text{absr}], \quad (3.31)$$

where $FM_0 = 2.1949$, and $C_{LC_{50}(FM)_k}$ are the first-order group contributions accounting for fathead minnow 96-h LC_{50} ($LC_{50}(FM)$) developed by Hukkerikar *et al.* [150] and listed in Table 3.5.

Equations (3.25a), (3.25b) and (3.26) are linear in $n_{k,j}$ and hence can be used directly in the MILP optimisations without the need for linearisation. It should also be noted that to match the parameters for some groups. A correction term is introduced to account for different group databanks. [167] For instance, the group contributions for GWP, ODP and LC_{50} developed by Hukkerikar *et al.* [150] always depends on the hydrocarbon group next to it, whether it is $-CH_2$, $>CH-$ as it can be noticed in Table 3.5. Thus, a correction must be considered to match the main databank deployed. For example, if the $>CH_2$ and $-NH_2$ amongst the groups for a given substance, the group contributions of GWP, ODP and LC_{50} for $-NH_2$ should be corrected by deducting the contribution of $>CH_2$ (*e.g.*, $C_{LC_{50},NH_2} = C_{LC_{50},-CH_2NH_2} - C_{LC_{50},>CH_2}$).

Table 3.5: Group contributions for auto-ignition temperature (C_{AIT_k}), global warming potential (C_{GWP_k}), ozone depletion potential (C_{ODP_k}) and lethal concentration ($C_{LC_{50}_k}$) for functional organic groups considered in this study taken from Refs. [150, 152]. A correction must be considered to match the main databank deployed. For example, if the $>CH_2$ and $-NH_2$ amongst the groups for a given substance, the group contributions of GWP, ODP and LC_{50} for $-NH_2$ should be corrected by deducting the contribution of $>CH_2$ (*e.g.*, $C_{LC_{50},NH_2} = C_{LC_{50},-CH_2NH_2} - C_{LC_{50},>CH_2}$).

Group	C_{AIT_k}	C_{GWP_k}	C_{ODP_k}	$C_{LC_{50}(FM)_k}$
$-CH_3$	-1.0952	0.388	-0.9453	0.0972
$>CH_2$	-0.8995	-1.0699	0	0.2885
$>CH-$	0.4397	0	0	0.2441
$=CH_2$	0.1432	0	0	0.8395
$=CH-$	-2.5374	0	0	0.1945
$-OH$	-0.4083	0	0	-0.6115
$-CH_2OH$	-1.3078	0	0	-0.323
$-CH_2-NH_2$	n/a*	0	0	-0.0246
$>CH-NH_2$	n/a	0	0	-0.0983
CH_3-NH-	n/a	0	0	-0.4593
$-CH_2-NH-$	n/a	0	0	0.0524
$>CH-NH-$	n/a	0	0	0
$-NH_2$ except as above	-0.7274	0	0	0.113
$>NH$	0.264	n/a	n/a	n/a

* n/a = not applicable

3.2.4 MINLP solution algorithm

As mentioned earlier, the CAMD-DAR framework implies a mixed-integer nonlinear optimisation problem. If the working fluid mixture is predefined, the MINLP problem reduces to an NLP that requires optimising only continuous decision variables listed in Table 3.3. In this study, the hybrid stochastic-deterministic method implemented in gPROMS [126] for solving global optimisation problems is adopted to combine the advantages of both approaches mentioned earlier. A flowchart of the hybrid stochastic-deterministic optimisation method used for solving the MINLP CAMD-DAR problem is shown in Figure 3.4.

The hybrid optimisation algorithm mentioned above uses the stochastic multi-start optimisation method available within the gPROMS modelling environment. This method relies on computing as many local optima while returning their best optimum. The more the initial guesses, the more likely that the best optimum point returned by the optimiser is the global optimal point. The algorithm is initialised by solving the (MI)NLP problem using user-defined initial guess ($\theta^{(0)}$ and $\beta^{(0)}$). The (MI)NLP is solved using an appropriate gradient-based optimisation algorithm specified at the next level of the hybrid optimisation algorithm. Then, as long as the number of initial guesses (which is specified by the user) is not exceeded (*i.e.*, $i < i_{\max}$); the optimiser generates a random initial guess ($\theta_i^{(0)}$ and $\beta_i^{(0)}$). The solver uses the quasi-random Sobol [269] number generator to generate the initial guess from a randomly distributed decision-variable space between its lower and upper bounds to provide an even space of unique sample points (as much as possible). The generated local optima are ranked, and this rank is continuously updated. The current study considers optimal alternatives which are similar within 1% as a single optimal point. The number of initial guesses (listed in Table 3.6) is tuned to ensure that the best optimum point is achieved at least twice during the optimisation run, provided that the initial guesses are unique. This practice has been proven to be successful in applying a similar stochastic method while fitting parameters for developing models in SAFT- γ -Mie. The choice of the maximum initial guess also considers the compromise of computation time with convergence within the vicinity of global optima.

At each iteration of the multi-start optimisation algorithm, the gradient-based OAERAP algorithm described by Viswanathan and Grossmann [207] is deployed to find the local optima for MINLP problems where the sequential quadratic program (SQP) [225] is used to solve the fully-relaxed (FR) and primal problems (PR) NLPs entitled to be solved within each OAERAP

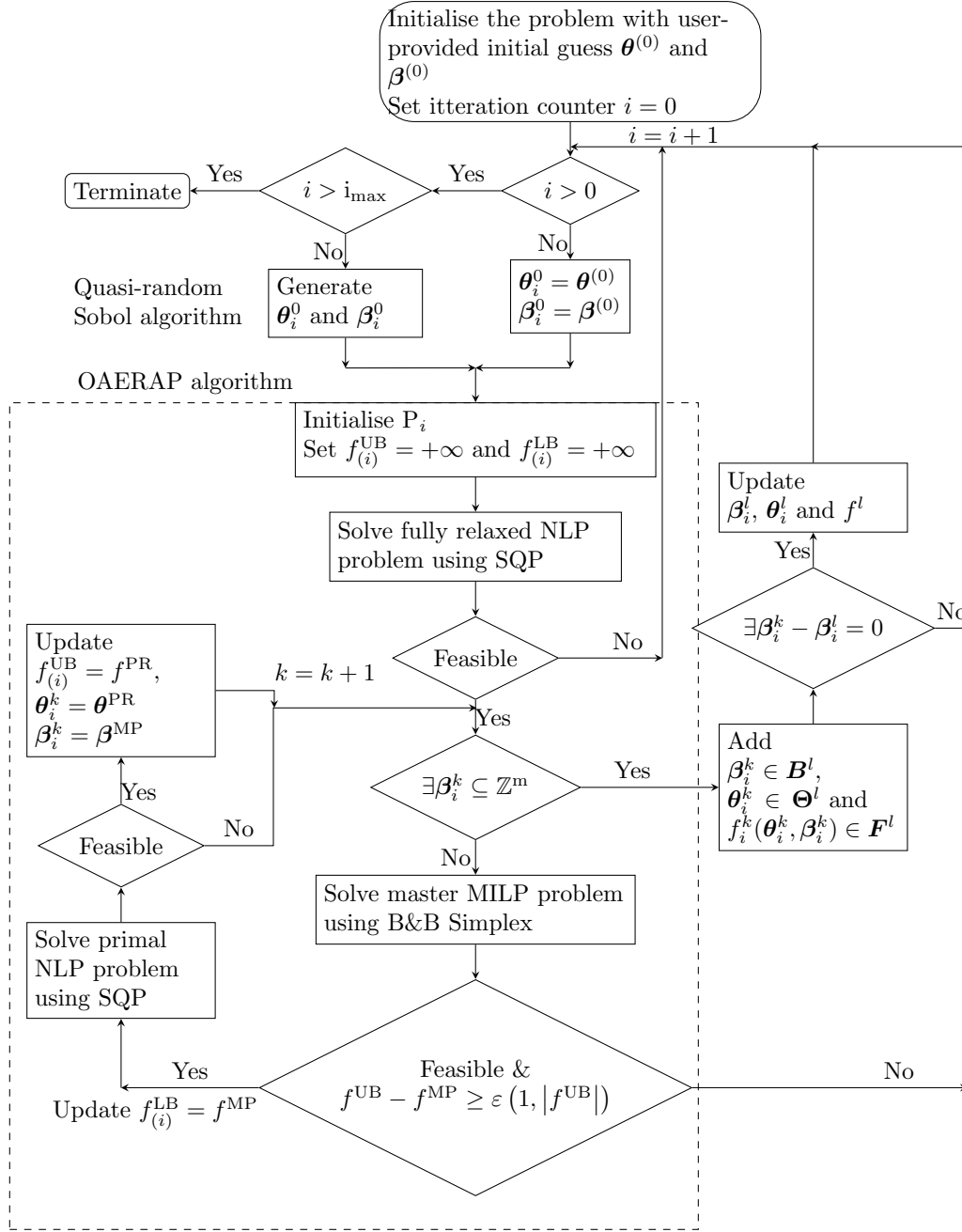


Figure 3.4: A flowchart of the hybrid stochastic-deterministic optimisation method used as implemented in gPROMS [126] based on the outer approximation–equation relaxation–augmented penalty OAERAP algorithm developed by Viswanathan and Grossmann [207] for solving the MINLP CAMD-DAR problem (considering minimising objective function). The multiple initial guesses are generated randomly using a quasi-random Sobol algorithm [269]. The OAERAP algorithm implements a sequential quadratic program (SQP) (*see* Ref. [225]) for NLP problems and mixed-integer linear programming (MILP) solver based on the revised simplex method and the Branch-and-bound (B&B) method for the integers [270].

optimisation. The implemented mixed-integer linear programming (MILP) solver is based on the revised simplex and Branch-and-bound methods developed by Berkelaar *et al.* [270]. For obvious reasons, in the set parametric NLP optimisations (discussed in the following section),

the gradient-based SQP optimisation algorithm is deployed instead of the OAERAP algorithm. To reduce computation time, parallel workers are used to solve the multi-start optimisation problems since initial guesses are generated randomly and independently.

3.3 Parametric NLP and MINLP for CAMD-DAR

Before demonstrating the MINLP optimisation results of the complete CAMD-DAR framework shown in Figure 3.1, a series of parametric NLP and MINLP optimisations are presented. These parametric NLP and MINLP optimisations to maximise the cooling rate, $\dot{Q}_{\text{evap}}$ for some organic-family combinations listed in Table 3.7, where the structures of these organic families are already defined in Table 3.2. Not only do the parametric NLP and MINLP optimisations serve to justify the convenience of the proposed CAMD-DAR framework, but they also give insights into the size of refrigerant and absorbent molecules suitable for running DAR applications. In this section, a cooling temperature, T_{co} of 4 °C is considered, which resembles an average cabin temperature in a household fridge. Three ambient temperature, T_{a} levels are studied: 20 °C, 30 °C and 40 °C, to cover a wide range of temperatures for regions where DAR is intended to be used and to explore how the ambient temperature can shape the decision of the working-fluid selection.

Table 3.6: Number of user-defined initial guesses specified for the hybrid stochastic-deterministic optimisation.

CAMD-DAR optimisation	Number of initial guesses
NLP	20
Parametric MINLP	120
Full MINLP	500
Multi-objective MINLP	500

Table 3.7: Array of organic families combinations considered for NLP optimisations.

Refrigerant	Absorbent
	N-alkanes
N-alkanes	N-alkenes
	2-alkenes
	N-alkanes
N-alkenes	N-alkenes
	2-alkenes
	N-alkanes
2-alkenes	N-alkenes
	2-alkenes

3.3.1 Parametric NLP optimisations

For a given working-fluid combination in Table 3.7, the multiplicities of $>\text{CH}_2$ group in both refrigerant and absorbent, $n_{>\text{CH}_2,\text{refr}}$ and $n_{>\text{CH}_2,\text{absr}}$ are increased in increments of one and optimisations were completed for each generated pair considering both hydrogen and helium auxiliary gases ending up with four continuous decision variables which are listed in Table 3.3. Hence, the optimisation problem in Equation (3.14) reduces to:

$$\max_{\tilde{x}_{\text{rs}}, p_{\text{ch}}, \dot{P}_{\text{DAR}}, \bar{p}_9} \dot{Q}_{\text{evap}} \left\{ \tilde{x}_{\text{rs}}, p_{\text{ch}}, \dot{P}_{\text{DAR}}, \bar{p}_9, \mathbf{n}_{\text{ref}}, \mathbf{n}_{\text{absr}}, n_{\text{g}} \right\} \quad (3.14 \text{ revisited})$$

$$\text{s.t.} \quad u_{\text{L}} \leq u_{\text{L,bs}}, \quad (3.15\text{a})$$

$$u_{\text{V}} \leq u_{\text{V,an}}, \quad (3.15\text{b})$$

$$p_9 \leq p_{10} \leq p_{\text{evap,max}}, \quad (3.16\text{a}, 3.16\text{b})$$

$$p_{\text{min}} < p_{\text{ch}} < p_{\text{max}}, \quad (3.16\text{c}, 3.16\text{d})$$

$$T_{\text{bub,rs}} < T_{\text{gen,w}}, \quad (3.17\text{b})$$

$$x_{\text{ws}} < x_{\text{rs}}, \quad (3.18\text{a})$$

$$x_{\text{ws}} \leq x_{\text{ws,min}}, \quad (3.18\text{b})$$

$$\dot{Q}_{\text{evap,g}} \leq \dot{Q}_{\text{evap,refr}}, \quad (3.19)$$

$$T_{\text{gen,w}} + 30 \leq T_{\text{AIT}}. \quad (3.24\text{a})$$

For feasible working fluids, NLP optimisations described by Equation (3.14 revisited) converge to the best optima. It is also found that increasing the number of initial guesses (using multi-start optimisation) beyond 20 initial guesses does not improve the optimum DAR design or unleash new optimum alternatives. NLP optimisation results for aliphatic working fluids are displayed in Figures 3.5 to 3.7.

Optimal DAR systems and their thermodynamic performance

In Figure 3.5, optimum $\dot{Q}_{\text{evap}}$ is plotted for different working-fluid mixtures against the size of absorbent, quantified by their carbon-chain length. It can be observed in Figure 3.5 that when the ambient temperature is 20 °C, the theoretical maximum cooling rate, $\dot{Q}_{\text{evap}}$ is capped at 38 W to maintain cooling temperature at 4 °C. Results in this figure also reveal that refrigerants with

3.3. PARAMETRIC NLP AND MINLP FOR CAMD-DAR

four carbon atoms (C_4H_{10} and $2-C_4H_8$) are favoured. At the same time, the carbon-chain length of optimum absorbents for maximum cooling output varies between six and ten carbon atoms depending on the refrigerant molecule size and ambient temperature. It can also be observed in Figure 3.5 and subject to the constraints listed in Equation (3.14 revisited) that n -alkanes offer more flexible options for absorbent choice and can be paired with more refrigerant alternatives compared to alkenes as absorbents.

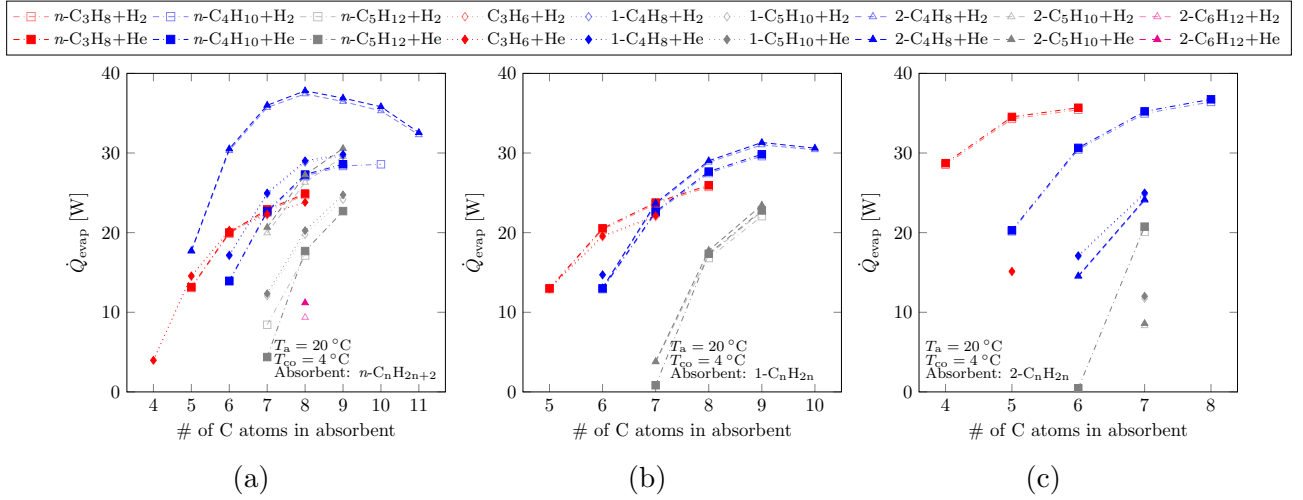


Figure 3.5: The effect of absorbent chain length on DAR maximum cooling rates, $\dot{Q}_{\text{evap}}$ for different straight-chain aliphatic refrigerants under ambient temperature, $T_a = 20^\circ\text{C}$ and cooling temperature, $T_{\text{co}} = 4^\circ\text{C}$. Three straight-chain aliphatic absorbents are considered: (a) n -alkanes ($n\text{-C}_n\text{H}_{2n+2}$); (b) 1-alkenes ($1\text{-C}_n\text{H}_{2n}$) and (c) 2-alkenes ($2\text{-C}_n\text{H}_{2n}$).

Higher DAR design powers promote higher $\dot{Q}_{\text{evap}}$. When Figure 3.6 is studied with Figure 3.5, it can be revealed that the maximum DAR power for a given working-fluid mixture is limited by vapour generation rate and the auto-ignition temperature of the absorbent. The constraint in Equation (3.15b) imposes a limit on the maximum DAR power for a given working-fluid mixture, which theoretically promotes annular flow in the bubble pump as earlier discussed in Chapter 2. In addition, for some working-fluid mixtures, especially those with $n\text{-C}_n\text{H}_{2n+2}$ - $n\text{-C}_n\text{H}_{2n+2}$ pairs, the theoretical temperature at the generator increases as the theoretical DAR power increases. Thus, the theoretical generator temperature tends to hit the safe bound of the absorbent auto-ignition temperature described by the constraint in Equation (3.24a). The auto-ignition temperature estimated by Equation (3.27) decreases as the carbon-chain length increases. These two reasons explain why absorbents with carbon-chain size greater than nine are not feasible except with the following refrigerants: $n\text{-C}_4\text{H}_{10}$; $1\text{-C}_4\text{H}_8$ and $2\text{-C}_4\text{H}_8$.

It can be demonstrated in Figures 3.5 to 3.7 that, for obvious reasons, maximum $\dot{Q}_{\text{evap}}$ monoton-

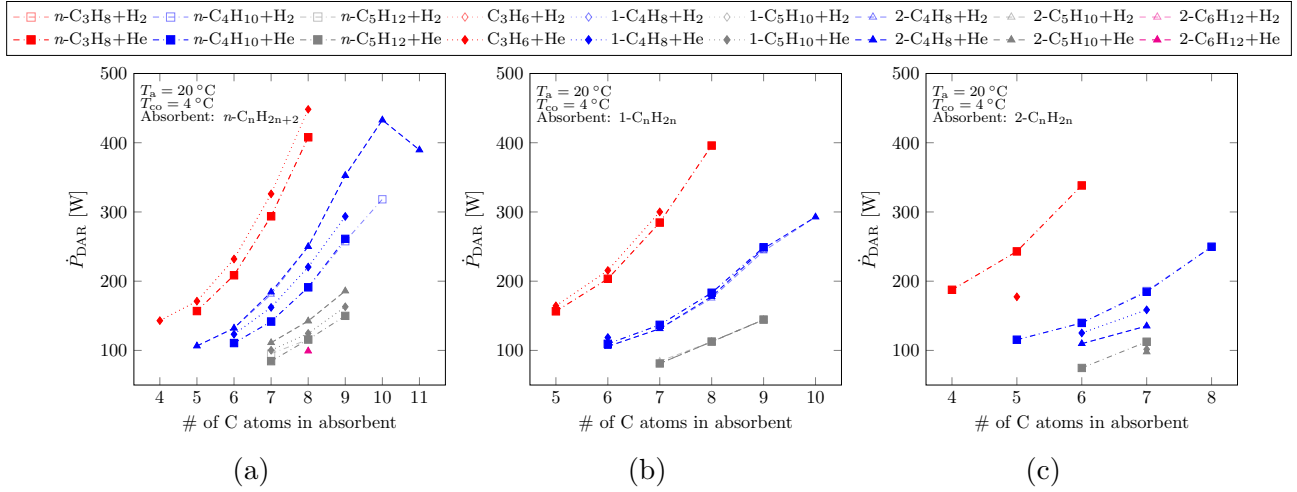


Figure 3.6: The effect of absorbent chain length on DAR design power, $\dot{P}_{\text{DAR}}$ required for maximum cooling rates, $\dot{Q}_{\text{evap}}$ considering different straight-chain aliphatic refrigerants under ambient temperature, $T_a = 20^\circ\text{C}$ and cooling temperature, $T_{co} = 4^\circ\text{C}$ for three straight-chain aliphatic absorbents: (a) n -alkanes ($n\text{-C}_n\text{H}_{2n+2}$); (b) 1-alkenes ($1\text{-C}_n\text{H}_{2n}$) and (c) 2-alkenes ($2\text{-C}_n\text{H}_{2n}$).

ically declines as the ambient temperature increases. It can also be revealed that thermodynamically under the design conditions, using helium as auxiliary gas introduces an imperceptible cooling rate enhancement over using hydrogen. This enhancement marginally increases as the ambient temperature increases. For example, for $2\text{-C}_4\text{H}_8\text{-}n\text{-C}_8\text{H}_{18}$, a helium-pressurised DAR system can produce 1 %, 2 % and 5 % higher cooling rates compared to a hydrogen-pressurised DAR system running with the same design parameters ($\dot{P}_{\text{DAR}}$, $\tilde{x}_{\text{rs}}$ and p_{ch}) but at different ambient temperatures, respectively: 20°C , 30°C and 40°C .

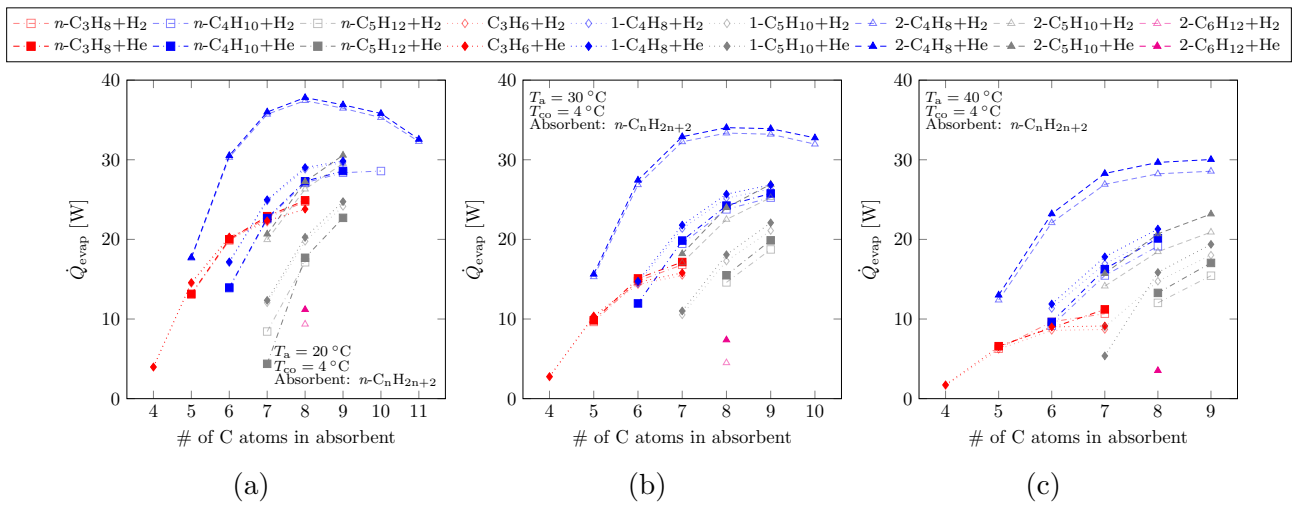


Figure 3.7: Variation of maximum cooling rates, $\dot{Q}_{\text{evap}}$ against carbon-chain length of the optimum absorbent in hydrocarbon-based working fluids [straight-chain aliphatic refrigerants + n -alkane ($n\text{-C}_n\text{H}_{2n+2}$) absorbent] for cooling temperature, $T_{co} = 4^\circ\text{C}$ and three ambient temperatures: (a) $T_a = 20^\circ\text{C}$; (b) $T_a = 30^\circ\text{C}$ and (c) $T_a = 40^\circ\text{C}$.

A sensitivity analysis based on the elementary effect (EE) method is deployed to validate the effect of different decision variables on the prediction of cooling rates using the model presented in Chapter 2. The elementary effect (EE) method has been developed by Morris [276] and modified by Campolongo *et al.* [277]. In EE analysis, sensitivities index for a decision variable (hereafter called factor i), X_i on response of sample j , Y_j , $EE_{i,j}$ is calculated based on the following approximation: [278]

$$EE_{i,j} = \frac{Y(X_1, \dots, X_i + \Delta, \dots, X_N) - Y(X_1, \dots, X_i, \dots, X_N)}{\Delta} \quad \forall i \in 1, \dots, N, \quad (3.32)$$

where Δ is the incremental change introduced to factor i and N is the number of sample realisation, $N = (N_{X_j} + 1)N$ with N_{X_j} is the number of studied factors (which are 9 factors for this study) listed in Table 3.8 and N_s is the number of samples specified as 100 and found sufficient to ensure convergence. For the N samples, the mean value of the elementary effect of factor i can be calculated as:

$$\mu_{EE,i} = \frac{1}{N} \sum_{j=1}^N EE_{i,j}. \quad (3.33)$$

To avoid cancellation effects of opposite-sign elementary-effect values, Campolongo *et al.* [277] proposed replacing $\mu_{EE,i}$ with the mean of absolute values of the elementary effects, $\mu_{EE,i}^*$:

$$\mu_{EE,i}^* = \frac{1}{N} \sum_{j=1}^N |EE_{i,j}|. \quad (3.34)$$

The standard deviation of the elementary effects is

$$\sigma_{EE,i} = \sqrt{\frac{1}{N-1} \sum_{j=1}^N (EE_{i,j} - \mu_{EE,i})^2}. \quad (3.35)$$

The mean $\mu_{EE,i}$ gives information about the overall influence of factor i on the model response. The mean $\mu_{EE,i}$ can be considered an approximation of the mean partial derivative. The value of standard deviation, $\mu_{EE,i}$ gives an indication about the ensemble of the factor's effects. If this factor likely interacts with other factors, $\mu_{EE,i}$ also indicates whether the response change monotonically as factor i changes or not. [278] The EE sensitivity analysis is completed in gPROMS and the results are presented in Figure 3.8 and Table 3.8.

From Figure 3.8, it can be observed that the carbon-chain length of the refrigerant, $n_{CH_2,refr}$ is

the most influential factor, not only for the working-fluid combinations displayed in Figure 3.8 but also for all investigated families. The values of $\mu_{EE,i}$ and $\mu_{EE,i}^*$ for $>\text{CH}_2$ multiplicity in both the refrigerant and absorbent suggest a non-monotonous relation between the predicted $\dot{Q}_{\text{evap}}$ and the chain lengths of refrigerant and absorbent which agrees with optimisation results presented in Figure 3.7. High $\sigma_{EE,\text{refr},\text{CH}_2}$ is attributed to the complexity of the model and how different factors are highly interactive. The results in Table 3.8 show that absolute values of $\sigma_{EE,i}$ for T_a and T_{co} coincide with their corresponding values of $\sigma_{EE,i}^*$. These results verify that cooling rate predictions monotonically increase as cooling temperatures increase and the ambient temperature decreases. The analysis shows that cooling rate predictions are less influenced by factors like n_g , $\bar{p}_9$.

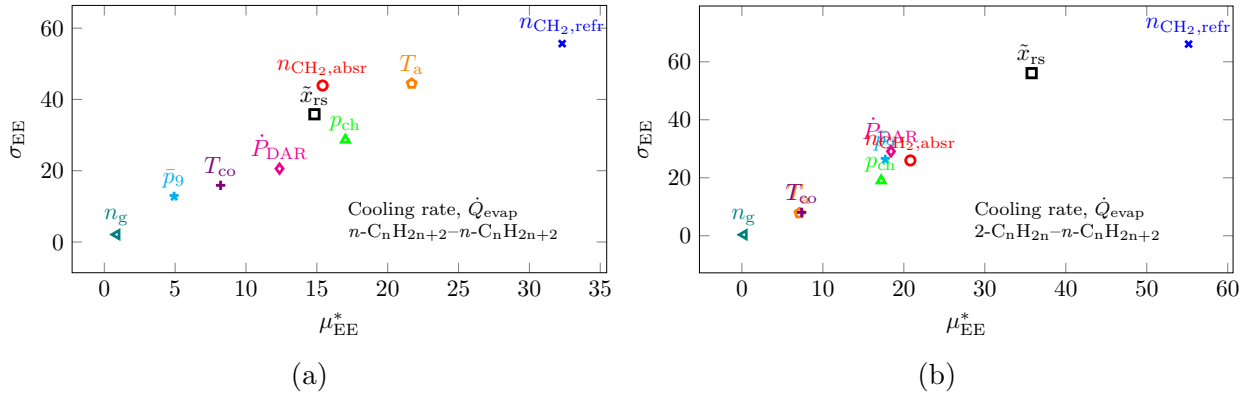


Figure 3.8: Elementary effect sensitivity analysis to study the effect of decision variables and model input variables on the prediction of cooling rates, $\dot{Q}_{\text{evap}}$ for two working-fluid combinations from Table 3.7: (a) $n\text{-C}_n\text{H}_{2n+2}-n\text{-C}_n\text{H}_{2n+2}$, and (b) $2\text{-C}_n\text{H}_{2n}-n\text{-C}_n\text{H}_{2n+2}$.

NLP optimisation results also recommend that alkanes can be coupled with different refrigerant options. The optimisation results also suggest working-fluid pairs are not recommended to be from the same family. In addition, the results suggest that the refrigerant and absorbent chain lengths are recommended to be at least two carbon atoms apart for optimum systems.

The – so far – best twelve identified DAR-system designs are listed in Table 3.9. It is observed that the cooling rates, $\dot{Q}_{\text{evap}}$ presented in this table tend to be lower than those reported earlier in Chapter 2. This observation is attributed to the fact that $\dot{Q}_{\text{evap}}$ reported in Chapter 2 have been considered for DAR systems charged with 20 mol % refrigerant-rich working fluid mixture. On one hand, reducing the rich solution composition (as observed in Table 3.9) results in lower $\dot{Q}_{\text{evap}}$. On the other hand, as it has been studied in Chapter 2, the absorption process is thermodynamically more favourable when the weak-solution composition is less, reflected by a lower Henry constant

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Table 3.8: Results of the elementary effect sensitivity of cooling rate, $\dot{Q}_{\text{evap}}$ predictions considering the effect of decision variables and model inputs for two working-fluid combinations from Table 3.7: (a) $n\text{-C}_n\text{H}_{2n+2}$ – $n\text{-C}_n\text{H}_{2n+2}$, and (b) $2\text{-C}_n\text{H}_{2n}$ – $n\text{-C}_n\text{H}_{2n+2}$.

Variable	Range	Unit	$n\text{-C}_n\text{H}_{2n+2}$ – $n\text{-C}_n\text{H}_{2n+2}$			$2\text{-C}_n\text{H}_{2n}$ – $n\text{-C}_n\text{H}_{2n+2}$		
			μ_{EE}	μ_{EE}^*	σ_{EE}	μ_{EE}	μ_{EE}^*	σ_{EE}
$\bar{p}_9$	[0.05:0.2]		−2.89	4.93	12.78	−176	17.71	26.35
$\tilde{x}_{\text{rs}}$	[0.1:0.38]		6.95	14.83	35.84	32.62	35.78	56.09
$\dot{P}_{\text{DAR}}$	[50:500]	W	−3.19	12.37	20.57	1.77	18.41	29.09
p_{ch}	[2:21]	bar	−7.31	17.01	28.67	−1665	17.2	19.02
n_{g}	[0:1]		−0.83	0.87	2.09	−0.04	0.25	0.35
$n_{\text{CH}_2, \text{absr}}$	[0:9]		4.28	15.41	43.9	14.45	20.81	25.97
$n_{\text{CH}_2, \text{refr}}$	[0:5]		−2757	32.31	55.66	−528	55.17	66.09
T_{a}	[10:40]	°C	−2169	21.69	44.46	−7.1	7.1	7.82
T_{co}	[−18:8]	°C	8.21	8.21	15.9	7.38	7.38	8.05

(calculated by Equation (2.31)). Thus, a limit on weak-solution composition of the organic pair is imposed to fall below 10 mol %, by the constraint in Equation (3.18b), to ensure thermodynamically-favourable absorption, this constraint limits the refrigerant-rich solution compositions to the values listed in Table 3.9 which vary between 11.5 mol % to 14.3 mol %.

The optimum charge pressure for the optimised systems listed in Table 3.9 falls between 2.35 bar to 9.29 bar. Most of the DAR designs reported in this table require theoretical charge pressures below 4 bar which are found to be around 40 % lower than the minimum theoretical charge pressure required by a similar $\text{NH}_3\text{--H}_2\text{O}$ DAR system (9.7 bar) operating at $T_{\text{a}} = 20^\circ\text{C}$. Exceptions that need relatively higher pressure are C_3H_8 -based DAR systems which need theoretical charge pressure of 9.29 bar due to the higher volatility of C_3H_8 . Whereas, DAR design running with $2\text{-C}_4\text{H}_8$ – $n\text{-C}_7\text{H}_{16}$ – H_2 requires the least theoretical charge pressure (2.35 bar).

It has been established from experimental studies for DAR systems, such as those carried out by Najjaran *et al.* [85] and Choi *et al.* [259], that DAR performance deteriorates as the charge pressure increases. According to Dalton’s law (*see* Equations (2.22a) and (2.23a)), refrigerant partial pressure is proportional to the system charge pressure. When the pressures across the evaporator are higher, the latent heat of the refrigerant is less, adversely affecting the evaporation capacity in the evaporator. Thus, the NLP model tends to converge towards lower charge pressures bounded by the constraints presented in Equation (3.16). As the ambient temperature increases, it is found that higher charge pressure is needed to ensure refrigerant condensation. This partially contributes to lower $\dot{Q}_{\text{evap}}$ predictions demonstrated in Figure 3.7.

Table 3.9: Results of NLP optimisations with the objective to maximise the predicted cooling rate, $\dot{Q}_{\text{evap}}$ for cooling temperature, $T_{\text{co}} = 4^\circ\text{C}$ and ambient temperature, $T_{\text{a}} = 20^\circ\text{C}$. Working-fluid mixtures are sorted in a descending order according to optimum cooling rates, $\dot{Q}_{\text{evap}}$.

Rank	Working fluid	$\dot{Q}_{\text{evap}}$ [W]	$\dot{P}_{\text{DAR}}$ [W]	p_{ch} [bar]	$\tilde{x}_{\text{rs}}$	$\bar{p}_9$	$\bar{T}_{\text{gen,w}}$ [°C]	$C_{\text{CU},0}$ [£]	SPC [£W ⁻¹]
1	2-C ₄ H ₈ - <i>n</i> -C ₈ H ₁₈ -He	37.8	249.9	2.70	0.135	0.063	106.9	566	15.00
2	2-C ₄ H ₈ - <i>n</i> -C ₈ H ₁₈ -H ₂	37.4	249.9	2.70	0.135	0.067	106.9	566	15.15
3	2-C ₄ H ₈ - <i>n</i> -C ₉ H ₂₀ -He	36.9	352.5	3.40	0.124	0.046	131.7	692	18.74
4	<i>n</i> -C ₄ H ₁₀ -2-C ₈ H ₁₆ -He	36.7	249.6	2.88	0.135	0.078	112.2	567	15.42
5	2-C ₄ H ₈ - <i>n</i> -C ₉ H ₂₀ -H ₂	36.5	353.1	3.42	0.124	0.054	131.9	692	19.00
6	<i>n</i> -C ₄ H ₁₀ -2-C ₈ H ₁₆ -H ₂	36.4	249.9	2.89	0.135	0.083	112.4	567	15.60
7	2-C ₄ H ₈ - <i>n</i> -C ₇ H ₁₆ -He	36.0	184.3	2.48	0.142	0.071	90.1	475	13.21
8	2-C ₄ H ₈ - <i>n</i> -C ₁₀ H ₂₂ -He	35.8	432.8	3.54	0.121	0.047	143.3	779	21.74
9	2-C ₄ H ₈ - <i>n</i> -C ₇ H ₁₆ -H ₂	35.7	181.0	2.35	0.143	0.081	87.6	470	13.17
10	C ₃ H ₈ -2-C ₆ H ₁₂ -He	35.7	338.3	9.29	0.115	0.105	114.5	675	18.92
11	C ₃ H ₈ -2-C ₆ H ₁₂ -H ₂	35.4	338.3	9.29	0.115	0.127	114.5	675	19.06
12	2-C ₄ H ₈ - <i>n</i> -C ₁₀ H ₂₂ -H ₂	35.3	432.8	3.54	0.121	0.052	143.3	779	22.06

Theoretical generator-wall temperatures, $\bar{T}_{\text{gen,w}}$ listed in Table 3.9 are predicted using Equation (2.33). Interestingly, these theoretical generator-wall temperatures are lower than temperatures needed to operate NH₃-H₂O DAR systems (*see* Refs. [42, 63, 85]). Generator-wall temperatures for optimum DAR designs range between 87.6 °C and 143.3 °C which are in line with some measured values in literature for similar organic pairs (*e.g.*, those measured and recently reported by Choi *et al.* [259], and in Kim *et al.* [92]). Unsurprisingly, the least generator-wall temperature for optimum operation is predicted for 2-C₄H₈-*n*-C₇H₁₆-H₂ mixture, for its low charge pressure and required operating power. Such low generator-wall temperatures are advantageous for coupling DAR with low-temperature heat sources such as evacuated-tube heat-pipe (ETC-HP) solar collectors [42, 74, 95].

Heat rejection from DAR systems

Although it is challenging to present an accurate sizing for the proposed DAR designs due to the justification presented in Section 3.2.1, it is still interesting to study the effect of working fluid selection on the rate of heat dissipation from different DAR-unit components. The breakdown of the heat dissipated from DAR systems of different designs is displayed in Figures 3.9 and 3.10. It can be inferred from these two plots that in general, the rate of dissipated from the bubble pump is higher for higher ambient temperatures which can be linked to higher generation

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temperatures needed to maximise $\dot{Q}_{\text{evap}}$. It is also observed from Figure 3.9 that for a given refrigerant, 2-C₄H₈, as the number of carbon atoms in the absorbent molecule increases, the predicted heat loss at the bubble pump increases.

From the exact figure, it can be revealed that the heat that needs to be rejected from the rectifier tends to decrease as the absorbent chain length increases, leading to less rectifier area requirement. It can be inferred that the difference between the sizes of absorbent and refrigerant increases, and the purity of the refrigerant vapour entering the rectifier increases, limiting the rectifier heat load. It can also be observed that both the condensation and absorption heat loads are mainly controlled by the rate of refrigerant circulated across the DAR cycle and less influenced by the absorbent size.

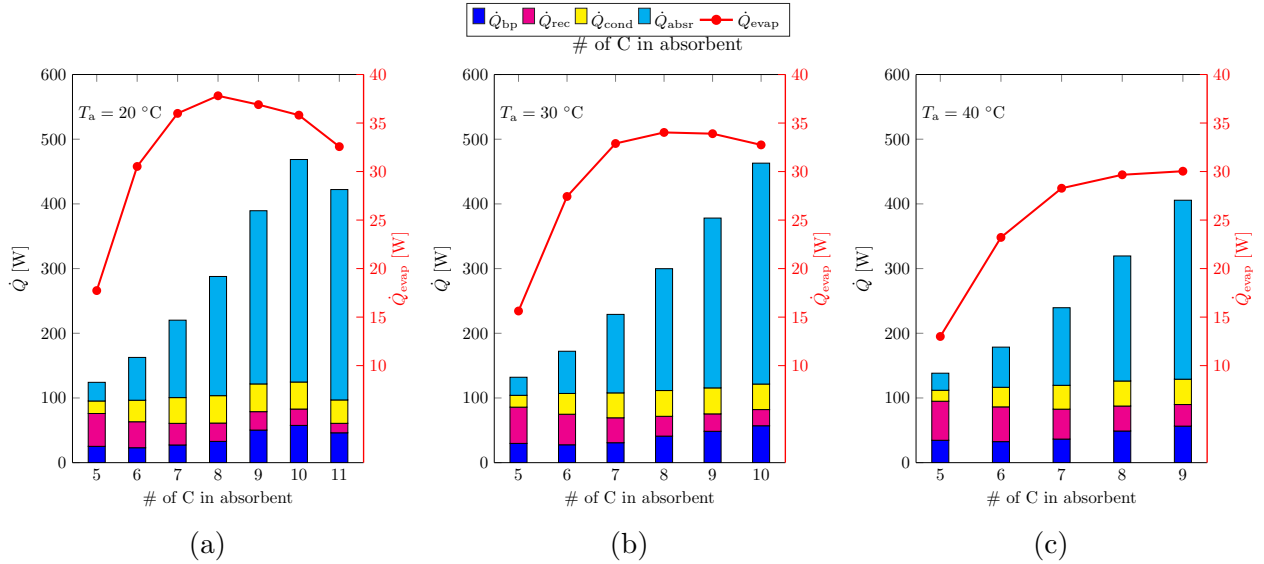


Figure 3.9: The effect of absorbent chain length on heat rejection rates (left ordinate) and cooling rate, $\dot{Q}_{\text{evap}}$ (right ordinate) from 2-C₄H₈- n -C_nH_{2n+2}-He DAR systems identified by the NLP model for cooling temperature, $T_a = 4^\circ\text{C}$ and three ambient temperatures: (a) $T_a = 20^\circ\text{C}$; (b) $T_a = 30^\circ\text{C}$ and (c) $T_a = 40^\circ\text{C}$.

On the other hand, it can be observed from Figure 3.10 that for a given absorbent, n -C₈H₁₆, the predicted heat dissipated from the bubble pump are proportional to the maximum refrigerant circulation rate that decreases as the refrigerant size increases. As interpreted from Figure 3.9, for a given absorbent, the heat should be rejected from the rectifier tends to increase as the number of carbon atoms in the refrigerant approaches that of the absorbent.

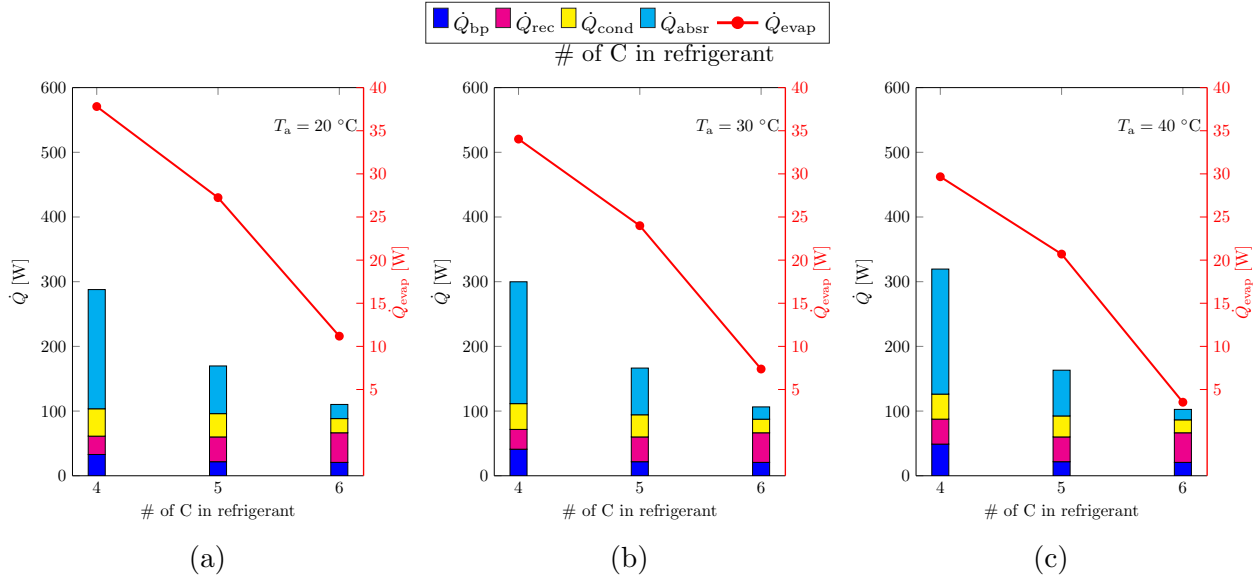


Figure 3.10: The effect of refrigerant chain length on heat rejection rates (left ordinate) and cooling rate, $\dot{Q}_{\text{evap}}$ (right ordinate) from 2- $\text{C}_n\text{H}_{2n}-n-\text{C}_8\text{H}_{18}$ -He DAR systems identified by the NLP model for cooling temperature, $T_a = 4^\circ\text{C}$ and three ambient temperatures: (a) $T_a = 20^\circ\text{C}$; (b) $T_a = 30^\circ\text{C}$ and (c) $T_a = 40^\circ\text{C}$.

Economic evaluation of optimal DAR systems

It is evident that there is a compromise between $\dot{Q}_{\text{evap}}$ and DAR system sizes. To economically evaluate different DAR designs listed in Table 3.9, the purchase costs, $C_{\text{CU},0}$ are predicted using Equation (3.3). To operate in ambient temperature of 20°C , the purchase costs corresponding to maximum $\dot{Q}_{\text{evap}}$ ranges between 470 £ and 780 £. Equation (3.13) is deployed to predict SPC corresponding to maximum $\dot{Q}_{\text{evap}}$ for the designs in this table. The 2- $\text{C}_4\text{H}_8-n-\text{C}_7\text{H}_{16}$ - H_2 DAR design results the least SPC (13.17 £W^{-1}) compared to 15 £W^{-1} for 2- $\text{C}_4\text{H}_8-n-\text{C}_8\text{H}_{18}$ -He DAR design. The specific purchase costs of cooling, SPC corresponding to maximum $\dot{Q}_{\text{evap}}$ are displayed in Figure 3.11. Unsurprisingly, it can be seen that the specific cooling cost, SPC , increases as the ambient temperature increases. This is attributed to the corresponding reduction in $\dot{Q}_{\text{evap}}$ (Figure 3.7) and the need for larger DAR systems to maximise $\dot{Q}_{\text{evap}}$.

It has been demonstrated in Table 3.9 and Figure 3.5 that maximum $\dot{Q}_{\text{evap}}$ can be obtained deploying 2- $\text{C}_4\text{H}_8-n-\text{C}_8\text{H}_{18}$ -He as a working fluid. However, this working fluid does not necessarily ensure lowest SPC as revealed in Figure 3.11. Instead, for $T_a = 20^\circ\text{C}$, 2- $\text{C}_4\text{H}_8-n-\text{C}_6\text{H}_{14}$ -He is identified with the least $SPC = 12.85 \text{ £W}^{-1}$. Whilst for $T_a = 30^\circ\text{C}$ and 40°C , 2- $\text{C}_4\text{H}_8-n-\text{C}_7\text{H}_{16}$ -He returns the least $SPC = 15 \text{ £W}^{-1}$ and 18 £W^{-1} , respectively. In this section, SPC presented here are not the ultimate minimum SPC obtained via optimisations;

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these are a function of maximum $\dot{Q}_{\text{evap}}$.

