Experimental and analytical assessment of a packed bed for thermal energy storage

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**EXPERIMENTAL AND ANALYTICAL ASSESSMENT
OF A PACKED BED FOR THERMAL ENERGY
STORAGE**

KHOR JUN ONN
Interdisciplinary Graduate School
Energy Research Institute @ NTU

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OF A PACKED BED FOR THERMAL ENERGY
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KHOR JUN ONN

**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

20 August 2020
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Date	Khor Jun Onn

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

27/08/2020	AR
Date	Assoc Professor Alessandro Romagnoli

Authorship Attribution Statement

This thesis contains material from 3 papers published/accepted in the following peer-reviewed journals where I was/will be the first and/or corresponding author.

Chapter 2.1 and 3 is published as Khor, J. O., Dal Magro, F., Gundersen, T., Sze, J. Y., and Romagnoli, A. "Recovery of cold energy from liquefied natural gas regasification: Applications beyond power cycles." *Energy conversion and management* 174 (2018): 336-355.

The contributions of the co-authors are as follows:

- Dr Fabio dal Magro provided the initial project idea and edited the manuscript drafts.
- I designed the study with Associate Professor Alessandro Romagnoli.
- I carried out the simulations required using ASPEN and carried out data analysis.
- I prepared the manuscript drafts. The manuscript was revised by Associate Professor Alessandro Romagnoli.
- Dr Truls Gundersen and Dr Sze Jia Yin revised the manuscript as well as carried out the proofreadings.

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The contributions of the co-authors are as follows:

- I provided the main idea as well as study direction, while Associate Professor Alessandro Romagnoli provided idea on data tabulation and analysis.
- I built the simulation model using MATLAB as well as carried out all the required simulations and data analysis.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Sze Jia Yin.
- Dr Sze Jia Yin and Dr Li Yongliang proofread the paper.

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The contributions of the co-authors are as follows:

- I provided the main idea as well as study direction.
- I built the simulation model using MATLAB as well as carried out all the required simulations and data analysis.
- I wrote the drafts of the manuscript, which is revised by Dr Bakytzhan Akhmetov.
- Associate Professor Alessandro Romagnoli and Dr Bakytzhan Akhmetov revised the paper.

21 August 2020

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Date

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Khor Jun Onn

Abstract

Liquefied natural gas (LNG) is a preferred distribution method for natural gas, particularly for long distance transport. LNG is regasified before distributed to the final consumers, releasing vast amount of cold energy. Majority studies on recovery of LNG cold energy involve conversion of cold energy into electricity. Usage of other energy carriers such as working fluids and thermal energy storage (TES) are seldom considered. When cold demands exist, cold-to-cold transfer from LNG terminal to demands using electricity as energy carrier can be unfeasible due to extra conversion process required. A study is carried out to compare the performances of different energy carriers, including electricity, working fluids, solid-liquid type phase change materials (PCMs) storage and liquid air energy storage (LAES), to transport LNG cold energy to different cold demands.

Four cold demands (air separation, dry ice production, deep-freezing warehouse and district cooling system) are considered, with their setups altered to adapt with different energy carriers. Layouts and performances of different cold demands subjected to different cold carriers are investigated in detail. On overall, using working fluids and PCM TES energy carriers result in 38.0% and 37.0% reduction in carbon emissions, which can be attributed to the replacement of conventional cooling systems in most cold demands supported by these energy carriers. Using LAES yields only 6.0% reduction in carbon emissions, due to the energy-intensive liquid air production process. Considering the costs and feasibility between working fluids and TES for cold distribution, TES is chosen as the next subject of study due to its lower capital and operational costs.

TES systems have been widely investigated for heat applications, but less for cold storage, while majority of them focus on low-grade cold storage such as space cooling.

Study of TES systems for storage of LNG cold is the first-of-its-kind during the point the study was carried out. A numerical study is carried out using Galden HT-55 as liquid-state heat transfer fluid (HTF) and has operating temperature as low as -80°C . Cascaded PCM in packed bed configuration (different PCM arranged in series), known with higher operational efficiencies, is chosen with three PCMs with different melting temperatures (-49°C , -19.5°C and 6.5°C). The study serves two objectives: (1) to find out the performance of PCM storage for low-temperature cold storage, especially in the real life where PCM's thermophysical properties deteriorates with decrease of phase change temperature, and (2) to minimize the amount of PCMs for optimum performances. Such optimization study is important as a lot of the time, TES systems act as auxiliary systems to other thermal systems, and their parameters are seldom optimized. The performances of TES system are evaluated based on the operation time and cyclic efficiencies on different TES capacity for each PCM. Cyclic efficiency is found to be the highest when ratio of TES capacity for high-medium-low grade PCMs is 10:7:5. Besides, with all the simulated cases, a generalized map is presented. The map allows a user to predict the performance of a cascaded PCM system with pre-determined storage capacity for each PCM. Besides, if the user has desired performance for the system, the map can be used to determine the suitable allocation of TES capacity for each PCM.