Obviously, from Figures 3.7 and 3.11, it can be emphasised that the refrigerant selection is not influenced by whether maximum $\dot{Q}_{\text{evap}}$ or minimum SPC is considered. Further, the ambient temperature rise is not influenced by the refrigerant selection. So far, we find that the most optimal refrigerant is 2-C₄H₈ (a 2-alkene with four carbon atoms). However, the ambient temperature and the objective affect the choice of absorbent. To maximise $\dot{Q}_{\text{evap}}$, *n*-C₈H₁₈ is the optimal working fluid for ambient temperatures, T_a : 20 °C and 30 °C, and *n*-C₉H₂₀ for $T_a = 40$ °C. Seeking the least SPC , the absorbent choice shall be *n*-C₆H₁₄ for $T_a = 20$ °C, and *n*-C₇H₁₆ for ambient temperatures: T_a : 30 °C and 40 °C.

From Figure 3.11, it is observed that using C₃H₆-*n*-C₄H₈ as the working fluid incurs the highest SPC for all considered ambient temperatures as a result of its low cooling capacity shown in Figure 3.7. In general, predicted $\dot{Q}_{\text{evap}}$ in Tables 3.9 and 3.12 is comparable to $\dot{Q}_{\text{evap}}$ of a 250-W DAR unit that uses NH₃-H₂O. [129, 130, 258]

It should be emphasised that, although there are high uncertainties in the cost estimation as discussed in Section 3.2.1 and the absence of other reliable economic evaluation methods for DAR systems, the presented SPC values are useful in presenting a thermo-economic evaluation for such emerging cooling technology. The presented CAMD-DAR framework can be easily adapted to consider more reliable costing methods whenever available.

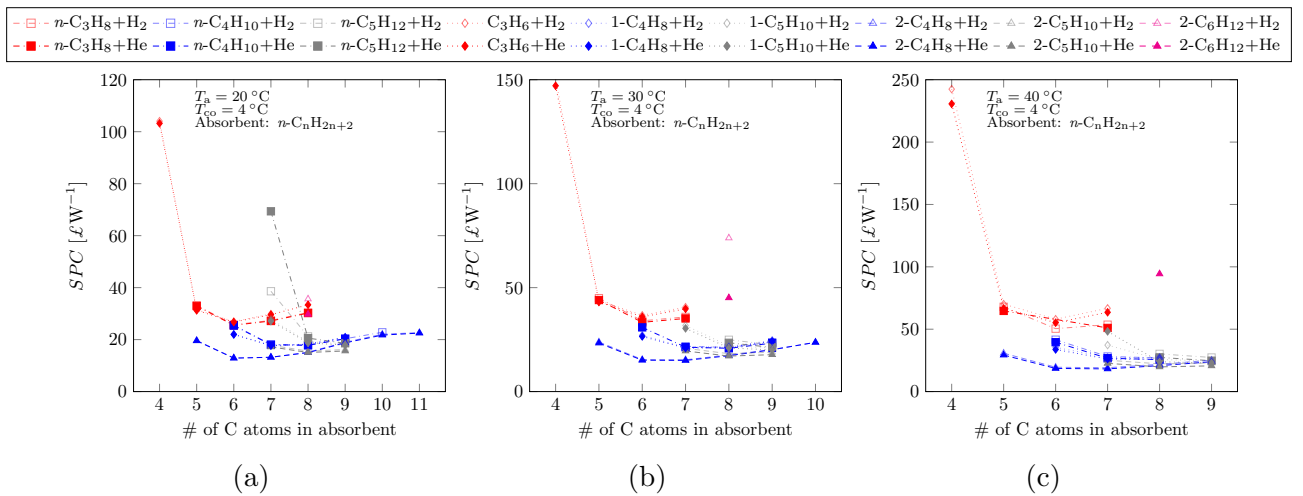


Figure 3.11: Specific purchase cost of cooling, SPC for DAR designs presented in Figure 3.7 for cooling temperature, $T_{\text{co}} = 4$ °C and three ambient temperatures: (a) $T_a = 20$ °C; (b) $T_a = 30$ °C and (c) $T_a = 40$ °C.

3.3.2 Parametric MINLP optimisations

Before using the full-scale MINLP CAMD-DAR framework, the framework is validated against the results of the NLP optimisations. For a given working-fluid combination in Table 3.7, the multiplicities of $>\text{CH}_2$ group in both refrigerant and absorbent, $n_{>\text{CH}_2,\text{refr}}$ and $n_{>\text{CH}_2,\text{absr}}$ and the auxiliary gas identity, n_g are now moved to the decision-variable space ending up with four continuous decision variables and four integer decision variables which are listed in Table 3.10. Hence, the optimisation problem in Equation (3.14) reduces to:

$$\max_{\substack{\tilde{x}_{\text{rs}}, p_{\text{ch}}, \dot{P}_{\text{DAR}}, \bar{p}_9 \\ n_{>\text{CH}_2,\text{refr}}, n_{>\text{CH}_2,\text{absr}}, \mathbf{n}_g}} \dot{Q}_{\text{evap}} \left\{ \tilde{x}_{\text{rs}}, p_{\text{ch}}, \dot{P}_{\text{DAR}}, \mathbf{n}_{\text{refr}}, \mathbf{n}_{\text{absr}}, \mathbf{n}_g \right\} \quad (3.14 \text{ revisited})$$

$$\text{s.t.} \quad u_{\text{L}} \leq u_{\text{L,bs}}, \quad (3.15a)$$

$$u_{\text{V}} \leq u_{\text{V,an}}, \quad (3.15b)$$

$$p_9 \leq p_{10} \leq p_{\text{evap,max}}, \quad (3.16a, 3.16b)$$

$$p_{\text{min}} < p_{\text{ch}} < p_{\text{max}}, \quad (3.16c, 3.16d)$$

$$T_{\text{sat,refr}} < T_{\text{bub,rs}}, \quad (3.17a)$$

$$T_{\text{bub,rs}} < T_{\text{gen,w}}, \quad (3.17b)$$

$$T_{\text{sat,refr}} < T_{\text{sat,absr}}, \quad (3.17c)$$

$$\tilde{x}_{\text{ws}} < \tilde{x}_{\text{rs}}, \quad (3.18a)$$

$$\tilde{x}_{\text{ws}} \leq \tilde{x}_{\text{ws,min}}, \quad (3.18b)$$

$$\dot{Q}_{\text{evap,g}} \leq \dot{Q}_{\text{evap,refr}}, \quad (3.19)$$

$$n_{\text{H}_2} + n_{\text{He}} = 1, \quad (3.23)$$

$$T_{\text{gen,w}} + 30 \leq T_{\text{AIT}}, \quad (3.24a)$$

$$\Gamma_j \leq 0.8, \quad (3.24b)$$

$$\log_{10}(GWP_j) \leq \log_{10}(150), \quad (3.25a)$$

$$\log_{10}(ODP_j) \leq \log_{10}(0.2), \quad (3.25b)$$

$$1 < \log_{10}(LC_{50}). \quad (3.26)$$

The parametric MINLP optimisations described by Equation (3.14 revisited) converge to the best optima. It is found that increasing the number of initial guesses (using multi-start optimisation)

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Table 3.10: Optimisation decision variable for DAR case studies with their lower and upper bounds definition and ranges for parametric MINLP (updating Table 3.3).

Variable	Description	Lower bound	Upper bound	Units
$\dot{P}_{\text{DAR}} = \dot{Q}_{\text{gen}}$	Generator heat rate	50	500	W
p_{ch}	Charging pressure	2	25	bar
$\tilde{x}_{\text{rs}}$	Rich solution molar composition	0.1	0.38	–
$\bar{p}_9$	Relative low evaporator pressure	0.02	0.2	–
$n_{>\text{CH}_2, \text{refr}}$	Multiplicity of $>\text{CH}_2$ in the refrigerant	0	5	–
$n_{>\text{CH}_2, \text{absr}}$	Multiplicity of $>\text{CH}_2$ in the absorbent	0	9	–
n_{H_2}	choice of H_2 as an auxiliary gas	0	1	–
n_{He}	choice of He as an auxiliary gas	0	1	–

beyond 120 initial guesses (*see* Table 3.6) does not improve the optimum DAR design. The parametric MINLP optimisation results for aliphatic working fluids are compared to the results obtained from NLP optimisations presented earlier in this chapter, and the comparison is displayed in Figure 3.12.

It can be observed in Figure 3.12 that for each organic working-fluid combination, the optimal working fluid identified by the MINLP optimisation coincides with the best working fluid identified using NLP optimisations, except for 1-alkene–1-alkene (*i.e.*, 1- C_nH_{2n} –1- C_nH_{2n}) working-fluid mixtures. The working fluid identified by NLP optimisation for the three considered ambient temperatures (C_3H_6 –1- C_7H_{14} – He). On the other hand, the optimum working fluids suggested by the MINLP are 1- C_4H_8 –1- C_9H_{18} – He for $T_{\text{a}} = 20^\circ\text{C}$ and 1- C_4H_8 –1- C_8H_{16} – He for $T_{\text{a}} = 30^\circ\text{C}$ and 40°C . Interestingly, these working fluids identified through MINLP optimisations correspond to 34 %, 59 % and 99 % more cooling than the working fluid identified through NLP optimisations.

3.3.3 Small-scale MINLP optimisation problem

The MINLP CAMD-DAR framework is further tested considering extending the decision-variable space to maximise cooling power output under ambient conditions of $T_{\text{a}} = 20^\circ\text{C}$ and cooling temperature, $T_{\text{co}} = 4^\circ\text{C}$. The following groups are varied for both absorbent and refrigerant: $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $=\text{CH}_2$ and $=\text{CH}-$. Two auxiliary gases were considered: hydrogen (H_2) and helium (He). The new decision-variable space consists of four continuous and ten integer

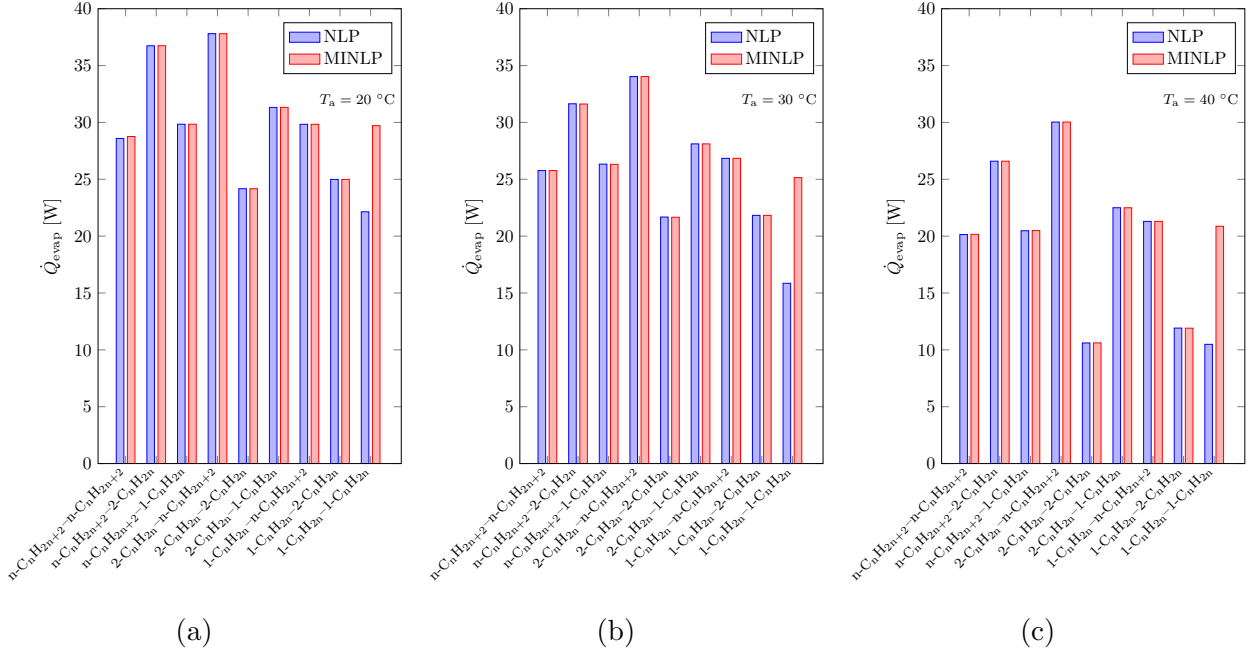


Figure 3.12: Comparison of MINLP and NLP results for selected refrigerant and absorbent families.

decision variables. The optimisation problem in Equation (3.14) can be defined as:

$$\begin{aligned}
 & \max_{\substack{\tilde{x}_{rs}, p_{ch}, \dot{P}_{DAR} \\ \mathbf{n}_{refr}, \mathbf{n}_{absr}, \mathbf{n}_g}} \quad \dot{Q}_{evap} \left\{ \tilde{x}_{rs}, p_{ch}, \dot{P}_{DAR}, \mathbf{n}_{refr}, \mathbf{n}_{absr}, \mathbf{n}_g \right\} & (3.14 \text{ revisited}) \\
 & \text{s.t.} \quad \mathbf{h}(\boldsymbol{\theta}, \boldsymbol{\beta}) = 0, \\
 & \quad \mathbf{g}(\boldsymbol{\theta}, \boldsymbol{\beta}) \leq 0, \\
 & \quad \boldsymbol{\theta} \in [\boldsymbol{\theta}^{LB}, \boldsymbol{\theta}^{UB}] \subseteq \mathbb{R}^n, \\
 & \quad \boldsymbol{\beta} \in [\boldsymbol{\beta}^{LB}, \boldsymbol{\beta}^{UB}] \subseteq \mathbb{Z}^m,
 \end{aligned}$$

where $\mathbf{h}(\boldsymbol{\theta}, \boldsymbol{\beta}) = 0$, and $\mathbf{g}(\boldsymbol{\theta}, \boldsymbol{\beta}) \leq 0$, respectively, represent the sets of equality and inequality constraints relevant to the DAR system listed in Table 3.4. The vectors $\boldsymbol{\theta}^{LB}$, $\boldsymbol{\theta}^{UB}$, $\boldsymbol{\beta}^{LB}$, $\boldsymbol{\beta}^{UB}$ are lower bounds and upper bounds imposed on the continuous and integer decision variables which are listed in Tables 3.10 and 3.11. As polar groups are not considered in this MINLP, the constraints in Equation (3.22) become redundant and do not affect the optimisation results.

The optimisation results are presented in Table 3.12. It can be observed that there is a very good match between the optimum working fluid in this table and the results of the NLP optimisations in Table 3.9. Further, the order in which the MINLP optimisation ranks the best working-fluid mixtures compares well with the ranking generated by the NLP optimisations within the first six

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Table 3.11: Upper and lower bounds for integer decision variables considered in small-scale MINLP problem. Variables not listed in this table take the same bounds listed in Table 3.10.

j		$n_{-\text{CH}_3,j}$	$n_{>\text{CH}_2,j}$	$n_{=\text{CH}_2,j}$	$n_{=\text{CH}-,j}$
“refr”	LB	0	0	0	0
	UB	2	5	1	2
“absr”	LB	0	0	0	0
	UB	2	9	1	2

optimum alternatives. It should be recalled that the hybrid stochastic-deterministic optimisation method used in this study attempts to solve the optimisation problem as many times as the number of initial guesses provided, while these initial guesses (apart from the very initial one) are randomly generated by the solver using a Sobol algorithm. Thus, the MINLP problem is solved as often as the solver succeeds in converging to an optimal solution. Employing an adequate number of initial guesses ensures not only reaching a non-dominated optimal solution but also a list of alternative optimal working fluids; thus, it is not necessary to employ integer cuts to explore new alternatives.

Table 3.12: Ranking of optimum working fluids for cooling temperature, $T_{\text{co}} = 4^\circ\text{C}$ and ambient temperature, $T_{\text{a}} = 20^\circ\text{C}$. Working fluid pairs are sorted in descending order according to optimum cooling rates, $\dot{Q}_{\text{evap}}$.

MINLP Rank	NLP Rank	Working fluid	$\dot{Q}_{\text{evap}}$ [W]	$\dot{P}_{\text{DAR}}$ [W]	p_{ch} [bar]	$\tilde{x}_{\text{rs}}$	$\bar{p}_9$	$C_{\text{CU},0}$ [£]	SPC [£W^{-1}]
1	1	2-C ₄ H ₈ - <i>n</i> -C ₈ H ₁₈ -He	37.8	248.5	2.70	0.135	0.064	564	14.93
2	2	2-C ₄ H ₈ - <i>n</i> -C ₈ H ₁₈ -H ₂	36.6	260.5	2.90	0.129	0.064	579	15.84
3	3	2-C ₄ H ₈ - <i>n</i> -C ₉ H ₂₀ -He	36.5	313.2	2.70	0.127	0.065	645	17.68
4	5	2-C ₄ H ₈ - <i>n</i> -C ₉ H ₂₀ -H ₂	36.5	343.7	3.20	0.124	0.057	680	18.66
5	6	<i>n</i> -C ₄ H ₁₀ -2-C ₈ H ₁₆ -H ₂	36.3	239.8	2.60	0.136	0.095	552	15.20
6	4	<i>n</i> -C ₄ H ₁₀ -2-C ₈ H ₁₆ -He	35.9	257.2	3.00	0.129	0.074	575	16.03

The thermodynamic cycle of the DAR with the optimum working fluid in Table 3.12, 2-C₄H₈-*n*-C₈H₁₈-He identified by the MINLP optimisation, is represented using the Oldham diagram displayed in Figure 3.13. Oldham diagrams are commonly used to represent absorption refrigeration cycles, [104] in which equilibrium temperatures, pressures and compositions of the 2-C₄H₈-*n*-C₈H₁₈ working fluid are plotted at different system states (defined in Figure 3.3). From Figure 3.13, it can be observed that the partial refrigerant pressure ranges from 0.17 bar to 2.7 bar, corresponding to expansion and total system pressures, respectively. It can be observed from Figure 3.13 that the refrigerant partial pressure increases during the evaporation step due to the auxiliary gas, which pressure drops along the evaporation step, so the system pressure remains unchanged.

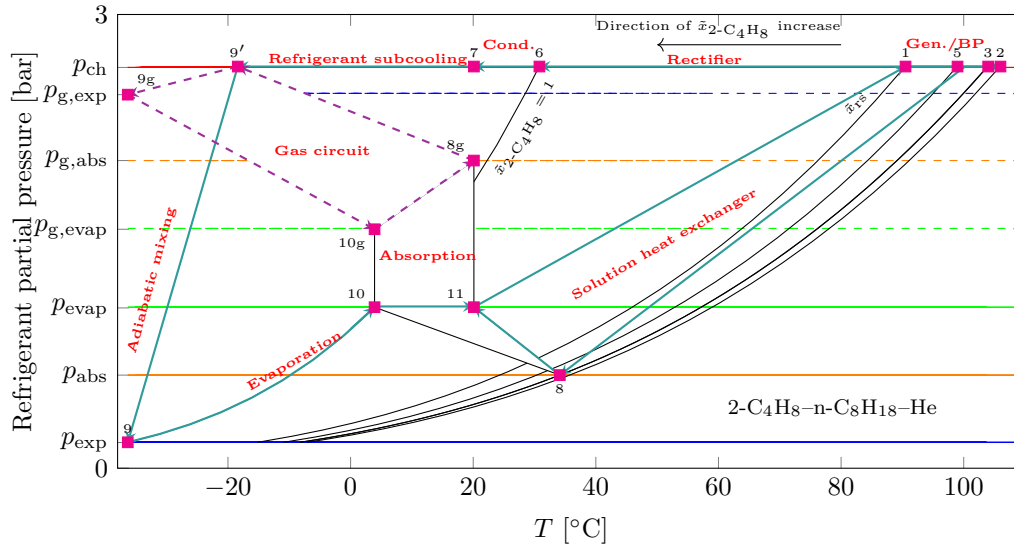


Figure 3.13: Oldham diagram describing the thermodynamic DAR cycle based on the configuration in Figure 3.3 with the optimum working fluid, 2-C₄H₈-n-C₈H₁₈-He from Table 3.12.

Comparison of objective functions on working-fluid selection

It can be concluded from the above discussion that the objective function can shape the decision of the working fluid selection and, probably, the DAR system design. To evaluate the effect of the objective function, MINLP optimisations are carried out solving Equation (3.14 revisited) but for two other objective functions, to minimise the purchase cost, $C_{CU,0}$ and minimise the specific purchase cost of cooling, SPC . When the purchase cost, $C_{CU,0}$ is minimised, a lower bound on the cooling rate is set to $\dot{Q}_{\text{evap}} \geq 5 \text{ W}$ to ensure positive $\dot{Q}_{\text{evap}}$.

Different objective functions are compared in Table 3.13. Again, the results in this table establish that the refrigerant selection is not affected by the change in the objective function, where 2-C₄H₈ is the optimum refrigerant for all objective functions studied. On the other hand, absorbent selection depends on the objective function. When maximum $\dot{Q}_{\text{evap}}$ is called, the optimum absorbent is n-C₈H₁₈, while if minimum purchase cost is called, 2-C₆H₁₂ is selected, whilst n-C₆H₁₄ is promoted as the optimum absorbent for minimum SPC . It can be realised that DAR design variables ($\dot{P}_{\text{DAR}}$, p_{ch} and $\tilde{x}_{\text{rs}}$) also depend on the objective function.

Clearly, for minimum purchase cost, the NLP convergence toward the smallest DAR size characterised by its power, $\dot{P}_{\text{DAR}}$ (50 W), whereas, when SPC is minimised, the DAR size (132 W) falls between the largest DAR for maximum $\dot{Q}_{\text{evap}}$ (250 W) and the size for minimum purchase cost (50 W). The DAR design for minimum SPC coincides with that if the COP is maximised. In the

3.4. SUMMARY

current framework, the purchase cost calculated using Equation (3.3) is a function in DAR design power only. Thus, minimising SPC is almost the same problem as maximising the coefficient of performance, which has been confirmed by running the MINLP for maximum COP. Notably, SPC is the highest for the system with the minimum purchase cost, $C_{CU,0}$.

From Table 3.13, it can be observed that the optimisation objective influences less the rich-solution composition; nonetheless, it is more influenced by the constraint in Equation (3.18b) and the working fluid. Interestingly, the predicted generator temperature is the lowest for the system with a minimum T_{gen} (69 °C) due to the low charge pressure and rich-solution composition required to charge the system.

Table 3.13: Results of parametric NLP optimisations for $T_a = 20$ °C with three different objectives to: minimise the purchase cost, $C_{CU,0}$ and minimise the specific purchase cost of cooling, SPC

Objective function	Working fluid	$\dot{Q}_{evap}$ [W]	$\dot{P}_{DAR}$ [W]	p_{ch} [bar]	$\tilde{x}_{rs}$	$\bar{T}_{gen,w}$ [°C]	$C_{CU,0}$ [£]	SPC [£W ⁻¹]
max $\dot{Q}_{evap}$	2-C ₄ H ₈ - <i>n</i> -C ₈ H ₁₈ -He	37.8	249.9	2.70	0.135	106.9	566	15.00
min $C_{CU,0}$	2-C ₄ H ₈ -2-C ₆ H ₁₂ -He	5.3	50.0	3.31	0.142	100.77	222	44.48
min SPC_{CU}	2-C ₄ H ₈ - <i>n</i> -C ₆ H ₁₄ -He	30.5	132.2	2.22	0.157	69.22	391	12.80

The results in Table 3.13 emphasise the importance of considering the trade-off between maximising the cooling power output and minimising the purchase cost of the DAR system. The presented set of MINLP optimisations offers alternative working fluids that can perform as well as standard DAR units with NH₃-H₂O in terms of $\dot{Q}_{evap}$. Moreover, the NLP optimisations suggested working fluids that can be generated with relatively lower temperatures compared to temperatures required by NH₃-H₂O DAR systems.

3.4 Summary

In this chapter, an integrated computer-aided molecular design and DAR system optimisation framework for DAR systems (CAMD-DAR framework) is presented to simultaneously design working fluid and DAR systems. The CAMD-DAR framework is based on the DAR mathematical model and the molecular-based, group-contribution SAFT- γ Mie equation of state, which has been described in Chapter 2. Computer-aided molecular design using SAFT- γ Mie has not been applied to such a framework for the thermal-powered domestic refrigeration system. Without

appropriate sizing methods, a simple costing correlation is presented based on market prices for diffusion absorption refrigeration units to assess different working-fluid systems economically. In addition, relevant process and molecular feasibility constraints are included in other relevant environmental, safety and toxicity constraints. Having formulated the MINLP problem, a hybrid stochastic-deterministic optimisation method is described, which has not been applied to such a framework for thermal-powered domestic refrigeration before.

To validate the presented framework, the MINLP solution for the presented CAMD-DAR framework is compared against the solution of parametric NLP optimisations. Optimisations were carried out for refrigerant and absorbent mixtures of simple hydrocarbons considering homologous series of simple hydrocarbons (n -alkanes, 1-alkenes and 2-alkenes) for both refrigerant and absorbent molecules. Three ambient temperatures: 20 °C, 30 °C and 40 °C are considered and a cooling temperature of 4 °C is considered to resemble mean temperature in a domestic refrigeration chamber.

In addition, a sensitivity analysis based on elementary effects was applied, which supported NLP optimisation results in understanding how different decision variables and model inputs influence the cooling rate, $\dot{Q}_{\text{evap}}$ as the objective function. Understanding the effect of decision variables on the objective functions helps to set the appropriate bounds for the decision-variable space to make the best use of the stochastic-deterministic MINLP method while limiting the risk of missing any of the feasible space. The CAMD-DAR framework shows that the cooling rate monotonically decreases as ambient temperature increases or as cooling temperature decreases, which agrees with the elementary-effect sensitivity analysis for two representative working-fluid systems.

The presented MINLP results demonstrate the suitability of the proposed CAMD-DAR framework for the integrated working fluid and DAR process design using a hybrid stochastic-deterministic optimisation method. The presented results also confirm that simple organic working-fluid mixtures are great alternatives to the commonly used ammonia–water mixture for their low heat-source temperature and low charging pressure requirements. Maximum $\dot{Q}_{\text{evap}}$ can be obtained using a 250 W DAR unit charged with 2-butene– n -octane–He for a 38 W cooling rate, corresponding to a specific purchase cost of cooling of £ 15 per W. The presented working fluids offer comparable cooling rates relative to commercial ammonia–water systems of similar sizes. The predicted cooling rates agree with similar DAR system cooling rates reported in the literature. Organic-based DAR systems can offer SPC as low as £ 13 per W of cooling. The

3.4. SUMMARY

CAMD-DAR framework demonstrates that the optimum DAR system for maximum cooling does not necessarily coincide with the optimum DAR system for the minimum specific purchase cost of cooling. The optimisations suggest that hydrocarbons with four carbon atoms perform well in most cases and can be coupled with many organic absorbents.

the presented costing method, though its high uncertainty, is a valuable tool for the thermo-economic assessment of DAR systems based on different working-fluid alternatives. The CAMD-DAR framework can be easily modified to include more accurate costing methods. In general, the CAMD-DAR formulation is a helpful tool that paves the way toward designing novel working fluids for DAR systems.

Chapter 4

Case Studies in CAMD for Domestic Diffusion Absorption Refrigeration

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4.1 Introduction

As reviewed in Chapter 1, DAR is a thermally-driven refrigeration technology (depicted in Figure 3.3) suitable for electricity-free operation. DAR systems have great merits as they do not have moving parts. DAR systems are favoured for hotel installations for their quiet operation, long lifetimes and minimal running (maintenance/operation) costs. As mentioned in Chapter 3, DAR are manufactured and sold as single units, resulting in low capital costs. [38,65,66] DAR systems sold in market use $\text{NH}_3\text{-H}_2\text{O}$ with H_2 or helium as the auxiliary gas. As it has been highlighted in Chapter 3, DAR cooling system market prices range considerably based on system size and options between £ 300 and £ 1800 . [71,72]

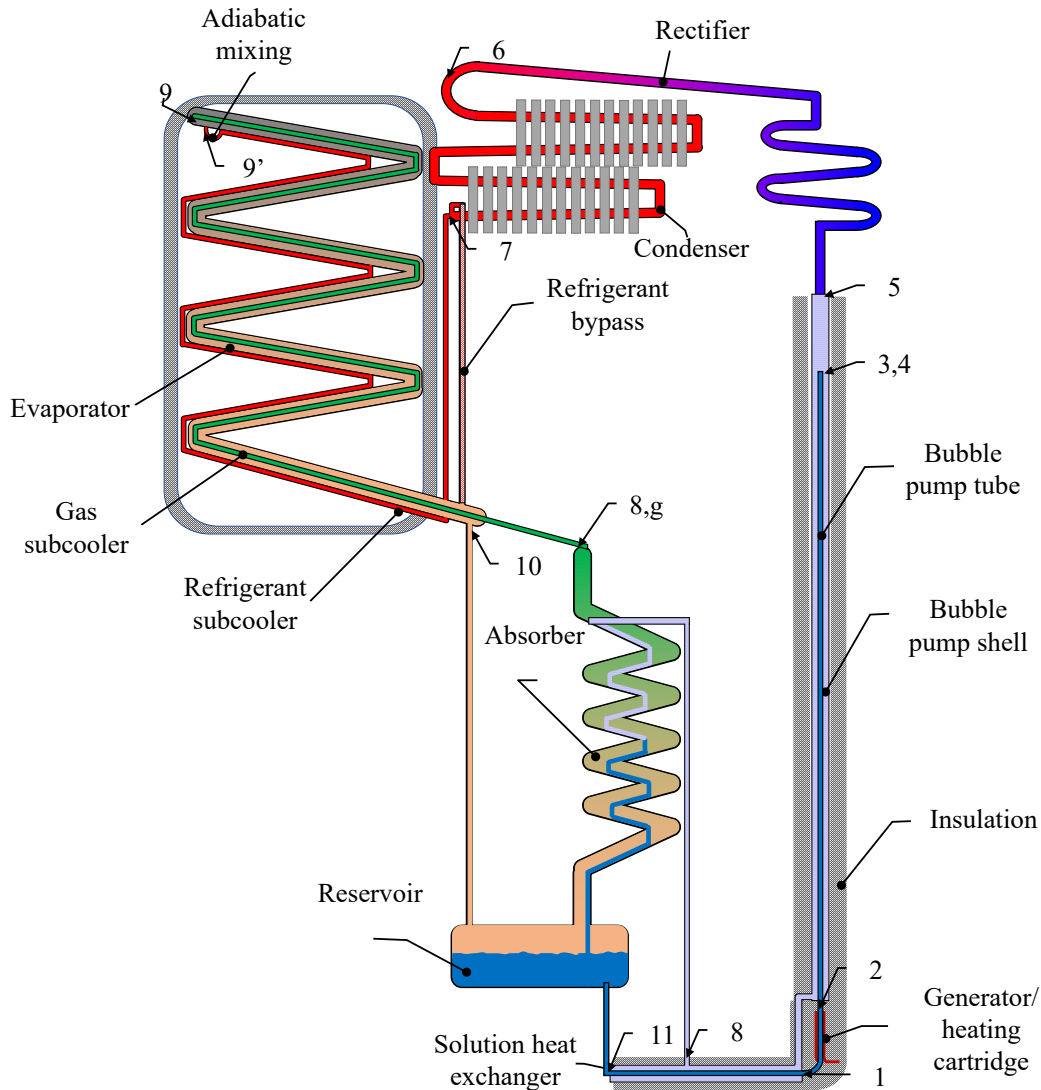


Figure 3.3: A schematic diagram for a typical DAR system with a semi-attached generator. (repeated from page 96)

High-temperature heat sources needed by DAR units limit its market for solar applications since the performance of the bubble pump limits DAR cooling capacity. [66, 73] Heat-source temperatures in the range of 140 °C to 200 °C are typically required to drive DAR systems with $\text{NH}_3\text{-H}_2\text{O-H}_2$ as the working-fluid mixture, due to the system pressures and temperatures required for the operation of the bubble-pump and condenser. As suggested earlier in Chapter 1, meeting low-temperature heat sources motivates us to explore more working fluid mixtures to lower temperature and pressure requirements for more flexible DAR operation. [38, 63, 64].

To assess DAR systems operated by different heat sources using variant working fluid systems, integrated models are needed to model different working performances. There have been few contributions towards presenting a validated integrated-DAR model that can be used systematically to explore various working fluids for DAR operation. In addition, apart from work presented by Harraz *et al.* [63, 64] modelling working fluids for a DAR system using a group-contribution (GC) equation of state (EoS) such as SAFT- γ Mie has not been considered before.

To the best of the author’s knowledge, there is almost no CAMD study that considers DAR systems and how alternative working-fluid selection can matter with their thermo-economic performance and safety consideration. Integrated computer-aided molecular design (CAMD) and DAR system optimisation via MINLP optimisation has not been applied before to diffusion absorption refrigeration systems.

Previously, Harraz *et al.* [63, 212] conceptualised a CAMD-DAR modelling framework that can be used to identify optimal working-fluid mixtures considering thermo-economic and environmental limitations. This CAMD-DAR framework has been presented and implemented in Chapter 3. Thermodynamic properties of working-fluid mixtures are estimated using SAFT- γ Mie EoS [184, 195, 230]. In contrast, some other needed properties like surface tension and critical properties are calculated using appropriate GC methods described in Chapter 2. The CAMD-DAR thermodynamic model has been presented in Chapter 2 and is valid against experiments performed at Imperial College London and other data from the literature. [212]

To solve the presented MINLP-CAMD-DAR optimisation problem, an MINLP optimisation method is needed. It has been discussed in Chapter 3 that using most deterministic gradient-based MINLP optimisation algorithms do not guarantee a globally optimal solution, except at the cost of using expensive global optima algorithms due to the curse of dimensionality usually encountered in big combinatorial MINLP problems. [202, 220, 224] In contrast, stochastic

4.1. INTRODUCTION

MINLP optimisation algorithms (*i.e.* genetic algorithms, simulated annealing) are more likely to find or approach global optima with randomly generated initial guesses; though, stochastic optimisation methods are susceptible to premature termination. [225,226] Thus, implementing a hybrid stochastic-deterministic optimisation method combines the advantages of both stochastic and deterministic approaches.

The objective of this chapter is to use the CAMD-DAR framework developed in Chapter 3 (depicted again in Figure 3.1 for convenience and clarity) in the context of domestic refrigeration. The adapted CAMD-DAR framework is implemented to explore more organic-based working fluid mixtures suitable for DAR domestic use. The MINLP CAMD-DAR problem is solved using the hybrid stochastic-deterministic optimisation method described in Chapter 3, where multi-start optimisations are considered; randomly generated initial guesses generated by a Sobol algorithm [269] are used to solve a series of MINLP optimisations using the gradient-based outer approximation–equality relaxation–Augmented penalty (OAERAP) optimisation method described by Viswanathan and Grossmann [207].

In this chapter, two main case studies are considered. The first case presents a working-fluid design for a medium-scale domestic 10-ft³ DAR. The MINLP-CAMD-DAR problem is solved to design working-fluid mixtures and charging settings (*e.g.*, p_{ch} and $\tilde{x}_{\text{rs}}$) under variant ambient temperatures and for a wide range of refrigeration and freezing temperatures. Optimal and sub-optimal working fluids and corresponding DAR charging settings are presented and compared to an NH₃–H₂O DAR system to demonstrate different trade-offs between thermodynamic performance, required heat source temperature and *SPC*. Further, more NLP optimisations are applied to the optimal working fluids identified by the MINLP-CAMD-DAR problem to investigate the optimum DAR charging settings for different DAR sizes. The results present a set of alternative working fluids for low heat-source temperature applications.

In the second case study, the trade-off between the DAR size (hence the purchase cost) and the cooling rate is considered. The DAR size, V_{CU} (alternatively the DAR rated power, $\dot{P}_{\text{DAR}}$) is considered as a decision variable, and the MINLP-CAMD-DAR problem is solved to design working-fluid mixtures and charging settings (*e.g.*, p_{ch} and $\tilde{x}_{\text{rs}}$) for different objective functions ($\max \dot{Q}_{\text{evap}}$, $\min C_{\text{CU},0}$ and $\min \text{SPC}$). Further, multi-objective optimisation is considered to highlight the trade-off between maximising the cooling rate, $\dot{Q}_{\text{evap}}$ and minimising the purchase cost, $C_{\text{CU},0}$ to obtain a set of non-dominated design alternatives.

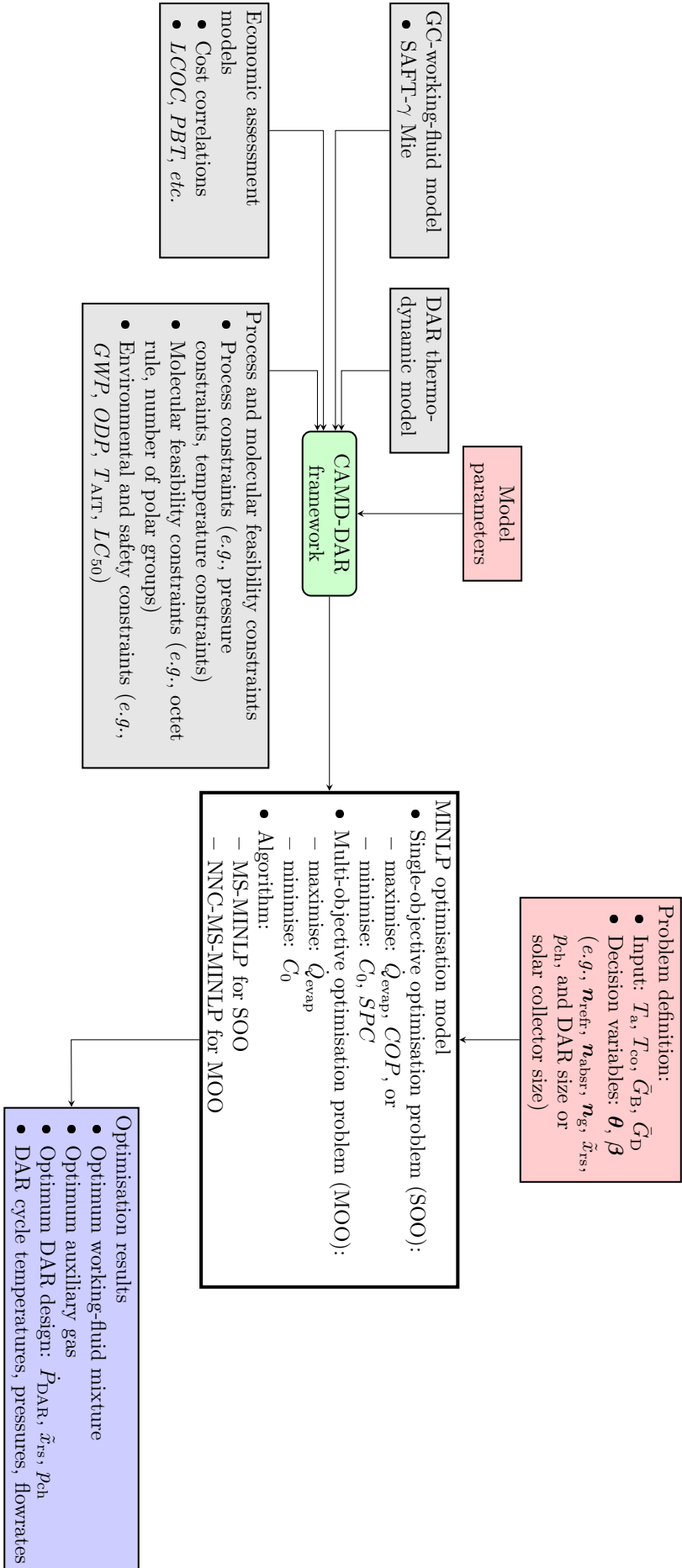


Figure 3.1: The proposed computer-aided molecular and system design for DAR systems (CAMD-DAR). (repeated from page 93)

4.2 Problem definition

The CAMD-DAR framework presented in Figure 3.1 has been developed in Chapter 3. The CAMD-DAR framework is built up of five main components: a DAR system model, which is presented in Chapter 2; a working-fluid model based on SAFT- γ Mie GC-EoS [195, 230]; costing method, system and molecular constraints proposed in Chapter 3; and finally, an optimisation method which also presented in Chapter 3.

Following the same consideration adopted in Chapter 3, the DAR shown in Figure 3.3 is specified by having a semi-attached bubble pump configuration as it has been recommended by Zohar *et al.* [70] and tested by Kim *et al.* [92]. The input model parameters which are represented by Equations (3.4) to (3.12) in Table 3.1 are considered, and has been described in Chapter 3.

Table 3.1: DAR-system model inputs for considered thermo-economic optimisation and analysis. (repeated from page 97)

DAR model input	Description	
$T_1 = T_{\text{bub}}(p_{\text{ch}}, x_{\text{rs}})$	Generator inlet temperature	(3.4)
$\Delta T_{\text{gen,o}} = T_{\text{gen,w}} - T_2 = \Delta T_{\text{lo}}$	Generator outlet temperature	(3.5)
$T_3 = T_4 = T_2 - 2$	Bubble-pump outlet temperature	(3.6)
$T_5 = T_3 - 5$	Rectifier liquid temperature	(3.7)
$T_6 = T_{\text{sat,refr}}(p_{\text{ch}})$	Rectifier vapour temperature	(3.8)
$\Delta T_{\text{cond,o}} = T_7 - T_{\text{a}} = \Delta T_{\text{lo}}$	Condenser outlet temperature	(3.9)
$T_{8,\text{g}} = T_{\text{a}} + 0.1$	Desorbed gas temperature	(3.10)
$\Delta T_{\text{exp}} = T_{9'} - T_9 = (18.5 - 0.15 \times p_{\text{ch}})$	Expansion temperature drop	(3.11)
$T_{11} = T_7$	Reservoir temperature	(3.12)

In this chapter, the CAMD-DAR framework is extended to consider a wider molecular space for both refrigerant and absorbent, allowing branched and polar molecular structures to be considered. Thus, the following groups are considered for both absorbent and refrigerant: $-\text{CH}_3$, $>\text{CH}_2$, $=\text{CH}_2$, $=\text{CH}-$, $>\text{CH}-$, $-\text{OH}$, $-\text{CH}_2\text{OH}$, $-\text{NH}_2$ and $>\text{NH}$. For the added groups (*i.e.*, $=\text{CH}-$, $-\text{OH}$, $-\text{CH}_2\text{OH}$, $-\text{NH}_2$ and $>\text{NH}$), a lower bound is set to zero on their multiplicity to ensure that simple aliphatic hydrocarbons explored in Chapter 3 are included. While an upper bound is set to one for these groups to limit secondary effects that might arise from complex groups that could not be handled¹. [231]

The objective of the MINLP-CAMD-DAR problem defined here is to seek an optimal working fluid and optimum charging conditions to fit in a given commercial DAR unit that has a

¹SAFT- γ Mie is employed via gSAFT/gProperties tool provided by gPROMS which is a black-box and switching group parameters during the optimisations has not been possible in this study

nominal volumetric capacity, V_{CU} corresponding to DAR rating power, $\dot{P}_{\text{DAR}} = 43.8V_{\text{CU}}$ (see Section 3.2.1). The integrated design must provide a maximum cooling rate at a set cooling temperature, T_{co} in an environment with ambient temperature, T_{a} . Hence, the optimisation problem described in Equation (3.14) can be written as:

$$\begin{aligned}
 & \max_{\substack{\tilde{x}_{\text{rs}}, p_{\text{ch}}, \\ \mathbf{n}_{\text{refr}}, \mathbf{n}_{\text{absr}}, \mathbf{n}_{\text{g}}}} \dot{Q}_{\text{evap}} \{ \tilde{x}_{\text{rs}}, p_{\text{ch}}, V_{\text{CU}}, \mathbf{n}_{\text{refr}}, \mathbf{n}_{\text{absr}}, \mathbf{n}_{\text{g}} \} & (3.14 \text{ revisited}) \\
 & \text{s.t.} \quad \mathbf{h}(\boldsymbol{\theta}, \boldsymbol{\beta}) = 0, \\
 & \quad \mathbf{g}(\boldsymbol{\theta}, \boldsymbol{\beta}) \leq 0, \\
 & \quad \boldsymbol{\theta} \in [\boldsymbol{\theta}^{\text{LB}}, \boldsymbol{\theta}^{\text{UB}}] \subseteq \mathbb{R}^n, \\
 & \quad \boldsymbol{\beta} \in [\boldsymbol{\beta}^{\text{LB}}, \boldsymbol{\beta}^{\text{UB}}] \subseteq \mathbb{Z}^m,
 \end{aligned}$$

where, as mentioned earlier, $\mathbf{h}(\boldsymbol{\theta}, \boldsymbol{\beta}) = 0$, and $\mathbf{g}(\boldsymbol{\theta}, \boldsymbol{\beta}) \leq 0$, respectively, represent the sets of equality and inequality constraints relevant to the DAR system listed in Table 3.4 presented in Chapter 3 to ensure system, molecular feasibility, environmental and safety-related limitations are all met. The vectors $\boldsymbol{\theta}^{\text{LB}}$, $\boldsymbol{\theta}^{\text{UB}}$, $\boldsymbol{\beta}^{\text{LB}}$, $\boldsymbol{\beta}^{\text{UB}}$ are lower bounds and upper bounds imposed on the continuous and integer decision variables which are listed in Table 4.1.

Table 4.1: Optimisation decision variable for DAR case studies with their lower and upper bounds definition and ranges for parametric MINLP.

Variable	Description	Lower bound	Upper bound	Units
p_{ch}	Charging pressure	2	25	bar
$\tilde{x}_{\text{rs}}$	Rich solution molar composition	0.1	0.38	–
$\bar{p}_9$	Relative low evaporator pressure	0.02	0.2	–
n_{H_2}	choice of H_2 as an auxiliary gas	0	1	–
n_{He}	choice of He as an auxiliary gas	0	1	–

j	$n_{-\text{CH}_3,j}$ $n_{>\text{CH}_2,j}$ $n_{=\text{CH}_2,j}$ $n_{=\text{CH}-,j}$ $n_{>\text{CH}-,j}$ $n_{-\text{OH},j}$ $n_{-\text{CH}_2\text{OH},j}$ $n_{-\text{NH}_2,j}$ $n_{>\text{NH},j}$								
“refr”	LB	0	0	0	0	0	0	0	0
	UB	2	5	1	2	1	1	1	1
“absr”	LB	0	0	0	0	0	0	0	0
	UB	2	9	1	2	1	1	1	1

The results of solving Equation (3.14 revisited) are presented here for a 10-ft³ DAR unit using the CAMD-DAR framework for ambient temperatures ranging from 10 °C to 40 °C and for cooling temperatures ranging from −12 °C to 8 °C which resemble a wide range of ambient conditions and domestic-use refrigeration activities (*i.e.*, food and beverage chilling, storage and freezing). The identified optimum working fluids are further considered via a series of NLP optimisations to

4.3. MINLP SOLUTION OF THE CAMD-DAR FRAMEWORK FOR MAXIMUM COOLING

examine the effect of DAR size, which is characterised by the rate of heat power needed to activate the bubble pump. on charging settings (*e.g.*, p_{ch} and $\tilde{x}_{\text{rs}}$) for a particle combination of cooling and ambient temperature ($T_{\text{a}} = 20\text{ }^{\circ}\text{C}$ and $T_{\text{co}} = 4\text{ }^{\circ}\text{C}$). Further, the total and specific purchase cooling-unit cost ($C_{\text{CU},0}$ and SPC_{CU} of optimal and sub-optimal DAR systems are considered when economically assessing the proposed DAR designs, and the costing method presented in Section 3.2.1 is used to estimate DAR unit purchase based on its design heat power.

To evaluate the performance of optimum working fluid systems proposed by the CAMD-DAR framework, the mentioned optimum designs are compared against $\text{NH}_3\text{--H}_2\text{O}$ -based DAR system pressurised at 15.5 bar and charged with 30 wt% (31 mol%) refrigerant-rich solution. It has been established that DAR performance declines as the charge pressure increases; however, high charging pressures are required if the DAR unit runs at high ambient temperature to ensure complete recovery of the refrigerant in the rectifier. Thus, a DAR system is chosen to compromise the need for high pressure to ensure complete refrigerant condensation while maintaining a decent amount of cooling based on the experiments done by Najjaran [258]. [38, 63] For sake of comparison, it is assumed that the $\text{NH}_3\text{--H}_2\text{O}$ DAR system is still capable of recovering all the refrigerant as long as the ambient temperature is lower than NH_3 saturation temperature at charging pressure (*i.e.*, $\approx 40\text{ }^{\circ}\text{C}$).