Liquid HTF based TES system has higher operating temperature and is unable to fully utilize all exergy of LNG cold, despite the high energy density of the HTF. Gaseous type HTF is thus investigated for charging an in-house-developed PCM. Due to lack of reported experiment for cold storage at temperature as low as -160°C , a packed bed TES experimental setup using in-house-developed PCM is thus built to achieve two purposes: (1) to obtain experimental results for more accurate validation of 3-D

simulation models due to clearer understanding on the operating conditions and (2) to investigate a high-grade cold TES system using gaseous type HTF. This TES for such high-grade cold storage (PCM with melting temperature of -118°C) is the first-of-its-kind.

From the experiments, the large void space in between the encapsulated PCMs which contributed to zero TES capacity and low efficiency of the system is identified as a key improvement area. Granular quartzite pebbles are inserted into the void space to reduce the void fraction. Experiments are then carried out to validate a new numerical model which considers two TES materials in a same numerical grid. Consideration of homogenous mixture of granular materials with PCM is never considered to improve performance of a packed bed PCM TES system. Thus, numerical studies are carried out to identify the influence of different granular materials under systems with different PCMs, encapsulation size and HTF flow rate. Insertion of granular materials improves the TES efficiency by up to 25%, particularly when the PCMs have ultra-low phase change temperature, due to materials' limitations with thermo-physical properties. Granular materials allow for increase in encapsulation size by up to 60% and decreases encapsulation cost by up to 75% without deteriorating performance of the system. Alumina particles are found to be the best granular material due to the extra storage capacity it provides due to its high density. Using micro-encapsulated PCM (n-decane) brings the highest improvement in cyclic efficiency, however, it is found that if micro-encapsulated PCM with lower phase change temperature is developed, the system performance can be further improved.

Thus far, 1-dimensional model has been used for numerical studies. However, some parameters of the TES system cannot be studied with 1-dimensional model, such as development of radial temperature profile due to energy loss via the tank wall, as well

as additional of inlet from the side where radial flow component needs to be studied. A 3-dimensional COMSOL simulation model is built and validated with the experimental results to study the development of temperature profile in both axial and radial directions of a TES tank, as well as change in performance of system under influence of auxiliary input with different HTF flow direction. Due to the thermal energy via tank wall, it is found that the temperature gradient along HTF axial-flow direction increases, which elongates the charge time of a TES system as PCMs near the tank wall is subjected to reduced thermal power. Side injection inlets are thus proposed to supply HTF with high-grade cold energy directly, to increase the thermal power in the region near the tank wall. However, usage of side inlet alone is unable to solve the problem directly, as mixing occurs between diverted flow from the side inlet and the flow from the main inlet, resulting in great exergy losses, especially if the resultant mixture has temperature higher than the PCM phase change temperature. Thus, operational parameters are also considered where at the beginning of the charging stage, only main inlet is used. After a certain amount of time, part of the flow entering the main inlet is redirected to the side inlet, while maintaining the total flow rate into the system. Such configuration is found to able to decrease the charge time by up to 13.4%.

The abovementioned study identified three aspects on how a TES system designed for cryogenic cold storage can be designed and improved. When all the aspects are considered during design stage, there is no doubt that an optimized TES system, not only for storage of LNG cold, but also for a generic storage of thermal energy can be designed.

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Nomenclature

Acronyms

A-CAES	Adiabatic CAES	LAES	Liquid air energy storage
AAV	Ambient air vaporizer	LHTES	Latent heat TES
CAES	Compressed air energy storage	LNG	Liquefied natural gas
CC	Combustion chamber	LPC	Low pressure column
CHP	Combined heat and power	MSHE	Multi-stream heat exchanger
COP	Coefficient of performance	ODP	Ozone depleting potential
CP	Compressor	ORC	Organic Rankine cycle
CSP	Concentrated solar power	ORV	Open rack vaporizer
EP	Expander	PBTES	Packed bed TES
GUI	Graphical user interface	PCM	Phase change material
GWP	Global warming potential	PHES	Pumped hydroelectricity storage
HC	Hydrocarbon	PP	Pump
HCFC	Hydrochlorofluorocarbon	PTES	Pumped thermal electrical storage
HFC	Hydrofluorocarbon	PV	Photovoltaic
HFO	Hydrofluoroolefin	RTD	Resistance temperature detector
HPC	High-pressure column	SCV	Submerged combustion vaporizer
HRSG	Heat recovery steam generator	SHTES	Sensible heat TES