4.3 MINLP solution of the CAMD-DAR framework for maximum cooling

The results for a domestic 10-ft³ DAR unit are presented in Figure 4.1 where the MINLP-CAMD-DAR problem is solved for ambient temperatures ranging from 10 °C to 40 °C and cooling temperatures ranging from −12 °C to 8 °C which resemble a wide range of ambient conditions and domestic-use refrigeration activities (*i.e.*, food and beverage chilling, storage and freezing).

4.3.1 Optimal DAR working fluids for domestic DAR unit

In Figure 4.1, for a 10-ft³ DAR unit (corresponding to $\approx 440\text{ W}$ rated power), four optimum working fluid mixtures can be identified for maximum cooling rates over the range of considered

ambient and cooling temperatures. Notably, the refrigerants in these four working fluids are non-polar hydrocarbons: 2-butene ($2\text{-C}_4\text{H}_8$); 1-butene ($1\text{-C}_4\text{H}_8$); propane (C_3H_8) and 4-methyl,2-pentene ($[\text{CH}_3]_2>\text{CHCH}=\text{CHCH}_3$). On the other hand, optimum absorbents tend to contain a polar group. For the considered temperature space, the identified absorbents are limited to: ethanol ($\text{C}_2\text{H}_5\text{OH}$); 1-aminopropylene ($\text{CH}_3\text{CH}=\text{CHNH}_2$); aminoethylene ($\text{CH}_2=\text{CHNH}_2$) and 1-aminobutadiene ($\text{CH}_2=\text{CHCH}=\text{CHNH}_2$). Unsurprisingly, helium is elected as the auxiliary gas in all the optimisations. Pressuring organic-based DAR systems can be safer using helium than hydrogen. The latter might become reactive with some organic compounds under high temperature and pressure. All optimal and sub-optimal working fluids considered in the rest of this chapter are assigned using the prefix “WF” followed by a number.

From Figure 4.1a, it can be demonstrated that optimum cooling rates monotonically decrease as ambient temperature increases or cooling temperature decreases. It is also revealed that, thermodynamically, working fluid, WF1 (2-butene–ethanol–helium, *a.k.a.*, $2\text{-C}_4\text{H}_8\text{--C}_2\text{H}_5\text{OH--He}$) offers an optimum working fluid for a wide range of ambient and cooling temperatures (*i.e.*, $20 \leq T_a \leq 40$ and $-4 \leq T_{co} \leq 8$) with cooling rates ranging between 70 W and 154 W.

Working fluid, WF2 (1-butene–1-aminopropylene–helium, *a.k.a.*, $1\text{-C}_4\text{H}_8\text{--CH}_3\text{CH}=\text{CHNH}_2\text{--He}$) is identified by the CAMD-DAR framework to be the optimum working fluid for very low cooling temperatures (-18°C) and high ambient temperatures ($\geq 30^\circ\text{C}$) which makes it the right choice for applications for food freezing in remote hot regions like Sub-Saharan Africa or Gulf region where a 10-ft^3 DAR unit running with WF2 can provide theoretical cooling rates of 43 W to 70 W depending on the operating conditions. Contrarily, working fluid, WF3 (propane–aminoethylene–helium, *a.k.a.*, $\text{C}_3\text{H}_8\text{--CH}_2=\text{CHNH}_2\text{--He}$) is recommended by the framework for lower ambient temperatures ($T_a \leq 20^\circ\text{C}$) and a wide range of low cooling temperatures ($T_{co} < 0^\circ\text{C}$) with cooling rates ranging from 105 W to 146 W.

Working fluid, WF4 (4-methyl,2-pentene–1-aminobutadiene–helium, *a.k.a.*, $[\text{CH}_3]_2>\text{CHCH}=\text{CHCH}_3\text{--CH}_2=\text{CHCH}=\text{CHNH}_2\text{--He}$) is identified by the CAMD-DAR to be an optimum working fluid to meet cooling at 8°C in ambient temperature of 10°C .

The results in Figure 4.1a also reveal that all the suggested optimum working fluids are deemed to produce more cooling than the benchmark $\text{NH}_3\text{--H}_2\text{O}$ DAR system by more than 50 %. It can be observed in Figure 4.1b that optimum rich-solution compositions needed are less than 31 mol % ($\tilde{x}_{rs} \leq 14\%$). It should be recalled that these low compositions are limited by

4.3. MINLP SOLUTION OF THE CAMD-DAR FRAMEWORK FOR MAXIMUM COOLING

the constraints in Equations (3.18a) and (3.18b) which impose a limit on the weak-solution compositions to ensure proper absorption in the absence of a detailed absorber model which is out the scope of this study. Bounded weak-solution compositions drive the optimisations towards less charging compositions. The reported compositions agree well with theoretical and experimental charging compositions reported in the literature. For similar absorption refrigeration systems running using similar organic working fluids. [92, 145, 259]

Further, from Figure 4.1c, the theoretical charge pressure required by each of the optimum DAR systems for maximum cooling is much less than 15.5 bar ($4 \leq p_{\text{ch}} \leq 9.5$ bar). Lower charging pressure reduces the generator's load, promotes a higher cooling rate, and ensures safer operation, provided that this pressure is sufficient to ensure complete condensation of the corresponding refrigerant at all operating ambient temperatures.

From Figure 4.1d, it can be revealed that for the suggested optimum DAR designs, the

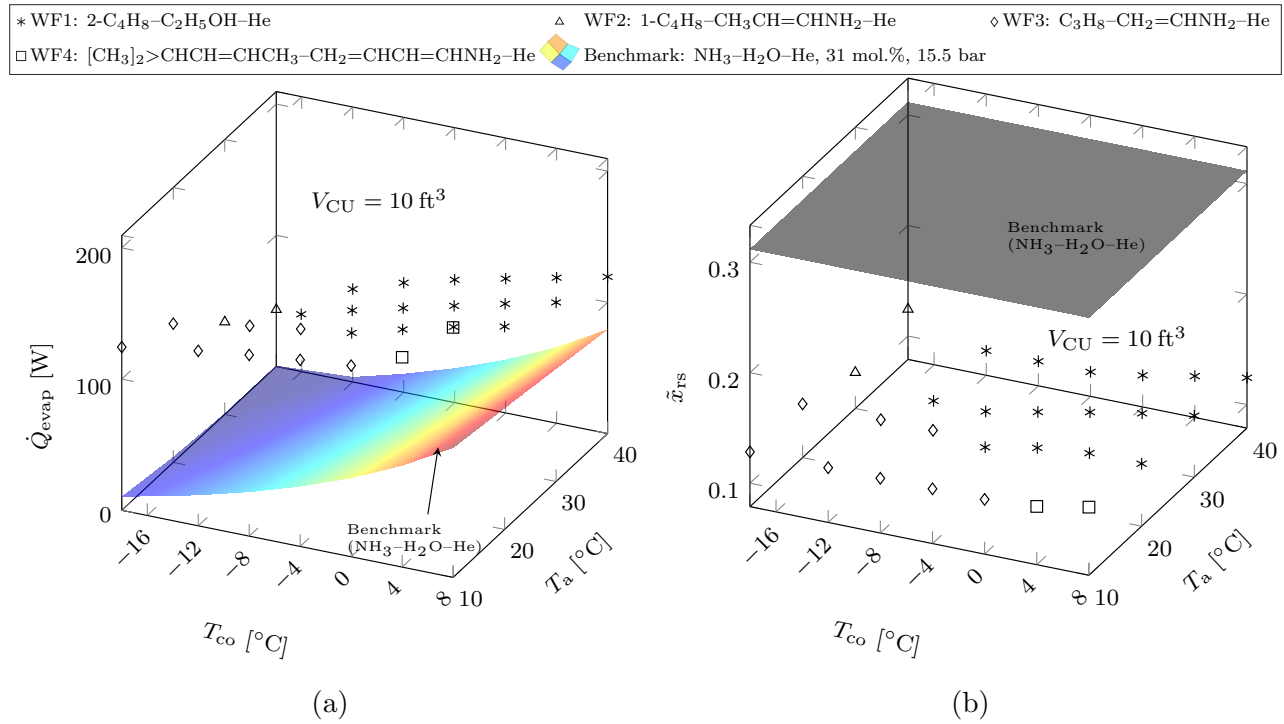


Figure 4.1: Mapping results of the MINLP CAMD-DAR problem described in Equation (3.14 revisited) to design optimal organic working-fluid mixtures and corresponding charging settings for a 10-ft³ DAR unit (corresponding to ≈ 440 W rated power) under a wide range of ambient and cooling temperatures. Optimum working fluids are distinguished by symbols and tagged with the prefix “WF”. The optimal systems are compared to an NH₃-H₂O DAR system charged with 31 mol % rich solution under 15.5 bar described by the surface plots: (a) cooling rate, $\dot{Q}_{\text{evap}}$; (b) DAR charge composition, $\tilde{x}_{\text{rs}}$; (c) DAR charge pressure, p_{ch} and (d) lowest temperature in the evaporator, T_9 .

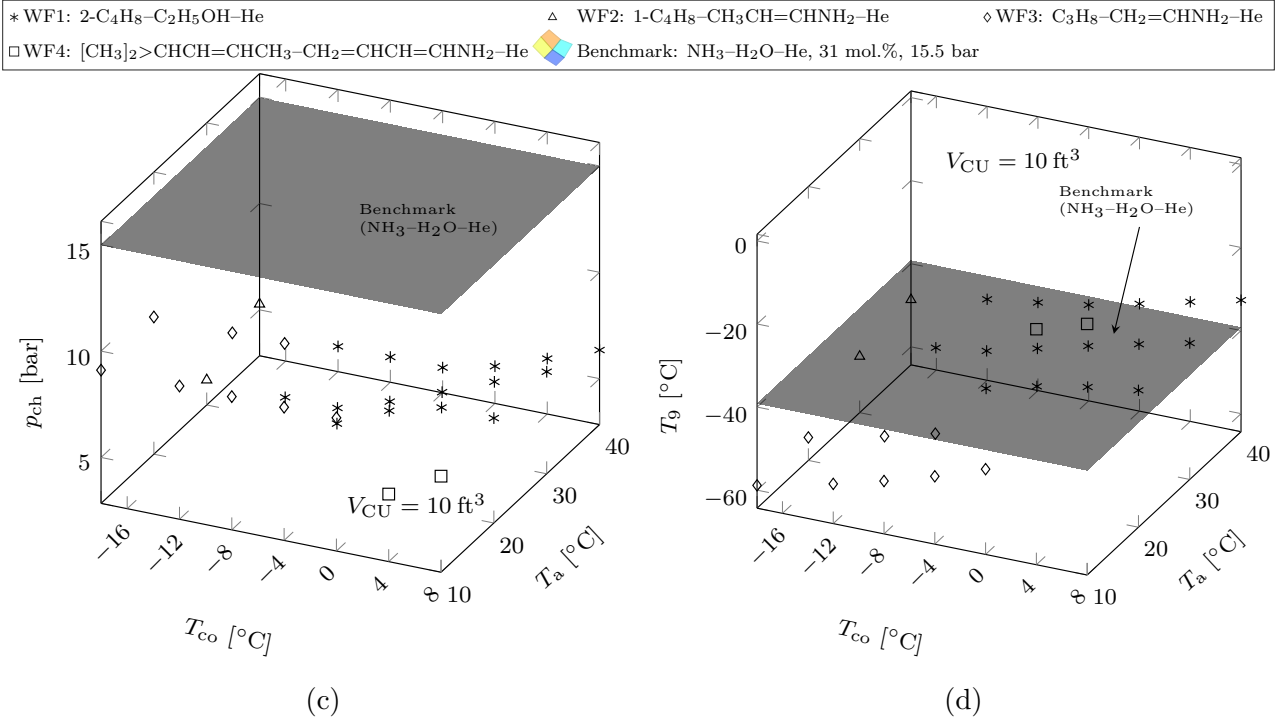


Figure 4.1: (*Continued.*)

temperature drop resulting from the adiabatic mixing of refrigerant and auxiliary gas is, in most cases, comparable to evaporator temperatures in the NH₃-H₂O DAR system considered for comparison. Low evaporator temperatures allow multi-purpose operation (*e.g.*, freezing and refrigeration), as long as the lowest temperature in the evaporator is above the refrigerant's freezing point, a condition which is met for all proposed working fluid mixtures.

Generally, it can be concluded that small-sized non-polar refrigerants are favoured due to their relative volatility compared to polar molecules of the same carbon-chain length. Results in this chapter combined with results presented in Chapter 3 suggest that 2-alkenes and branched hydrocarbons offer higher cooling capacity compared to *n*-alkanes due to their higher latent heat of vapourisation, which makes them preferred choices as a refrigerant. This observation agrees with the results reported by [161,178] for designing working fluids for ORC systems and the recent study published by Papadopoulos *et al.* [179], in which working fluid mixtures are considered for optimum absorption refrigeration system design.

On the other hand, it can be observed that polar hydrocarbons are preferred to non-polar hydrocarbons as absorbents, as their polarity introduces more relative volatility difference with non-polar refrigerants at the generator temperature making it easier to rectify the refrigerant and may eliminate the need for the rectifier.

4.3.2 Effect of DAR size on charging settings

A relevant question is about which DAR size and corresponding charging conditions should be considered to maximise the cooling output for a given purpose and location. As an example, if one considers food refrigeration ($\bar{T}_{\text{co}} = 4^\circ\text{C}$) in a temperature-cooled space ($T_{\text{a}} = 20^\circ\text{C}$). Suppose the DAR size is an integer decision variable in addition to the variables listed in Table 4.1. In that case, the MINLP CAMPD problem suggests that a 10-ft³ DAR should be the optimum charged with WF1 is recommended. MINLP results shown in Section 4.3.2 demonstrate that the decisions about the working fluid and DAR size are irrelevant to the ambient temperature change. In contrast, charging settings should be tuned to maximise the cooling rate for a particular ambient temperature.

To evaluate the thermo-economic impact of DAR size for the four working fluid mixtures mentioned above (*i.e.*, WF1, WF2, WF3 and WF4), a series of NLP optimisations are presented for each DAR size available in the market. In these cases, the ambient and cooling temperatures are set to $T_{\text{a}} = 20^\circ\text{C}$ and $T_{\text{co}} = 4^\circ\text{C}$, respectively. The optimisation results are presented in Figure 4.2.

The results in Figure 4.2a suggest that for working fluids, WF1 and WF2, a 10-ft³ (corresponding to $\approx 440\text{ W}$) DAR unit can produce maximum cooling rates, $\dot{Q}_{\text{evap}}$ if charged using charge pressure and compositions displayed Figure 4.2a. It can be observed that a 12-ft³ DAR unit charged with WF3 is predicted to produce maximum cooling compared to other DAR sizes charged with the same working fluid. Results depicted in Figures 4.2a and 4.2b reveal that a 12-ft³ DAR unit charged with WF1 or WF3 perform comparably. For WF4-charged DAR systems, it can be observed that maximum cooling can be achieved using a 14-ft³ DAR unit. It can be observed that all the optimised systems produce more cooling than the benchmark NH₃–H₂O DAR system, though suggested charging compositions, $\tilde{x}_{\text{rs}}$ are much lower than the typical NH₃–H₂O DAR charging composition as demonstrated in Figure 4.2c. The reason for that is believed to be attributed to the higher relative volatility of the selected working-fluid pairs and the high latent heat of vapourisation of each of the selected refrigerants.

From Figure 4.2a, it can be revealed that beyond the optimum DAR size, for each working fluid, the cooling rate declines. For design considerations, the DAR generator size cannot be scaled proportionally to the design power input to ensure bubble-pump operation (correlated to the DAR fridge size). Thus, the temperature in the generator is primarily influenced by

charging pressure and design power according to Equation (2.33). Accordingly, as the generator temperature increases, as it can be observed in Figure 4.3, more absorbent is likely to be entrapped with the refrigerant at the cost of a lower refrigerant circulation rate. It can also be observed that using 18-ft³ DAR units becomes no option for either of the working fluids, mainly due to the risk of overheating the working fluid and approaching the auto-ignition temperature of the absorbent. For similar reasons, working fluids WF1 and WF3 are unsuitable for 16-ft³ DAR systems. Although it is out of the scope of this thesis, it becomes interesting to integrate the optimisation of the generator dimensions ($d_{\text{gen,in}}$ and l_{gen}) to maximise the refrigerant circulation rate. Working fluid, WF4 cannot be used to charge small-scale DAR units (*i.e.*, $V_{\text{CU}} \leq 6 \text{ ft}^3$), as the optimisations suggest that theoretical DAR power cannot activate such working fluids (*i.e.*, the constraint in Equation (3.15a) could not be fulfilled).

The coefficients of performance that correspond to maximum cooling for the considered working fluids are depicted in Figure 4.2c. It can be observed that WF2 ensures a maximum coefficient of

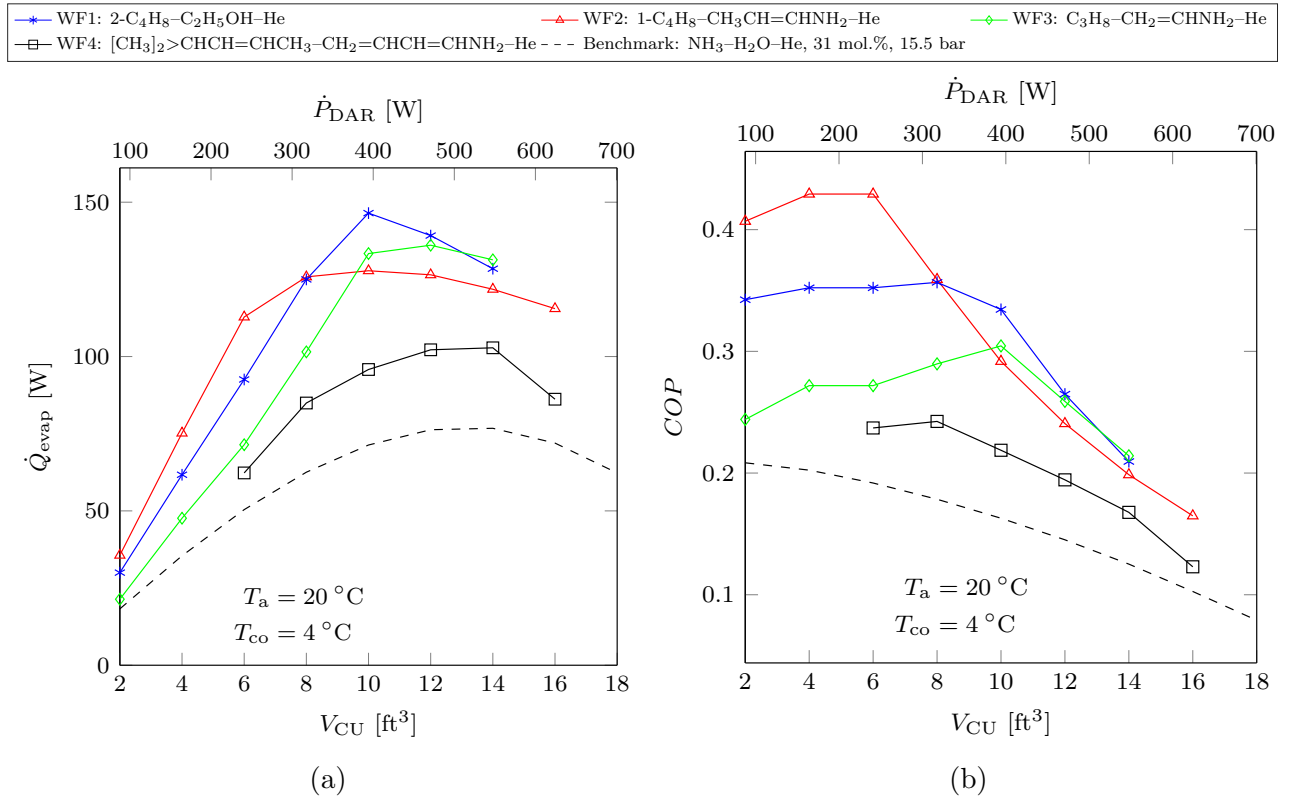


Figure 4.2: Effect of optimised DAR size on: (a) Optimum cooling rate, $\dot{Q}_{\text{evap}}$ and corresponding: (b) Coefficient of performance, COP ; (c) DAR charge composition, $\tilde{x}_{\text{rs}}$ and (d) required charge pressure, p_{ch} for the four working fluids identified in Figure 4.1. NLP optimisations are considered for ($T_a = 20^\circ\text{C}$ and $T_{\text{co}} = 4^\circ\text{C}$). Optimum cooling rates and optimised variables are compared against the benchmark NH₃-H₂O DAR system described above.

4.3. MINLP SOLUTION OF THE CAMD-DAR FRAMEWORK FOR MAXIMUM COOLING

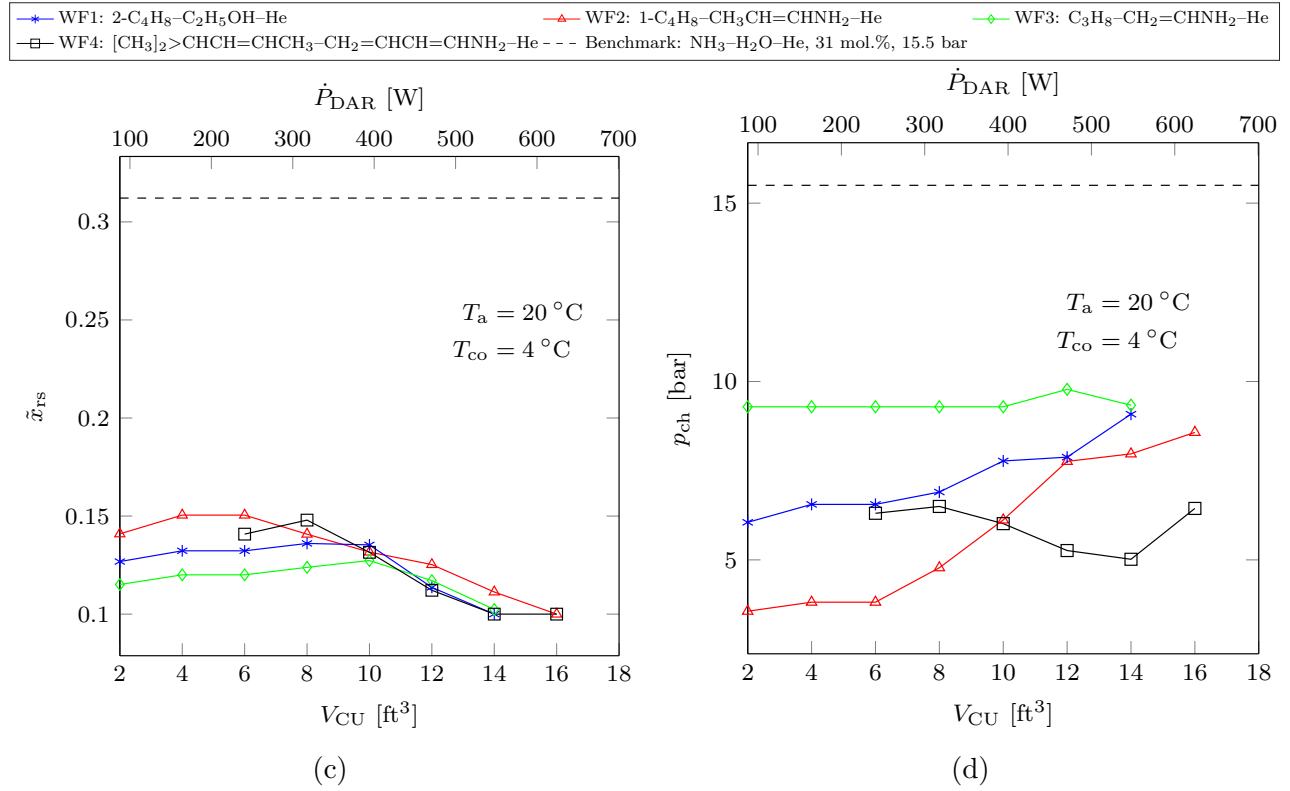


Figure 4.2: (*Continued.*)

performance over other working fluids. It can also be confirmed that all the predicted coefficients of performance are higher than the coefficient of performance received by the NH₃-H₂O DAR system used for comparison.

It can be revealed that for each working fluid, there is a DAR size that ensures maximum COP.² For instance, for the same considered ambient and cooling temperature, if the maximum coefficient of performance is of concern, the solution of the MINLP-CAMD-DAR problem suggests using WF2 with a 6-ft³ DAR unit. In contrast, if the maximum cooling rate is considered, the MINLP-CAMD-DAR problem solution suggests using WF1 with a 10-ft³ DAR unit. These results of the MINLP optimisations fully agree with the NLP optimisation results presented in Figure 4.2.

To achieve maximum cooling rates, the corresponding optimum system charging pressures and compositions are presented in Figures 4.2c and 4.2d for each of the four considered working fluids. From these figures, it can be easily observed that optimal charging compositions vary below 15%. Interestingly, optimised charge compositions displayed in Figure 4.2c are at least 50% than

²It is worth mentioning that in Figure 4.2b, COP is not the objective function. Instead, these are COPs that correspond to maximum cooling rates depicted in Figure 4.2a

standard $\text{NH}_3\text{--H}_2\text{O}$ DAR charge composition. As it has been presented in Chapters 2 and 3, the optimised DAR charge pressures for organic-based systems are much lower than that required for $\text{NH}_3\text{--H}_2\text{O}$ DAR systems. This is attributed to the fact that the considered refrigerants are less volatile compared to NH_3 . However, polar absorbents require higher charging pressures than the non-polar working fluid systems presented in Chapter 3.

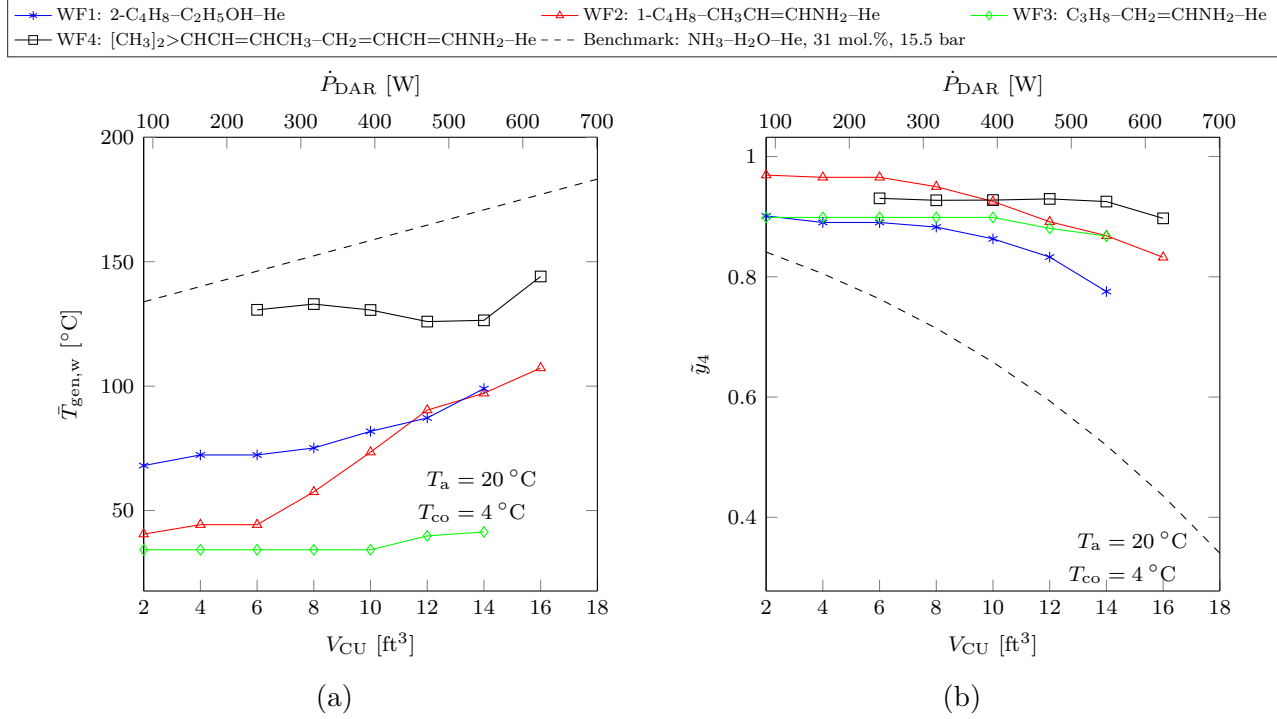


Figure 4.3: Effect of optimised DAR size for on (a) predicted generator wall temperature, $\bar{T}_{\text{gen,w}}$; (b) predicted purity of refrigerant leaving the bubble pump, $\tilde{y}_4$ four working fluids identified in Figure 4.1 corresponding to maximum cooling rates. NLP optimisations are considered for ($T_a = 20^\circ\text{C}$ and $T_{co} = 4^\circ\text{C}$). Predicted generator wall temperatures are compared against those temperatures predicted for the benchmark $\text{NH}_3\text{--H}_2\text{O}$ DAR system described above.

As mentioned earlier, should the DAR rated power increase, the predicted generator temperature increases, as it can be observed in Figure 4.3a. Nevertheless, predicted generator temperatures for the four organic working fluids are observed to be lower than predicted for the $\text{NH}_3\text{--H}_2\text{O}$ DAR system used as a benchmark for all the considered DAR sizes. Interestingly, for WF3, the predicted generator temperature is very low due to the high relative volatility of the propane+1-aminobutadiene mixture, which is easily generated using low-temperature heat sources.

As the thermodynamic analysis suggests in Figure 4.3b, compared to $\text{NH}_3\text{--H}_2\text{O}$ DAR systems, most of the refrigerant can be recovered in the bubble pump, provided that the bubble pump is operating efficiently. The purity of vapour leaving the bubble pump can suppress 80 % and

4.3. MINLP SOLUTION OF THE CAMD-DAR FRAMEWORK FOR MAXIMUM COOLING

reach 98 % for some working fluids like WF2 in small-sized DAR. This explains why rectifier heat loads for organic-based DAR systems are much lower than rectifier heat loads for $\text{NH}_3\text{--H}_2\text{O}$ DAR systems, as observed in the results observed in Figure 4.4 suggest.

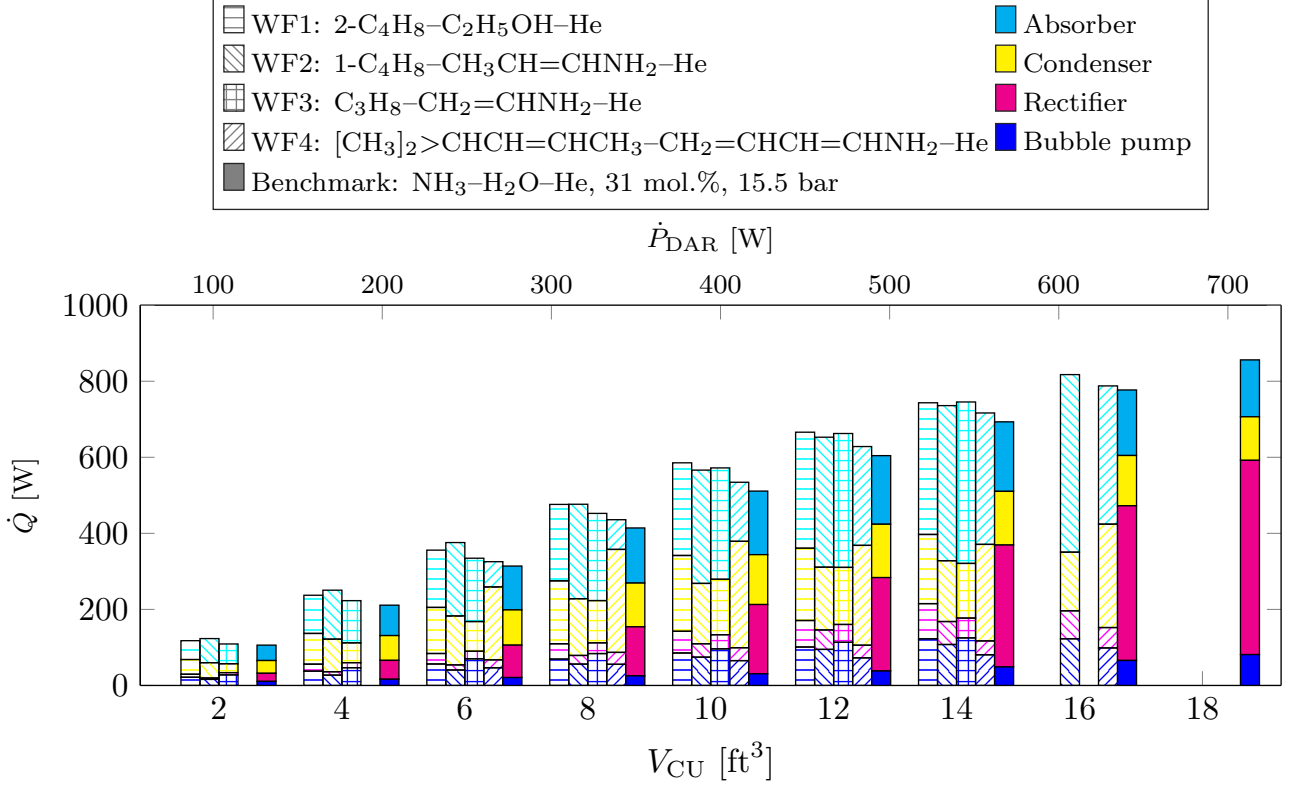


Figure 4.4: Effect of optimised DAR size on heat dissipation from different DAR components for four working fluids identified in Figure 4.1 corresponding to maximum cooling rates. NLP optimisations are considered for ($T_a = 20^\circ\text{C}$ and $T_{\text{co}} = 4^\circ\text{C}$). Heat losses for different working fluids are compared against the benchmark $\text{NH}_3\text{--H}_2\text{O}$ DAR system described above. The patterns identify different working fluids as indicated in the legend, whereas different colours represent different DAR components from which heat is rejected.

For a 10-ft^3 DAR unit, using organic-based working fluids can reduce the rectifier heat load by 70 % to 80 % compared to the benchmark DAR system. It can also be noticed that most of the rectifier area of commercially available DAR units (especially small-sized ones) can be insulated when charged with one of the presented organic working fluids.

On the other hand, it can also be observed in Figure 4.4 that the heat rejection from the condenser to the ambient for organic-DAR systems is, in general, higher than that encountered in $\text{NH}_3\text{--H}_2\text{O}$ -based DAR systems. This can be attributed to the lower charging pressures suggested by the optimisations compared to the benchmark DAR system pressure. For instance, a 10-ft^3 DAR unit charged with WF3 should reject 11% more heat from the condenser to the

ambient compared to the $\text{NH}_3\text{--H}_2\text{O}$ -based DAR system. WF4 can reject up to 110% more than the $\text{NH}_3\text{--H}_2\text{O}$ -based DAR system.³

It can also be noticed in Figure 4.4 that, except for DAR units with sizes $V_{\text{CU}} \leq 10$ charged with WF4, absorber heat loads from organic-based DAR systems are also significantly higher than the heat loads for $\text{NH}_3\text{--H}_2\text{O}$ -based DAR systems which suggest the need to modify already available DAR units to install larger absorber areas to accommodate the high heat rejection.

In general, it can be concluded that organic-based working fluids can replace $\text{NH}_3\text{--H}_2\text{O}$ system for lower generation temperature, less required rectifier heat load, lower operating pressures, easy refrigerant recovery and most importantly, higher cooling rates. However, most of these organic-based DAR systems reject more heat during condensation and absorption steps, which implies the possible need for a larger condenser and absorber. Preliminary calculations indicate that the air-side heat transfer coefficient limits heat rejection in DAR systems compared to the heat-transfer resistance encountered by the fluid flow. For instance, commercially available DAR units come with a bank of finned-tube condensers. The large area provided by the air-cooled finned condenser can ensure complete condensation of the refrigerant for a DAR unit operating at its design point.

Nevertheless, It can still be interesting for future research to consider more detailed condenser and absorber design. Since the thermodynamic evaluation suggests that most of the heat rejected in organic-based DAR systems is dissipated from the condenser and absorber, it shall be of great importance to study how far these two components, in particular, can be game changers. Proper design of these components should consider minimising the needed sizes while maximising the cooling rate. For example, Rattner and Garimella [84] suggested using a finned-absorption circuit instead of the coiled one to increase the transfer area, promoting better absorption.

Although the presented CAMD-DAR framework relies mainly on thermodynamic analysis of DAR systems and does not consider the detailed design of system components, it remains a powerful tool for suggesting alternative working fluids to replace ammonia–water pairs to retrofit commercially available DAR units.

³In the thermodynamic analysis, the refrigerant is assumed to approach ambient temperature for all organic-based and $\text{NH}_3\text{--H}_2\text{O}$ -based DAR system.

4.3.3 Economic assessment of optimal DAR working fluids

In order to complement the thermodynamic analysis presented above, the specific cooling cost, *SPC* for optimum DAR systems of 10-ft³ size (corresponding to ≈ 440 W rated power) is presented in Figures 4.5 and 4.6. In this study, *SPC* is estimated by dividing the purchase cost of the DAR unit (calculated using Equation (3.3)) by the maximum cooling rate predicted by the CAMD-DAR model. The specific cooling cost, *SPC* for optimum DAR designs identified in Figure 4.1 are mapped in Figure 4.5. It can be observed that the considered NH₃–H₂O DAR system demonstrates a relatively high *SPC* compared to the organic working fluids proposed in Chapter 3 and this chapter. As the cooling temperature decreases, *SPC* increases exponentially.

It can also be realised from Figure 4.5 that for the considered NH₃–H₂O DAR system, *SPC* is less affected by the ambient temperature variation than the cooling temperature effect. It can be easily recognised that the optimum DAR designs suggested by the CAMD-DAR framework can offer lower *SPC* than what NH₃–H₂O DAR units can offer. For example, for 20 °C ambient temperature and 4 °C cooling temperature, the optimum DAR system charged with WF1 is predicted to have a £ 5.3 per W which is 50 % less than the anticipated *SPC* of using the benchmark NH₃–H₂O DAR unit for the same ambient and cooling temperatures. Obviously, the organic-working working fluids presented in this chapter offer lower *SPC* than the simple working fluids considered in Chapter 3.

Following the discussion presented in the previous subsection, *SPC* for the four optimal working fluids identified in Figure 4.1 are plotted in Figure 4.2b against various DAR sizes for which the cooling rate is maximised considering ambient and cooling temperatures, 20 and 4 °C, respectively. It can be noticed from the figure that all the proposed working fluids can result in 15 % to 50 % reduction in predicted *SPC* compared to a benchmark NH₃–H₂O DAR unit of the same size. It can be easily realised that Figure 4.1 is a mirror for Figure 4.2b. Similar to the earlier discussion, It can be revealed from this figure that a 6-ft³ DAR unit charged with WF2 has the lowest *SPC* of £ 5.1 per W, which is 55 % less than *SPC* of using an NH₃–H₂O DAR unit of the same size and 3 % less than *SPC* of using the 10-ft³ DAR unit charged with WF1 (for which the cooling rate is maximised).

As discussed in Chapter 3, an advantage of using multi-start hybrid stochastic-deterministic optimisation methods, such as the one deployed in this study, is that it can provide a list of

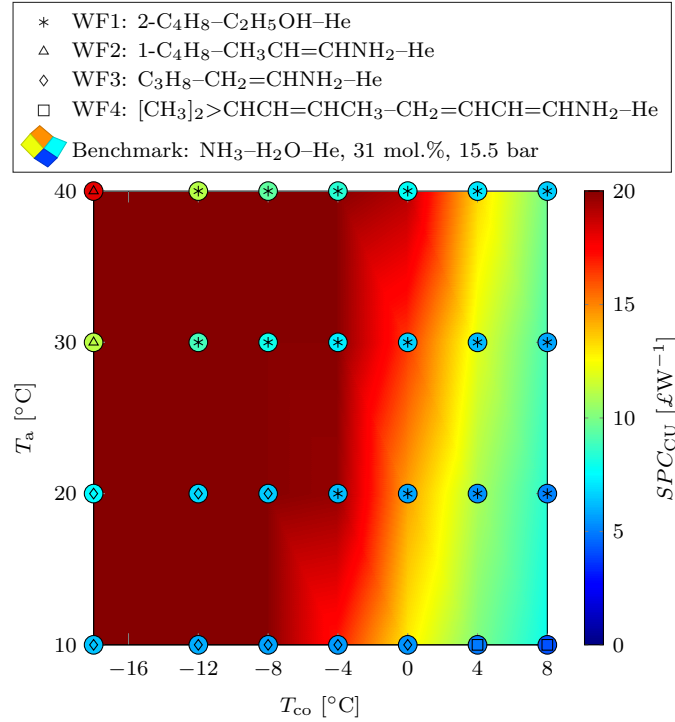


Figure 4.5: Effect of ambient temperature and cooling temperature on SPC for optimal organic working-fluid mixtures and corresponding charging settings presented in Figure 4.1, where a 10-ft^3 DAR unit (corresponding to $\approx 440\text{ W}$ rated power) is considered. Optimum working fluids are distinguished by symbols and tagged with the prefix “WF” followed by a number. The optimal systems are compared to SPC predicted for the benchmark $\text{NH}_3\text{-H}_2\text{O}$ DAR system charged with 31 mol % rich solution under 15.5 bar described by the surface plot.

sorted alternative optimal solutions without the need to apply integer cuts. For example, the best ten integrated DAR designs generated by the CAMD-DAR framework for the 10-ft^3 -DAR unit operating at $T_a = 20^\circ\text{C}$ to deliver cooling at $T_{co} = 4^\circ\text{C}$ are presented in Table 4.2.⁴

It can be observed that the CAMD-DAR framework selects some inferior polar refrigerants. For instance, for $T_a = 20^\circ\text{C}$ and $T_{co} = 4^\circ\text{C}$, WF5 contains aminoethylene ($\text{C}_2\text{H}_5\text{NH}_2$) as the refrigerant with a primary amine group ($-\text{NH}_2$). Also, WF6 contains di-methylamine (CH_3NHCH_3) as the refrigerant with a secondary amine group ($>\text{NH}$). It can also be observed that none of the refrigerants in the first ten optimal solutions (actually, none at all) are alcohols. The CAMD-DAR framework suggests that alcohols cannot be used as refrigerants, limited by the ability of the generator to initiate the bubble pump to circulate alcohol-based DAR systems. However, simple alcohols (*i.e.*, methanol and ethanol) can be used as refrigerants with some ionic-liquid absorbents for conventional absorption refrigeration systems as evaluated by Boman *et al.* [279]. But due to the passive nature of DAR cycles in contrast to absorption-refrigeration cycles, the choice of refrigerant-absorbent pair

⁴Tables of MINLP results for other ambient and cooling temperatures are presented in Appendix A.

4.3. MINLP SOLUTION OF THE CAMD-DAR FRAMEWORK FOR MAXIMUM COOLING

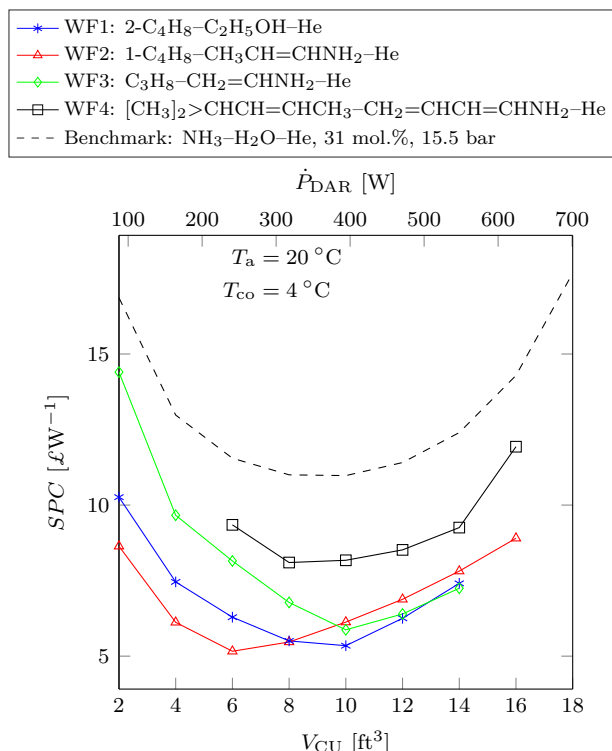


Figure 4.6: Effect of optimised DAR size for on specific purchase cost of cooling, SPC . four working fluids identified in Figure 4.1 corresponding to maximum cooling rates. NLP optimisations are considered for ($T_a = 20^\circ\text{C}$ and $T_{co} = 4^\circ\text{C}$). Optimum cooling rates and optimised variables are compared against the benchmark $\text{NH}_3\text{-H}_2\text{O}$ DAR system described above.

is limited by the bubble-pump operation.

It can also be noticed in Table 4.2, although it is not frequent, a non-polar organic pair is identified, WF9 which is a mixture of 3-methylbutene ($[\text{CH}_3]_2\text{>CHCH=CH}_2$) as the refrigerant 2,4-hex-di-ene ($2,4\text{-C}_6\text{H}_{10}$) as the absorbent. 3-methylbutene is a branched alkene with a single terminal double bond and five carbon atoms, while 2,4-hex-di-ene is a linear alkene with two internal double bonds. The comparison between the optimal working fluids identified in Table 3.12 in Chapter 3 and Table 4.2 suggest that complex hydrocarbon systems which have polar absorbents are more thermodynamically favoured for maximising the cooling rates. Unsurprisingly, most of the selected refrigerants have four carbon atoms, which agrees well with the results presented in Chapter 3. The results presented in this chapter and the results presented in Chapter 3 suggest the advantage of having olefin refrigerants to maximise the cooling rate. It can also be demonstrated that helium is thermodynamically more favourable than hydrogen.

For three different ambient temperatures, $T_a = 20^\circ\text{C}$, 30°C and 40°C and three different cooling temperatures, $T_{co} = -4^\circ\text{C}$, 0°C and 4°C , for maximum cooling, MINLP optimisations for the

Table 4.2: Results of MINLP optimisations for 10-ft³ DAR unit with $T_a = 20^\circ\text{C}$ and $T_{co} = 4^\circ\text{C}$. Helium is identified as the auxiliary gas for all the presented working fluids. Rank refers to the order in which the multi-start optimiser sorts the optimal solutions; two optimal solutions are the same if their objective function values and arguments are similar within 1%.

Rank	ID	Refrigerant	Absorbent	$\dot{Q}_{\text{evap}}$ [W]	p_{ch} [bar]	$\tilde{x}_{\text{rs}}$	$\bar{p}_9$	$T_{\text{gen,w}}$ [°C]	SPC [£W ⁻¹]
1	WF1	2-C ₄ H ₈	C ₂ H ₅ OH	146	7.77	0.135	0.026	82	5.36
2	WF2	1-C ₄ H ₈	CH ₃ CH=CHNH ₂	128	6.12	0.132	0.042	73	6.12
3	WF5	C ₂ H ₅ NH ₂	CH ₂ =CHCH=CHNH ₂	120	4.75	0.13	0.022	102	6.53
4	WF6	CH ₃ NHCH ₃	C ₂ H ₅ CH=CHNH ₂	113	8.36	0.126	0.025	77	6.93
5	WF7	2-C ₄ H ₈	CH ₂ =CHCH=CHNH ₂	100	3.61	0.131	0.046	94	7.83
6	WF4	[CH ₃] ₂ >CHCH=CHCH ₃	CH ₂ =CHCH=CHNH ₂	96	6.02	0.132	0.014	131	8.16
7	WF8	1-C ₄ H ₈	CH ₂ =CHCH ₂ OH	96	4.83	0.13	0.052	90	8.16
8	WF9	[CH ₃] ₂ >CHCH=CH ₂	2,4-C ₆ H ₁₀	89	4.73	0.115	0.025	100	8.8
9	WF10	1-C ₄ H ₈	CH ₂ =CH=CH[CH ₂] ₂ NH ₂	78	3.97	0.132	0.065	70	10.04
10	WF11	i-C ₄ H ₁₀	[CH ₃] ₂ >CHOH	76	6.7	0.127	0.048	104	10.3

integrated CAMD-DAR framework suggest 45⁵ unique DAR designs based on working-fluid combinations of 14 distinct refrigerants and 25 distinct absorbents (which are available in Appendix A). All the 45 designs, theoretically, require lower generation temperature compared to the simulations carried out for NH₃–H₂O benchmark DAR unit, where most of the suggested working-fluid systems can offer cooling rates superior to the benchmark NH₃–H₂O DAR unit.

4.3.4 Environmental-impact evaluation of optimum and sub-optimal DAR working fluids

As presented in Chapter 3, the integrated CAMD-DAR framework considers different environmental and safety limitations to ensure that optimised DAR systems comply with environmental and safety regulations.

The global warming and ozone depletion potentials ensure that working fluid is environmentally friendly. Global warming potential for refrigerants and absorbents is limited by 150 as an upper bound. [149] Many refrigerants and absorbents considered by the CAMP-DAR have almost zero GWP.

In this study, the ODP should not exceed 0.2. However, it can be revealed that should this limit be stricter, allowing only zero-ODP molecules to be considered, none of the presented refrigerants shall be selected. It should be mentioned that should fluorinated, and hydrofluorinated groups are considered, GWP and ODP can play a more significant role in designing the working fluid.

For safe DAR operation, it is important to ensure that the working fluid is not ignitable and less likely to burn at the risk of any leakage. To avoid super flammable working fluids, the flammability number, Γ -number calculated using the method developed by Kondo *et al.* [151] should not exceed 0.8. Unsurprisingly, most of the recommended working-fluid systems are strongly flammable.

Polar refrigerants are favoured over non-polar refrigerants for being relatively less flammable but at the cost of reducing the cooling capacity. For the same reason, amine absorbents are favoured over alcohols for their lower Γ -number. In addition to that, the designed refrigerants and absorbents have high enough auto-ignition temperatures compared to the predicted generator temperature.

⁵The number of unique optimal DAR designs can marginally increase subject to the increase in the number of initial guesses. The number of distinct designs can also increase if smaller solution tolerance is considered. The solution tolerance is set to 1% in this study.

Only low-toxic refrigerants and absorbents are selected. All the designed refrigerants have high LC50 to ensure they are not toxic for handling and at the risk of leakage.

4.4 DAR design from multi-objective optimisation for DAR units

It has been discussed in Chapter 3, how important the objective function for the proposed integrated CAMD-DAR framework considers the trade-off between the purchase cost, $C_{CU,0}$ and theoretical cooling rate, $\dot{Q}_{\text{evap}}$. The results presented in Table 3.13 in Chapter 3 unleash this trade-off considering minimising the specific purchase cooling cost, SPC . Moreover, the selected optimum working fluid is found to be affected by the objective function considered, and the minimum SPC does not necessarily correspond to neither maximum $\dot{Q}_{\text{evap}}$ or minimum $C_{CU,0}$.

To extend the above discussion, multi-objective optimisation (MOO) is applied to offer a set of alternative designs that compromise the cooling rate and the cost. The developed CAMD-DAR framework is used and an MINLP problem is formulated considering two simultaneous objective functions: minimising $C_{CU,0}$ and minimising $-\dot{Q}_{\text{evap}}$ (*i.e.*, maximising $\dot{Q}_{\text{evap}}$). The multi-objective optimisation problem can be expressed as:

$$\begin{aligned}
 \min_{\boldsymbol{\theta}, \boldsymbol{\beta}} \quad & -\dot{Q}_{\text{evap}}, C_{CU,0} \\
 \text{s.t.} \quad & \mathbf{h}(\boldsymbol{\theta}, \boldsymbol{\beta}) = 0, \\
 & \mathbf{g}(\boldsymbol{\theta}, \boldsymbol{\beta}) \leq 0, \\
 & \boldsymbol{\theta} \in [\boldsymbol{\theta}^{\text{LB}}, \boldsymbol{\theta}^{\text{UB}}] \subseteq \mathbb{R}^n, \\
 & \boldsymbol{\beta} \in [\boldsymbol{\beta}^{\text{LB}}, \boldsymbol{\beta}^{\text{UB}}] \subseteq \mathbb{Z}^m.
 \end{aligned} \tag{4.1}$$

After solving the multi-objective optimisation, a set of non-dominated solutions are obtained. Being a non-dominated optimal solution means that there is no other better solution in one of the objectives' values without worsening the other objectives. A Pareto front is the set of all non-dominated solutions obtained by solving the multi-objective optimisation problem. This Pareto front provides a powerful tool for selecting a DAR system based on the relative importance of the cost and cooling rate.

To solve the MINLP MOO problem, it is important to ensure the generation of evenly-distributed non-dominated points to generate the Pareto front. [219, 280] It is common to use scalarisation methods, such as weighted sum, in CAMD and CAMPD problems; however, these methods may not be able to generate an evenly-distributed set of solutions on the Pareto front. On the other hand, [280] van Kleef *et al.* [178] applied a non-dominated genetic algorithm (NSGA) to consider ORC's thermodynamic and economic performance by designing working fluids. The NSGA is a stochastic optimisation algorithm that inherits the limitations of stochastic optimisation algorithms. Lee *et al.* [219] reviewed different MINLP MOO approaches for the CAMD problem, where they presented trade-offs between different MOO algorithms in terms of convergence and computational time.

In this study, the normalised normal constraint (NNC) algorithm developed by Messac *et al.* [280] is used to formulate the MOO problem into a single-objective function problem. The NNC method ensures a nice evenly spaced set of non-dominated optimal solutions. In addition, the NNC algorithm allows the handling of two or more multi-objective functions. The formulated single-objective problem is solved using the hybrid optimisation algorithm described in Chapter 3, where all the obtained local and global optimum solutions are passed to a dominance filter proposed by Messac *et al.* [280] to generate the optimal Pareto front with non-dominated optimal solutions (the NNC algorithm with dominance filter is well described in Ref. [280]).

In this section, two cases are considered. In the two cases, the size of the DAR is a decision variable. In the first case, the size of the DAR unit is identified by its rated power, $\dot{P}_{\text{DAR}}$ and is allowed to vary continuously, where a continuous Pareto front is generated and displayed in Figure 4.7. While in the second case, following the argument presented earlier in this chapter, the size of the DAR unit is identified by its rated volume, V_{CU} as available in the market and takes an integer value between 2 and 10 ft³, and a discrete Pareto front is generated and displayed in Figure 4.8.

From Figure 4.7, the best *SPC* is obtained by DAR systems with cooling capacity ≈ 120 W running with WF2 (1-C₄H₈-CH₃CH=CHNH₂-He). This result matches the results displayed in Figure 4.6, where WF2 is identified to have the least *SPC*. It can also be observed that the minimum *SPC* is only 1 % less than *SPC* for the working fluid with maximum cooling rate, $\dot{Q}_{\text{evap}}$.

The results in Figure 4.7 reveals that 1-aminopropene (CH₃CH=CHNH₂) and allylamine (1-amino-2-propene or CH₂=CHCH₂NH₂) are the most selected molecules as absorbents. Although

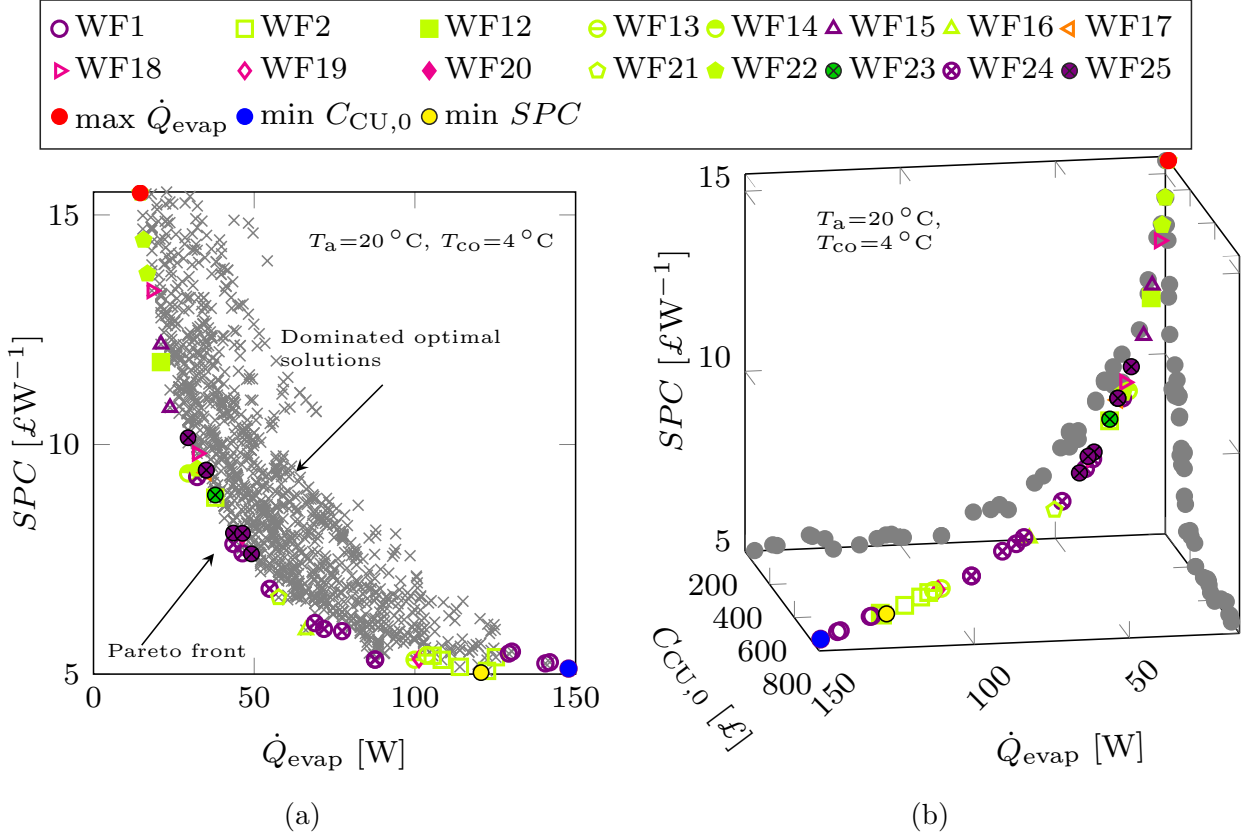


Figure 4.7: Results of multi-essential optimisations for $\dot{P}_{\text{DAR}}$ as a continuous decision variable, ambient temperature, $T_a = 20^\circ\text{C}$ and cooling temperature, $T_{co} = 4^\circ\text{C}$ with two objective functions: $\max \dot{Q}_{\text{evap}}$ and $\min C_{\text{CU},0}$. (a) SPC against $\dot{Q}_{\text{evap}}$ demonstrating dominated and non-dominated optimal solutions; (b) three-dimensional plot of $C_{\text{CU},0}$ (x -axis) against $\dot{Q}_{\text{evap}}$ (y -axis) against SPC (z -axis), and 2D projections (in grey) of the Pareto front on $x-z$ and $y-z$ planes. Working fluids are listed in Table A.1.

both aminopropenes passed environmental, toxicity and safety checks considered in this study, the National Center for Biotechnology Information [281] identifies allylamine as toxic with a low flash point which implies that working fluids with allylamine should be considered with more caution. In agreement with the results displayed Figure 4.2a, short chain alcohols are also recommended by the MINLP optimisations. Unsurprisingly, it can be observed from Table A.1 and Figure 4.7 that all refrigerants that fall on the Pareto front are non-polar. It is also not surprising that most non-dominated DAR designs use helium as the pressurising gas though hydrogen can still be used.

The Pareto front in Figure 4.7 gives an insight into which DAR design should be adopted. If high cooling rates $> 100\text{ W}$ are required, then DAR systems with WF1 or WF2 are recommended, while if low purchase cost is of interest, working fluids like WF12 and WF22 are recommended to be used with the corresponding charging settings.

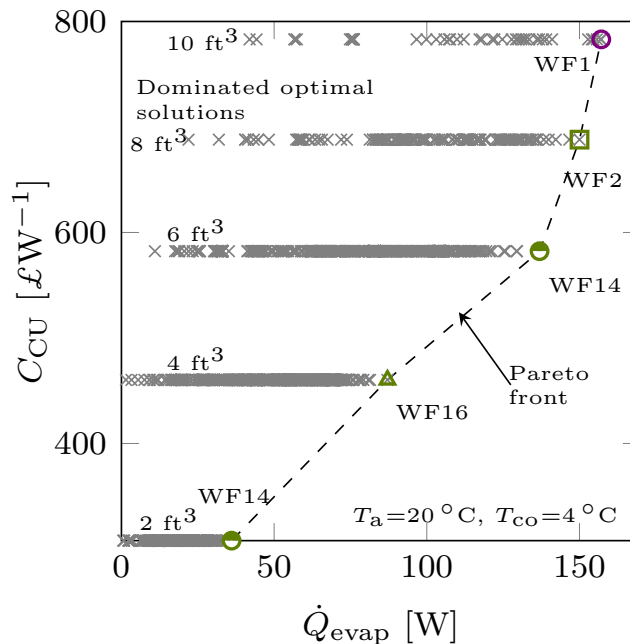


Figure 4.8: Results of multi-objective optimisations for V_{CU} as an integer decision variable, ambient temperature, $T_a = 20^\circ\text{C}$ and cooling temperature, $T_{co} = 4^\circ\text{C}$ with two objective functions: $\max \dot{Q}_{\text{evap}}$ and $\min C_{CU,0}$. (a) $C_{CU,0}$ against $\dot{Q}_{\text{evap}}$ demonstrating dominated and non-dominated optimal solutions. Working fluids are listed in Table A.1.

When the decision variable describing the DAR-unit size is discretised, the Pareto front is reduced to the frontier displayed in Figure 4.8. Minimum SPC is obtained by charging a 6-ft³ DAR unit with WF14, 1-pentane-1-aminopropylene-H₂ (1-C₅H₁₀-CH₃CH=CHNH₂-H₂) which differs from the optimal working fluid (WF2) for minimum SPC identified in Figure 4.7. The optimal SPC identified in Figure 4.7 consider a DAR unit that receives 282 W which lies between the power needed to operate 6 ft³ to 8 ft³ DAR cooling unit and the appropriate DAR size rounds to the larger size and hence higher SPC . This explains why WF2 is dominated by WF14 when the discretised space of DAR size is considered. It can be observed from Figure 4.8 and Table A.1 that 1-aminopropene dominates other absorbents except for 10-ft³ DAR unit.

4.5 Summary

Having the CAMD-DAR framework for domestic refrigeration developed and tested in Chapter 3, the framework is extended to consider more organic groups, including polar organic groups. Single and multi-objective MINLP optimisations are carried out using the integrated CAMD-DAR framework to maximise DAR cooling rate through working-fluid and charging settings (*e.g.*,

p_{ch} and $\tilde{x}_{\text{rs}}$) design under variant ambient and cooling temperatures. It has been demonstrated that non-polar+polar working fluid mixtures are favoured for maximum cooling rates. Cooling rates up to 146 W if 2-C₄H₈-C₂H₅OH-He is charged under charge pressure around 7.8 bar with *SPC* down to £ 5.36 per W of cooling. Other sub-optimal working fluids and corresponding DAR charging settings have also been identified. Most identified refrigerants have 3 to 5 carbon atoms. In addition, olefin refrigerants are preferred for their higher cooling rates. Compared to an NH₃-H₂O DAR system, The DAR system based on 2-C₄H₈-C₂H₅OH-He provides more cooling. Optimisations have shown that the required generator temperatures for optimum organic working fluids can be much lower than those needed to activate the NH₃-H₂O DAR system. All the identified working-fluid mixtures are environmentally friendly, but many refrigerants are highly flammable, with flammability numbers between 0.6 and 0.8.

The trade-off between the DAR size (hence the purchase cost) and the cooling rate has been considered by carrying out multi-objective optimisation with two different objective functions ($\max \dot{Q}_{\text{evap}}, \min C_{\text{CU},0}$). Further, multi-objective optimisation highlights the trade-off between maximising the cooling rate, $\dot{Q}_{\text{evap}}$ and minimising the purchase cost, $C_{\text{CU},0}$ to obtain a set of non-dominated design alternatives. Results from multi-objective optimisations suggest that 1-aminopropene (CH₃CH=CHNH₂) and allylamine (1-amino-2-propene or CH₂=CHCH₂NH₂) are the most selected molecules as absorbents on the Pareto front. In contrast, all non-dominated refrigerants that fall on the Pareto front are non-polar.

The presented CAMD-DAR framework can be extended by introducing more organic groups and environmental and safety constraints. The CAMD-DAR framework can be upgraded by expanding the multi-objective optimisation to include more independent objective functions to involve environmental objectives.

Chapter 5

Dynamic Modelling and Thermo-economic Evaluation of Solar-Driven Diffusion Absorption Refrigeration Systems

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5.1 Introduction

Domestic refrigeration is primarily driven by non-renewable energy in the MENA region, while the MENA region is responsible for high global warming gas emissions. [19] The escalating energy demands and prices associated with the depletion of fossil fuels motivate the use of alternative thermally-driven refrigeration systems powered by renewable energy. As discussed earlier in Chapter 1, most MENA countries lie on the solar belt having high average annual solar irradiation that ranges between 2000 W and 3000 W [31]. There are also ambitious goals in the MENA region to increase the share of solar energy in covering energy demands. Thus, there is great potential in the MENA region to decarbonise domestic refrigeration using abundant solar insolation. Refrigeration technologies powered by cheap solar collectors are promising for rural areas with limited access to electricity. Many regions like sub-Saharan Africa are deprived of proper refrigeration due to a lack of electricity access and high upfront installation costs. [1]

Solar thermal-sorption refrigeration is more cost-effective than solar electric and thermo-mechanical refrigeration, [48] considering that expanding solar-energy technologies brings down energy costs. For example, the levelised cost of energy (LCOE) of CSP declined from US\$ 0.34 kWh⁻¹ to US\$ 0.108 kWh⁻¹ between 2010 and 2020, [52] which falls in the range of fuel-fired power generation. This low LCOE can promote the investigation of solar-powered refrigeration systems for household applications.

Solar cooling systems based on absorption or adsorption cycles are still at a relatively early stage of uptake, with the majority of applications being for air conditioning, with cooling capacities >1 kW. [38] (H₂O–LiBr) absorption refrigeration systems are suitable for space cooling as water (the refrigerant) freezes at 0 °C. [65] Water is often used as the solar heat source fluid, and systems may be combined with domestic water heating. The hot water storage tank also provides buffering during intermittent solar availability.

Diffusion absorption refrigeration (DAR) is a thermal absorption refrigeration which has been thoroughly discussed in Section 1.2. Some studies considered adapting DAR systems for optimal performance in solar applications. DAR can provide off-grid cooling with zero electrical input at a relatively low cost, provided it is coupled with low-cost solar collectors. The types of solar collectors most suitable are non-tracking collectors that use natural (or thermally-driven) fluid circulation to deliver heat to the generator. [38, 42]. Dammak *et al.* [131] Jakob [41] and

5.1. INTRODUCTION

Schmid *et al.* [74] studied how solar collector and bubble pump can be integrated into a single component to heat the working fluid directly with solar radiation.

Many authors have investigated solar-powered diffusion-absorption refrigeration technologies. [14, 41–44] Absorption refrigeration is among these environment-friendly technologies. [45]

Solar-powered refrigeration can be either electrically driven or thermally driven. It can be observed in Figure 5.1 that solar thermal cooling systems rely on three main components: a heat-driven refrigeration system, a cooling medium, and solar thermal collectors. Solar thermal cooling systems may additionally use thermal storage (hot-water tanks, phase-change material or ice storage).

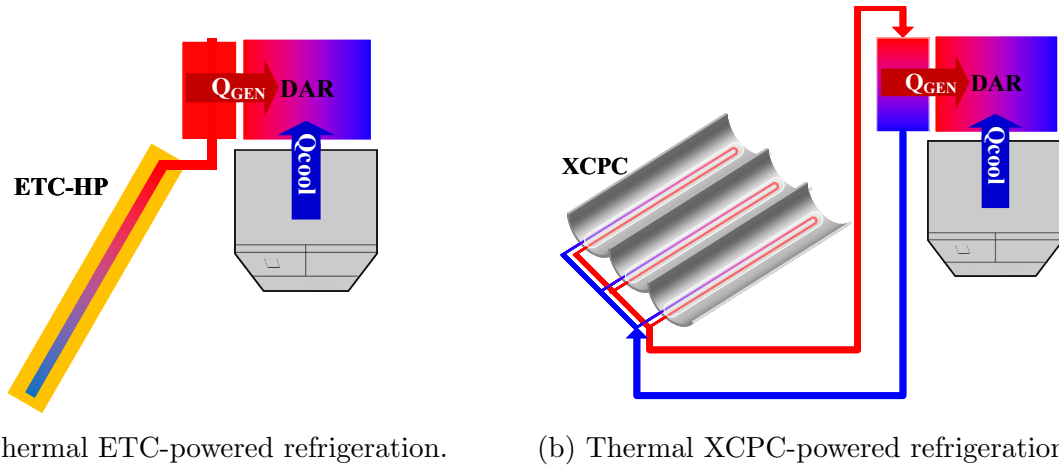


Figure 5.1: Some possible configurations of solar-powered DAR systems studied in this chapter.

Acuña *et al.* [43, 132] investigated the use of different solar-collector types to run DAR systems. Among the considered solar-collector types are compound parabolic concentrator (CPC), evacuated tube collectors (ETC) and flat-plate solar collector (FPC). Their simulations for a couple of inorganic working fluids suggest that ETC results in higher solar energy conversion than CPC and FPC. Freeman [42] considered low-cost evacuated-tube heat pipe collectors (ETC-HP) to power solar-DAR systems. Their results highlight trade-offs in DAR performance under considering different operating and design parameters like solar collector area and DAR charge pressure. [38]

As reviewed in Chapter 1, Jakob *et al.* [41] and Schmid *et al.* [74] suggested that multi-tube bubble pumps are beneficial for solar-powered DAR systems. Schmid *et al.* [74] developed a solar-driven $\text{NH}_3\text{--H}_2\text{O}$ DAR machine with an integrated multi-tube generator where the working fluid flows instead of the heat transfer fluid in the ETC heat pipes. This integrated design

showed low solar-collector efficiency compared to a DAR design with a plate heat exchanger. The plate heat exchanger has a dry interface with the generator that delivers heat from the solar collector array to the DAR unit. Schmid's latter DAR design can produce a cooling capacity of up to 228 W with 11.4 % solar irradiance converted to cooling power.

Apart from the work presented by Freeman *et al.* [42, 95] who developed a quasi-transient DAR model for $\text{NH}_3\text{-H}_2\text{O}$ solar DAR system, no other studies considered the dynamic simulation of solar-powered DAR systems. All the analysis presented in literature are either experimental (*e.g.*, Refs. [41, 74]) or steady-state simulations (*e.g.*, Refs. [43, 132]). Whereas, a transient or quasi-transient universal solar-DAR model can play an important role in investigating different working fluid mixtures and various DAR configurations under variant climatic and operating conditions.

It is relevant to review some DAR dynamic models in the literature. Mansouri *et al.* [113] devised a simple black box dynamic model for a dynamic DAR system based on the first-order response function with a delay time. They considered a hotel-size DAR unit (2 ft^3). Their DAR unit showed a 40 min to 68 min delay until cooling starts. Similarly, Jemaa *et al.* [112] presented a similar model. Their DAR unit showed a 20 min to 60 min delay. Both Mansouri *et al.* [113] and Jemaa *et al.* [112] correlated the DAR system time constant and time delay to the power input and their model demonstrated good agreement with their measurements. The correlations between the dynamic constant and the power input differ in the two studies. This observation suggests that the devised correlations are very specific and cannot be extended to describe different DAR systems.

On the other hand, Adjibade *et al.* [114] presented a parametrised dynamic model for a simple DAR system based on a system of algebraic differential equations. Adjibade *et al.* [114] also considered a small-scale DAR unit (1.4 ft^3) with a 1 g s^{-1} refrigerant-rich solution flow. Unlike the work presented by Mansouri *et al.* [113] and Jemaa *et al.* [112], the model devised by Adjibade *et al.* [114] cannot capture the delay observed in the response of DAR performance.

One of the scopes of this thesis is to demonstrate the suitability of DAR technology for refrigeration in the Middle East. To complete the analysis, the thermo-economic evaluation of solar-DAR systems is a useful tool to complete the picture. Yıldız *et al.* [162] presented an economic assessment for an LPG-powered DAR system based on exergic analysis. However, their analysis does not capture the assessment of the technology throughout the system's

lifetime. Najjaraan [258] presented an economic assessment to compare ammonia–water-based DAR unit to conventional vapour-compression refrigeration unit for refrigeration purposes. While underestimated DAR installed prices are considered, the levelised cost of cooling of DAR ($LCOC < \$0.4 \text{ kWh}^{-1}$) competes with solar-powered vapour-compression refrigeration with or without energy storage. Nevertheless, due to higher energy requirements, solar-DAR cooling power per floor area of the solar collector is shown to be almost half that of the solar-powered vapour compression refrigeration unit. However, the thermo-economic assessment of organic-based DAR systems was beyond the scope of his study.

Due to the particular importance of the dynamic performance of DAR systems, particularly solar-powered DAR, the work presented by Freeman *et al.* [42,95] is extended to devise a more generalised quasi-transient model for solar-powered DAR systems. The quasi-transient model is devised to simulate the performance of the DAR unit with a particular focus on start-up and shutdown performance in response to the intermittency of solar irradiance.

The proposed model can be used to assess different working-fluid mixtures under various operating conditions. Unlike Freeman’s model, the presented model considers the transient behaviour of the solar collector array. A simple algorithm is considered to shed light on the start-up and shutdown of solar-powered DAR units. It is sufficient to consider a quasi-transient model, as most of the thermal mass is concentrated in the hot side of the solar-DAR unit (heat source, heat delivery assembly, and generator wall) compared to other DAR-unit components. This can be obviously observed in how temperatures measured behave at various points in a solar-powered DAR which is demonstrated in Figure 5.3.

Further, A thermo-economic assessment is also considered to shed light on the suitability of solar-DAR based on organic working fluids, with a particular interest in the Egyptian climate for optimum working-fluid system identified through MINLP solution of the CAMD-DAR framework presented in Chapter 4.

5.2 Modelling and optimisation methodology

A schematic diagram of the studied solar-DAR system is displayed in Figure 5.2. The solar DAR system consists of two main sections: the solar collector and the DAR unit. The solar

collector harnesses heat from the sun, which the DAR cycle converts into cooling.

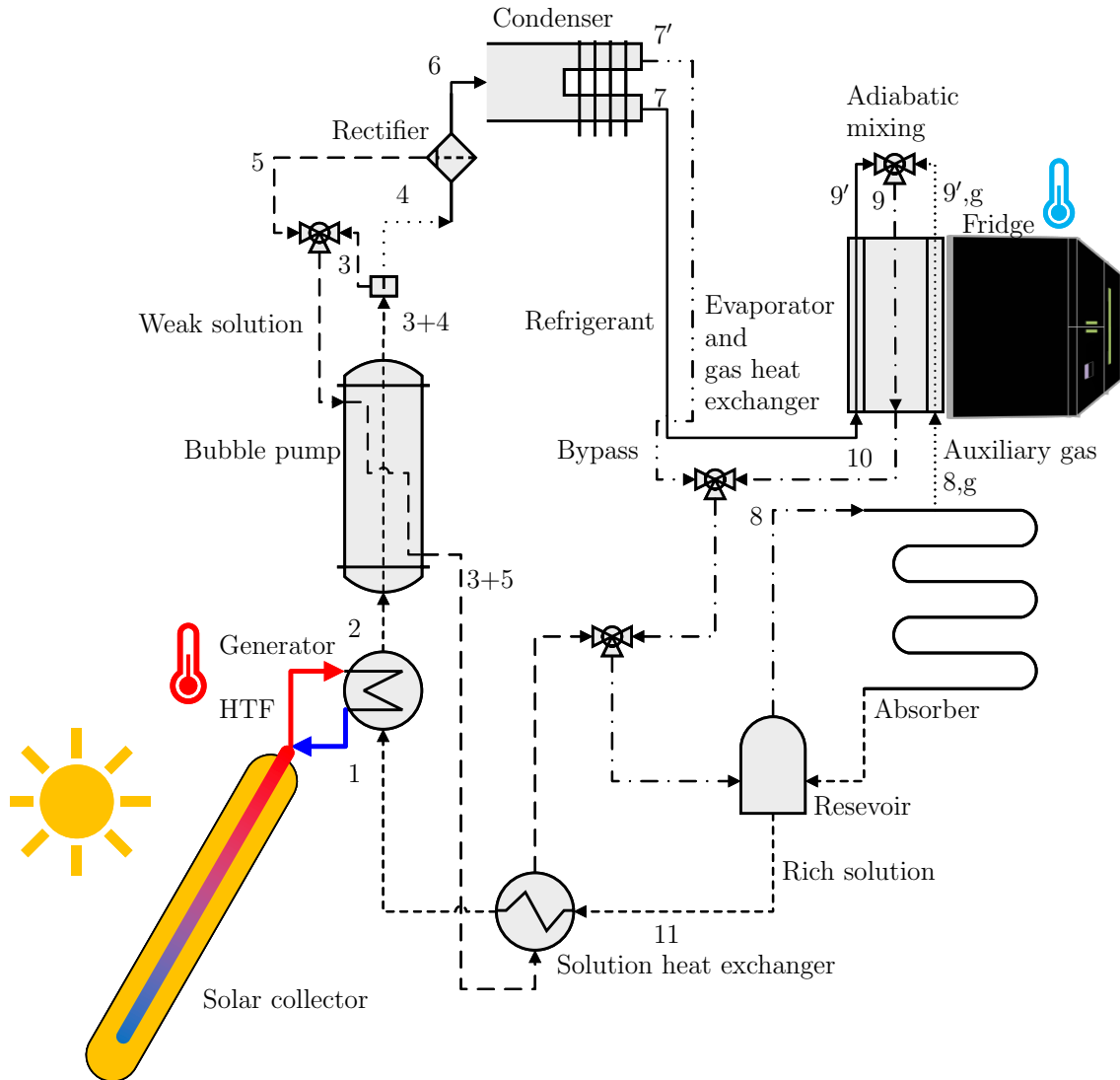


Figure 5.2: Schematic diagram of main unit operations in the solar-DAR system considered in this chapter. The solar collector can vary from being an evacuated tube collector heat pipe (ETC) to an external compound parabolic concentrator (XCPC).

in the current study, the DAR generator is coupled to the solar collector array through a dry interface. The DAR working fluid is heated in the generator by exchanging heat with the heat-transfer fluid (HTF), typically water, that circulates through the solar collector array. Like in Chapter 4, a semi-attached generator is adopted (*see* Figure 3.3). The generated working fluid is lifted by the bubble pump, separating into a weak-solution stream that flows down into the absorber and a refrigerant-concentrated vapour stream. The refrigerant in the vapour stream is purified by partial condensation in an air-cooled rectifier. Then, the refrigerant vapour flows into an air-cooled finned-tube condenser. Any uncondensed refrigerant bypasses the evaporator and flows down into

the reservoir. The condensed refrigerant enters the gas heat exchanger, where the evaporating stream subcools it. The subcooled refrigerant mixes adiabatically with an auxiliary-gas stream at the top of the evaporator. This adiabatic mixing results in a drop in the temperature and refrigerant partial pressure. The heat removed from the fridge evaporates the refrigerant flowing into the DAR evaporator. The stream leaving the evaporator is received in the reservoir. The evaporated refrigerant is absorbed in the weak solution flowing down from the bubble pump. The auxiliary gas escapes from the absorber, and the refrigerant-rich liquid drains down the absorber returning to the generator to complete the cycle. A solution heat exchanger is used to preheat the rich-solution stream leaving the absorber by the weak-solution stream flowing into the absorber.

The transient performance of DAR is identified by its start-up and shut-down time. In a relevant study, Najjaran *et al.* [130] investigated the effect of heat-input supply and charging conditions on the startup of a lab-scale DAR unit. It can be concluded from their study that higher heat inputs can shorten startup times; however, the DAR performance becomes more oscillating for high heat-input supply and the coefficient of performance declines as well. Their study also reveals that during the startup phase, thermal heat is accumulated at the generator wall until the DAR is activated. Hence, the heat supply is associated with refrigerant circulation through the DAR cycle resulting in a drop in the generator wall temperature. The same observation has been recorded for solar-powered DAR systems examined by Freeman *et al.* [42,95] and Najjaran measurements [282] as shown in Figure 5.3. From the same figure, the shutdown phase is also significant and limited by the rate of heat-input supply to the solar-DAR as shall be discussed in Section 5.2.2. Relevant component models and economic models are identified in the following sections.

5.2.1 Solar collectors

Two types of non-tracking thermal solar collectors are considered in this study: (i) evacuated-tube collectors with heat pipes (ETC-HP); and (ii) external compound parabolic concentrators (XCPC). The commercial Strebel AS 100 HP16 ETC designed by Thermostrom Energietechnik GmbH [283] and XCPC designed by ArticSolar [284], respectively, are considered, and their design parameters are given in Table 5.1.

Evacuated-tube solar collectors are glass pipes which are evacuated to reduce heat losses from the tubes. As it can be seen in Figure 5.3, an ETC pipe has two concentric tubes. The outer

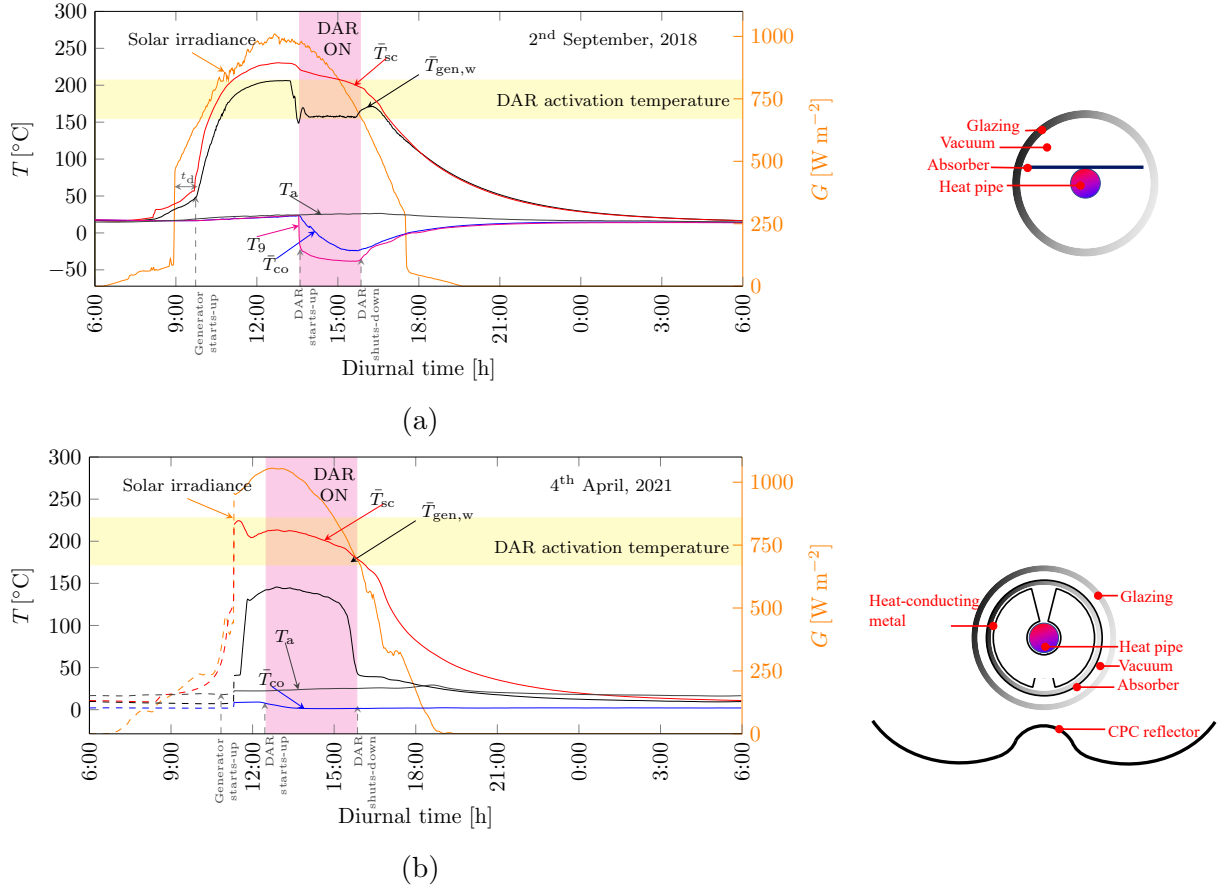


Figure 5.3: Diurnal plot for temperature variation in a solar-powered DAR. (a) a DAR powered by four tubes of ETC-HP on a sunny day (2nd of September 2018) obtained from [95]. (b) a DAR powered by a XCPC module on 4rd of April, 2021 provided by Najjaran *et al.* [282].

tube is a transparent glass one, while the inner tube has a selective coating layer for higher light absorbance and lower reflection. Solar irradiance crosses the glass tube and the inner tube traps the heat to heat the heat-transfer fluid (HTF), which evaporates and conveys this thermal heat to the end user. [285] An external compound parabolic concentrator (XCPC) is a modification to the ETC. An external non-imaging reflector is coupled to the heat pipes to concentrate the received solar irradiance. [286]

The thermal efficiency of the solar collector as a function of the solar irradiance, I_{sol} , the solar collector temperature, $\bar{T}_{sc}$ and ambient temperature T_a is computed using the classical second-order expression [288]:

$$\eta_{sc} = \eta_{th,0} - \eta_{th,1} \frac{(\bar{T}_{sc} - \bar{T}_a)}{I_{sol}} - \eta_{th,2} \frac{(\bar{T}_{sc} - \bar{T}_a)^2}{I_{sol}}, \quad (5.1)$$

where I_{sol} is the global irradiance for ETC-HP and direct normal irradiance for XCPC. The term

5.2. MODELLING AND OPTIMISATION METHODOLOGY

Table 5.1: Design parameters for ETC-HP and XCPC solar collectors considered in this thesis. Incident angle modifier for K_{Bt} and K_{Dt} calculations are obtained from Refs. [283,287] for ETC and XCPC respectively.

Parameter	Unit	Value	Description
ETC [283]			
a_{ETC}	m ² per collector	2.957	Aperture area per collector
$\eta_{th,0}$	–	0.74	Zero-loss (optical) efficiency
$\eta_{th,1}$	W m ⁻² K ⁻¹	1.52	First-order heat loss coefficient
$\eta_{th,2}$	W m ⁻² K ⁻²	0.0052	Second-order heat loss coefficient
MC_{sc}	kJ m ⁻² K ⁻¹	3.69	Thermal capacity of solar collector
I_{sol}	W m ⁻²	$K_B G_{Bt} + K_D G_{Dt}$	Solar irradiance
MC_{hd}	kJ K ⁻¹	10	Thermal capacity of solar collector
$UA_{sc-gen,w}$	W K ⁻¹	4.5	Overall heat transfer coefficient through heat delivery assembly (solar collector header) to generator wall
$UA_{gen,w-amb}$	W K ⁻¹	1	Overall heat transfer coefficient accounting heat losses between generator wall and ambient
XCPC-EW [284]			
a_{XCPC}	m ² per collector	2.41	Aperture area per collector
$\eta_{th,0}$	–	0.74	Zero-loss (optical) efficiency
$\eta_{th,1}$	W m ⁻² K ⁻¹	0.54	First-order heat loss coefficient
$\eta_{th,2}$	W m ⁻² K ⁻²	3.98×10^{-6}	Second-order heat loss coefficient
MC_{sc}	kJ m ⁻² K ⁻¹	2.13	Thermal capacity
I_{sol}	W m ⁻²	$K_B G_{Bt}$	Solar irradiance
MC_{sc}	kJ m ⁻² K ⁻¹	3.69	Thermal capacity of solar collector
MC_{hd}	kJ K ⁻¹	1	Thermal capacity of solar collector
$UA_{sc-gen,w}$	W K ⁻¹	2.5	Overall heat transfer coefficient through heat delivery assembly (solar collector header) to generator wall
$UA_{gen,w-amb}$	W K ⁻¹	1	Overall heat transfer coefficient accounting heat losses between generator wall and ambient

$\eta_{th,0}$ is the zero-loss (optical) efficiency, $\eta_{th,1}$ is the first-order loss coefficient, and $\eta_{th,2}$ is the second-order loss coefficient. Unlike work presented by Freeman *et al.* [42], The thermal capacity of solar collectors is considered. Hence, the quasi-dynamic energy balance for the solar collector is

$$\dot{Q}_u = \eta_{sc} I_{sol} A_{sc} - MC_{sc} \frac{d\bar{T}_{sc}}{dt}, \quad (5.2)$$

where MC_{sc} is the thermal capacity of the solar collector available from the manufacturer specification sheet for ETC [283], and fitted for XCPC as demonstrated in Appendix B. In Equation (5.2), A_{sc} is the aperture area of the solar collector array and $\dot{Q}_u$ is the useful heat

transferred by HTF in the heat delivery assembly to the generator wall:

$$\dot{Q}_u = UA_{sc-gen,w}(\bar{T}_{sc} - \bar{T}_{gen,w}), \quad (5.3)$$

with $UA_{sc-gen,w}$ defined in Table 5.1 and calibrated as shown in Appendix B, and $\bar{T}_{gen,w}$ is the mean generator wall temperature.

5.2.2 Solar-DAR system

A DAR unit with dimensions given in Table C.1 in Appendix C is considered in this analysis. The DAR steady-state thermodynamic model presented in Section 2.3.2 is modified to account for the DAR unit's transient behaviour. In the presented model, besides the solar collector array, the generator and heat delivery assembly are considered (collectively) as the main dynamic component where all the thermal capacity, MC_{hd} of the DAR is accumulated. Thus, Equation (2.33) in the steady-state model is replaced by the dynamic balance for the generator and heat-delivery assembly section:

$$MC_{hd} \frac{d\bar{T}_{gen,w}}{dt} = \dot{Q}_u - \dot{Q}_{gen} - \dot{Q}_{gen,w-amb}, \quad (5.4)$$

where $\dot{Q}_{gen,w-amb}$ is the rate of heat dissipated from the generator wall to the ambient:

$$\dot{Q}_{gen-amb} = UA_{gen,w-amb}(\bar{T}_{gen,w} - T_a), \quad (5.5)$$

with $UA_{gen,w-amb}$ is the overall heat transfer coefficient accounting for the heat losses between the generator wall and the ambient.

As discussed earlier, refrigerant circulation starts when the heat delivered to the generator is enough to create a two-phase slug flow. [42, 212] To simulate this, the conditions in Figure 5.4 and earlier discussed in Section 2.3.2 should be met to anticipate rich solution flowrate, $\dot{n}_{rs}$. The calculated generator wall temperature, $\bar{T}_{gen,w}$, rich solution flowrate, $\dot{n}_{rs}$ and heat-input power received by the DAR unit at the generator, $\dot{Q}_{gen}$ are introduced to the model previously discussed in Section 2.3.2.

Preliminary analysis suggested that the heat transfer coefficients in the rectifier and the condenser

are mainly controlled by the air-side heat transfer resistance. Thus, in order to simplify the model, the overall heat transfer coefficient for the rectifier and condenser. The assumption in Equation (3.8) is replaced by solving the heat balance equation for the rectifier

$$\dot{Q}_{\text{rect}} = UA_{\text{rect}}\Delta T_{\text{rect,mean}} \quad (5.6)$$

where $UA_{\text{rect}} = h_{\text{air}}\pi d_{\text{rect,o}}l_{\text{rect}}$ with h_{air} is approximately 10 W for indoor [289], and $\Delta T_{\text{rect,mean}}$ using Chen's [290] approximation to avoid solver failure at diminishing temperature difference. Instead of deploying Equation (3.9) for the temperature of the refrigerant leaving the condenser, heat balance is solved for the condenser outlet temperature:

$$\dot{Q}_{\text{cond}} = UA_{\text{cond}}\Delta T_{\text{cond,mean}} \quad (5.7)$$

The condenser in DAR units is typically an air-cooled rectangular-finned condenser. Hence, the method proposed by Godinho de Rezende *et al.* [291] is used to estimate the corrected overall heat transfer coefficient UA_{cond} on the air-side of the condenser and $\Delta T_{\text{cond,mean}}$ using Chen's [290] approximation to avoid solver failure at diminishing temperature difference.

In the solar-powered DAR experiments, the temperature in the cold box was not controlled unlike the set of indoor experiments, where the generator was electrically heated. [130, 258] Thus a dynamic expression for the cold box is introduced

$$\text{MC}_{\text{co}} \frac{d\bar{T}_{\text{co}}}{dt} = -\dot{Q}_{\text{evap}} - \dot{Q}_{\text{co-amb}}, \quad (5.8)$$

where MC_{co} is set to 10 kJ K⁻¹ and the rate at which heat leaks from the ambient to the fridge, $\dot{Q}_{\text{co-amb}}$ is

$$\dot{Q}_{\text{co-amb}} = UA_{\text{co-amb}}(\bar{T}_{\text{co}} - T_{\text{a}}), \quad (5.9)$$

with a value of 0.75 W K⁻¹ is considered for $UA_{\text{co-amb}}$. It should be highlighted that for real-time operation, the value of MC_{co} relies on fridge loading, while $UA_{\text{co-amb}}$ value depends on the frequency at which the fridge door is opened. However, for sake of comparison, it is sufficient to preset these parameters.

The presented model is devised to take design parameters (UA's, MC's) and climate data for a given location (*e.g.*, London, Alexandria, Cyprus). In this study, unless mentioned, hourly climate data

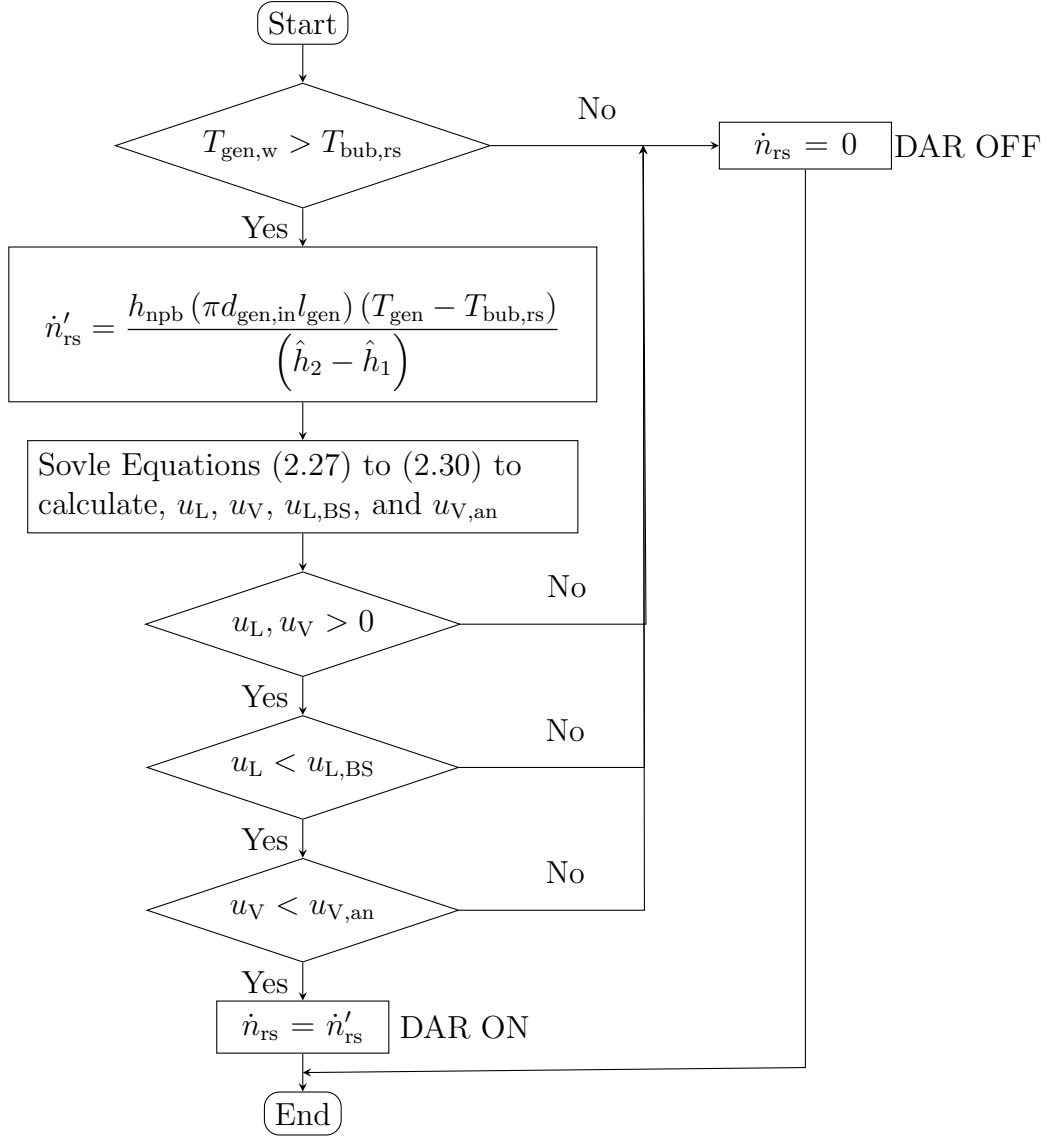


Figure 5.4: Algorithm for identifying refrigerant-rich solution flowrate.

for a given city (ambient temperature, direct-beam and diffuse irradiance and other location-relevant information) are obtained from the climate database available in EnergyPlus [292]. Given the aforementioned inputs, the quasi-transient DAR thermodynamic model is solved.

5.2.3 Economic and environmental analysis

For solar-powered DAR systems, in addition to the specific installed cost of DAR unit, SPC , which has been considered in Chapter 3, the levelised cost of cooling, $LCOC$, is used to assess the convenience of using a cooling technology for a given economy. The $LCOC$ is the discounted lifetime cost of the cooling system (here the solar-DAR system) and operating maintenance cost

5.2. MODELLING AND OPTIMISATION METHODOLOGY

of the system, expressed as a cost per unit of cooling produced in $\text{£ Wh}_{\text{co}}^{-1}$. It considers all the capital, operating and financing costs attributed to the operating cooling system throughout its lifetime. $LCOC$ is calculated as: [58, 59, 293]

$$LCOC = \frac{\sum C_0 + \sum_{t=1}^{LT} \sum C_{O\&M} (1 + i_f)^{t-1} \cdot (1 + i_d)^{-t}}{\sum_{t=1}^{LT} E_{\text{co,annual}} \cdot (1 + i_d)^{-t}}, \quad (5.10)$$

Table 5.2: Cost parameters for DAR module and solar collectors considered in this thesis.

Parameter	Description	Unit	Value
DAR *			
$C_{\text{DAR},0}$	Installed cost	£	$23\dot{P}_{\text{DAR}}^{0.58}$
$C_{\text{DAR},O\&M}$	Maintenance cost	£ year^{-1}	0
ETC † [42, 95]			
$C_{\text{ETC},0}$	Installed cost	£ m^{-2}	251
$C_{\text{ETC},O\&M}$	Maintenance cost	£ year^{-1}	$0.01C_{\text{ETC},0}$
XCPC †			
$C_{\text{XCPC},0}$	Installed cost	£ m^{-2}	414.93
$C_{\text{XCPC},O\&M}$ ‡	Maintenance cost	£ year^{-1}	$0.01C_{\text{ETC},0}$

* Already discussed in Section 3.2.1.

† Estimation based on information provided by the supplier.

‡ Estimated.

where E_{co} is the annual refrigeration capacity in kWh year^{-1} , $\sum C_0$ is the total installation cost of the solar-DAR system including installation of the solar-collector array, $\sum C_{O\&M}$ is the annual operating and maintenance costs attributed to running the solar-DAR system, i_d is the discount rate and i_f is the inflation rate. Relevant cost parameters are listed in Table 5.2. Another economic metric is the levelised cost of saving, LCS over the lifetime, estimating the savings that can be made over the useful lifetime of the system:

$$LCS = C_s \cdot (i_d - i_f)^{-1} \cdot \left[1 - \left(\frac{1 + i_f}{1 + i_d} \right) \right] - C_0, \quad (5.11)$$

where C_s is the annual savings due to avoiding the use of electricity:

$$C_s = E_{\text{gen}} \cdot c_{\text{elec}} - \sum C_{O\&M}, \quad (5.12)$$

with $E_{\text{gen}} = \int \dot{Q}_{\text{gen}}$ is the annual heat-input received by the DAR generator. The payback time, PBT is the number of years over which the initial investment can be recovered and is calculated

as:

$$PBT = \frac{\ln \left[\frac{C_0(i_f - i_d)}{C_s} + 1 \right]}{\ln \left(\frac{1+i_f}{1+i_d} \right)} \quad (5.13)$$

Table 5.3: List of economic and environmental parameters for consideration in this study, where the parameters describe Egyptian prices and economy

Parameter	Description	Unit	Value	Ref.
i_f	Average inflation rate, 2019	%	9.273	[294]
i_d	Discount rate, 2019	%	9.75	[294]
c_{elec}	Electricity selling price	pence kWh ⁻¹	3*	[36]
f_{CO_2e}	CO ₂ electricity emission factor	kgCO _{2e} kWh ⁻¹	0.628	[295]
c_{CO_2}	CO ₂ emission cost	£ tCO _{2e} ⁻¹	62.696	[296]

*LE 0.65 kWh_e⁻¹ converted to pence kWh_e⁻¹ at 2019-average exchange rate (GB£ 1=LE 21.4825) [294], customer service charge of LE 6 per month is added.

One of the motivations mentioned in Chapter 1 is reducing CO₂ emissions. There is a general move to encourage governments to enforce carbon pricing to reduce CO₂ emissions. The total environmental penalty cost saving, *EPCS*, over the lifetime of the solar-DAR unit, [297] an important measure that signifies the potential reduction of CO₂ emissions by avoiding the use of electricity to power the DAR system:

$$EPCS = E_{gen} \cdot f_{CO_2e} \cdot c_{CO_2} \cdot (i_d - i_f)^{-1} \cdot \left[1 - \left(\frac{1+i_f}{1+i_d} \right) \right], \quad (5.14)$$

where f_{CO_2e} is CO₂ emission factor which accounts for CO₂ attributed to unit kWh, while c_{CO_2} is the penalised cost (or tax) of emitting CO₂ to the atmosphere. These are geographically-related parameters and are listed in Table 5.3. The carbon pricing ranges from as low as less than £ 1 up to more than £ 100. [298]

5.3 Results and discussion

The results in Chapter 4 are extended in Section 5.3.1 to study the effect of solar collector type and DAR size associated with optimum working fluid and charging settings on the theoretical design solar collector temperature requirements and how the solar collector and DAR design (size + working fluid + charging setting) reflects on cooling rates, solar-DAR thermal efficiencies, and economic metrics for a standard solar irradiance. Further, in Section 5.3.1, The solar-DAR quasi-transient model presented in Section 5.2.2 is used with the optimal organic-based DAR

design considering time-varying solar-DAR performance for typical winter and summer weeks in Alexandria, Egypt. In Section 5.3.2, optimum working fluids from the CAMD-DAR framework in Chapter 4 are thermo-economically and environmentally assessed for Alexandria, Egypt.

5.3.1 Solar collector choice for solar-powered DAR

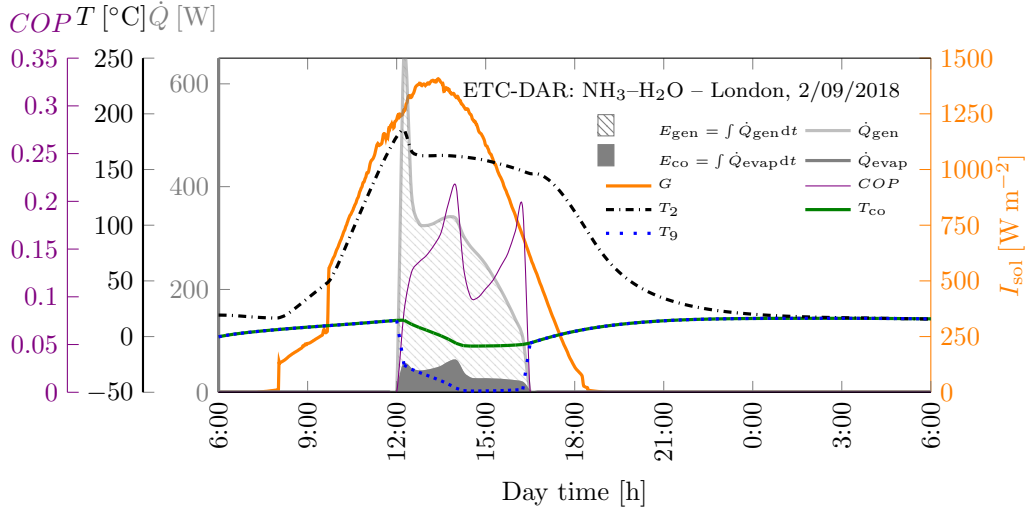
In this section, one-minute ambient temperatures, T_a and solar irradiance, G data measured by Freeman *et al.* [95] on a sunny day in London (2nd September) is considered. The measured climatic data are used to carry out one-minute simulations to assess the suitability of the two thermal solar collector types (ETC and XCPC) which have been experimentally evaluated using the DAR experimental facility at Imperial College London.

To carry out simulations, the solar-DAR model presented in Section 5.2.2 is used to investigate the impact of solar-collector type and size on the performance of a solar-powered DAR unit. To this end, two solar-DAR configurations discussed in Section 5.1: ETC and XCPC solar collectors are considered with standard ammonia–water DAR unit. One-minute solar-DAR simulations shown in Figure 5.5 suggest that for the given climatic conditions, Despite the aperture area of the ETC array being almost half the aperture area of the XCPC array, the ETC-DAR system can produce more cooling compared to the XCPC-DAR system. For the systems in Figure 5.5, ETC-DAR system produces 145 Wh of cooling on this specific day; whereas XCPC-DAR system produces 30 Wh of cooling.

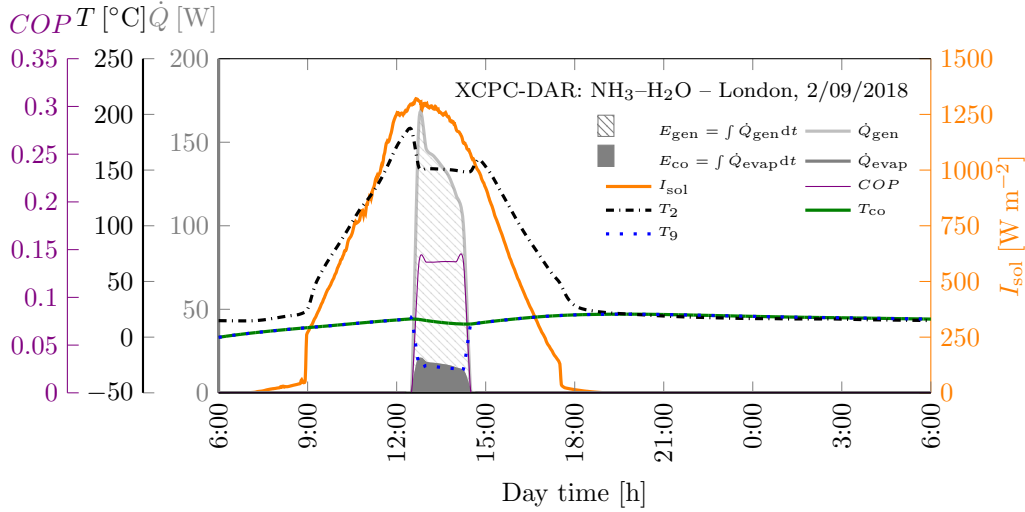
It can also be observed from the figure, that the ETC-DAR system can result in a wider operating window. Compared to Figure 5.3, simulations indicate that having two more ETC tubes can extend the system operation time by almost an hour. cooling energy per day. solar-DAR can go modular. The results suggest the importance of investigating the effect of solar-collector size.

For a fixed size DAR unit, it can be observed in by comparison with Figure 5.3a, that on this specific day, doubling the number of ETC tubes from 6 to 12 tubes results in cooling capacity from 145 Wh day^{-1} to 170 Wh day^{-1} (*i.e.*, 16 % more cooling). In contrast, doubling the aperture area of the solar collector array to power a single DAR unit results in a reduction in the coefficient of performance as shown in Figure 5.6.

On the other hand, simulations show that XCPC with an aperture area less than the area of



(a)



(b)

Figure 5.5: Simulation results for solar-powered DAR simulations on a sunny day in London (2nd of September 2018). Solar irradiance values are measured values taken from Ref. [95]. (a) A solar-DAR unit powered by 6 ETC-HP tubes, and (b) a solar-DAR unit powered by a single XCPC array.

one array cannot activate the DAR system. The useful heat collected is insufficient to bring the refrigerant-rich mixture to a boil ensuring two-phase slug flow in the bubble pump. For the same DAR size, doubling the size of the XCPC array results result in an increase in cooling capacity from 30 Wh day^{-1} to 45 Wh day^{-1} (*i.e.*, 53 % more cooling). It can also be shown that increasing the XCPC aperture area does not significantly change the number of operating hours on a scale of one hour.

In general, the results presented in Figure 5.6 confirm that for a given DAR system, the available simulations demonstrate that using ETC is more convenient for small-scale cooling

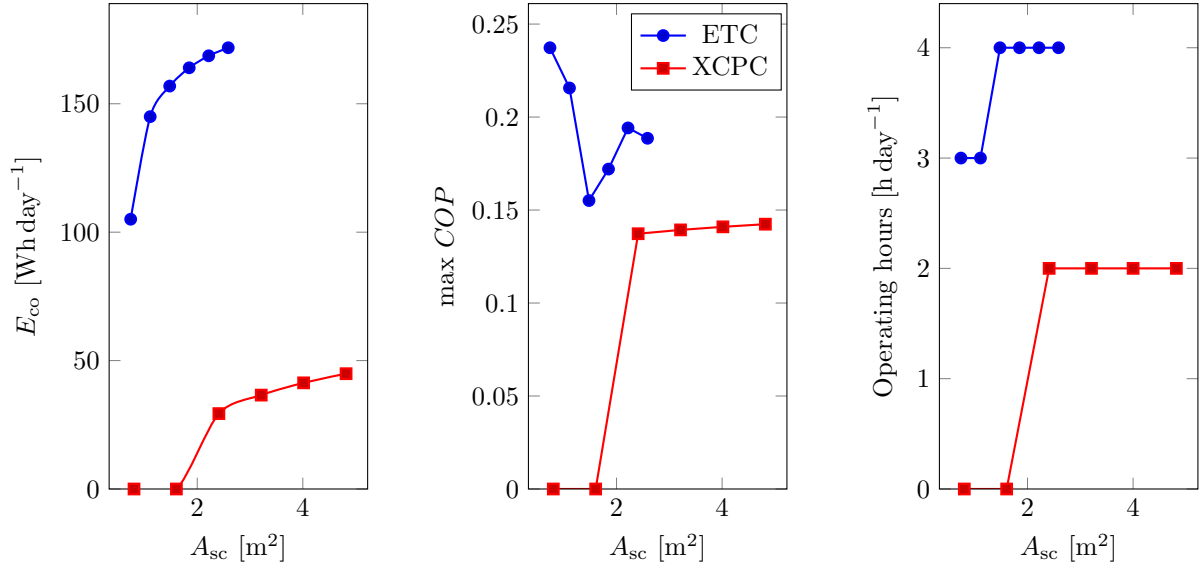


Figure 5.6: Effect of solar-collector array area on DAR performance for an ammonia–water solar-powered DAR on a sunny day in London (2nd of September 2018). Solar irradiance values are measured values taken from Ref. [95].

using NH₃–H₂O-charged DAR systems. XCPC is likely more suitable for large duty systems like DAR systems for space cooling rather than refrigeration, such as air-conditioning applications as considered by Li *et al.* [299].

5.3.2 Case study: Organic-based solar-powered DAR refrigeration for different regions

The analysis in this section considers a 10-ft³ solar-DAR unit. With given importance to the MENA region, weather data for Alexandria, Egypt is considered to investigate the convenience of the DAR system in general and proposed organic-based DAR systems specifically. For Alexandria, ASHRAE [300] identifies the typical summer week can be considered as the week between 26 September and 2 October. Whereas a typical winter week is a week between 8 and 14 of March.

Solar-DAR performance under different weather conditions

The MINLP CAMD-DAR optimisations in Chapter 4 suggest the use of 10-ft³ DAR unit charged with 2-C₄H₈–C₂H₅OH–He for maximum cooling rate. A recognised feature about this working-fluid mixture, as demonstrated in Chapter 4, is its suitability for a wide range of ambient and cooling temperatures. Thus, this DAR system with charging settings (listed in

Table 5.4) is carried forward in the rest of this chapter as a representative case. Two solar collector arrays are considered. The first one is the 6-tube ETC array with aperture area $\approx 1\text{m}^2$. The second solar-collector is a single XCPC array with an aperture area of 2.4m^2 . These two solar collector systems are tested and their design parameters (listed in Table 5.1) are calibrated in Appendix B.

Table 5.4: Description of organic-based solar DAR systems under consideration.

	Unit	Alexandria, EG	
		ETC-HP	XCPC-EW
Working fluid		2-C ₄ H ₈ -C ₂ H ₅ OH-He	
DAR size, V_{CU}	ft ³	10	
Charge pressure, p_{ch}	bar	7.8	
Charge composition, x_{rs}	wt%	17	
Number of solar collector tubes	tubes	6	3
Solar-collector aperture area, A_{sc}	m ²	1	2.4

The results in Figure 5.7 compare 2-C₄H₈-C₂H₅OH solar DAR system to NH₃-H₂O solar DAR system for the typical summer week (26 September and 2 October) using 6-tube ETC array. It can be observed that unlike the NH₃-H₂O solar DAR system, The DAR system with the organic working fluid can provide cooling throughout the whole week. The NH₃-H₂O solar-DAR unit can provide only 161 Wh_{co} of cooling over two days with only 3.5 h of cooling per week. For the considered NH₃-H₂O solar-DAR unit, it can be revealed that on a summer day, at least 850 W m⁻² incident on the tilted ETC to activate the DAR unit. In contrast, the organic-based solar-DAR unit can provide 1441 Wh_{co} of cooling over the week. It can be easily observed in Figure 5.7, that operating time is longer than the NH₃-H₂O solar-DAR unit. The organic-based DAR unit can operate up to 43 h of cooling per week with a mean of 6.14 h per day.

Unlike the case of using ETC, The results in Figure 5.8 suggest the inconvenience of using a single XCPC array to run the NH₃-H₂O solar DAR system in Alexandria. Even for the organic-based DAR system, the cooling output of the XCPC-powered fridge (77 Wh_{co}) is much lower than the cooling output of the ETC-powered fridge. This can be partially attributed to the XCPC model deployed accounts for a lot of unavoi ded heat losses from the HTF circulating between the solar collector array and the generator wall. This also explains why the cooling output of the ETC-powered DAR system is higher than the XCPC-powered DAR system, although the thermal efficiency of XCPC is higher than ETC's. Thus, it is interesting, though it is out of the scope of this thesis, to adopt a more detailed model that can investigate and optimise the heat delivery process for different

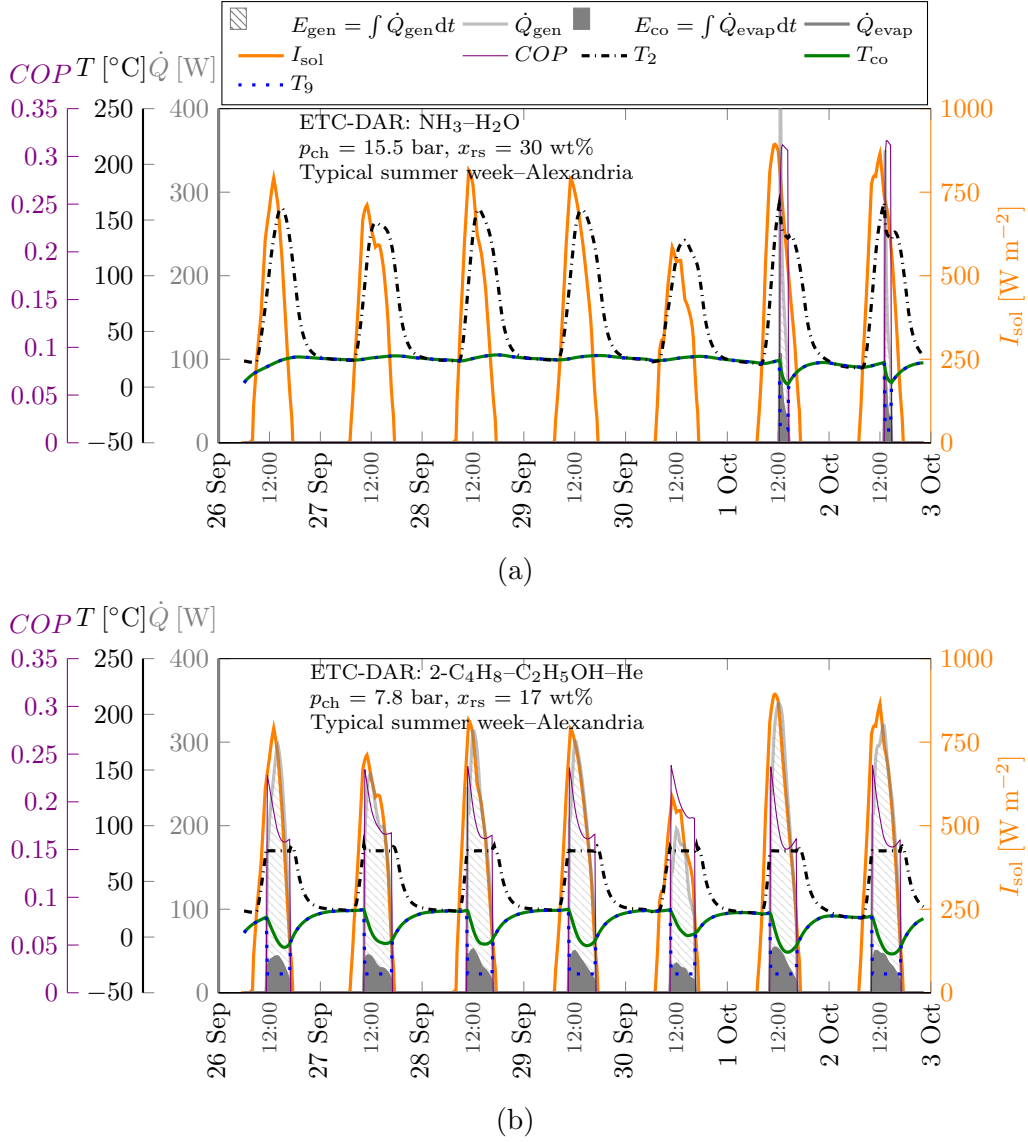


Figure 5.7: Solar irradiance and solar-DAR operation during a typical summer week in Alexandria based on a solar-DAR powered by a 6-tube ETC array for two DAR systems with rated DAR power ($\dot{P}_{\text{DAR}} = 440 \text{ W}$: (a) benchmark DAR system charged with 30 wt% $\text{NH}_3\text{-H}_2\text{O}$ solution under 15.5 bar, and (b) DAR system with optimum working fluid identified in Chapter 4: $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ with x_{rs} 17 wt% refrigerant rich solution under 7.8 bar.

solar-DAR configurations (especially for XCPC-powered systems) to minimise the heat losses and benefit from the high collector efficiency.

For the same reasons mentioned above, it can be easily observed in Figure 5.8 that the operating window of XCPC-DAR is shorter than ETC-DAR. The organic XCPC-DAR is shown to provide only 8.25 h of cooling, which is only 20 % of the operating window offered by the organic ETC-DAR system. By comparing Figure 5.8 to Figure 5.7, even the time-varying coefficient performance of the XCPC-DAR system is lower than the coefficient of performance of the ETC-DAR system.

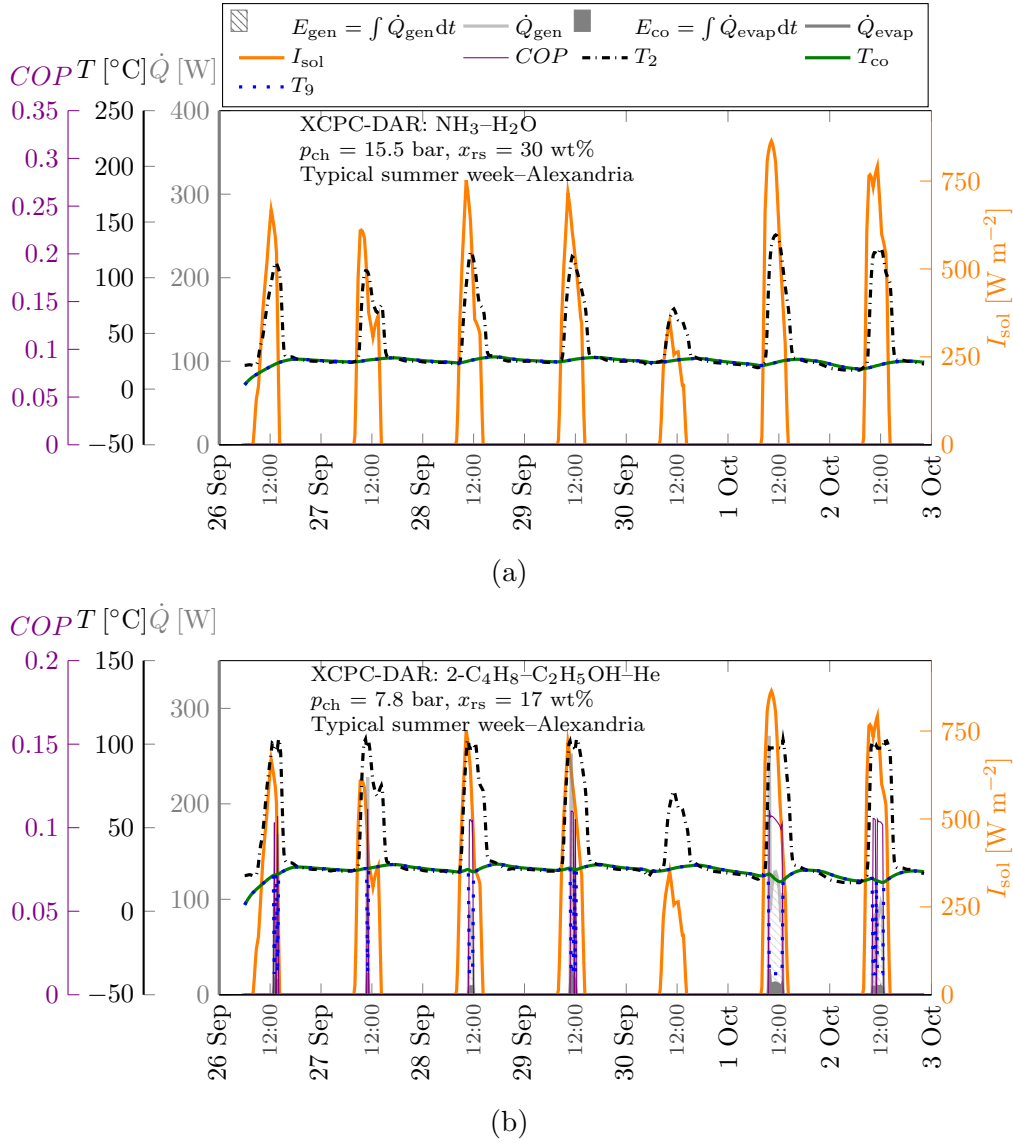


Figure 5.8: Solar irradiance and solar-DAR operation during a typical summer week in Alexandria based on a solar-DAR powered by a single XCPC array for two DAR systems with rated DAR power ($\dot{P}_{\text{DAR}} = 440$ W: (a) benchmark DAR system charged with 30 wt% $\text{NH}_3\text{-H}_2\text{O}$ solution under 15.5 bar, and (b) DAR system with optimum working fluid identified in Chapter 4: $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ with x_{rs} 17 wt% refrigerant rich solution under 7.8 bar.

The results in Figure 5.9 show the performance of solar-DAR systems coupled with ETC solar collectors during a typical winter week in Alexandria, Egypt. In contrast to the results depicted in Figure 5.7, the $\text{NH}_3\text{-H}_2\text{O}$ solar-DAR system can produce more cooling ($543 \text{ Wh}_{\text{co}}$ per week). This can be a consequence of the higher solar irradiance, I_{sol} during the typical winter week compared to the typical summer week. It can be easily observed in Figure 5.9, that the operating window of $\text{NH}_3\text{-H}_2\text{O}$ solar DAR system can reach 11.5 h of cooling per typical winter week. It can also be observed that for a given DAR system, the coefficient of performance is higher in winter than in summer, obviously influenced by the lower ambient temperatures experienced in winter.

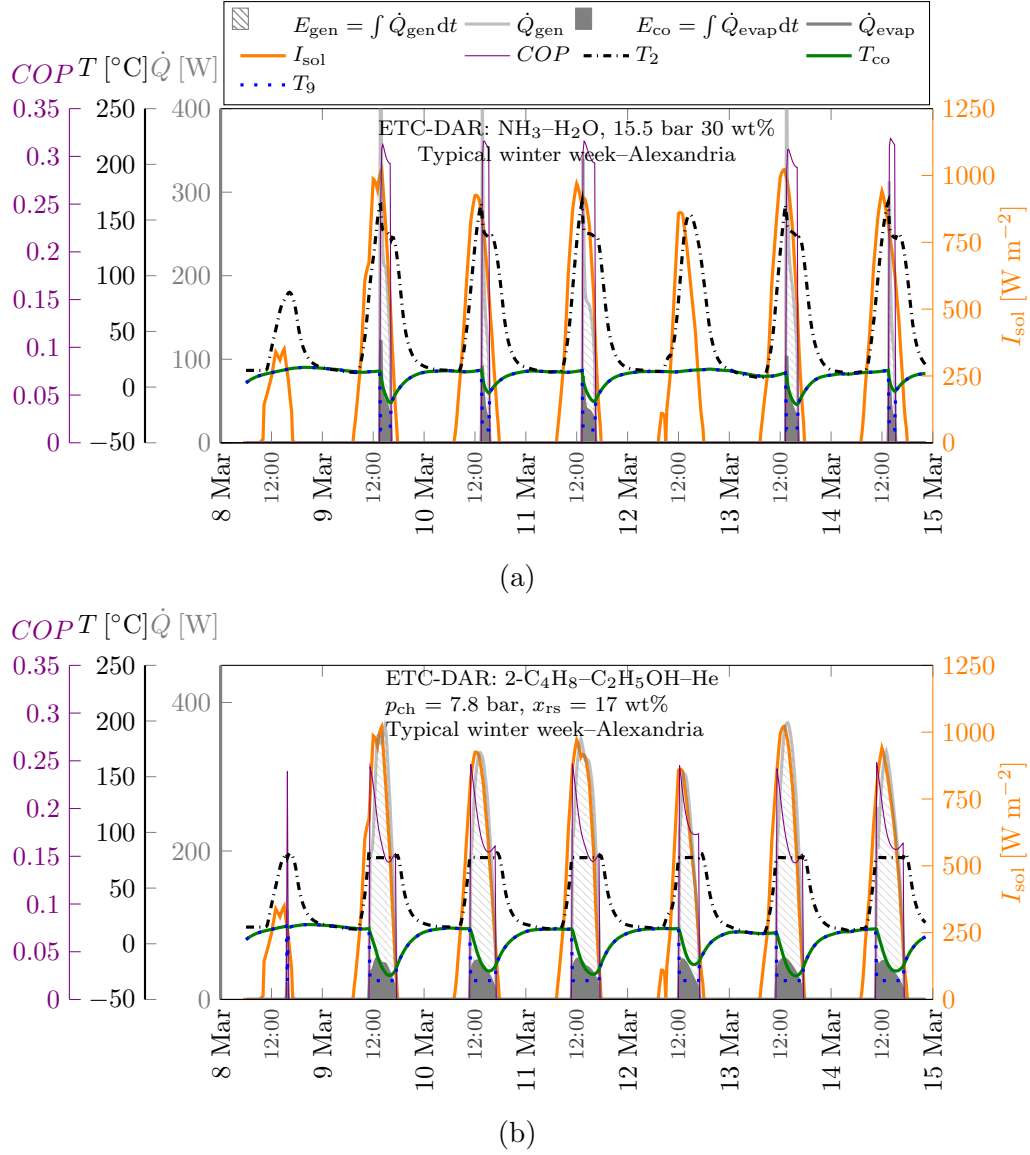


Figure 5.9: Solar irradiance and solar-DAR operation during a typical winter week in Alexandria based on a solar-DAR powered by a 6-tube ETC array for two DAR systems with rated DAR power ($\dot{P}_{DAR} = 440$ W): (a) benchmark DAR system charged with 30 wt% NH_3-H_2O solution under 15.5 bar, and (b) DAR system with optimum working fluid identified in Chapter 4: $2-C_4H_8-C_2H_5OH$ with x_{rs} 17 wt% refrigerant rich solution under 7.8 bar.

The results in Figure 5.9 also reveal that the organic-based solar-DAR system powered by ETC produces marginally less cooling per week ($1433 Wh_{co}$) in winter compared to the same design in summer. This can be attributed to the lower levels of diffusive solar irradiance in winter compared to summer; lower ambient temperatures in winter, in contrast, promote more cooling production and higher coefficients of performance. In addition, due to shorter daytime in winter, the operating window of the organic-based solar-powered DAR systems can be narrower by about 16 % compared to summer.

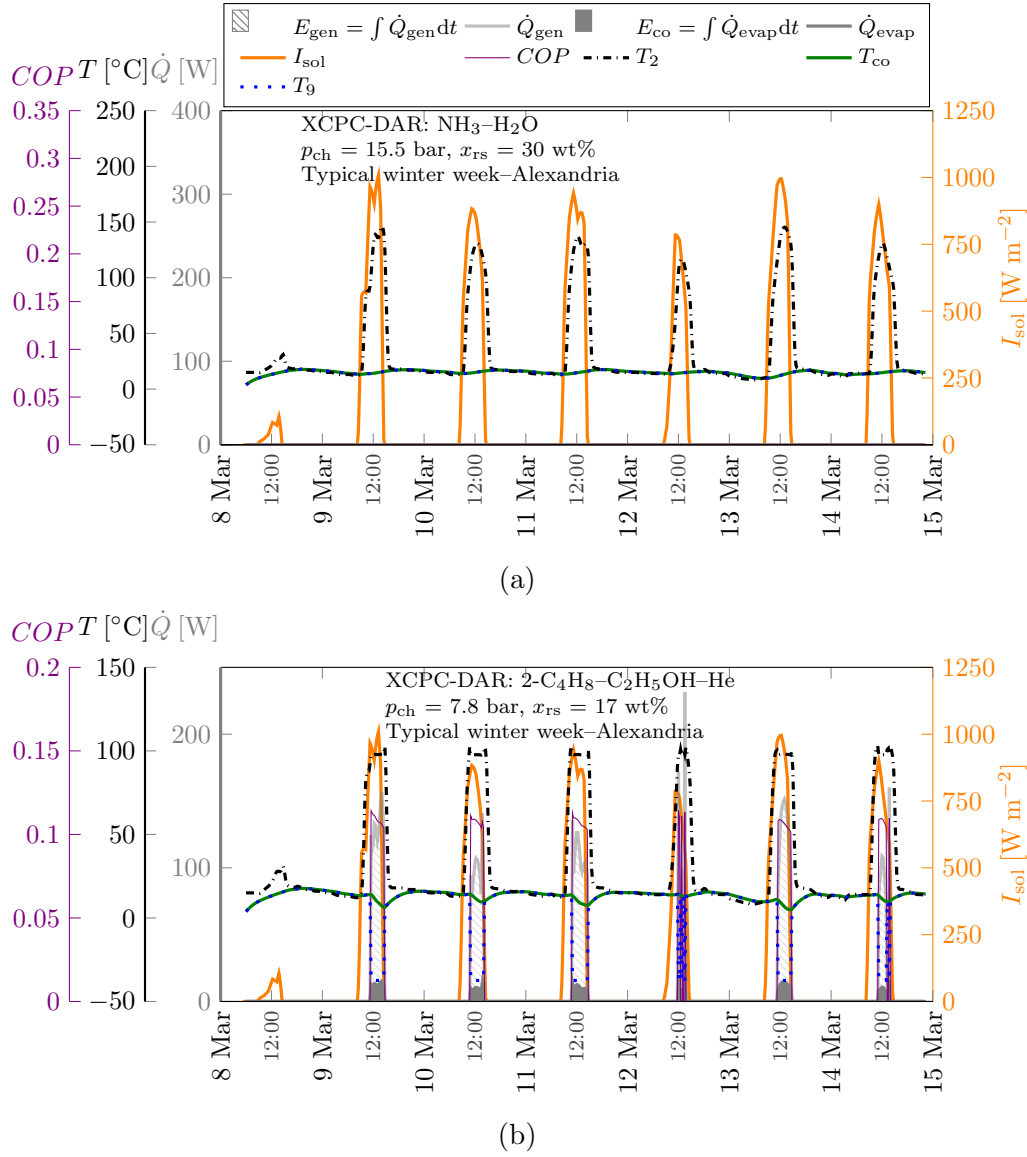


Figure 5.10: Solar irradiance and solar-DAR operation during a typical winter week in Alexandria based on a solar-DAR powered by a single XCPC array for two DAR systems with rated DAR power ($\dot{P}_{\text{DAR}} = 440$ W: (a) benchmark DAR system charged with 30 wt% $\text{NH}_3\text{-H}_2\text{O}$ solution under 15.5 bar, and (b) DAR system with optimum working fluid identified in Chapter 4: $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ with $x_{\text{rs}} = 17$ wt% refrigerant rich solution under 7.8 bar.

The simulations in Figure 5.10 confirm that the adopted XCPC-DAR design is not feasible with $\text{NH}_3\text{-H}_2\text{O}$ for Alexandria, Egypt. Interestingly, the organic-based solar-DAR system powered by XCPC can produce more cooling ($182 \text{ Wh}_{\text{co}}$) during a typical winter week compared to the same design operating in a typical summer week. This is possibly attributed to higher normal beam irradiance in winter than in summer. It can be noticed in Figure 5.10, that no cooling is observed on 8th of March due to very low solar irradiance. On 12th of March, the DAR performance is highly intermittent; this is caused by low solar heat compared to other days.

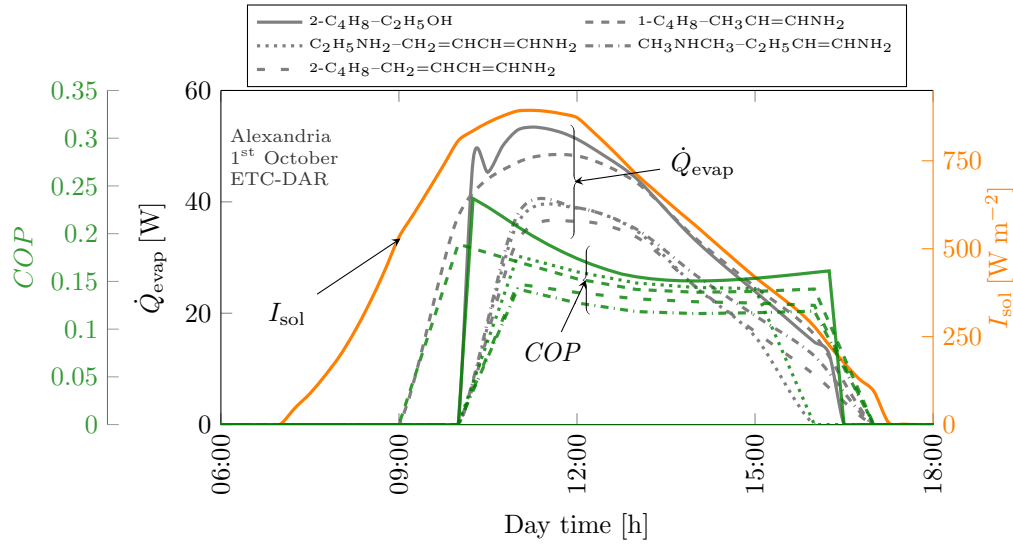


Figure 5.11: Hourly cooling production for ETC-powered DAR system based on working fluids listed in Table 4.2. The simulations consider a 6-tube ETC array for comparison. Simulations are for 1st of October with climate data for Alexandria, Egypt. All designs are charged with helium.

It can be observed from the results presented in Figures 5.7 to 5.10, that $\text{NH}_3\text{--H}_2\text{O}$ -based solar-DAR systems usually start in the afternoon (after 12:00 PM) with two to three hours of operation on days with cooling production. In contrast, organic-based solar DAR systems tend to start earlier and show longer operating times which allows for more cooling production, as confirmed by the simulations in Figure 5.11.

Simulations presented in Figure 5.11 compares the diurnal performance of ETC-powered DAR charged with the five-best working-fluid systems listed in Table 4.2. A typical summer in Alexandria, Egypt (1st of October) is considered. It can be observed that $2\text{-C}_4\text{H}_8\text{--C}_2\text{H}_5\text{OH}$ and $1\text{-C}_4\text{H}_8\text{--CH}_3\text{CH=CHNH}_2$ provide similar cooling production for longer operating time, respectively, $235 \text{ Wh}_{\text{co}}$ and $232 \text{ Wh}_{\text{co}}$ per day. The other three DAR designs with working fluids: $\text{C}_2\text{H}_5\text{NH}_2\text{--CH}_2\text{=CHCH=CHNH}_2$; $\text{CH}_3\text{NHCH}_3\text{--C}_2\text{H}_5\text{CH=CHNH}_2$; and $2\text{-C}_4\text{H}_8\text{--CH}_2\text{=CHCH=CHNH}_2$ can produce cooling $150 \text{ Wh}_{\text{co}}$, $182 \text{ Wh}_{\text{co}}$ and $155 \text{ Wh}_{\text{co}}$, respectively. Confirming what is observed for $2\text{-C}_4\text{H}_8\text{--C}_2\text{H}_5\text{OH}$, operating times for organic-based working fluids can reach 5 h to 6 h, thanks to lower generator temperatures needed to activate the DAR system compared to $\text{NH}_3\text{--H}_2\text{O}$ systems. The simulations confirm that for a typical summer day, the DAR design based on $2\text{-C}_4\text{H}_8\text{--C}_2\text{H}_5\text{OH}$ proves to outperform other assessed working fluids.

Annual solar-DAR system operation for organic-based systems

The solar-DAR system based on 2-C₄H₈-C₂H₅OH as the working-fluid mixture is further assessed by considering the annual DAR performance. The climate data for Alexandria, Egypt, are obtained from the weather databank in EnergyPlus [292]. Hourly ambient temperatures, T_a , direct beam solar irradiance, G_{Bn} and diffuse solar irradiance, G_D are depicted in Figure 5.12. Alexandria, Egypt, enjoys about 3,300 hours of sunshine annually.

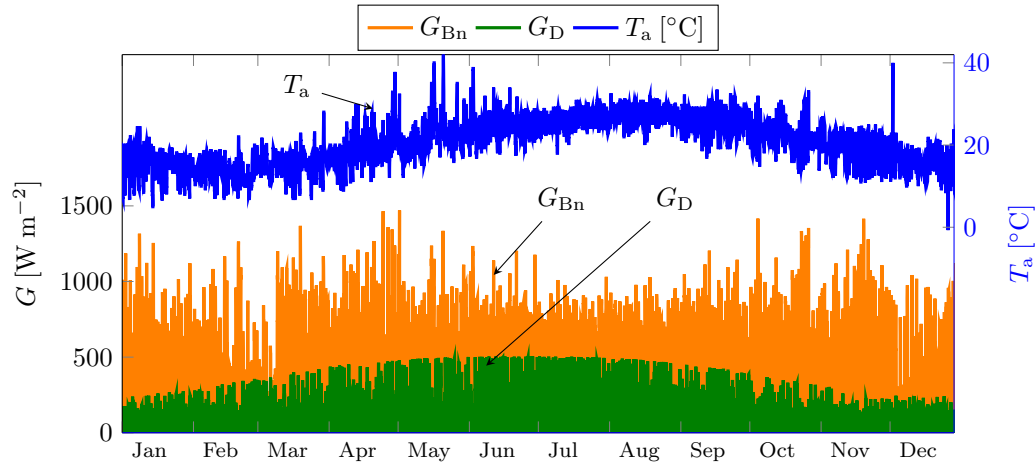


Figure 5.12: Hourly climate data for Alexandria, Egypt obtained from the weather databank available in EnergyPlus [292].

Annual DAR performance is displayed in Figure 5.13 for two solar-collector arrays: 6-tube ETC array and a single XCPC array. It can be observed from the presented results that for the same fridge size, the temperature in the fridge powered by ETC is, in general, lower than temperatures in the fridge powered by the XCPC. It can also be observed that for both solar collectors, cooling production is limited in winter. This is partially attributed to shorter day lengths in winter and less diffusive solar irradiance (especially for ETC-powered DAR systems). The Solar-DAR system powered by XCPC show narrower operating times compared to the ETC-powered DAR system.

The results in Figure 5.14 show simulated monthly cooling production for the two solar-DAR designs listed in Table 5.4. It can be observed that for both systems, maximum cooling is produced during May with cooling capacities 7.7 kWh_{co} and 2.2 kWh_{co}, for ETC and XCPC-powered DAR systems, respectively. In contrast, for both systems, the least amount of cooling is produced in December, 2.2 kWh_{co} and 0.58 kWh_{co} of cooling is produced by ETC and XCPC-powered DAR systems, respectively.

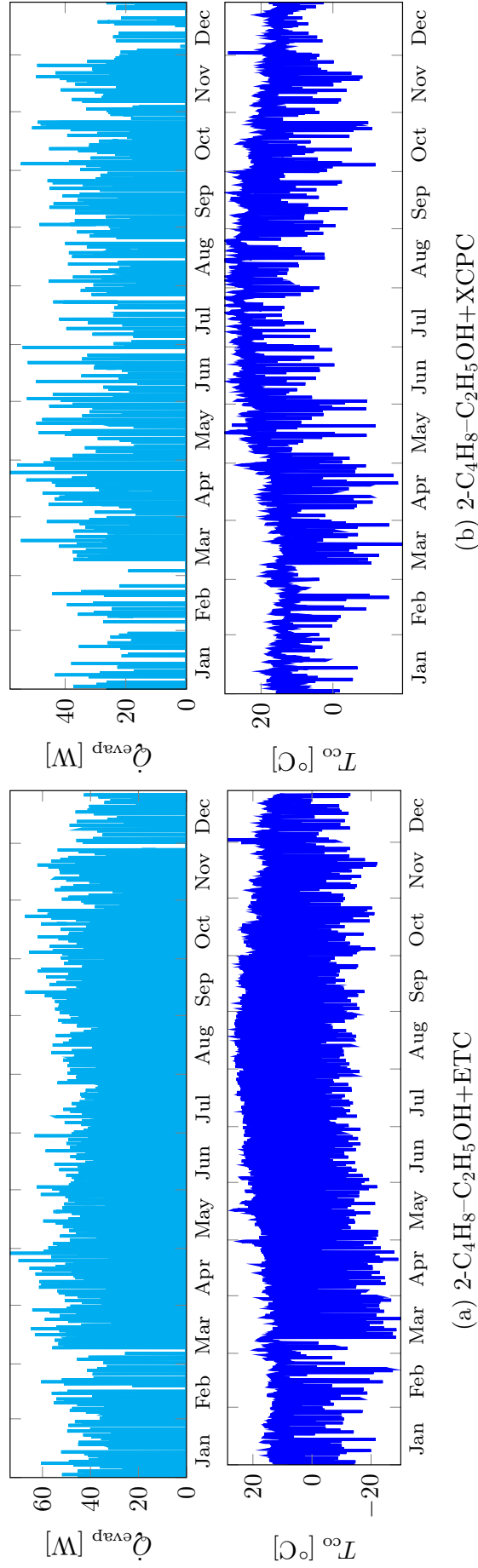


Figure 5.13: Hourly simulations of solar-powered DAR system performance with climate data for Alexandria, Egypt. DAR units are identical but powered by two different solar collector array types: (a) $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH+ETC}$ and (b) $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH+XCPC}$. Solar-DAR systems are described in Table 5.4.

The results in Figure 5.14 also reveal that between April and July, cooling production and cooling hours of the XCPC-DAR system decline sharply, then increase again. Despite longer daytime in summer, this observation can be attributed to the lower corrected solar irradiance for tilted surfaces absorbed by the XCPC. The cooling production decreases slightly between May and July for the ETC-DAR system. Nevertheless, maximum operating hours can be obtained in the ETC-DAR system in July, which suggests benefiting more from more prolonged sunshine in summer when cooling is more needed. The ETC-DAR charged with $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ can annually produce 1393 h of cooling compared to only 790 h of cooling produced by the XCPC-DAR charged with the same working-fluid mixture.

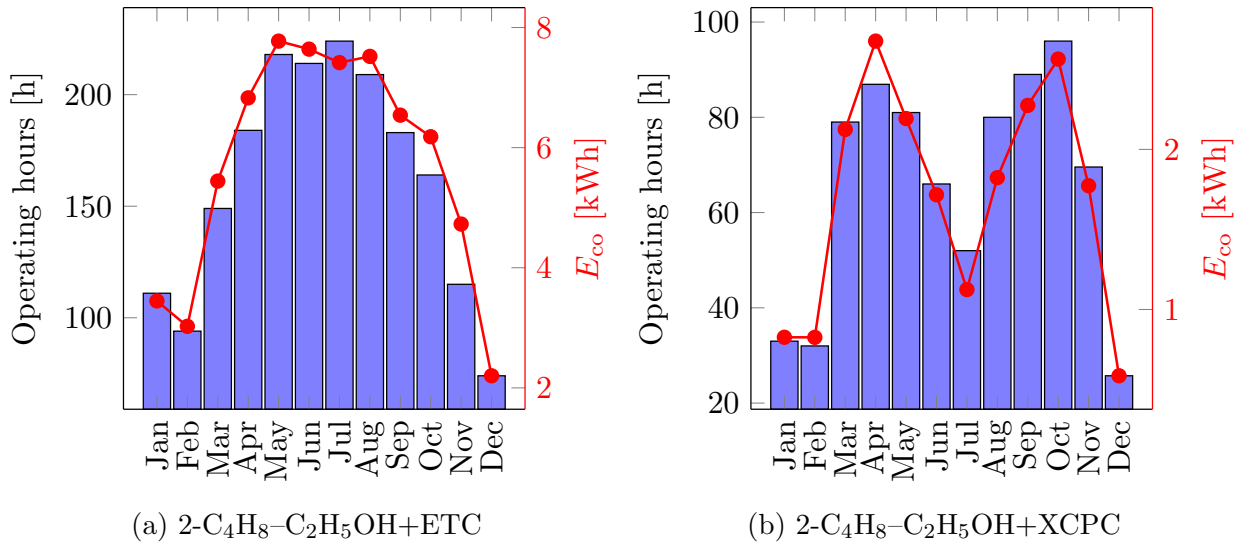


Figure 5.14: Monthly cooling production of solar-DAR systems based on (a) ETC and (b) XCPC. Both solar-DAR systems are charged with $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ and charging settings described in Table 5.4. The results consider hourly weather data for Alexandria, Egypt.

The cumulated energy usage in ETC-DAR and XCPC-DAR is presented in Figure 5.15. More useful energy, E_u , can be supplied to the DAR powered by the ETC array compared to the XCPC-DAR system; since the connections in the ETC-powered system are better insulated than the XCPC-powered system. In contrast, due to less energy received by the generator, E_{gen} , the energy conversion is higher in the XCPC-powered DAR system resulting in a higher coefficient of performance, COP_E compared to the ETC-powered DAR system.

It should be reminded that the investigated solar collector systems are limited to the systems tested at Imperial College London. It shall be interesting to consider more solar collectors in the future. Despite its simplicity, the presented solar-DAR quasi-transient model is a powerful tool to assess different working fluids rather than relying on steady-state simulations that cannot

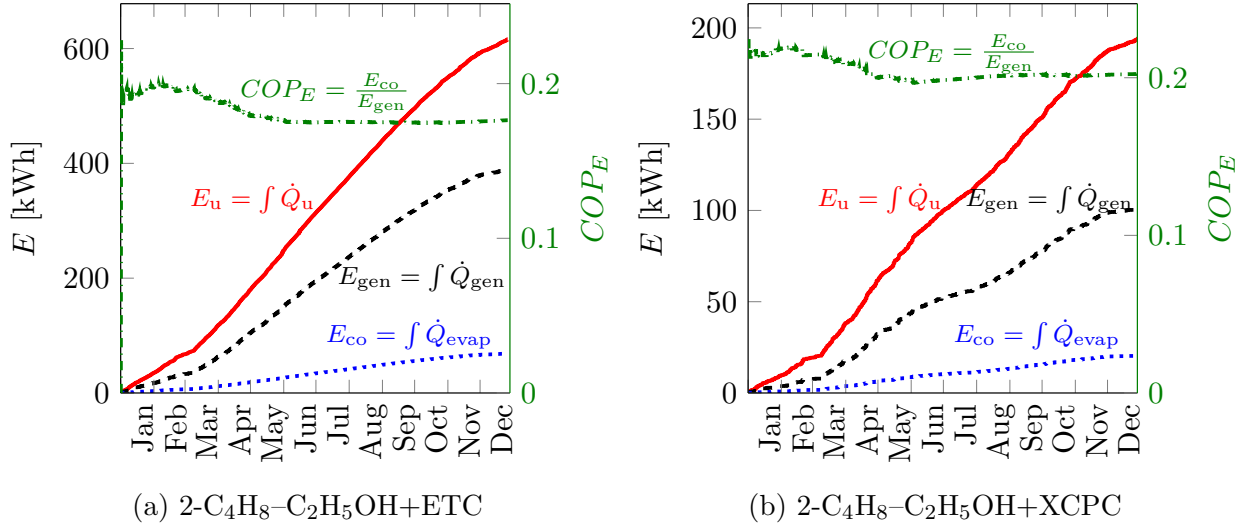


Figure 5.15: Annual cumulated solar-DAR system performance based on (a) ETC and (b) XCPC. Both solar-DAR systems are charged with 2-C₄H₈-C₂H₅OH and charging settings described in Table 5.4. The results consider hourly weather data for Alexandria, Egypt.

capture start-up and shut-down phases of particular importance in modelling solar-powered DAR systems. As discussed earlier, It shall be interesting in the future to consider the heat transfer between the solar collector and the generator wall in more detail. The presented quasi-transient model can also be integrated into the CAMD-DAR framework to consider the variation in solar irradiance while optimising the DAR system.

Economic evaluation of organic-based solar-DAR systems

In this section, two solar-DAR designs are economically assessed for use in Alexandria, Egypt. It is important to discuss the economic feasibility of the considered solar-powered DAR systems, especially for evolving economies like Egypt. Some economic indicators are described in Section 5.2.3. Based on the economic parameters listed in Table 5.3, the payback time (calculated using Equation (5.13)) of the proposed system exceeds 100 years for both designs. This is mainly attributed to the low electricity pricing in Egypt.

In Egypt, consumption bracketing is adopted for electricity pricing. For example, electricity for the third tier households consumers was sold for LE 0.65 per kWh_e (£ 0.031 per kWh_e) in 2019. This price is to increase to reach LE 0.97 per kWh_e (£ 0.045 per kWh_e) following the Egyptian energy subsidy reduction plan. Nevertheless, these prices are relatively lower compared to international electricity prices. For instance, in 2019, electricity is sold in the UK at an average

rate of £ 0.193 per kWh_e. [301]. Considering UK electricity pricing, the payback time reduces to only 15 years for the ETC-DAR system, which is less than the system lifetime; nevertheless, the payback time for the XCPC-DAR system remains much greater than 100 years due to its low annual specific cooling capacity per unit solar collector aperture area. As demonstrated in Figure 5.16, for this specific ETC-DAR design, the PBT is less than 20 years for electricity prices greater than £ 0.15 per kWh_e.

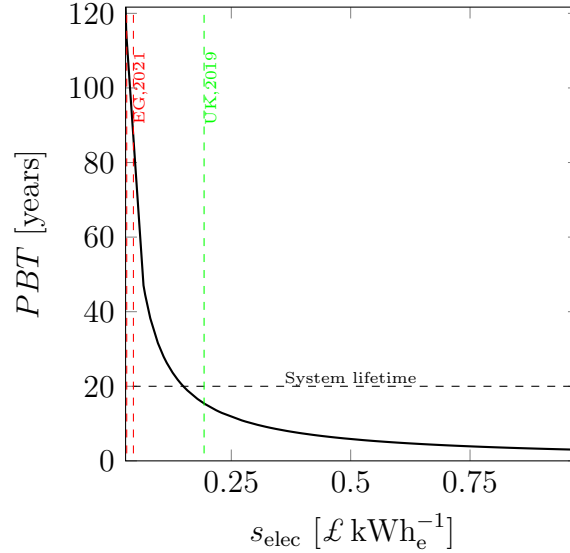


Figure 5.16: The Effect of the electricity purchase price on the payback time of solar-DAR system based on 6-tube ETC array considering climate data for Alexandria, Egypt.

For the same reason (low electricity prices), there is no positive levelised cost of saving (calculated using Equation (5.11)) throughout the lifetime of the DAR design unless electricity prices are greater than £ 0.15 per kWh_e. In the Middle East, More incentives for using thermal solar collectors in the domestic sector can also bring down the *PBT* and increase the *LCS*.

The levelised cost of cooling of the given systems is £ 1.93 per kWh_{co} and 11.7 per kWh_{co}, respectively, for the investigated ETC and XCPC-powered DAR systems. Li *et al.* [299] reported *LCOC* for solar-powered air-conditioning systems lower than \$ 1 per kWh_{co}. Najjaraan *et al.* [258] reported *LCOC* with similar order of magnitude for solar-DAR systems as he underestimated the purchase cost of the DAR cooling unit and considered energy storage. The *LCOC* of the ETC-DAR system can be further reduced by considering a larger ETC area or incorporating energy storage. Thus, it is interesting to consider in the future the trade-off between additional costs incurred by adding thermal storage and the resulting reduction in the levelised cost of cooling caused by increasing the system's cooling capacity.

It is also essential to consider how beneficial it is to use solar-DAR systems to avoid CO₂ emissions. Since 2019, Egypt has been among the countries that pledged to consider international and domestic carbon pricing initiatives, though such initiatives have not yet been brought into action. According to the Central Agency for Public Mobilization and Statistics (CAPMAS) in Egypt, the environmental impact of CO₂ is approximately worth \$ 80 per tCO_{2e}.¹ It worth to mention that the UK CO₂ price is £13.15 per tCO_{2e} for the same year [302] and, recently, jumped to £78 per tonne CO₂. Based on the parameters in Table 5.4, The *EPCS* that can be saved by using the ETC-powered DAR system is estimated by Equation (5.14) as £ 14 compared to only £ 3.6 saved by the XCPC-powered design.

5.4 Summary

In this chapter, the DAR thermodynamic model presented in Chapter 2 is adapted, and a quasi-transient DAR model is devised to simulate the performance of solar-powered DAR systems with a particular interest in the start-up and shut-down phases. The presented model considers the thermal capacity stored in the solar collector module and the generator with the heat delivery assembly. A simple algorithm was devised to determine solar-powered DAR units' start-up and shutdown times. Two solar-collector systems are considered: an array of 6 tubes of evacuated tube collectors (ETC); and a single module of external compound parabolic concentrators (XCPC) to power DAR unit charged with a 17 % mixture of 2-C₄H₈-C₂H₅OH and pressurised by helium under 7.8 bar. For these solar-collector types, the objective is to use this quasi-transient model to compare the performance of both solar collectors in powering the organic-based DAR system compared to NH₃-H₂O DAR system using climate data for Alexandria, Egypt. Further, the thermo-economic suitability of solar-DAR systems based on organic working fluids in Egypt is also discussed to shed light on how ready DAR technology is for use in the Egyptian market.

The results suggest that for NH₃-H₂O systems, doubling the area of ETC from 6 to 12 tubes results in 16 % more cooling capacity on a sunny day at the cost of a reduction in the coefficient of performance. Whereas doubling the area of XCPC can result in 53 % more cooling capacity on the same sunny day. In general, the transient simulations for typical winter and summer weeks

¹This value is estimated by the Egyptian Ministry of Petroleum and Mineral Resources, converted to GB£ using 2019 average exchange rate \$ 1= £ 0.7837

in Alexandria, Egypt, suggests that the ETC array outperforms the XCPC array. Furthermore, DAR systems based on the organic working fluid produce more cooling than the $\text{NH}_3\text{--H}_2\text{O}$ DAR system powered by the same solar-collector array. Operating times for organic-based working fluids can reach 5 h to 6 h, thanks to lower generator temperatures needed to activate the DAR system compared to $\text{NH}_3\text{--H}_2\text{O}$ systems. The simulations confirm that for a typical summer day, the DAR design based on $2\text{-C}_4\text{H}_8\text{--C}_2\text{H}_5\text{OH}$ proves to outperform other assessed working fluids. The hourly simulations of solar-DAR simulations suggest that the DAR unit charged with $2\text{-C}_4\text{H}_8\text{--C}_2\text{H}_5\text{OH}$ and powered by a 6-tube ETC array can produce 68 kWh of cooling per year compared to only 20 kWh_{co} that can be produced when XCPC is used to power the DAR system. The simulations also suggest that the ETC-powered organic-based DAR system can produce 1939 h of cooling per year compared to only 750 h of cooling per year that the XCPC-powered organic-based DAR system can produce.

The economic assessment of solar-DAR systems suggests that the ETC-powered organic-based DAR unit is more economically feasible for use in Egypt, thanks to the lower cost of ETC arrays and more cooling produced by the ETC-powered DAR system. Nevertheless, lower electricity prices in Egypt do not encourage the use of solar-powered DAR systems for their very long payback time and negative levelised cost of savings. The presented solar-powered DAR systems based on ETC can become more attractive in countries with high electricity prices or by introducing more incentives to promote solar-powered DAR systems. The levelised cost of cooling for the ETC-powered organic-based DAR system is estimated to be £ 1.93 per kWh_{co}, while the environmental penalty cost savings are estimated to be only around £ 14.

These simulations and thermo-economic assessment have demonstrated that the current quasi-transient model based on group-contribution methods can be used for the time-varying performance of any given solar-powered DAR system charged with any organic-based working fluid. This tool can assess different solar-collector types and working fluid combinations under other climatic conditions.

Chapter 6

Conclusions and Recommendations

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6.1 Summary of thesis objectives

The soaring energy crisis with the continuous need for refrigeration has led to a growing interest in studying refrigeration technologies that can be powered by renewable energy to secure sustainable refrigeration, particularly for developing economies to reduce food waste, and improve quality of life. The MENA region enjoys plenty of solar insolation throughout the year. Thus solar-powered refrigeration systems can play a great role in reducing energy bills and carbon emissions.

Diffusion absorption refrigeration (DAR) is one of the attractive low-carbon refrigeration technologies that can be powered using solar thermal collectors. Nevertheless, DAR systems usually have a lower performance coefficient than conventional refrigeration technologies. Commercial DAR units usually use $\text{NH}_3\text{--H}_2\text{O}$ mixture that requires temperatures higher than 150°C to initiate cooling. Thus, it is interesting to explore alternative environment-friendly working fluids that can allow DAR activation using low-temperature heat sources ($< 150^\circ\text{C}$) for coupling with low-cost solar collectors.

Organic working fluids can be used with DAR systems for their lower generation temperature requirements. This research aims to identify these optimal working fluids to replace the commercially used $\text{NH}_3\text{--H}_2\text{O}$ mixture. The aims and objectives of this thesis were identified in Section 1.6. In the following sections, a summary of the results obtained from this research is presented.

6.2 Summary of thesis results

6.2.1 DAR modelling based on group-contribution methods

A validated DAR steady-state thermodynamic model based on the GC SAFT- γ Mie EoS was presented in Chapter 2. One of the objectives of this model is to assess low-GWP organic working fluids that require low-temperature heat sources to run DAR systems. The DAR thermodynamic model was validated and can predict cooling rates within $\pm 16\%$. Some organic working-fluid pairs, based on some pre-selected refrigerants and absorbents of normal and branched alkanes, were considered and compared to $\text{NH}_3\text{--H}_2\text{O}$ in terms of cooling output, charging pressure and generator temperature requirements. The considered working fluids are formed of normal alkanes and 2-methylalkanes. Among the fluids considered, for a more-flexible

operation, butanes are recommended for use as refrigerants under variant heat-input conditions. On the other hand, pentanes are preferred for their higher *COPs* (up to 0.27, depending on the prevailing ambient temperature). The presented thermodynamic models are found suitable to be integrated into a computer-aided molecular and system design framework to incorporate optimisation approaches and explore optimal working-fluid pairs and charging conditions under different operating conditions.

6.2.2 Computer-aided molecular and system design for DAR systems

Exploring new working-fluid mixtures paves the way towards innovative solar-powered DAR systems. To this end, an integrated computer-aided molecular and system design framework for DAR systems was presented Chapter 3 to design alternative working-fluid mixture and seek optimum DAR size. The CAMD-DAR framework was developed based on the DAR mathematical model and the molecular-based, group-contribution SAFT- γ Mie equation of state presented in Chapter 2. In the absence of appropriate sizing methods, a simple costing correlation was presented based on market prices for diffusion absorption refrigeration units to assess different working-fluid systems economically. The CAMD-DAR framework is formulated as an MINLP problem which can be solved using a hybrid stochastic-deterministic optimisation method. Under different ambient and cooling temperatures, the CAMD-DAR framework was used to carry out NLP and MINLP optimisations. Considering only non-polar organic compounds, the CAMD-DAR framework recommends the use of 2-butene-*n*-octane-He ($2\text{-C}_4\text{H}_8\text{-}n\text{-C}_8\text{H}_{18}\text{-He}$) to charge a DAR unit powered by 250 W. The CAMD-DAR framework suggests that organic-based DAR systems that use non-polar working fluid pairs have *SPC* of £ 13 per W of cooling with low generator temperatures ($< 100^\circ\text{C}$). The optimisations suggest that hydrocarbons with four carbon atoms perform well in most cases and can be coupled with many organic absorbents.

Including more polar organic groups into the CAMD-DAR framework allows the framework to identify cooling rates up to 146 W if $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH-He}$ under charge pressure around 7.8 bar with *SPC* down to £ 5.36 per W of cooling. Other sub-optimal working fluids and corresponding DAR charging settings are also identified. The CAMD-DAR framework suggests that small-size refrigerant molecules with 3 to 5 carbon atoms have been the most favoured. Moreover, olefin refrigerants are preferred for their higher cooling rates. The DAR system based on $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH-He}$ can provide more cooling compared to a standard $\text{NH}_3\text{-H}_2\text{O}$ system.

The CAMD-DAR framework suggests organic-working fluids with lower generator-temperature requirements than those needed to activate the $\text{NH}_3\text{-H}_2\text{O}$ DAR system.

Further, multi-objective optimisations with two different objective functions ($\max \dot{Q}_{\text{evap}}$, $\min C_{\text{CU},0}$) were considered to obtain a set of non-dominated design alternatives. The multi-objective-optimisation results suggest that 1-aminopropene ($\text{CH}_3\text{CH=CHNH}_2$) and allylamine (1-amino-2-propene or $\text{CH}_2=\text{CHCH}_2\text{NH}_2$) are the most selected absorbents, while all non-dominated refrigerants are short-carbon chain non-polar hydrocarbons.

6.2.3 Dynamic performance of solar-powered DAR systems

Due to the particular importance of the dynamic performance of solar-powered DAR systems, a dynamic model for solar-powered DAR systems was devised based on the quasi-transient analysis of the DAR model with a particular interest in the start-up and shut-down phases. Two representative cases of solar collector systems were considered: an array of 6 tubes of evacuated tube collectors (ETC); and a single module of external compound parabolic concentrators (XCPC). The DAR unit considered for the analysis is the DAR system design identified by the CAMD-DAR framework in Chapter 4 (charged with 17 % mixture of 2- $\text{C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ and pressurised by helium under 7.8 bar). The objective of the quasi-transient model was also to compare the performance of different solar collectors in powering the organic-based DAR system compared to $\text{NH}_3\text{-H}_2\text{O}$ DAR system using climate data for Alexandria, Egypt.

The simulations suggest that doubling the aperture area of the solar collector contributes to a fractional increase in cooling capacity. Increasing the aperture area also tends to reduce the solar-DAR coefficient of performance. In general, the transient simulations for typical winter and summer weeks in Alexandria, Egypt, suggest that the ETC array should be used rather than the considered XCPC collectors for their smooth operation. The simulations also recommend that DAR systems based on the organic working fluid can produce more cooling and longer operating times (5 h to 6 h) than the $\text{NH}_3\text{-H}_2\text{O}$ DAR system powered by the same solar-collector array. The transient simulations confirm that for a typical summer day, the DAR design based on 2- $\text{C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ produces more cooling (68 kWh of cooling per year) than other organic working fluids when powered by a 6-tube ETC array. Whereas the DAR design based on 2- $\text{C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ can produce only 20 kWh_{co} when XCPC was used to power

the DAR system. The simulations also suggest that the ETC-powered organic-based DAR system can produce up to 1939 h of cooling per year compared to only 750 h of cooling per year that the XCPC-powered organic-based DAR system can produce.

The economic assessment of solar-DAR systems suggests that ETC-powered organic-based DAR systems can be economically feasible for use in Egypt. Nevertheless, lower electricity prices in Egypt do not encourage households to use solar-powered DAR systems for their very long payback time and negative levelised cost of savings. The thermo-economic analysis also suggests that the presented solar-powered DAR systems based on ETC can be more attractive with rising electricity prices or by introducing more incentives that can promote solar-powered DAR systems. The levelised cost of cooling for the ETC-powered organic-based DAR system is estimated to be £ 1.93 per kWh_{co}, while the environmental penalty cost saving is estimated to be only around £ 14.

In general, the presented CAMD-DAR framework presented in Chapters 3 and 4 supplemented by the quasi-transient DAR model shown in Chapter 5 offers a great tool to investigate alternative working fluids for solar-powered DAR systems that can be extended to consider other working fluids and variant solar collectors. In this regard, some of the potential directions for future research are identified in the following section.

6.3 Possible directions for future research

Any CAMD framework for mixture design is limited by the molecular groups available and proper group-interaction groups defined. Beyond the explored molecular groups, more molecular groups can be considered like carboxyl groups, fluoro and hydrofluoro hydrocarbons. Further, with the current developments of SAFT- γ Mie EoS to model electrolytes and inorganic molecules, more inorganic working fluids, which have been out of the scope of this study, can be explored for solar-powered DAR applications, particularly for air-conditioning applications. The CAMD-DAR framework can also be extended by introducing other environmental and safety constraints. It can be upgraded by expanding the multi-objective optimisation to include more independent objective functions to involve more environmental objectives. It is also suggested to explore different optimisation approaches rather than mentioned in this thesis and assess their performance in solving the MINLP problems that describe the CAMD-DAR framework.

A limitation of the presented transient model is the unavailability of sufficient experimental data for DAR systems. Most available experiments in the literature are concerned with temperature measurements. In contrast, experimental studies involving flowrate measurements, whenever available, consider idealised operating conditions (low pressure, single fluid, usually water,...etc.). Thus, it can be incredibly beneficial to consider flowrate measurements for an operating DAR system. Flowrate measurements can be challenging because of small DAR-tube diameters and the inability to install conventional inline flowmeters. Another challenge is the passivity of the system (*i.e.*, flowrates cannot be controlled). Thus, it is recommended to consider non-intrusive two-phase flow and composition measurements. The availability of flowrate and composition measurements across the DAR cycle, especially across the absorber, provides more reliable data that can be used to develop mechanistic models for the absorber to incorporate into the CAMD-DAR framework. Further, flowrate measurements combined with temperature measurements can help to establish suitable mechanistic heat and mass transfer models for different DAR components. Reliable validated models can lead to more accurate design and costings.

The presented time-varying simulations demonstrate that the current quasi-transient model based on group-contribution methods can be used for considering the time-varying performance of any given solar-powered DAR system charged with any organic-based working fluid. This model can assess different solar-collector and working fluid combinations under a given climatic condition. It is also recommended to consider energy-storage systems extending refrigeration cooling times. Further, it is interesting to integrate the presented quasi-transient DAR model within the CAMD-DAR framework so that optimised working fluids and system design consider maximum cooling production, taking into account that the intermittency of solar energy is overlooked by the steady-state design model deployed in the current CAMD-DAR framework.

Another research direction which is worth consideration is the extension of the presented CAMD-DAR framework into a super-structure CAMD-Refrigeration framework in which different refrigeration technologies can be considered (*i.e.*, vapour compression, absorption refrigeration, adsorption refrigeration, DAR...etc.). The CAMD-Refrigeration framework can be formulated so that for a given refrigeration duty, optimum refrigeration technology is identified with corresponding refrigerants and refrigeration unit sizes, considering the trade-off covering the refrigeration demand and associated expenses.

References

- [1] IRENA, IEA, and REN21, “Renewable energy policies in a time of transition: Heating and cooling.” <https://www.iea.org/reports/renewable-energy-policies-in-a-time-of-transition-heating-and-cooling>, 2020. IRENA, OECD/IEA and REN21.[Last accessed on : 1/12/2020].
- [2] L. T. Biarreau, L. W. Davis, P. Gertler, and C. Wolfram, “Heat exposure and global air conditioning,” *Nature Sustainability*, vol. 3, pp. 25–28, 2020.
- [3] UK Department for Business, Energy & Industrial Strategy, “Electrical products data tables (excel).” https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1061638/2021_Electrical_Products_tables_March_2022_update.xlsx, 2021. ECUK, UK, 2021 [Last accessed on: 1/6/2022].
- [4] US Energy Information Administration, “Electricity explained: Use of electricity.” <https://www.eia.gov/energyexplained/electricity/use-of-electricity.php>, 2021. [Last accessed on: 2/12/2021].
- [5] IIR, “The role of refrigeration in worldwide nutrition - 6th informatory note on refrigeration and food.” <https://iifiir.org/en/fridoc/142029>, 2020. International Energy Agency, Paris, [Last accessed on: 1/11/2021].
- [6] WMO, “State of the global climate 2020.” <https://public.wmo.int/en/our-mandate/climate/wmo-statement-state-of-global-climate>, 2020. [Last accessed on: 2/12/2021].
- [7] A. Kitous and J. Després, “Assessment of the impact of climate change on residential energy demand for heating and cooling,” tech. rep., European Union, 2018.
- [8] IEA, “The future of cooling: Opportunities for energy-efficient air conditioning [Online].” available from <https://www.iea.org/reports/the-future-of-cooling>, 2018. [Last accessed on: 1/12/2018].
- [9] United Nations, Department of Economic and Social Affairs, Population Division, “Proba-

- bilistic population projections rev. 1 based on the world population prospects 2019.” <https://population.un.org/wpp/Download/Probabilistic/Population/>, 2019. [Last accessed on: 1/10/2020].
- [10] Mordor Intelligence, “Household refrigerators and freezers market-growth, trends, covid-19 impact, and forecasts (2021-2026).” <https://www.mordorintelligence.com/industry-reports/household-refrigerators-and-freezers-market>, 2020. [Last accessed on: 24/11/2021].
- [11] Allied Analytics LLP, “Solar freezer market by type, capacity and end use, household, infrastructure, commercial and other end uses: Global opportunity analysis and industry forecast, 2021-2030.” <https://www.researchandmarkets.com/reports/5439730/solar-freezer-market-by-type-capacity-and-end>, 2020. [Last accessed on: 24/11/2021].
- [12] Mordor Intelligence, “Refrigerants market - growth, trends, covid-19 impact, and forecasts (2021 - 2026).” <https://www.mordorintelligence.com/industry-reports/refrigerants-market>, 2020. [Last accessed on: 24/11/2021].
- [13] L. Kitinoja, “Use of cold chains for reducing food losses in developing countries, PEF white paper No. 13-03,” tech. rep., The Postharvest Education Foundation (PEF), 2013. [Last accessed on: 1/11/2020].
- [14] K. E. N’Tsoukpoe, D. Yamegueu, and J. Bassole, “Solar sorption refrigeration in Africa,” *Renewable & Sustainable Energy Reviews*, vol. 35, pp. 318–335, 2014.
- [15] IEA, “Cooling.” <https://www.iea.org/reports/cooling>, 2021. International Energy Agency, Paris, [Last accessed on: 1/11/2021].
- [16] IIR, “The carbon footprint of the cold chain, 7th informatory note on refrigeration and food.” <https://iifir.org/en/fridoc/the-carbon-footprint-of-the-cold-chain>, 2021. International Energy Agency, Paris, [Last accessed on: 1/11/2021].
- [17] M. Indraganti and D. Boussaa, “A method to estimate the heating and cooling degree-days for different climatic zones of Saudi Arabia,” *Building Services Engineering Research and Technology*, vol. 38, no. 3, pp. 327–350, 2017.
- [18] H. Radhi and S. Sharples, “Quantifying the domestic electricity consumption for air-conditioning due to urban heat islands in hot arid regions,” *Applied Energy*, vol. 112, pp. 371–380, 2013.
- [19] S. ElHag, M. Bououd, R. ElGuindy, I. Abo Khhodeir, A. AlMohamadi, R. Rizk, E. Adel, and K. Bakry, “Assessment of appliances share of the total energy consumptions in the Southern and Eastern Mediterranean countries – special focus on air condi-

- tioning appliances.” <https://www.rcreee.org/content/assessment-appliances-share-total-energy-consumptions-semcs—special-focus-air-conditioning>, 2020. [Last accessed on: 28/11/2021].
- [20] MEDENER and RCREEE, “Energy efficiency for appliances with a focus on air-conditioning.” <https://www.rcreee.org/content/energy-efficiency-appliances-focus-air-conditioning>, 2020. [Last accessed on: 28/11/2021].
- [21] M. A. Moradi, H. Shakouri G., and A. M. Aboutaleb, “Developing the electricity demand model for Iran’s residential sector; based on leap,” in *28th International Power System Conference*, (Tehran, Iran), 11 2013.
- [22] Y. M. Y. Ameen, O. S. Al-Yozbaky, and M. S. M. Al-Hafidh, “Energy efficiency enhancement for residential sector: Case study of lighting in Iraq,” *Al-Rafidain Engineering Journal*, vol. 26, no. 1, pp. 53–62, 2021.
- [23] M. S. M. Al-Hafidh, M. A. Al-Mama, and A. S. Al-Fahadi, “Determination of residential electrical load components in Iraqi north region,” *Iraqi Journal for Electrical and Electronic Engineering*, vol. 13, no. 2, pp. 161–165, 2017.
- [24] T. Alajam and P. Phelan, “Modeling and forecasting end-use energy consumption for residential buildings in Kuwait using a bottom-up approach,” *Energies*, vol. 13, p. 1981, 2020.
- [25] IEA, “Energy policies beyond IEA countries - Morocco.” <https://www.iea.org/reports/energy-policies-beyond-iea-countries-morocco-2019>, 2019. International Energy Agency, Paris, [Last accessed on: 1/11/2021].
- [26] O. Alrawi, I. S. Bayram, and M. Koc, “High-resolution electricity load profiles of selected houses in Qatar,” in *2018 IEEE 12th International Conference on Compatibility, Power Electronics and Power Engineering (CPE-POWERENG 2018)*, (Doha, Qatar), 4 2021.
- [27] A. Alaidroos and M. Kararti, “Optimal design of residential building envelope systems in the Kingdom of Saudi Arabia,” *Energy and Buildings*, vol. 86, pp. 104–117, 2015.
- [28] K. K. Esmail, M. S. Alshitawi, and R. A. Almasri, “Analysis of energy consumption pattern in Saudi Arabia’s residential buildings with specific reference to Qassim region,” *Energy Efficiency*, vol. 12, pp. 2123–2145, 2019.
- [29] RECREE, “National energy efficiency programs for household electrical appliances in member states of the regional center for renewable energy and energy efficiency.” <https://www.rcreee.org/ar/content/national-energy-efficiency-programs-for-household-electrical-appliances-in-member-states-of-RCREEE>, 2012. In Arabic [Last

- accessed on: 28/11/2021].
- [30] The Policy Unit (IRENA), L. El-Katiri, A. Khalid, R. Mills, M. Salman, R. Ibrahim, and R. Ferroukhi, “Renewable energy market analysis: GCC 2019.” <https://www.irena.org/publications/2019/Jan/Renewable-Energy-Market-Analysis-GCC-2019>, 2019. International Renewable Energy Agency (IRENA), [Last accessed on: 1/11/2021].
 - [31] The World Bank, “Solar resource maps of middle east and north africa.” <https://solargis.com/maps-and-gis-data/download/middle-east-and-north-africa>, 2020. Source: Global Solar Atlas 2.0, Solar resource data: Solargis, [Last accessed on: 10/12/2021].
 - [32] MEDENER and RCREEE, “Energy efficiency and renewable energy strategies and polices.” https://www.rcreee.org/sites/default/files/meetmed_report_a1_1_final_191009.pdf, 2019. [Last accessed on: 28/11/2021].
 - [33] R. Ferroukhi, A. Khalid, D. Hawila, D. Nagpal, L. El-Katiri, V. Fthenakis, and A. Al-Fara, “Renewable energy market analysis: GCC 2016.” <https://www.irena.org/publications/2016/Jan/Renewable-Energy-Market-Analysis-The-GCC-Region>, 2016. International Renewable Energy Agency (IRENA), [Last accessed on: 1/11/2021].
 - [34] Egyptian Ministry of Planning and Economic Development, “Egypt’s vision 2030.” <https://www.mped.gov.eg/EgyptVision?lang=en>, 2015. [Last accessed on: 1/10/2019].
 - [35] IRENA, “Renewable energy outlook: Egypt.” <https://www.irena.org/publications/2018/Oct/Renewable-Energy-Outlook-Egypt>, 2018. [Last accessed on: 1/6/2019].
 - [36] EEHC, “Egyptian electricity holding company annual report 2019/20.” www.moe.gov.eg/english_new/EEHC_Rep/finalaEn19-20.pdf, 2020. [Last accessed on: 8/7/2021].
 - [37] M. Zeyghami, D. Y. Goswami, and E. Stefanakos, “A review of solar thermo-mechanical refrigeration and cooling methods,” *Renewable & Sustainable Energy Reviews*, vol. 51, pp. 1428–1445, 2015.
 - [38] A. Najjaran, A. A. Harraz, J. Freeman, N. Mac Dowell, and C. N. Markides, “Numerical and experimental investigation of diffusion absorption refrigeration systems for Use with low-temperature heat sources,” in *ECOS 2018: Proceedings of the 31st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems* (J. C. Teixeira, ed.), (Guimarães, Portugal), p. 323, 6 2018.
 - [39] T. Jaruwongwittaya and G. Chen, “A review: Renewable energy with absorption chillers in Thailand,” *Renewable & Sustainable Energy Reviews*, vol. 14, pp. 1437–1444, 2010.
 - [40] J. Deng, R. Wang, and G. Han, “A review of thermally activated cooling technologies for combined cooling, heating and power systems,” *Progress in Energy and Combustion*

- Science*, vol. 37, pp. 172–203, 2011.
- [41] U. Jakob, U. Eicker, D. Schneider, A. H. Taki, and M. J. Cook, “Simulation and experimental investigation into diffusion absorption cooling machines for air-conditioning applications,” *Applied Thermal Engineering*, vol. 28, no. 10, pp. 1138–1150, 2008.
 - [42] J. Freeman, A. Najjaran-Kheirabadi, R. Edwards, M. Reid, R. Hall, A. Ramos, and C. N. Markides, “Testing and simulation of a solar diffusion-absorption refrigeration system for low-cost solar cooling in india,” in *ISES Solar World Congress*, 2017.
 - [43] A. Acuña, F. Lara, N. Velázquez, and J. Cerezo, “Optimum generator temperature to couple different diffusion absorption solar cooling systems,” *Energy Economics*, vol. 45, pp. 128–135, 2014.
 - [44] Z. Sayadi, B. Thameur, M. Bourouis, A. Bellagi, N. B. Thameur, M. Bourouis, and A. Bellagi, “Performance optimization of solar driven small-cooled absorption–diffusion chiller working with light hydrocarbons,” *Energy Conversion and Management*, vol. 74, pp. 299–307, 2013.
 - [45] D. Keppler, “Absorption chillers as a contribution to a climate-friendly refrigeration supply regime: Factors of influence on their further diffusion,” *Journal of Cleaner Production*, vol. 172, pp. 1535–1544, 2018.
 - [46] P. Srihirin, S. Aphornratana, and S. Chungpaibulpatana, “A review of absorption refrigeration technologies,” *Renewable & Sustainable Energy Reviews*, vol. 5, no. 4, pp. 343–372, 2001.
 - [47] R. Best and N. Ortega, “Solar refrigeration and cooling,” *Renewable Energy*, vol. 16, no. 1, pp. 685–690, 1999.
 - [48] D. Kim and C. Infante Ferreira, “Solar refrigeration options – a state-of-the-art review,” *International Journal of Refrigeration*, vol. 31, no. 1, pp. 3–15, 2008.
 - [49] M. S. Owen, ed., *2014 ASHRAE[®] Handbook–Refrigeration, SI Edition*. American Society of Heating, Refrigeration and Air Conditioning Engineers, 2014.
 - [50] I. Sarbu and C. Sebarchievici, “Review of solar refrigeration and cooling systems,” *Energy and Buildings*, vol. 67, pp. 286–297, 2013.
 - [51] IRENA, “Renewable power generation costs in 2020.” <https://www.irena.org/publications/2021/Jun/Renewable-Power-Costs-in-2020>, 2020. [Last accessed on : 1/12/2021].
 - [52] IRENA, “World energy transitions outlook: 1.5°C pathway.” <https://www.irena.org/publications/2021/Jun/World-Energy-Transitions-Outlook>, 2021. [Last accessed on : 1/12/2021].

-
- [53] T. P. Kitching, “Development of a tracking compound parabolic collector for a solar-driven diffusion absorption cycle,” Master’s thesis, North-West University, Potchefstroom, South Africa, 2018.
 - [54] S. S. Christopher, R. Santosh, M. Ponrajan Vikram, R. Prabakaran, A. K. Thakur, and H. Xu, “Optimization of a solar water heating system for vapor absorption refrigeration system,” *Environmental Progress & Sustainable Energy*, vol. 40, no. 1, p. e13489, 2021.
 - [55] “TRNSYS : Transient System Simulation Tool.” <http://www.trnsys.com/>.
 - [56] I. Baniasad Askari, H. Ghazizade-Ahsaee, and M. Ameri, “Thermo-economic analysis of a solar-powered absorption refrigeration integrated with a humidification–dehumidification desalination,” *Environment, Development and Sustainability*, vol. 24, 2022.
 - [57] A. Ramos, M. A. Chatzopoulou, I. Guarracino, J. Freeman, and C. N. Markides, “Hybrid photovoltaic-thermal solar systems for combined heating, cooling and power provision in the urban environment,” *Energy Conversion and Management*, vol. 150, pp. 838–850, 2017.
 - [58] M. Herrando, A. M. Pantaleo, K. Wang, and C. N. Markides, “Solar combined cooling, heating and power systems based on hybrid PVT, PV or solar-thermal collectors for building applications,” *Renewable Energy*, vol. 143, pp. 637–647, 2019.
 - [59] A. A. Harraz, A. Najjaran, K. Wang, A. M. Pantaleo, and C. N. Markides, “Optimal integration of solar refrigeration in food processing: Techno-economic comparison of PV, PV-T and hybrid solar cooling in a dairy farm,” in *The 15th Conference on Sustainable Development of Energy, Water and Environment Systems (SDEWES)*, (Cologne, Germany), 9 2020.
 - [60] K. Wang, A. M. Pantaleo, M. Herrando, M. Faccia, I. Pesmazoglou, B. M. Franchetti, and C. N. Markides, “Spectral-splitting hybrid PV-thermal (PVT) systems for combined heat and power provision to dairy farms,” *Renewable Energy*, vol. 159, pp. 1047–1065, 2020.
 - [61] UNICEF, “Solar direct drive refrigeration systems price data.” <https://www.unicef.org/supply/media/9396/file/Solar-direct-drive-refrigeration-systems-price-data.pdf>, 2020. [Last accessed on:1/2/2021].
 - [62] S. McCarney, J. Robertson, J. Arnaud, K. Lorensen, and J. Lloyd, “Using solar-powered refrigeration for vaccine storage where other sources of reliable electricity are inadequate or costly,” *Vaccine*, vol. 31, no. 51, pp. 6050–6057, 2013.
 - [63] A. A. Harraz, J. Freeman, K. Wang, N. Mac Dowell, and C. N. Markides, “Diffusion-absorption refrigeration cycle simulations in gPROMS using SAFT- γ Mie,” *Energy Proce-*

- dia*, vol. 158, pp. 2360–2365, 2019.
- [64] A. A. Harraz, A. Najjaran, R. Sacks, J. Freeman, A. V. Olympios, N. Mac Dowell, and C. N. Markides, “Experimentally validated simulations of a diffusion absorption refrigeration system,” in *ECOS 2019: Proceedings of the 32nd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems*, (Wroclaw, Poland), 6 2019.
 - [65] R. Rademacher, K. E. Herold, R. Radermacher, and S. A. Klein, *Absorbtion Chillers and Heat Pumps*. CRC, 2016.
 - [66] J. L. Rodríguez-Muñoz and J. M. Belman-Flores, “Review of diffusion-absorption refrigeration technologies,” *Renewable & Sustainable Energy Reviews*, vol. 30, pp. 145–153, 2014.
 - [67] B. C. V. Platen and C. G. Munters, “Absorption refrigerating apparatus,” US-Patent 1620843, 1923.
 - [68] B. C. V. Platen and C. G. Munters, “Refrigeration,” US-Patent 1678277, 1928.
 - [69] B. C. V. Platen and C. G. Munters, “Refrigerator,” US-Patent 1685764, 1928.
 - [70] A. Zohar, M. Jelinek, A. Levy, and I. Borde, “The influence of the generator and bubble pump configuration on the performance of diffusion absorption refrigeration (DAR) system,” *International Journal of Refrigeration*, vol. 31, no. 6, pp. 962–969, 2008.
 - [71] “RV cooling unit warehouse.” <https://rvcoolingunit.com/> [Last accessed on: 8/7/2021].
 - [72] “CamperID - Refrigerator parts.” <https://www.camperid.com/refrigerator-parts.html> [Last accessed on: 8/7/2021].
 - [73] G. Vicatos and A. Bennett, “Multiple lift tube pumps boost refrigeration capacity in absorption plants,” *Journal of Energy in Southern Africa*, vol. 18, no. 4, pp. 49–57, 2007.
 - [74] F. Schmid, B. Bierling, and K. Spindler, “Development of a solar-driven diffusion absorption chiller,” *Solar Energy*, vol. 177, pp. 483–493, 2019.
 - [75] J. Freeman, A. Ramos, N. Mac Dowell, and C. N. Markides, “An experimentally validated model of a solar-cooling system based on an ammonia-water diffusion-absorption cycle,” in *The 8th International Conference on Applied Energy – ICAE2016*, (Beijing, China), 2016.
 - [76] H. Wang, “A new style solar-driven diffusion absorption refrigerator and its operating characteristics,” *Energy Procedia*, vol. 18, pp. 681–692, 2012.
 - [77] N. B. Ezzine, R. Garma, and A. Bellagi, “A numerical investigation of a diffusion-absorption refrigeration cycle based on R124-DMAC mixture for solar cooling,” *Energy*, vol. 35, no. 5,

- pp. 1874–1883, 2010.
- [78] E. Özbaş, “Experimental study of diffusion absorption refrigeration systems using solar energy,” *Journal of Polytechnic*, vol. 21, no. 2, pp. 291–297, 2018.
 - [79] J. Freeman, *Solar-thermal combined energy systems for distributed small-scale applications*. PhD thesis, Imperial College London, London, UK, 2017.
 - [80] K. G. Narayankhedkar and M. P. Maiya, “Investigations on triple fluid vapour absorption refrigerator,” *International Journal of Refrigeration*, vol. 8, no. 6, pp. 335–342, 1985.
 - [81] J. Chen, K. J. Kim, and K. E. Herold, “Performance enhancement of a diffusion-absorption refrigerator,” *International Journal of Refrigeration-revue Internationale Du Froid*, vol. 19, pp. 208–218, 1996.
 - [82] A. Sathe, “Experimental and theoretical studies on a bubble pump for a diffusion-absorption refrigeration system mechanical engineering list of contents,” Master’s thesis, Institut für Thermodynamik und Wärmetechnik, Universität Stuttgart, Germany, 2001.
 - [83] P. Sriksirin and S. Aphornratana, “Investigation of a diffusion absorption refrigerator,” *Applied Thermal Engineering*, vol. 22, no. 11, pp. 1181–1193, 2002.
 - [84] A. S. Rattner and S. Garimella, “Low-source-temperature diffusion absorption refrigeration. Part I: Modeling and cycle analysis,” *International Journal of Refrigeration*, vol. 65, pp. 287–311, 2016.
 - [85] A. Najjaran, J. Freeman, A. Ramos, and C. N. Markides, “Experimental investigation of an ammonia-water-hydrogen diffusion absorption refrigerator,” *Applied Energy*, vol. 256, 2019.
 - [86] B. Chaouachi and S. Gabsi, “Design and simulation of an absorption diffusion solar refrigeration unit,” *American Journal of Applied Sciences*, vol. 4, no. 2, pp. 85–88, 2007.
 - [87] J. Pais, “Simulation and numerical optimization of diffusion-absorption refrigeration (DAR) cycle powered by solar energy,” Master’s thesis, The University of Pau and the Adour Region, Pau, France, 2009.
 - [88] W. I. A. Aly, M. Abdo, G. Bedair, and A. E. Hassaneen, “Thermal performance of a diffusion absorption refrigeration system driven by waste heat from diesel engine exhaust gases,” *Applied Thermal Engineering*, vol. 114, pp. 621–630, 2017.
 - [89] R. Farzadi and M. Bazargan, “Experimental study of a diffusion absorption refrigeration cycle supplied by the exhaust waste heat of a sedan car at low engine speeds,” *Heat and Mass Transfer/Waerme- und Stoffuebertragung*, vol. 56, no. 4, pp. 1353–1363, 2020.
 - [90] M. Kumar and R. Das, “Experimental analysis of absorption refrigeration system driven by waste heat of diesel engine exhaust,” *Thermal Science*, vol. 23, no. 1, pp. 149–157,

- 2019.
- [91] A. Koyfman, M. Jelinek, A. Levy, and I. Borde, “An experimental investigation of bubble pump performance for diffusion absorption refrigeration system with organic working fluids,” *Applied Thermal Engineering*, vol. 23, no. 15, pp. 1881–1894, 2003.
 - [92] G. Kim, H. W. Choi, G. Lee, J. S. Lee, and Y. T. Kang, “Experimental study on diffusion absorption refrigeration systems with low GWP refrigerants,” *Energy*, vol. 201, p. 117626, 2020.
 - [93] Y. Taitel, D. Bornea, and A. E. Dukler, “Modelling flow pattern transitions for steady upward gas-liquid flow in vertical tubes,” *AIChE Journal*, vol. 26, no. 3, pp. 345–354, 1980.
 - [94] A. S. Rattner and S. Garimella, “Coupling-fluid heated bubble pump generators: Experiments and model development,” *Science and Technology for the Built Environment*, vol. 21, no. 3, pp. 332–347, 2015.
 - [95] J. Freeman, “Towards an off-design model of a diffusion absorption refrigeration (DAR) system for solar-cooling applications,” tech. rep., Imperial College London, London, UK, 2018.
 - [96] P. Bourseau and R. Bugarel, “Réfrigération par cycle à absorption-diffusion: comparaison des performances des systèmes $\text{NH}_3\text{--H}_2\text{O}$ et $\text{NH}_3\text{--NaSCN}$,” *International Journal of Refrigeration*, vol. 9, no. 4, pp. 206–214, 1986.
 - [97] G. Starace and L. De Pascalis, “An advanced analytical model of the diffusion absorption refrigerator cycle,” *International Journal of Refrigeration*, vol. 35, no. 3, pp. 605–612, 2012.
 - [98] A. Zohar, M. Jelinek, A. Levy, and I. Borde, “Numerical investigation of a diffusion absorption refrigeration cycle,” *International Journal of Refrigeration*, vol. 28, no. 4, pp. 515–525, 2005.
 - [99] A. Benhmidene, B. Chaouachi, and S. Gabsi, “A review of bubble pump technologies,” *Journal of Applied Sciences(Faisalabad)*, vol. 10, no. 16, pp. 1806–1813, 2010.
 - [100] B. Bierling, F. Schmid, and K. Spindler, “Influence of different heating types on the pumping performance of a bubble pump,” *Heat and Mass Transfer*, vol. 55, no. 1, pp. 67–79, 2019.
 - [101] S. V. Shelton, S. W. Stewart, D. C. Erickson, and L. A. Schaefer, “Bubble pump design for single pressure absorption refrigeration cycles,” *ASHRAE Transactions*, vol. 108, pp. 867–876, 2002.
 - [102] B. Gurevich, “Bubble pump models verification based on the experimental results,” *Journal*

- of Energy and Power Engineering*, vol. 11, pp. 665–669, 2017.
- [103] A. S. Rattner and S. Garimella, “Low-source-temperature diffusion absorption refrigeration. Part II: Experiments and model assessment,” *International Journal of Refrigeration*, vol. 65, pp. 312–329, 2016.
 - [104] A. Taieb, K. Mejbri, and A. Bellagi, “Theoretical analysis of a diffusion-absorption refrigerator,” *International Journal of Hydrogen Energy*, vol. 41, no. 32, pp. 14293–14301, 2016.
 - [105] G. Starace and L. De Pascalis, “An enhanced model for the design of diffusion absorption refrigerators,” *International Journal of Refrigeration*, vol. 36, no. 5, pp. 1495–1503, 2013.
 - [106] M. Jelinek, A. Levy, and I. Borde, “The influence of the evaporator inlet conditions on the performance of a diffusion absorption refrigeration cycle,” *Applied Thermal Engineering*, vol. 99, pp. 979–987, 2016.
 - [107] Z. Long, Y. Luo, H. Li, X. Bu, and W. Ma, “Performance analysis of a diffusion absorption refrigeration cycle working with TFE–TEGDME mixture,” *Energy and Buildings*, vol. 58, pp. 86–92, 2013.
 - [108] B. M. Ziapour and M. Tavakoli, “Performance study on a diffusion absorption refrigeration heat pipe cycle,” *International journal of thermal sciences*, vol. 50, no. 4, pp. 592–598, 2011.
 - [109] A. Zohar, M. Jelinek, A. Levy, and I. Borde, “The influence of diffusion absorption refrigeration cycle configuration on the performance,” *Applied Thermal Engineering*, vol. 27, no. 13, pp. 2213–2219, 2007.
 - [110] A. Zohar, M. Jelinek, A. Levy, and I. Borde, “Performance of diffusion absorption refrigeration cycle with organic working fluids,” *International Journal of Refrigeration*, vol. 32, no. 6, pp. 1241–1246, 2009.
 - [111] A. Taieb, K. Mejbri, and A. Bellagi, “Detailed thermodynamic analysis of a diffusion-absorption refrigeration cycle,” *Energy*, vol. 115, pp. 418–434, 2016.
 - [112] R. Ben Jemaa, R. Mansouri, and A. Bellagi, “Dynamic testing and modeling of a diffusion absorption refrigeration system,” *International Journal of Refrigeration*, vol. 67, pp. 249–258, 2016.
 - [113] R. Mansouri, M. Bourouis, and A. Bellagi, “Experimental investigations and modelling of a small capacity diffusion-absorption refrigerator in dynamic model,” *Applied Thermal Engineering*, vol. 113, pp. 653–662, 2017.
 - [114] M. I. S. Adjibade, A. Thiam, C. Awanto, B. A. Ndiogou, and V. Sambou, “Dynamic investigation of the diffusion absorption refrigeration system $\text{NH}_3\text{-H}_2\text{O-H}_2$,” *Case Studies*

REFERENCES

- in Thermal Engineering*, vol. 10, pp. 468–474, 2017.
- [115] R. Mansouri, M. Bourouis, and A. Bellagi, “Steady state investigations of a commercial diffusion-absorption refrigerator: Experimental study and numerical simulations,” *Applied Thermal Engineering*, vol. 129, pp. 725–734, 2018.
- [116] “Aspen Plus®.” <https://www.aspentech.com/en/products/engineering/aspen-plus>.
- [117] M. Elsayed, A. Attia, and S. Tawfeek, “Steady state numerical simulation and studying performance of a modified diffusion absorption refrigeration cycle,” *Alexandria Engineering Journal*, vol. 61, no. 4, pp. 2591–2600, 2022.
- [118] “Aspen HYSYS®.” <https://www.aspentech.com/en/products/engineering/aspen-hysys>.
- [119] F. Chaves, M. Moreira, R. Koury, L. Machado, and M. Cortez, “Experimental study and modeling within validation of a diffusion absorption refrigerator,” *International Journal of Refrigeration*, vol. 101, pp. 136–147, 2019.
- [120] V. Pérez-García, J. Rodríguez-Muñoz, J. Belman-Flores, C. Rubio-Maya, and J. Ramírez-Minguela, “Theoretical modeling and experimental validation of a small capacity diffusion-absorption refrigerator,” *International Journal of Refrigeration*, vol. 104, pp. 302–310, 2019.
- [121] “EES: Engineering Equation Solver - F-Chart Software.” <https://fchartsoftware.com/ees/>.
- [122] “MATLAB - MathWorks - MATLAB & Simulink.” <https://uk.mathworks.com/products/matlab.html>.
- [123] “Fortran programming language.” <https://fortran-lang.org/>.
- [124] A. W. Westerberg, H. P. Hutchison, R. L. Motard, and P. Winter, *Process Flowsheeting*. Cambridge University Press, 2011.
- [125] M. M. Martín, *Introduction to software for chemical engineers*. CRC Press, 2014.
- [126] “PSE: gPROMS - Home - Process Systems Enterprise.” <https://www.psenterprise.com/products/gproms> [Last accessed on: 1/6/2018].
- [127] K. Mejbri and A. Bellagi, “Modelling of the thermodynamic properties of the water-ammonia mixture by three different approaches,” *International Journal of Refrigeration*, vol. 29, pp. 211–218, 2006.
- [128] J. Pátek and J. Klomfar, “Simple functions for fast calculations of selected thermodynamic properties of the ammonia-water system,” *International Journal of refrigeration*, vol. 18, no. 4, pp. 228–234, 1995.

-
- [129] A. Najjaran, A. A. Harraz, J. Freeman, R. Sacks, and C. N. Markides, “Experimental study of a diffusion absorption refrigeration unit at different charge-pressures,” in *ACEC 2019 Annual Clean Energy Conference*, pp. 1–8, Shiraz University, 2019.
- [130] A. Najjaran, A. A. Harraz, P. Sapin, K. Wang, and C. N. Markides, “Experimental investigation on the start-up time of a small-scale diffusion absorption refrigeration (DAR) unit,” in *14th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics*, (Wicklow, Ireland), 07 2019.
- [131] N. Dammak, B. Chaouachi, S. Gabsi, and M. Bourouis, “Optimization of the geometrical parameters of a solar bubble pump for absorption-diffusion cooling systems,” *American Journal of Engineering and Applied Sciences*, vol. 3, no. 4, 2010.
- [132] A. Acuña, N. Velázquez, D. Saucedo, P. Rosales, A. Suastegui, and A. Ortiz, “Influence of a compound parabolic concentrator in the performance of a solar diffusion absorption cooling system,” *Applied Thermal Engineering*, vol. 102, pp. 1374–1383, 2016.
- [133] A. Acuña, N. Velázquez, and J. Cerezo, “Energy analysis of a diffusion absorption cooling system using lithium nitrate, sodium thiocyanate and water as absorbent substances and ammonia as the refrigerant,” *Applied Thermal Engineering*, vol. 51, no. 1-2, pp. 1273–1281, 2013.
- [134] A. Najjaran, J. Freeman, A. Ramos, and C. N. Markides, “Experimental performance analysis of an ammonia-water diffusion absorption refrigeration cycle,” in *13th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics* (J. P. Mayer, ed.), (Portorož, Slovenia), pp. 951–955, 2017.
- [135] N. Ben Ezzine, R. Garma, and A. Bellagi, “Experimental and numerical investigation on absorption-diffusion refrigeration machine based on light hydrocarbons,” in *Proceedings of SEBUA-12 ICHMT International Symposium on Sustainable Energy in Buildings and Urban Areas*, pp. 329–334, 2012.
- [136] A. Yıldız and M. A. Ersöz, “Energy and exergy analyses of the diffusion absorption refrigeration system,” *Energy*, vol. 60, pp. 407–415, 2013.
- [137] B. Zhang, W. Chen, Q. Sun, and Z. Miao, “Numerical evaluation of thermal performances of diffusion-absorption refrigeration using 1,3-dimethylimidazolylium dimethylphosphate/methanol/helium as working fluid,” *Energy Conversion and Management*, vol. 152, pp. 201–213, 2017.
- [138] A. Stegou-Sagia, “A computational method for the methyl amine/H₂ gas mixture concentrations in methyl amine/H₂O/H₂ absorption refrigeration units,” *Applied Thermal*

- Engineering*, vol. 16, no. 8, pp. 707–718, 1996.
- [139] Q. Wang, L. Gong, J. Wang, T. Sun, K. Cui, and G. Chen, “A numerical investigation of a diffusion absorption refrigerator operating with the binary refrigerant for low temperature applications,” *Applied Thermal Engineering*, vol. 31, no. 10, pp. 1763–1769, 2011.
 - [140] H. Dardour, P. Cézac, J.-M. Reneaume, M. Bourouis, and A. Bellagi, “Numerical investigation of an absorption-diffusion cooling machine using C_3H_8/C_9H_{20} as binary working fluid,” *Oil & Gas Science and Technology – Revue d’IFP Energies nouvelles*, vol. 68, no. 2, pp. 249–254, 2013.
 - [141] S. Mazouz, R. Mansouri, and A. Bellagi, “Experimental and thermodynamic investigation of an ammonia/water diffusion absorption machine,” *International Journal of Refrigeration*, vol. 45, pp. 83–91, 2014.
 - [142] B. Agostini, F. Agostini, and M. Habert, “Modeling of a Von Platen-Munters diffusion absorption refrigeration cycle,” *Journal of Physics: Conference Series*, vol. 745, p. 032053, 2016.
 - [143] S. V. Wankhede, J. A. Hole, and B. L. Patil, “Performance of tetrafluoroethane (R134a)-dimethyl formamide (DMF) diffusion absorption air cooling system with variable power input,” *International Journal of Ambient Energy*, vol. 0, no. 0, pp. 1–7, 2020.
 - [144] H. Li, P. Lin, S. Du, and L. Wang, “Modelling and thermodynamic analysis of a hot-cold conversion pipe using R134a-DMF-He as the working pair,” *Journal of Thermal Science*, vol. 30, no. 1, pp. 64–75, 2021.
 - [145] G. Lee, H. W. Choi, and Y. T. Kang, “Cycle performance analysis and experimental validation of a novel diffusion absorption refrigeration system using R600a/n-octane,” *Energy*, vol. 217, p. 119328, 2021.
 - [146] T. Tiwari, Ajiit, and Gianender, “A review of working fluid combinations used in diffusion absorption refrigeration technologies,” *International Journal for Research in Applied Science and Engineering Technology*, vol. 5, no. Xi, pp. 2105–2111, 2017.
 - [147] R. Mbarek and W. Mbarek, “Building and experimentation of diffusion absorption refrigeration machines,” *International Journal of Basics and Applied Sciences*, vol. 1, no. 3, pp. 605–612, 2013.
 - [148] B. H. Gebreslassie, G. Guillén-Gosálbez, L. Jiménez, and D. Boer, “Design of environmentally conscious absorption cooling systems via multi-objective optimization and life cycle assessment,” *Applied Energy*, vol. 86, no. 9, pp. 1712–1722, 2009.
 - [149] J. Schilling, D. Tillmanns, M. Lampe, M. Hopp, J. Gross, and A. Bardow, “From molecules to dollars: integrating molecular design into thermo-economic process design

- using consistent thermodynamic modeling,” *Molecular System Design and Engineering*, vol. 2, pp. 301–320, 2017.
- [150] A. S. Hukkerikar, S. Kalakul, B. Sarup, D. M. Young, G. Sin, and R. Gani, “Estimation of environment-related properties of chemicals for design of sustainable processes: Development of group-contribution+ (GC+) property models and uncertainty analysis,” *Journal of Chemical Information and Modeling*, vol. 52, no. 11, pp. 2823–2839, 2012. PMID: 23039255.
- [151] S. Kondo, Y. Urano, K. Tokuhashi, A. Takahashi, and K. Tanaka, “Prediction of flammability of gases by using *F*-number analysis,” *Journal of Hazardous Materials*, vol. 82, no. 2, pp. 113–128, 2001.
- [152] T. A. Albahri and R. S. George, “Artificial neural network investigation of the structural group contribution method for predicting pure components auto ignition temperature,” *Industrial & Engineering Chemistry Research*, vol. 42, no. 22, pp. 5708–5714, 2003.
- [153] United Nations, *Globally harmonized system of classification and labelling of chemicals (GHS)*. New York, USA: Occupational Safety and Health Administration, United States of America. OSHA, fourth ed., 2011.
- [154] B. H. Gebreslassie, G. Guillén-Gosálbez, L. Jiménez, and D. Boer, “Economic performance optimization of an absorption cooling system under uncertainty,” *Applied Thermal Engineering*, vol. 29, no. 17-18, pp. 3491–3500, 2009.
- [155] B. H. Gebreslassie, G. Guillén-Gosálbez, L. Jiménez, and D. Boer, “A systematic tool for the minimization of the life cycle impact of solar assisted absorption cooling systems,” *Energy*, vol. 35, no. 9, pp. 3849–3862, 2010.
- [156] B. H. Gebreslassie, G. Guillén-Gosálbez, L. Jiménez, and D. Boer, “Solar assisted absorption cooling cycles for reduction of global warming: A multi-objective optimization approach,” *Solar Energy*, vol. 86, no. 7, pp. 2083–2094, 2012.
- [157] L. M. Chávez-Islas and C. L. Heard, “Optimization of a simple ammonia- water absorption refrigeration cycle by application of mixed-integer nonlinear programming,” *Industrial & engineering chemistry research*, vol. 48, no. 4, pp. 1957–1972, 2009.
- [158] L. M. Chávez-Islas and C. L. Heard, “Design and analysis of an ammonia/water absorption refrigeration cycle by means of an equation-oriented method,” *Industrial & engineering chemistry research*, vol. 48, no. 4, pp. 1944–1956, 2009.
- [159] “PubChem: National Library of Medicine – National Center for Biotechnology Information.” <https://pubchem.ncbi.nlm.nih.gov/> [Last accessed on: 1/2/2021].
- [160] M. T. White, O. A. Oyewunmi, A. J. Haslam, and C. N. Markides, “Industrial waste-heat

- recovery through integrated computer-aided working-fluid and ORC system optimisation using SAFT- γ Mie,” *Energy Conversion and Management*, vol. 150, pp. 851–869, 2017.
- [161] O. A. Oyewunmi, *Heat Recovery and Conversion Technologies with Organic Fluid Cycles: Optimal Working Fluid and System Design*. PhD thesis, Imperial College London, London, UK, 2018.
- [162] A. Yildiz, “Thermoeconomic analysis of diffusion absorption refrigeration systems,” *Applied Thermal Engineering*, vol. 99, pp. 23–31, 2016.
- [163] A. Bejan, G. Tsatsaronis, and M. J. Moran, *Thermal design and optimization*. John Wiley & Sons, 1995.
- [164] N. D. Austin, N. V. Sahinidis, and D. W. Trahan, “Computer-aided molecular design: An introduction and review of tools, applications, and solution techniques,” *Chemical Engineering Research and Design*, vol. 116, pp. 2–26, 2016.
- [165] L. Y. Ng, F. K. Chong, and N. G. Chemmangattuvalappil, “Challenges and opportunities in computer-aided molecular design,” *Computers & Chemical Engineering*, vol. 81, pp. 115–129, 2015.
- [166] R. Gani, B. Nielsen, and A. Fredenslund, “A group contribution approach to computer-aided molecular design,” *AIChE Journal*, vol. 37, no. 9, pp. 1318–1332, 1991.
- [167] L. Achenie, V. Venkatasubramanian, and R. Gani, eds., *Computer aided molecular design: theory and practice*. Elsevier, 2002.
- [168] O. Odele and S. Macchietto, “Computer aided molecular design: a novel method for optimal solvent selection,” *Fluid Phase Equilibria*, vol. 82, pp. 47–54, 1993.
- [169] N. Churi and L. Achenie, “On the use of a mixed integer non-linear programming model for refrigerant design,” *International Transactions in Operational Research*, vol. 4, no. 1, pp. 45–54, 1997.
- [170] M. Kernén, L. L. Lee, and H. Perez-Blanco, “A computer-aided molecular design of fluids that optimize absorption cycle COP,” *Journal of Energy Resources Technology*, vol. 117, pp. 156–160, 06 1995.
- [171] Y. Khetib, O. Larkeche, A.-H. Meniai, and A. Radwan, “Group contribution concept for computer-aided design of working fluids for refrigeration machines,” *Chemical Engineering & Technology*, vol. 36, no. 11, pp. 1924–1934, 2013.
- [172] Y. Khetib, A.-H. Meniai, A. Gari, and K. Sedraoui, “Refrigerants design for an absorption refrigeration machine using group contribution methods,” *Chemical Engineering Communications*, vol. 0, no. 0, pp. 1–19, 2021.
- [173] N. Churi and L. E. K. Achenie, “Novel mathematical programming model for computer

- aided molecular design,” *Industrial & Engineering Chemistry Research*, vol. 35, no. 10, pp. 3788–3794, 1996.
- [174] A. Duvedi and L. Achenie, “On the design of environmentally benign refrigerant mixtures: a mathematical programming approach,” *Computers & Chemical Engineering*, vol. 21, no. 8, pp. 915–923, 1997.
- [175] I. Louaer, A. Meniai, O. Larkeche, and M. Bencheikh-Lehocine, “Computer-aided design and test of new refrigerants for an absorption cycle using group contribution methods,” *Desalination*, vol. 206, no. 1, pp. 620–632, 2007. EuroMed 2006.
- [176] E. A.-H. Tora, “Computer-aided design and simulation of working fluid pairs for absorption refrigerators,” *International Journal of Scientific & Engineering Research*, vol. 4, no. 4, pp. 1306–1310, 2013.
- [177] J. Schilling, M. Lampe, J. Gross, and A. Bardow, “1-stage CoMT-CAMD: An approach for integrated design of ORC process and working fluid using PC-SAFT,” *Chemical Engineering Science*, vol. 159, pp. 217–230, 2017. iCAMD – Integrating Computer-Aided Molecular Design into Product and Process Design.
- [178] L. M. van Kleef, O. A. Oyewunmi, and C. N. Markides, “Multi-objective thermo-economic optimization of organic Rankine cycle (ORC) power systems in waste-heat recovery applications using computer-aided molecular design techniques,” *Applied Energy*, vol. 251, p. 112513, 2019.
- [179] A. I. Papadopoulos, A.-S. Kyriakides, P. Seferlis, and I. Hassan, “Integrated design of working fluid mixtures and absorption refrigeration cycles,” *Frontiers in Chemical Engineering*, vol. 3, 2021.
- [180] K. G. Joback and R. Reid, “Estimation of pure-component properties from group-contributions,” *Chemical Engineering Communications*, vol. 57, no. 1-6, pp. 233–243, 1987.
- [181] A. Fredenslund, R. L. Jones, and J. M. Prausnitz, “Group-contribution estimation of activity coefficients in nonideal liquid mixtures,” *AIChE Journal*, vol. 21, no. 6, pp. 1086–1099, 1975.
- [182] A. Fredenslund, J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria using UNIFAC: A Group-Contribution method*. Amsterdam: Elsevier, 1977.
- [183] U. Weidlich and J. Gmehling, “A modified UNIFAC model. 1. Prediction of VLE, h^E and γ^∞ ,” *Ind. Eng. Chem. Res.*, vol. 26, no. 7, pp. 1372–1381, 1987.
- [184] S. Dufal, T. Lafitte, A. Galindo, G. Jackson, and A. J. Haslam, “Developing intermolecular-potential models for use with the SAFT-VR Mie equation of state,” *AIChE Journal*,

REFERENCES

- vol. 61, no. 9, pp. 2891–2912, 2015.
- [185] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, “SAFT: Equation-of-state solution model for associating fluids,” *Fluid Phase Equilibria*, vol. 52, pp. 31–38, 1989.
- [186] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, “New reference equation of state for associating liquids,” *Industrial & Engineering Chemistry Research*, vol. 29, no. 8, pp. 1709–1721, 1990.
- [187] M. S. Wertheim, “Fluids with highly directional attractive forces: I. Statistical thermodynamics,” *Journal of Statistical Physics*, vol. 35, no. 1-2, pp. 19–34, 1984.
- [188] M. S. Wertheim, “Fluids with highly directional attractive forces: II. Thermodynamic perturbation theory and integral equations,” *Journal of Statistical Physics*, vol. 35, no. 1-2, pp. 35–47, 1984.
- [189] M. S. Wertheim, “Fluids with highly directional attractive forces: III. Multiple attraction sites,” *Journal of Statistical Physics*, vol. 42, no. 3-4, pp. 459–476, 1986.
- [190] M. S. Wertheim, “Fluids with highly directional attractive forces: IV. Equilibrium polymerization,” *Journal of Statistical Physics*, vol. 42, no. 3-4, pp. 477–492, 1986.
- [191] A. Lympieriadis, C. S. Adjiman, A. Galindo, , and G. Jackson, “. a group contribution method for associating chain molecules based on the statistical associating fluid theory (SAFT- γ),” *The Journal of Chemical Physics*, vol. 127, no. 23, p. 234903, 2007.
- [192] A. Lympieriadis, C. S. Adjiman, G. Jackson, and A. Galindo, “A generalisation of the SAFT- γ group contribution method for groups comprising multiple spherical segments,” *Fluid Phase Equilibria*, vol. 274, no. 1–2, pp. 85–104, 2008.
- [193] J. Vijande, M. M. Piñeiro, J. L. Legido, , and D. Bessi res, “Group-contribution method for the molecular parameters of the PC-SAFT equation of state taking into account the proximity effect. application to nonassociated compounds,” *Industrial and Engineering Chemistry Research*, vol. 49, no. 19, pp. 9394–9406, 2010.
- [194] J. Vijande, M. M. Piñeiro, and J. L. Legido, “Group-contribution method with proximity effect for pc-saft molecular parameters. 2. application to association parameters: Primary alcohols and amines,” *Industrial and Engineering Chemistry Research*, vol. 53, no. 2, pp. 909–919, 2014.
- [195] V. Papaioannou, *A molecular-based group contribution equation of state for the description of fluid phase behaviour and thermodynamic derivative properties of mixtures (SAFT- γ Mie)*. PhD thesis, Imperial College London, London, UK, 2012.
- [196] V. Papaioannou, T. Lafitte, C. A. no, C. S. Adjiman, G. Jackson, E. A. M ller, and A. Galindo, “Group contribution methodology based on the statistical associating fluid

- theory for heteronuclear molecules formed from mie segments,” *The Journal of Chemical Physics*, vol. 140, no. 5, p. 054107, 2014.
- [197] V. Papaioannou, F. Calado, T. Lafitte, S. Dufal, M. Sadeqzadeh, G. Jackson, C. S. Adjiman, and A. Galindo, “Application of the SAFT- γ Mie group contribution equation of state to fluids of relevance to the oil and gas industry,” *Fluid Phase Equilibria*, vol. 416, pp. 104–119, 2016.
- [198] R. Gani and E. Brignole, “Molecular design of solvents for liquid extraction based on unifac,” *Fluid Phase Equilibria*, vol. 13, pp. 331–340, 1983.
- [199] K. G. Joback, *Designing molecules possessing desired physical property values*. PhD thesis, Massachusetts Institute of Technology, 1989.
- [200] S. Stefanis, A. Buxton, A. Livingston, and E. Pistikopoulos, “A methodology for environmental impact minimization: Solvent design and reaction path synthesis issues,” *Computers & Chemical Engineering*, vol. 20, pp. S1419–S1424, 1996. European Symposium on Computer Aided Process Engineering-6.
- [201] K. G. Joback and G. Stephanopoulos, “Searching spaces of discrete solutions: The design of molecules possessing desired physical properties,” in *Intelligent Systems in Process Engineering Part I: Paradigms from Product and Process Design* (G. Stephanopoulos and C. Han, eds.), vol. 21 of *Advances in Chemical Engineering*, pp. 257–311, Academic Press, 1995.
- [202] J. Burger, V. Papaioannou, S. Gopinath, G. Jackson, A. Galindo, and C. S. Adjiman, “A hierarchical method to integrated solvent and process design of physical CO₂ absorption using the SAFT- γ Mie approach,” *AIChE Journal*, vol. 61, pp. 3249–3269, 2015.
- [203] S. Gopinath, A. Galindo, G. Jackson, and C. S. Adjiman, “A feasibility-based algorithm for computer aided molecular and process design of solvent-based separation systems,” *Computer-aided chemical engineering*, vol. 38, pp. 73–78, 2016.
- [204] M. T. White, O. A. Oyewunmi, M. A. Chatzopoulou, A. M. Pantaleo, A. J. Haslam, and C. N. Markides, “Computer-aided working-fluid design, thermodynamic optimisation and thermoeconomic assessment of ORC systems for waste-heat recovery,” *Energy*, vol. 161, pp. 1181–1198, 2018.
- [205] N. Churi and L. E. Achenie, “The optimal design of refrigerant mixtures for a two-evaporator refrigeration system,” *Computers & Chemical Engineering*, vol. 21, pp. S349–S354, 1997. Supplement to Computers and Chemical Engineering.
- [206] A. P. Duvedi and L. E. Achenie, “Designing environmentally safe refrigerants using mathematical programming,” *Chemical Engineering Science*, vol. 51, no. 15, pp. 3727–

- 3739, 1996.
- [207] J. Viswanathan and I. E. Grossmann, “A combined penalty function and outer-approximation method for minlp optimization,” *Computers & Chemical Engineering*, vol. 14, no. 7, pp. 769–782, 1990.
 - [208] C. S. Adjiman, C. A. Schweiger, and C. A. Floudas, “Mixed-integer nonlinear optimization in process synthesis,” in *Handbook of Combinatorial Optimization* (D. Z. Du and P. M. Pardalos, eds.), vol. 1, The Netherlands: Kluwer Academic publishers, 1998.
 - [209] O. Larkeche, A.-H. Meniai, and T. Cachot, “Modelling the absorption refrigeration cycle using partially miscible working fluids by group contribution methods,” *Molecular Physics*, vol. 110, no. 11-12, pp. 1305–1316, 2012.
 - [210] “PSEProCAMD - PSE.” https://www.pseforspeed.com/cpt_product/procamd/.
 - [211] L. Dong, D. Zheng, and X. Wu, “Working pair selection of compression and absorption hybrid cycles through predicting the activity coefficients of hydrofluorocarbon + ionic liquid systems by the unifac model,” *Industrial & Engineering Chemistry Research*, vol. 51, no. 12, pp. 4741–4747, 2012.
 - [212] A. A. Harraz, A. J. Haslam, A. Najjaran, N. Mac Dowell, and C. N. Markides, “An integrated computer-aided molecular design framework for diffusion-absorption refrigeration.” (*Unpublished*).
 - [213] M. Stavrou, M. Lampe, A. Bardow, and J. Gross, “Continuous molecular targeting–computer-aided molecular design (CoMT–CAMD) for simultaneous process and solvent design for CO₂ capture,” *Industrial & Engineering Chemistry Research*, vol. 53, no. 46, pp. 18029–18041, 2014.
 - [214] M. Lampe, M. Stavrou, H. M. Bücker, J. Gross, and A. Bardow, “Simultaneous optimization of working fluid and process for organic Rankine cycles using PC-SAFT,” *Industrial & Engineering Chemistry Research*, vol. 53, no. 21, pp. 8821–8830, 2014.
 - [215] M. Lampe, M. Stavrou, J. Schilling, E. Sauer, J. Gross, and A. Bardow, “Computer-aided molecular design in the continuous-molecular targeting framework using group-contribution PC-SAFT,” *Computers & Chemical Engineering*, vol. 81, pp. 278–287, 2015. Special Issue: Selected papers from the 8th International Symposium on the Foundations of Computer-Aided Process Design (FOCAPD 2014), July 13-17, 2014, Cle Elum, Washington, USA.
 - [216] J. Schilling, M. Entrup, M. Hopp, J. Gross, and A. Bardow, “Towards optimal mixtures of working fluids: Integrated design of processes and mixtures for organic Rankine cycles,” *Renewable and Sustainable Energy Reviews*, vol. 135, p. 110179, 2021.
 - [217] D. H. Bowskill, U. E. Tropp, S. Gopinath, G. Jackson, A. Galindo, and C. S. Adjiman,

- “Beyond a heuristic analysis: integration of process and working-fluid design for organic Rankine cycles,” *Mol. Syst. Des. Eng.*, vol. 5, pp. 493–510, 2020.
- [218] A. I. Papadopoulos, F. A. Perdomo, F. Tzirakis, G. Shavaliyeva, I. Tsivintzelis, P. Kazepidis, E. Nessi, S. Papadokostantakis, P. Seferlis, A. Galindo, G. Jackson, and C. S. Adjiman, “Molecular engineering of sustainable phase-change solvents: From digital design to scaling-up for CO₂ capture,” *Chemical Engineering Journal*, vol. 420, p. 127624, 2021.
- [219] Y. S. Lee, E. J. Graham, A. Galindo, G. Jackson, and C. S. Adjiman, “A comparative study of multi-objective optimization methodologies for molecular and process design,” *Computers & Chemical Engineering*, vol. 136, p. 106802, 2020.
- [220] S. Gopinath, G. Jackson, A. Galindo, and C. S. Adjiman, “Outer approximation algorithm with physical domain reduction for computer-aided molecular and separation process design,” *AIChE Journal*, vol. 62, no. 9, pp. 3484–3504, 2016.
- [221] A. I. Papadopoulos and P. Linke, “Multiobjective molecular design for integrated process-solvent systems synthesis,” *AIChE Journal*, vol. 52, no. 3, pp. 1057–1070, 2006.
- [222] A. I. Papadopoulos, M. Stijepovic, P. Linke, P. Seferlis, and S. Voutetakis, “Toward optimum working fluid mixtures for organic Rankine cycles using molecular design and sensitivity analysis,” *Industrial & Engineering Chemistry Research*, vol. 52, no. 34, pp. 12116–12133, 2013.
- [223] Q. Liu, L. Zhang, L. Liu, J. Du, A. K. Tula, M. Eden, and R. Gani, “OptCAMD: An optimization-based framework and tool for molecular and mixture product design,” *Computers & Chemical Engineering*, vol. 124, pp. 285–301, 2019.
- [224] N. V. Sahinidis, M. Tawarmalani, and M. Yu, “Design of alternative refrigerants via global optimization,” *AIChE Journal*, vol. 49, no. 7, pp. 1761–1775, 2003.
- [225] S. Dutta, *Optimization in Chemical Engineering*. Cambridge University Press, 2016.
- [226] T. Zhou, Y. Zhou, and K. Sundmacher, “A hybrid stochastic–deterministic optimization approach for integrated solvent and process design,” *Chemical Engineering Science*, vol. 159, pp. 207–216, 2017. iCAMD – Integrating Computer-Aided Molecular Design into Product and Process Design.
- [227] T. Zhou, J. Wang, K. McBride, and K. Sundmacher, “Optimal design of solvents for extractive reaction processes,” *AIChE Journal*, vol. 62, no. 9, pp. 3238–3249, 2016.
- [228] A. S. Drud, “CONOPT—A Large-Scale GRG Code,” *ORSA Journal on Computing*, vol. 6, no. 2, pp. 207–216, 1994.
- [229] B. E. Poling, J. M. Prausnitz, and J. P. O’Connell, *The properties of gases and liquids*. McGraw-Hill Education, 2001.

- [230] S. Dufal, V. Papaioannou, M. Sadeqzadeh, T. Pogiatzis, A. Chremos, C. S. Adjiman, G. Jackson, and A. Galindo, “Prediction of thermodynamic properties and phase behavior of fluids and mixtures with the SAFT- γ Mie group-contribution equation of state,” *Journal of Chemical and Engineering Data*, vol. 59, no. 10, pp. 3272–3288, 2014.
- [231] A. J. Haslam, A. González-Pérez, S. D. Lecce, S. H. Khalit, F. A. Perdomo, S. Kournopoulos, M. Kohns, T. Lindeboom, M. Wehbe, S. Febra, G. Jackson, C. S. Adjiman, and A. Galindo, “Expanding the applications of the SAFT- γ Mie group-contribution equation of state: Prediction of thermodynamic properties and phase behavior of mixtures,” *Journal of Chemical & Engineering Data*, vol. 65, no. 12, pp. 5862–5890, 2020.
- [232] A. Bagga and M. Teoh, “Thermodynamic modelling of ammonia and ammonia-water mixture using SAFT-VR Mie,” Master’s thesis, Imperial College London, London, UK, 2017.
- [233] P. Hutacharoen, S. Dufal, V. Papaioannou, R. M. Shanker, C. S. Adjiman, G. Jackson, and A. Galindo, “Predicting the solvation of organic compounds in aqueous environments: From alkanes and alcohols to pharmaceuticals,” *Industrial & Engineering Chemistry Research*, vol. 56, no. 38, pp. 10856–10876, 2017.
- [234] P. Hutacharoen, *Prediction of partition coefficients and solubilities of active pharmaceutical ingredients with the SAFT- γ Mie group-contribution approach*. PhD thesis, Imperial College London, London, UK, 2017.
- [235] S. Di Lecce, G. Lazarou, S. H. Khalit, C. S. Adjiman, G. Jackson, A. Galindo, and L. McQueen, “Modelling and prediction of the thermophysical properties of aqueous mixtures of choline geranate and geranic acid (CAGE) using SAFT- γ Mie,” *RSC Advances*, vol. 9, pp. 38017–38031, 2019.
- [236] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*. Butterworths & Co, third ed., 1982.
- [237] M. Conde Engineering, “Thermophysical properties of $\text{NH}_3+\text{H}_2\text{O}$ mixtures for the industrial design of absorption refrigeration equipment,” tech. rep., M. Conde Engineering, Zurich, 2006. last updated: November 2014.
- [238] S. R. S. Sastri and K. K. Rao, “A simple method to predict surface tension of organic liquids,” *The Chemical Engineering Journal and the Biochemical Engineering Journal*, vol. 59, no. 2, pp. 181–186, 1995.
- [239] IAPWS, “Revised release on surface tension of ordinary water substance,” tech. rep., International Association of Pure Water and Steam, 2014. [Last accessed on: 8/7/2018].
- [240] S. Sugden, “A relation between surface tension, density, and chemical composition,”

- Journal of the Chemical Society, Transactions*, vol. 125, pp. 32–41, 1924.
- [241] “NIST/TRC Web Thermo Tables (WTT).” <https://wtt-pro-nist-gov.iclibezp1.cc.ic.ac.uk/wtt-pro/>.
- [242] G. Liessmann, W. Schmidt, and S. Reiffarth, “Data compilation of the Saechsische Olefinwerke Boehlen (Germany),” *Recommended Thermophysical Data*, p. 1, 1995.
- [243] T. Klein, J. Cui, A. Kalantar, M. H. Chen, J. and Rausch, T. M. Koller, and A. P. Froeba, “Viscosity and surface tension of branched alkanes 2-methylnonane and 4-methylnonane,” *Journal of Chemical and Engineering Data*, vol. 63, no. 8, pp. 2833–2839, 2018.
- [244] E. W. Lemmon, , M. L. Huber, and M. O. McLinden, “NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.0, National Institute of Standards and Technology,” 2013.
- [245] C. L. Yaws, *Yaw’s Handbook of Thermodynamic and Physical Properties of Chemical Compounds*. Konvel, 2003.
- [246] P. Sies and J. Krafczyk, “The University of Oldenburg.” unpublished, 1992.
- [247] K. Tanaka and Y. Higashi, “Measurements of the surface tension for R290, R600a and R290/R600a mixture,” *International Journal of Refrigeration*, vol. 30, no. 8, pp. 1368–1373, 2007.
- [248] E. Graham, Edward J. and Forte, J. Burger, A. Galindo, G. Jackson, and C. S. Adjiman, “Multi-objective optimisation of equation of state parameters: SAFT-VR Mie models for water.” (*Unpublished*).
- [249] K. Levenberg, “A method for the solution of certain non-linear problems in least squares,” *Quarterly of Applied Mathematics*, vol. 2, no. 2, pp. 164–168, 1944.
- [250] D. W. Marquardt, “An algorithm for least-squares estimation of nonlinear parameters,” *Journal of the Society for Industrial and Applied Mathematics*, vol. 11, no. 2, pp. 431—441, 1963.
- [251] W. W. G.M. Gillespie, P.C.; Wilding, “Vapor liquid equilibrium measurements on the ammonia - water system from 313 K to 589 K,” in *AIChE Symposium Series*, pp. 97–127, 1987.
- [252] T. M. Smolen, D. B. Manley, and B. E. Poling, “Vapor-liquid equilibrium data for the ammonia-water system and its description with a modified cubic equation of state,” *Journal of Chemical and Engineering Data*, vol. 36, no. 2, pp. 202–208, 2002.
- [253] I. Fujita, T. Suzuki, and M. Uematsu, “Isobaric specific heat capacity of x H₂O + (1- x) NH₃ with x =(0.0000, 0.1566, 0.1597, 0.3030, 0.3048, 0.4956, 0.7061, and 0.8489) at T =(280, 300, 320, and 360) K over the pressure range from (0.1 to 15) MPa,” *The Journal*

- of Chemical Thermodynamics*, vol. 40, no. 2, pp. 260–264, 2008.
- [254] N. Mac Dowell, F. E. Pereira, F. Llovel, F. J. Blas, C. S. Adjiman, G. Jackson, and A. Galindo, “Transferable SAFT-VR models for the calculation of the fluid phase equilibria in reactive mixtures of carbon dioxide, water, and *n*-alkylamines in the context of carbon capture,” *Journal of Physical Chemistry B*, vol. 115, no. 25, pp. 8155–8168, 2011.
- [255] K. Kitaura and K. Morokuma, “A new energy decomposition scheme for molecular interactions within the hartree-fock approximation,” *International Journal of Quantum Chemistry*, vol. 10, no. 2, pp. 325–340, 1976.
- [256] H. Staudt, *Experimental Determination and Correlation of the Excess Enthalpy and the Excess Volume of Binary Aqueous Amine and Alcohol Systems and of the System Water - Ammonia, Depending on Pressure, Volume and Composition of the Mixture*. PhD thesis, Universität Kaiserslautern, Kaiserslautern, Germany, 1984.
- [257] I. S. Duff and J. K. Reid, “The design of MA48, a code for the direct solution of sparse unsymmetric linear systems of equations,” tech. rep., Computer and Information Systems Department, Rutherford Appleton Laboratory, Oxford, UK, 1995.
- [258] A. Najjaran, *Diffusion absorption refrigeration systems for thermally-driven cooling from low-temperature heat sources*. PhD thesis, Imperial College London, London, UK, 2020.
- [259] H. W. Choi, J. W. Lee, and Y. T. Kang, “Experimental study on diffusion absorption refrigerator achieving 0.2 coefficient of performance using low global warming potential refrigerant and low-grade heat source,” *Applied Thermal Engineering*, vol. 201, p. 117803, 2022.
- [260] A. D. Delano, *Design analysis of the Einstein refrigeration cycle*. PhD thesis, School of Mechanical Engineering, Georgia Institute of Technology, Georgia, USA, 1998.
- [261] M. Pfaff, R. Saravanan, M. Prakash Maiya, and S. Srinivasa Murthy, “Studies on bubble pump for a water–lithium bromide vapour absorption refrigerator,” *International Journal of Refrigeration*, vol. 21, no. 6, pp. 452–462, 1998.
- [262] S. J. White, “Bubble pump design and performance,” Master’s thesis, School of Mechanical Engineering, Georgia Institute of Technology, Georgia, USA, 2001.
- [263] K. W. Chan and M. McCulloch, “Analysis and modelling of water based bubble pump at atmospheric pressure,” *International Journal of Refrigeration*, vol. 36, no. 5, pp. 1521–1528, 2013.
- [264] J. Aman, P. Henshaw, and D. S. Ting, “Bubble-pump-driven LiBr-H₂O and LiCl-H₂O absorption air-conditioning systems,” *Thermal Science and Engineering Progress*, vol. 6, pp. 316–322, 2018.

- [265] J. D. Seader, E. J. Henley, and D. K. Roper, *Separation Process Principles: Chemical and Biochemical Operations*. John Wiley & Sons, Inc., third ed., 2011.
- [266] M. Cooper, “Saturation nucleate pool boiling - a simple correlation,” in *First U.K. National Conference on Heat Transfer* (H. C. Simpson, G. F. Hewitt, D. Boland, T. R. Bott, B. N. Furber, W. B. Hall, P. J. Heggs, P. N. Rowe, E. A. D. Saunders, and D. B. Spalding, eds.), The Institution of Chemical Engineers Symposium Series, pp. 785–793, Pergamon, 1984.
- [267] V. Guichet, S. Almahmoud, and H. Jouhara, “Nucleate pool boiling heat transfer in wickless heat pipes (two-phase closed thermosyphons): A critical review of correlations,” *Thermal Science and Engineering Progress*, vol. 13, p. 100384, 2019.
- [268] P. A. Kew and K. Cornwell, “Correlations for the prediction of boiling heat transfer in small-diameter channels,” *Applied Thermal Engineering*, vol. 17, no. 8, pp. 705–715, 1997.
- [269] I. M. Sobol’, D. Asotsky, A. Kreinin, and S. Kucherenko, “Construction and comparison of high-dimensional sobol’ generators,” *Wilmott*, vol. 2011, no. 56, pp. 64–79, 2011.
- [270] M. Berkelaar, J. Dirks, K. Eikland, P. Notebaert, J. Ebert, and H. Gourvest, “lpsolve: interface to ‘lp_solve’ v. 5.5 to solve linear/integer programs. r package version 5.6. 13.” <http://lpsolve.sourceforge.net/5.5/>, 2015.
- [271] J. Santiuste Martínez, “Development of a SAFT- γ Mie group-contribution approach to modelling working fluids and its application in the computer-aided molecular and process design of ORCs,” Master’s thesis, University OF Valladolid, Imperial College London, London, UK, 2020.
- [272] K. Flevaris and C. Chatzidoukas, “Optimal fed-batch bioreactor operating strategies for the microbial production of lignocellulosic bioethanol and exploration of their economic implications: A step forward towards sustainability and commercialization,” *Journal of Cleaner Production*, vol. 295, p. 126384, 2021.
- [273] G. F. Hewitt, G. L. Shires, and T. R. Bott, *Process Heat Transfer*. CRC Press, 1994.
- [274] W. D. Seider, D. R. Lewin, J. D. Seader, S. Widagdo, R. Gani, and K. M. NG, *Product and Process Design Principles: Synthesis, Analysis, and Evaluation*. John Wiley & Sons, Inc., fourth ed., 2017.
- [275] HM Revenue & Customs, “Guidance: Average for the year to 31 December 2019.” https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/877346/Average-for-the-year-to-December-2019.csv/preview, 2019. [Last accessed on: 5/5/2022].
- [276] M. D. Morris, “Factorial sampling plans for preliminary computational experiments,” *Technometrics*, vol. 33, no. 2, pp. 161–174, 1991.

- [277] F. Campolongo, J. Cariboni, and A. Saltelli, “An effective screening design for sensitivity analysis of large models,” *Environmental Modelling & Software*, vol. 22, no. 10, pp. 1509–1518, 2007. Modelling, computer-assisted simulations, and mapping of dangerous phenomena for hazard assessment.
- [278] A. Saltelli, M. Ratto, T. Andres, F. Campolongo, J. Cariboni, D. Gatelli, M. Saisana, and S. Tarantola, *Elementary Effects Method*, ch. 3, pp. 109–154. John Wiley & Sons, Ltd, 2007.
- [279] D. B. Boman, D. C. Hoysall, M. A. Staedter, A. Goyal, M. J. Ponkala, and S. Garimella, “A method for comparison of absorption heat pump working pairs,” *International Journal of Refrigeration*, vol. 77, pp. 149–175, 2017.
- [280] A. Messac, A. Ismail-Yahaya, and C. Mattson, “The normalized normal constraint method for generating the pareto frontier,” *Structural and Multidisciplinary Optimization*, vol. 25, no. 2, pp. 86–98, 2003.
- [281] PubChem [Internet]. Bethesda (MD): National Library of Medicine (US), National Center for Biotechnology Information, “PubChem Compound LCSS for CID 7853, Allylamine,” 2004. <https://pubchem.ncbi.nlm.nih.gov/compound/7853#datasheet=LCSS> [Last accessed on: 1/2/2022].
- [282] A. Najjaran, “Personal communication.” May 2021.
- [283] SPF Institute for Solar Energy, *Thermostrom Strebel AS 100 HP16. Solar collector factsheet C1112*. Accessed on: 14/6/2018.
- [284] Artic Solar, *Technology-Artic Solar*. [Last accessed on: 20/10/2020].
- [285] M. Sabiha, R. Saidur, S. Mekhilef, and O. Mahian, “Progress and latest developments of evacuated tube solar collectors,” *Renewable and Sustainable Energy Reviews*, vol. 51, pp. 1038–1054, 2015.
- [286] T. Osório, R. Pereira, A. Coelho, J. Marchã, J. Pereira, R. Silva, T. Eusébio, and M. Collares-Pereira, “A novel quasi-stationary CPC-type solar collector for intermediate temperature range applications for process heat: Simulation and experimental results,” *AIP Conference Proceedings*, vol. 2126, no. 1, p. 150006, 2019.
- [287] B. Widyolar, L. Jiang, J. Ferry, and R. Winston, “Non-tracking East-West XCPC solar thermal collector for 200 celsius applications,” *Applied Energy*, vol. 216, pp. 521–533, 2018.
- [288] “Bs en iso 9806:2017: Solar energy. solar thermal collectors. test methods,” 2018.
- [289] Y. Kurazumi, L. Rezgals, and A. Melikov, “Convective heat transfer coefficients of the human body under forced convection from ceiling,” *Journal of Ergonomics*, vol. 4, no. 1, 2014.

-
- [290] J. Chen, “Comments on improvements on a replacement for the logarithmic mean,” *Chemical Engineering Science*, vol. 42, no. 10, pp. 2488–2489, 1987.
 - [291] T. T. Godinho de Rezende, F. N. Teixeira, J. Antônio da Silva, L. G. Monteiro Guimarães, and M. dos Santos Guzella, “A non-intrusive method for evaluation ammonia mass flow rate in the condenser for diffusion-absorption refrigerators,” *Flow Measurement and Instrumentation*, vol. 72, p. 101695, 2020.
 - [292] “Weather Data — EnergyPlus.” <https://energyplus.net/weather>. [Last accessed on: 1/12/2021].
 - [293] M. MacDonald, “UK electricity generation costs update,” 2010.
 - [294] “Central Bank of Egypt.” <https://cbe.org.eg/en/>. [Last accessed on: 1/12/2020].
 - [295] L. Abdallah and T. El-Shennawy, “Evaluation of co₂ emission from Egypt’s future power plants,” *Euro-Mediterranean Journal for Environmental Integration*, vol. 5, no. 3, p. 49, 2020.
 - [296] “Egypt in figures 2018.” <https://www.sis.gov.eg/UP/Egypt%20in%20Figures%202018/egypt-in-numbers2018.pdf>, 2018. Central Agency for Public Mobilization and Statistics, [Last accessed on: 1/6/2020].
 - [297] K. Wang, M. Herrando, A. M. Pantaleo, and C. N. Markides, “Technoeconomic assessments of hybrid photovoltaic-thermal vs. conventional solar-energy systems: Case studies in heat and power provision to sports centres,” *Applied Energy*, vol. 254, p. 113657, 2019.
 - [298] World Bank Group, “State and trends of carbon pricing 2019,” 2019.
 - [299] Q. Li, C. Zheng, A. Shirazi, O. Bany Mousa, F. Moscia, J. A. Scott, and R. A. Taylor, “Design and analysis of a medium-temperature, concentrated solar thermal collector for air-conditioning applications,” *Applied Energy*, vol. 190, pp. 1159–1173, 2017.
 - [300] “2017 ASHRAE Handbook - fundamentals (SI): ASHRAE climatic design conditions 2009/2013/2017.” <http://ashrae-meteo.info/v2.0/>. [Last accessed on: 20/10/2020].
 - [301] UK Department for Business, Energy & Industrial Strategy, “Average variable unit costs and fixed costs for electricity for regions in the united kingdom.” https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1064502/table_224.xlsx, 2021. ECUK, UK, 2021 [Last accessed on: 1/6/2022].
 - [302] UK Department for Business, Energy & Industrial Strategy, “Updated short-term traded carbon values used for modelling purposes.” https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/794188/2018-short-term-traded-carbon-values-for-modelling-purposes.pdf,

REFERENCES

2019. ECUK, UK, 2021 [Last accessed on: 1/6/2022].
- [303] S. Kalogirou, *Solar Energy Engineering Processes and System*. Elsevier Academic Press, 2009.
- [304] “Solar collectors and photovoltaics in energypro.” <https://www.emd-international.com/files/energypro/HowToGuides/Solar%20collectors%20and%20photovoltaics%20in%20energyPRO.pdf>. [Last accessed on: 1/10/2021].

Appendix A

CAMD-DAR Optimal and Sub-optimal DAR Designs

Optimal and sub-optimal DAR designs recommended by proposed CAMD-DAR framework are presented in Figures A.1 and A.2

Table A.1: List of working fluids displayed in Figure 4.7 and Figure 4.8, WF1 and WF2 are defined in Table 4.2

ID	Refrigerant	Absorbent	Auxiliary gas
WF12	1-C ₄ H ₈	CH ₃ CH=CHNH ₂	H ₂
WF13	1-C ₅ H ₁₀	CH ₃ CH=CHNH ₂	He
WF14	1-C ₅ H ₁₀	CH ₃ CH=CHNH ₂	H ₂
WF15	[CH ₃] ₂ >CHCH=CH ₂	C ₂ H ₅ OH	He
WF16	[CH ₃] ₂ >CHCH=CH ₂	CH ₃ CH=CHNH ₂	He
WF17	2-C ₅ H ₁₀	1-C ₃ H ₇ OH	He
WF18	1-C ₄ H ₁₀	CH ₂ =CHCH ₂ NH ₂	He
WF19	<i>i</i> -C ₄ H ₁₀	CH ₂ =CHCH ₂ NH ₂	He
WF20	<i>i</i> -C ₄ H ₁₀	CH ₂ =CHCH ₂ NH ₂	H ₂
WF21	[CH ₃] ₂ >CHCH=CHCH ₃	CH ₃ CH=CHNH ₂	He
WF22	[CH ₃] ₂ >CHCH=CHCH ₃	CH ₃ CH=CHNH ₂	H ₂
WF23	2-C ₅ H ₁₂	CH ₂ =CHCH ₂ OH	H ₂
WF24	2-C ₅ H ₁₂	C ₂ H ₅ OH	He
WF25	2-C ₅ H ₁₂	C ₂ H ₅ OH	H ₂

- WF1: 2-C₄H₈-C₂H₅OH-He - WF5: C₂H₅NH₂-CH₂=CHCH=CHNH₂-He - WF9: [CH₃]₂>CHCH=CH₂-2,4-C₆H₁₀-He - WF27: C₃H₈-C₂H₅OH-He - WF31: CH₃NHCH₃-(CH₃)OH>CHCH=CH₂-He - WF35: C₃H₈-1-C₃H₇OH-He - WF39: CH₃NH₂-CH₃CH=CHNH₂-He - WF43: 2-C₄H₈-2-C₂H₅OH-He - WF47: C₃H₈-CH₂=CHCH₂NH₂-He - WF51: i-C₄H₁₀-C₂H₅OH-He - WF55: i-C₄H₁₀-1,2-C₇H₁₂-He - WF59: i-C₄H₁₀-1-C₆H₁₃OH-He	- WF2: 1-C₄H₈-CH₃CH=CHNH₂-He - WF6: CH₃NHCH₃-C₂H₅CH=CHNH₂-He - WF10: 1-C₄H₈-CH₂=CHCH=CH[CH₂]₂NH₂-He - WF28: C₃H₈-CH₃CH=CHNH₂-He - WF32: 1-C₄H₈-CH₂=CHCH=CHCH₂NH₂-He - WF36: CH₃NHCH₃-CH₂=CHCH₂OH-He - WF40: 2-C₂H₁₀-CH₂=CHCH=CHNH₂-He - WF44: C₃H₈-CH₂=CHCH₂OH-He - WF48: C₃H₈-CH₂=CHCH₂OH-He - WF52: i-C₄H₁₀-CH₂=CHCH₂OH-He - WF56: C₃H₈-[CH₃]₂>CHOH-He ★ Benchmark: NH₃-H₂O-He, 31 mol.%, 15.5 bar	- WF3: C₃H₈-CH₂=CHNH₂-He - WF7: 2-C₄H₈-CH₂=CHCH=CHNH₂-He - WF11: i-C₄H₁₀-[CH₃]₂>CHOH-He - WF29: i-C₄H₁₀-[CH₃]₂>CHCH=CHCH₂-He - WF33: 1-C₄H₈-CH₂=CHCH=CHCH₂OH-He - WF37: CH₃NHCH₃-C₃H₇CH=CHNH₂-He - WF41: CH₃NH₂-CH₂=CHCH=CHNH₂-He - WF45: [CH₃]₂>CHCH=CH₂-[CH₃]₂>CHCH=CHOH-He - WF49: i-C₄H₁₀-1,2-C₆H₁₀-He - WF53: [CH₃]₂>CHCH=CH₂-C₂H₅CH=CHNH₂-He - WF57: 1-C₄H₈-C₂H₅OH-He	- WF4: [CH₃]₂>CHCH=CHCH₃-CH₂=CHCH=CHNH₂-He - WF8: 1-C₄H₈-CH₂=CHCH₂OH-He - WF26: C₃H₈-CH₃CH=CHCH=CH₂-He - WF30: 2-C₄H₈-CH₃CH=CH[CH₂]₂NH₂-He - WF34: C₃H₈-C₂H₅OH-He - WF38: [CH₃]₂>CHCH=CH₂-CH₃CH=CHCH₂OH-He - WF42: 1-C₅H₁₀-NH₂CH₂CH=CHCH=CH₂-He - WF46: 1-C₄H₈-(CH₃)OH>CHCH=CH₂-He - WF50: 2-C₄H₈-CH₂=CHC₃H₇OH-He - WF54: CH₃NHCH=CH₂-CH₂=CHCH=CHNH₂-He - WF58: CH₂=CHCH=CHCH₂OH-He
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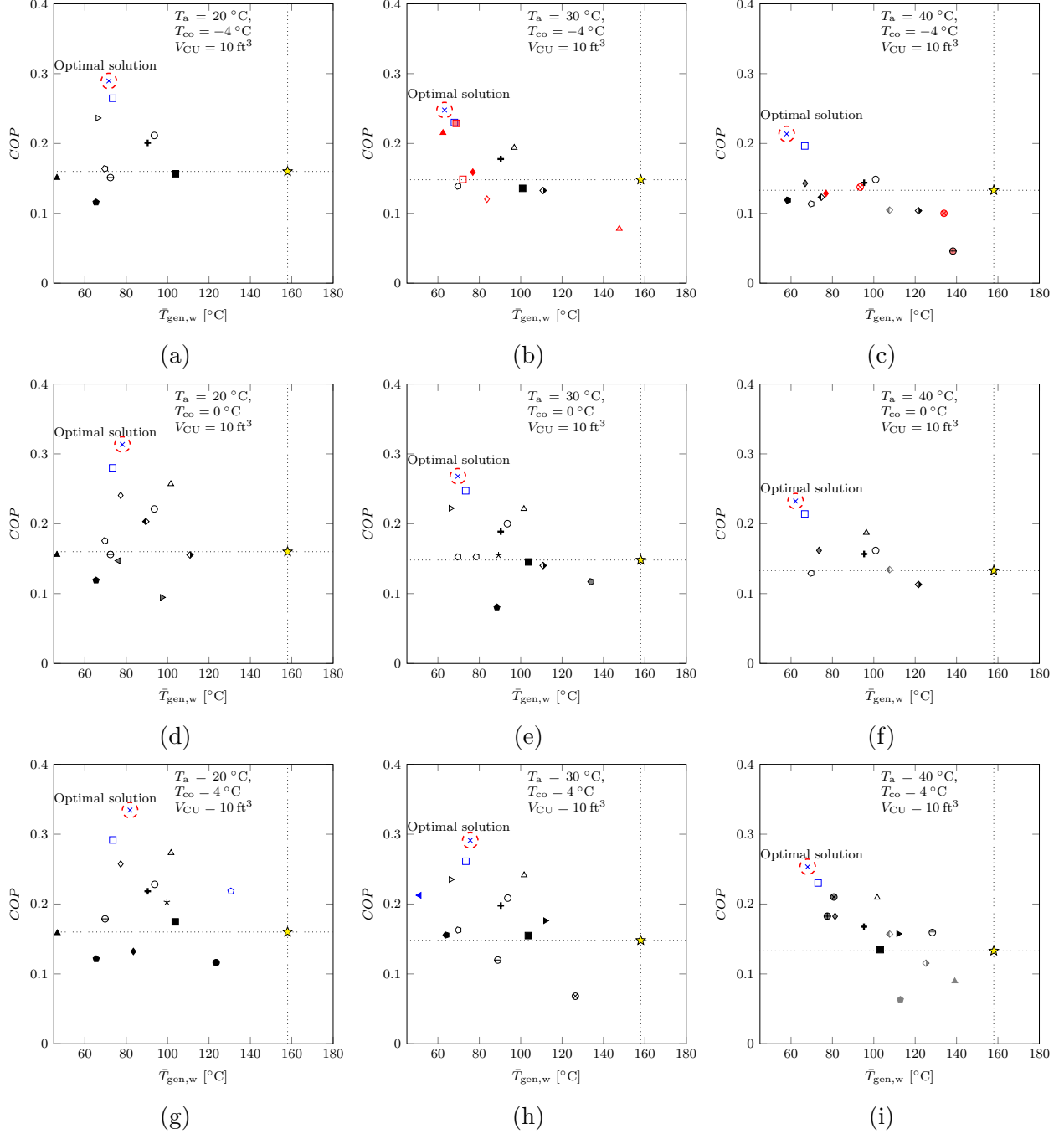


Figure A.1: Comparing optimal and sub-optimal results of MINLP optimisations to the benchmark NH₃-H₂O-DAR system simulations for three different ambient temperatures, $T_a = 20^\circ\text{C}$, 30°C and 40°C and three different cooling temperatures, $T_{co} = -4^\circ\text{C}$, 0°C and 4°C . The comparison presented in this figure considers comparing DAR coefficient of performance, COP against theoretical generator wall temperature, $T_{gen,w}$ for a 10-ft³ DAR unit (*i.e.*, ≈ 440 W rated power).

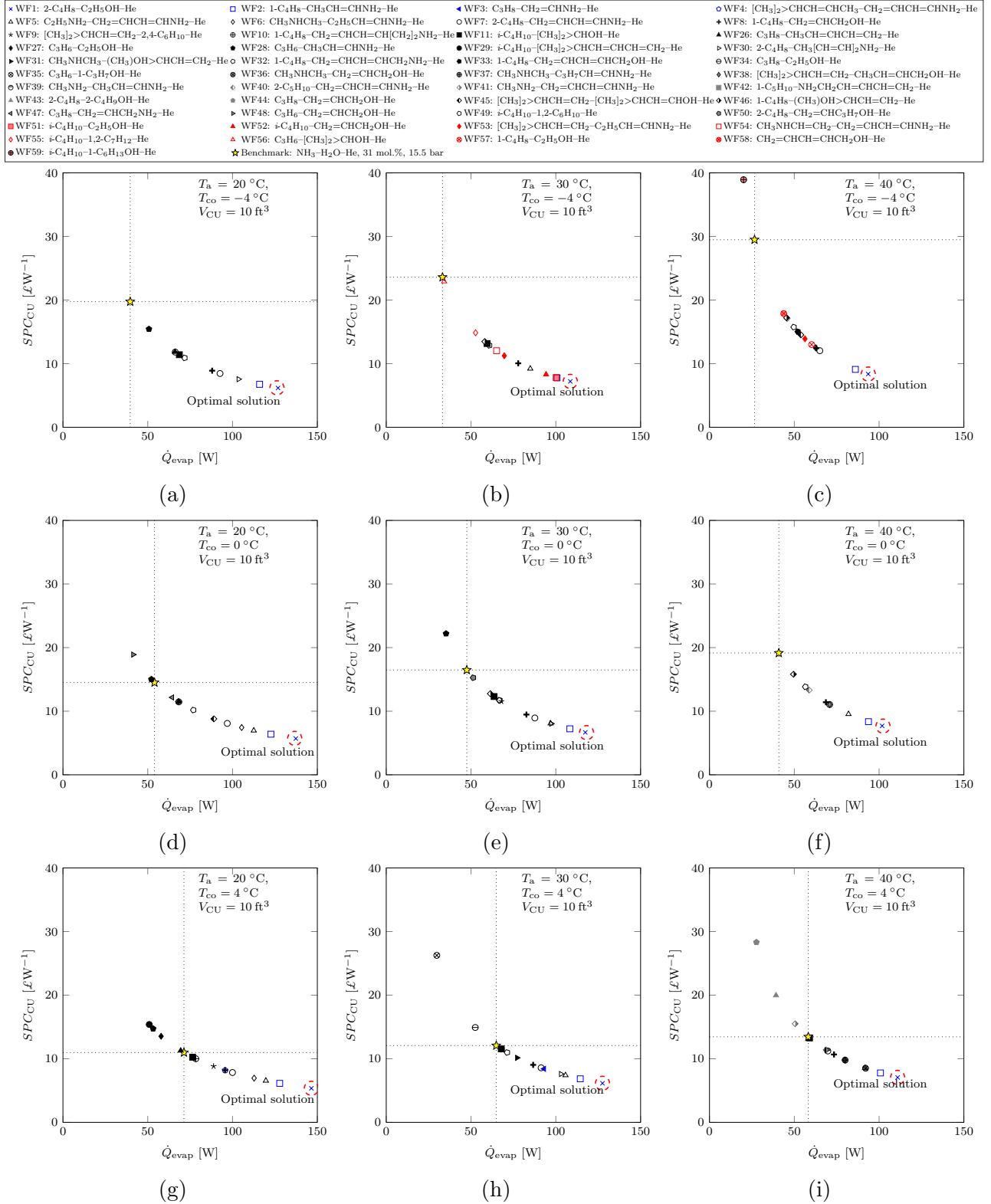


Figure A.2: Comparing optimal and sub-optimal results of MINLP optimisations to the benchmark $\text{NH}_3\text{-H}_2\text{O}$ DAR system simulations for three different ambient temperatures, $T_a = 20\text{ }^\circ\text{C}$, $30\text{ }^\circ\text{C}$ and $40\text{ }^\circ\text{C}$ and three different cooling temperatures, $T_{co} = -4\text{ }^\circ\text{C}$, $0\text{ }^\circ\text{C}$ and $4\text{ }^\circ\text{C}$. The comparison presented in this figure considers comparing the specific DAR purchased cost of cooling, SPC_{CU} against cooling rate, $\dot{Q}_{evap}$ for a 10-ft^3 DAR unit (*i.e.*, $\approx 440\text{ W}$ rated power).

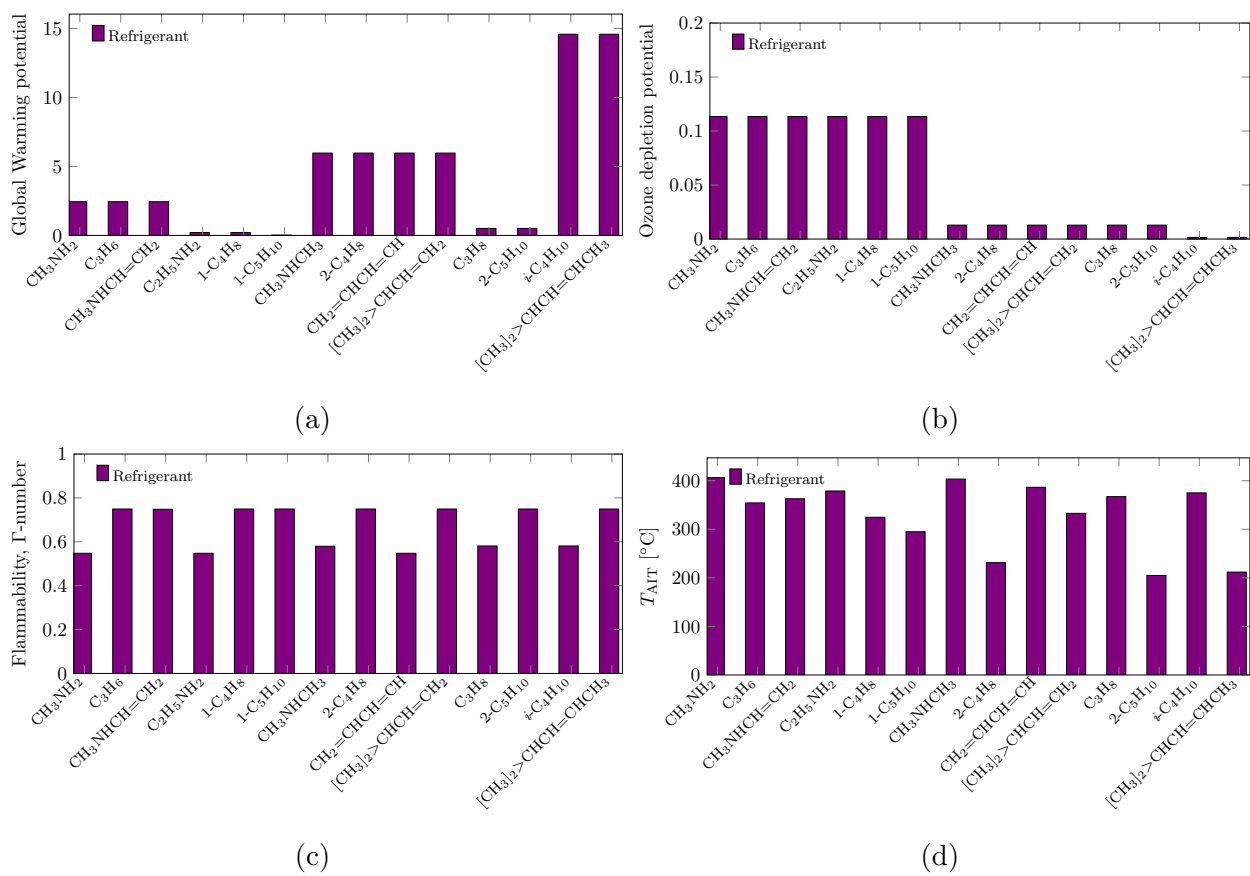


Figure A.3: Environmental and safety-relevant properties for refrigerants identified by the CAMD-DAR framework.

APPENDIX A. CAMD-DAR OPTIMAL AND SUB-OPTIMAL DAR DESIGNS

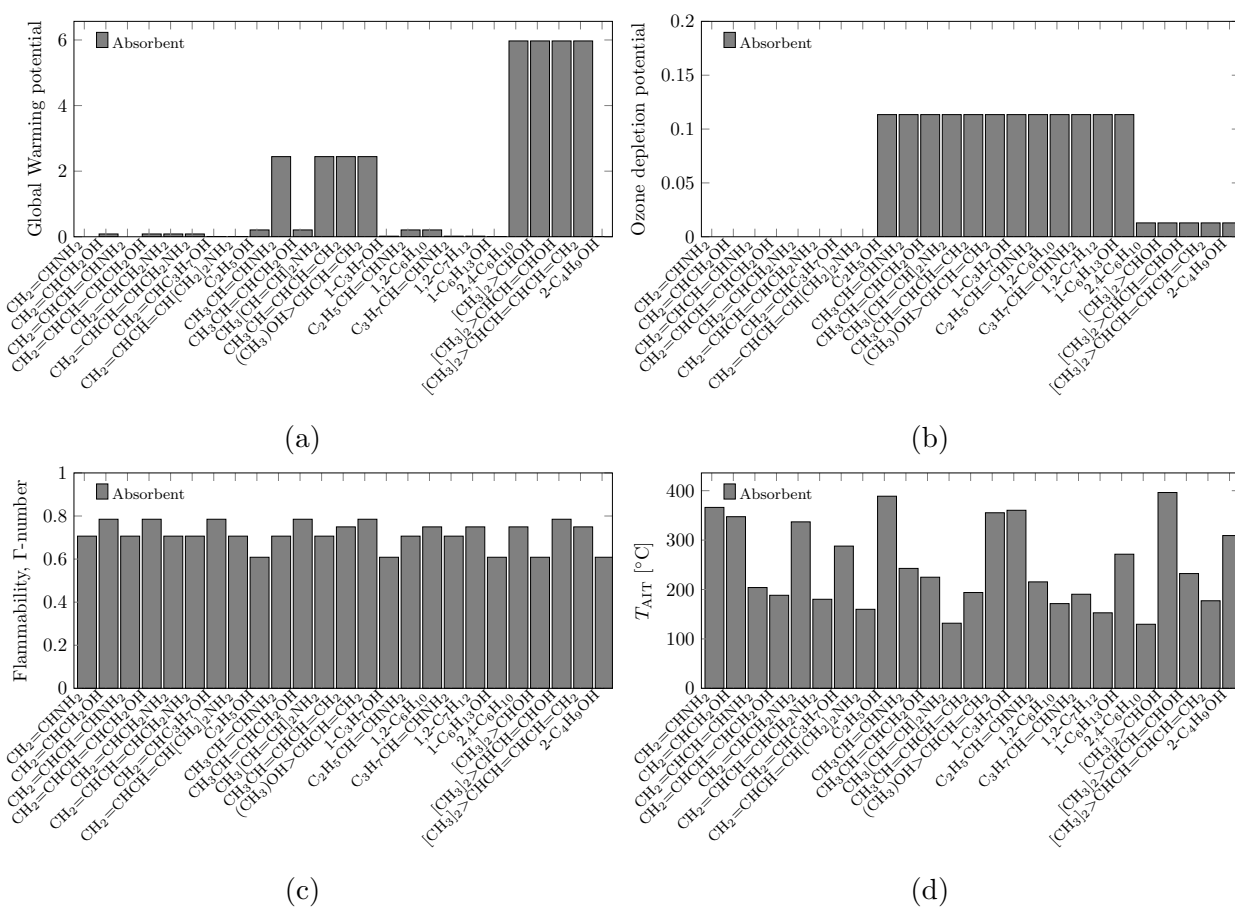


Figure A.4: Environmental and safety-relevant properties for absorbents identified by the CAMD-DAR framework.

Appendix B

Solar Calculations

Calculating incidence angle:

Input variables:

t	:	Time of the year	(h),
$month$	:	calendar month,	
$Hour$	:	hour of the day	[h],
N	:	day of the year (t/24),	
Lat	:	Latitude	(°),
$Long$	:	Longitude	(°),
TZ	:	Time Zone	(h),
DS	:	Day Light Saving	(min),
$tilt$	:	tilt angle ¹	(°),
orientation	:	orientation angle ²	(°).

The local longitude, LL in (°) is calculated from

$$LL = TZ \frac{180}{12} \quad (B.1)$$

The Equation of Time, ET , in min. is calculated as

$$ET = 9.87 \sin(2B) - 7.53 \cos(B) - 1.5 \sin(B) \quad (B.2)$$

where B in ($^{\circ}$) is calculated from the following equation

$$B = (N - 81) \frac{360}{365} \quad (\text{B.3})$$

Applying the daysaving (DS) when applicable, Calculate

$$\pm = \begin{cases} -1 & \text{if East} \\ +1 & \text{if West} \end{cases} \quad (\text{B.4})$$

The apparent solar time (AST) in hours

$$AST = LST + \frac{ET}{60} \pm 4(\text{Long} - LL) - \frac{DS}{60}, \quad (\text{B.5})$$

where $LST = \text{Hour}$. Kalogirou [303] calculated declination angle, δ in ($^{\circ}$) as

$$\delta = 23.45 \sin \left[\frac{360}{365} (284 + N) \right] \quad (\text{B.6})$$

While solar altitude angle, α in ($^{\circ}$) is

$$\alpha = \sin^{-1} [\sin(\text{Lat}) \sin \delta + \cos(\text{Lat}) \cos \delta \cos h] \quad (\text{B.7})$$

where h is the hour angle in ($^{\circ}$),

$$h = 15(AST - 12) \quad (\text{B.8})$$

The solar zenith angle, Φ in ($^{\circ}$) is $90 - \alpha$. The solar azimuth angle, z in ($^{\circ}$) is

$$z = \sin^{-1} \left(\frac{\cos \delta \sin h}{\cos \alpha} \right) \quad (\text{B.9})$$

For non-tracking collectors, the tilt angle in ($^{\circ}$), $\beta = \text{tilt}$, And the surface azimuth angle in ($^{\circ}$), $Z_s = \text{orientation}$. For non-tracking collectors the incidence angle can be computed from the following equation:

$$\theta = \cos^{-1} \left[\begin{array}{l} \sin(\text{Lat}) \sin \delta \cos \beta - \cos(\text{Lat}) \sin \delta \sin \beta \cos(Z_s) \\ + \cos(\text{Lat}) \cos \delta \cos h \cos \beta + \sin(\text{Lat}) \cos \delta \cos h \sin \beta \cos(Z_s) \\ + \cos \delta \sin h \sin \beta \sin(Z_s) \end{array} \right] \quad (\text{B.10})$$

$$R_b = \frac{\sin(\text{Lat} - \beta) \sin \delta + \cos(\text{Lat} - \beta) \cos \delta \cos h}{\sin(\text{Lat}) \sin \delta + \cos(\text{Lat}) \cos \delta \cos h} \quad (\text{B.11})$$

Following definitions from EMD document - Solar Collectors and Photovoltaic in energyPRO [304], the longitudinal incidence angle:

$$\theta_{\text{long}} = \tan^{-1} (\tan \Phi \cos(h - Z_s) - \beta) \quad (\text{B.12})$$

and transversal incidence angle

$$\theta_{\text{trans}} = \tan^{-1} \left(\frac{\sin \Phi \sin(h - Z_s)}{\cos \theta} \right) \quad (\text{B.13})$$

Longitudinal and transversal incidence angles are needed for incidence angle modifier calculations.

Calculating irradiance on tilted surfaces:

Input variables:

t	: Time of the year	(h),
G_{Bn}	: Direct Normal radiation	(Wm ⁻²),
G_{D}	: Diffusive horizontal radiation	(Wm ⁻²),
G_{on}	: Extraneous direct radiation	(Wm ⁻²),
Φ	: The solar zenith angle	(°)
θ	: The solar incidence angle	(°)
β	: The collector tilt angle	(°)
R_b	: beam tilt radiation factor	(°)

beam radiation on a horizontal surface, G_{B} in Wm⁻² is calculated as

$$G_{\text{B}} = G_{\text{Bn}} \cos \Phi \quad (\text{B.14})$$

$$G = G_{\text{B}} + G_{\text{D}} \quad (\text{B.15})$$

The isotropic ground reflectance, $\rho_g = 0.2$. Applying Reindl model, beam radiation on a tilted surface, G_{Bt} in Wm⁻²

$$G_{\text{Bt}} = R_b (G_{\text{B}} + G_{\text{D}} A) \quad (\text{B.16})$$

while diffuse radiation on tilted surface, G_{Dt} in Wm^{-2}

$$G_{Dt} = G_D(1 - A) \left[\frac{1 - \cos \beta}{2} \right] \left[1 + \sqrt{\frac{G_B}{G_B + G_D}} \sin^3 \left(\frac{\beta}{2} \right) \right] \quad (\text{B.17})$$

and Ground-reflected radiation on tilted surfaces, G_{Gt} in Wm^{-2}

$$G_{Gt} = (G_G + G_D) \rho_g \left[\frac{1 - \cos \beta}{2} \right] \quad (\text{B.18})$$

where the anisotropy index, A , is

$$A = \frac{G_{Bn}}{G_{on}} \quad (\text{B.19})$$

The total irradiance on a tilted surface can then be calculated using

$$G_t = G_{Bt} + G_{Dt} + G_{Gt} \quad (\text{B.20})$$

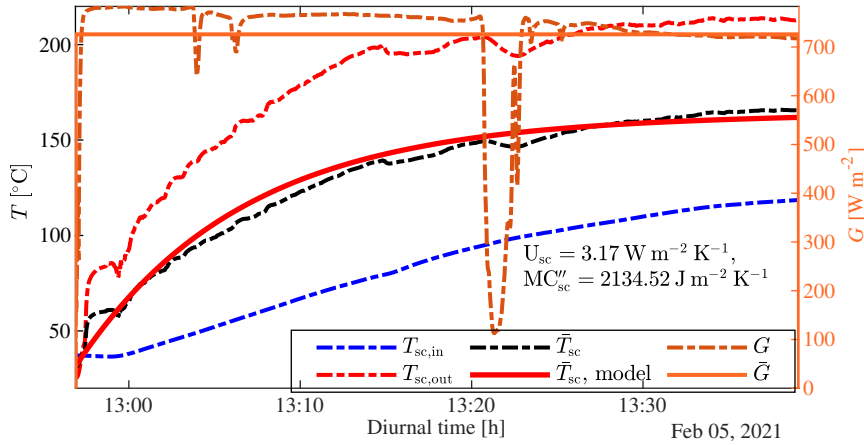


Figure B.1: Fitting parameters to model XCPC module on 2nd February 2021. The system cannot be well insulated and there is unavoidable heat losses from the solar collector system. Since there is no way for useful heat removal. The heat removed from the system is attributed to the losses from system connections to the ambient.

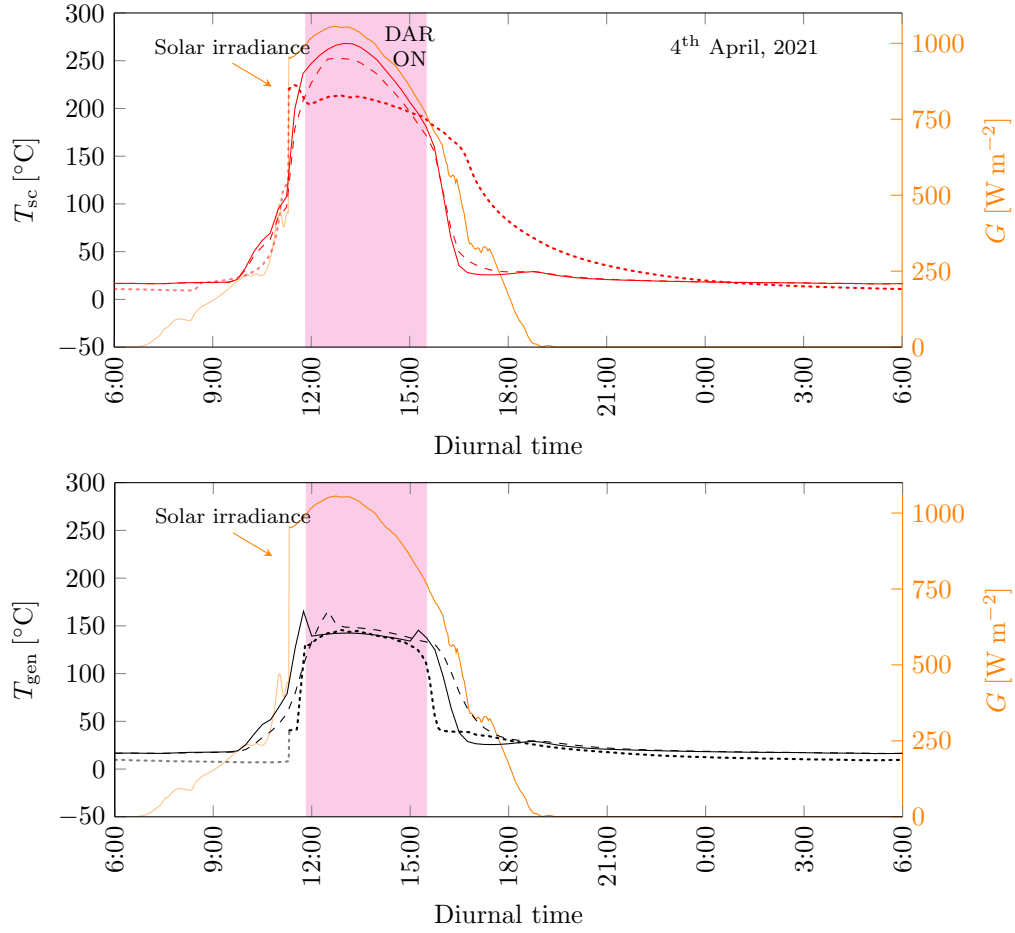


Figure B.2: Temperature measurement for solar-powered DAR systems against simulations on a sunny day in London (2nd of September 2018). Solar irradiance values were measured by Najjarian [282] using a solar-DAR unit powered by a single XCPC array.

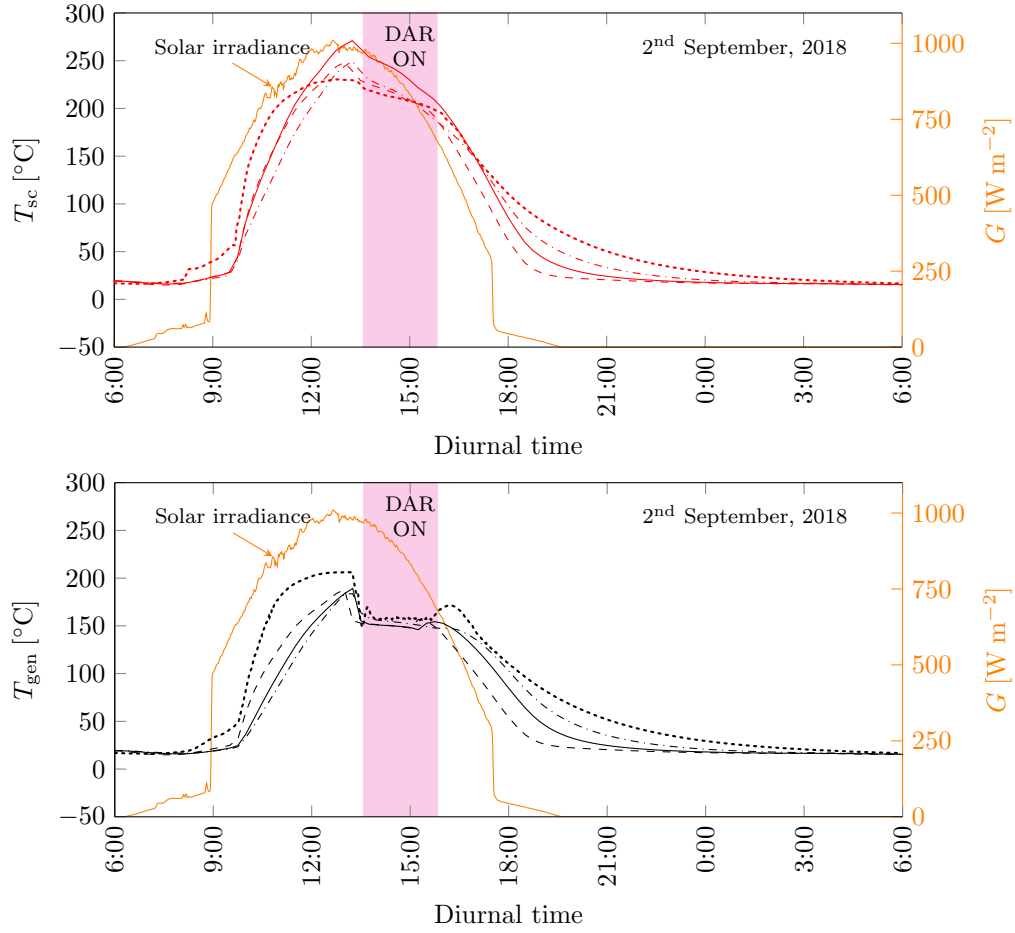


Figure B.3: Temperature measurement for solar-powered DAR systems against simulations on a sunny day in London (2nd of September 2018). Solar irradiance values are measured values taken from Ref. [95] using a solar-DAR unit powered by 4 ETC-HP tubes.

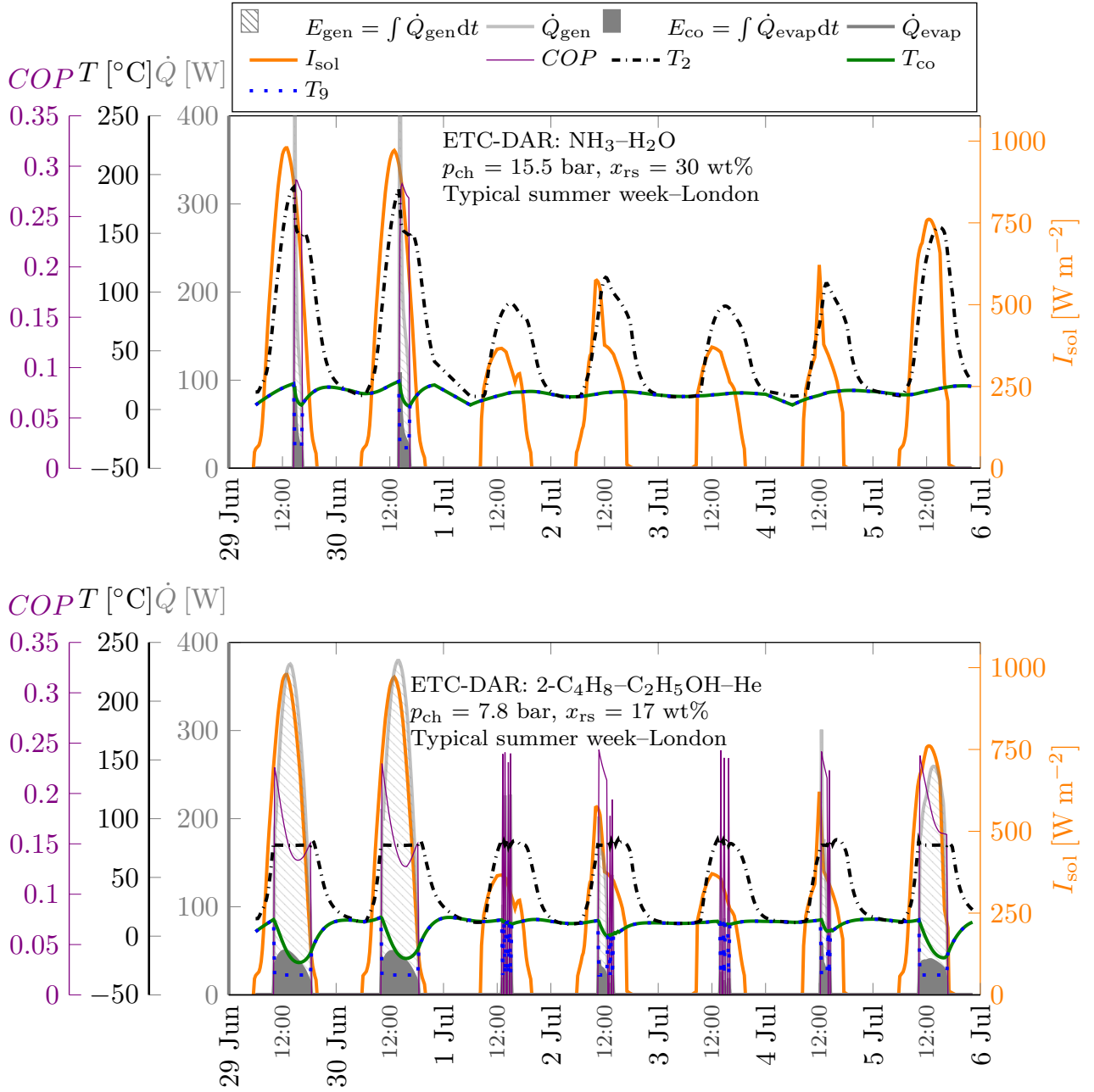


Figure B.4: Solar irradiance and solar-DAR operation during a typical summer week in London based on a solar-DAR powered by a 6-tube ETC array for two DAR systems with rated DAR power ($\dot{P}_{\text{DAR}} = 440 \text{ W}$): (a) benchmark DAR system charged with 30 wt% $\text{NH}_3\text{-H}_2\text{O}$ solution under 15.5 bar, and (b) DAR system with optimum working fluid identified in Chapter 4: $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ with $x_{\text{rs}} = 17 \text{ wt\%}$ refrigerant rich solution under 7.8 bar.

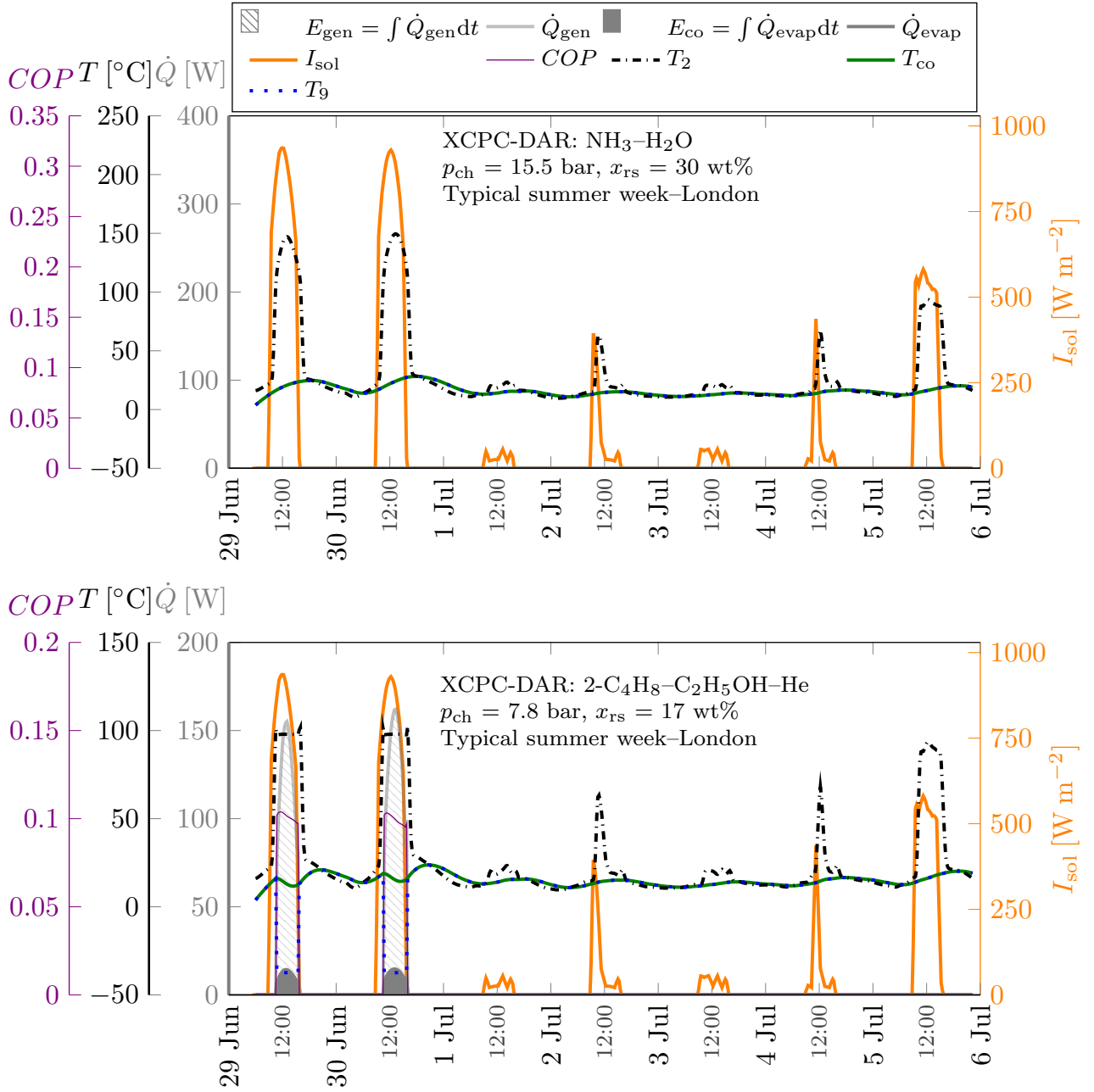


Figure B.5: Solar irradiance and solar-DAR operation during a typical summer week in London based on a solar-DAR powered by a single XCPC array for two DAR systems with rated DAR power ($\dot{P}_{\text{DAR}} = 440 \text{ W}$): (a) benchmark DAR system charged with 30 wt% $\text{NH}_3\text{-H}_2\text{O}$ solution under 15.5 bar, and (b) DAR system with optimum working fluid identified in Chapter 4: $2\text{-C}_4\text{H}_8\text{-C}_2\text{H}_5\text{OH}$ with $x_{\text{rs}} = 17 \text{ wt\%}$ refrigerant rich solution under 7.8 bar.

Appendix C

DAR Unit Dimensions

Table C.1: Typical DAR component sizes used in this study.

Component	Diameter	Length	Additional
Generator	$d_o = 6 \text{ mm}$ $d_{in} = 4 \text{ mm}$	$l = \begin{cases} 8 \text{ cm} & \text{if } V_{CU} \leq 4 \text{ ft}^3 \\ 10 \text{ cm} & \text{if } 4 \text{ ft}^3 < V_{CU} \leq 6 \text{ ft}^3 \\ 15 \text{ cm} & \text{if } V_{CU} > 6 \text{ ft}^3 \end{cases}$	
Bubble pump tube	$d_o = 6 \text{ mm}$ $d_{in} = 4 \text{ mm}$	$l = 90 \text{ cm}$	
Bubble pump shell	$d_o = 22 \text{ mm}$ $d_{in} = 19 \text{ mm}$	$l = 90 \text{ cm}$	
Rectifier	$d_o = 12 \text{ mm}$ $d_{in} = 10 \text{ mm}$	$l = 60 \text{ cm}$	
Condenser	$d_o = 12 \text{ mm}$ $d_{in} = 10 \text{ mm}$	$l = 360 \text{ cm}$	$N_{fins} = 48$ $t_{fin} = 0.5 \text{ mm}$ $w_{fin} = l_{fin} = 80 \text{ mm}$
Absorber	$d_o = 12 \text{ mm}$ $d_{in} = 10 \text{ mm}$	$l = 380 \text{ cm}$	
Evaporator	$d_o = 22 \text{ mm}$ $d_{in} = 19 \text{ mm}$	$l = 300 \text{ cm}$	
Reservoir	$d_o = 80 \text{ mm}$ $d_{in} = 76 \text{ mm}$	$l = 23 \text{ cm}$	

End of Thesis