HX	Heat exchanger	TES	Thermal energy storage
Chemical formula			
Al	Aluminum	LN ₂	Liquid nitrogen
Al ₂ O ₃	Aluminum oxide	LO ₂	Liquid oxygen
C	Carbon	N ₂	Nitrogen
CO ₂	Carbon dioxide	R1234yf	2,3,3,3-Tetrafluoropropene
H	Hydrogen	R1234ze	1,3,3,3-Tetrafluoropropene
HCl	Hydrogen chloride	R134a	1,1,1,2-Tetrafluoroethane
LiCl	Lithium chloride	R22	Chlorodifluoromethane

Parameters

a	Surface area to volume ratio	p	Thickness
A	Surface area	P	Pressure
c_p	Specific heat capacity	Pr	Prandtl number
d_p	Particle diameter	Q	Heat transfer
D	Tank/pipeline diameter	r	Radius
E	Exergy content	Ra	Rayleigh number
e	Specific exergy	Re	Reynolds number
ε	Void fraction	Res	Resistance
η	Efficiency	ρ	Density
F	Geometric factor	s	Specific entropy

h	Heat convection coefficient	t	Time
H	Enthalpy	T	Temperature
k	Thermal conductivity	U	Heat loss coefficient
K	Permeability	v	HTF velocity
L	Length	V	Volume
Nu	Nusselt number	W	Work done

Chapter 1. Introduction

1.1. Background studies

Fossil fuels, including coals, oils and natural gases have been the main driving force for major developments of the society in terms of technology and economy since the industrial revolution, and have remained so at the time-being due to their high energy density and availability. According to the British Petroleum statistical review of world energy [1], total primary energy consumption in 2018 was 13684.9 million tons of oil equivalent (MTOE), or 161.25 peta-Watt-hour (PWh) of energy. Fossil fuels contributed to 84.70% of the total primary energy consumption, which can be further divided into coals (27.21%), oils (33.62%) and natural gases (23.87%).

World energy consumption is projected to increase due to technology development and raise of living standards. According to the International Energy Agency (IEA) [2], world energy consumption is projected to increase by 50% between year 2018 and 2050 towards 911 quadrillion British thermal units (BTU), which is equivalent to 267.0 PWh of energy. Consumptions of coals, oils and gases are predicted to increase by 0.4%, 0.6% and 1.1% yearly. With the abovementioned growth rates for different energy sources, natural gas is projected to replace coal as the second largest fossil fuel-based primary energy source after oils in 2050. The growth of natural gas consumption is caused by policy calls and fuel costs [2]. In 2050, the consumption of natural gas is expected to increase by more than 40% compared to 2018 to 200 quadrillion BTU (58.6 PWh).

For Singapore, the main sources of primary energy consumption are oils and gases, which in 2016, 45.49% of primary energy consumption comes from oil products and 48.48% comes from natural gas [3, 4]. The main use of natural gas in Singapore is electricity generation, which consumes 86.01% of natural gas supply. Choice of natural

gas over other fossil fuels for electricity generation is due to a few reasons. Natural gas is cleaner than other fossil fuels as it is mainly composed of methane, with the smallest carbon to hydrogen (C-H) ratio [5]. During complete combustion, only one molecule of carbon dioxide (CO₂) is emitted from one methane molecule, which reduces the emissions compared to other fossil fuels. Other than that, power plants using natural gas as energy source is more versatile as it takes much less time to start and stop [6]. Also, IEA reported in 2016 that a gas-fired power plant is cheaper, as investment cost of gas-fired power plant costs less than US\$1,000 per kW compared to about \$3,600 per kW for a coal-fired power plant [7].

According to statistics from Singapore Energy Market Authority, 51.6 TWh of electricity was generated in 2016 in Singapore [3]. The electricity generation is projected to increase to between 60.6 and 64.1 TWh by 2027 [8], which indicates an increase between 17.4% and 24.2%. The consumption of natural gas will increase if the electricity generation portfolio remains unchanged and no major improvement on performance of gas-fired power plants. As a country with limited natural resource especially fossil fuel reserve, Singapore will continue to depend on natural gas import to keep up with the increase on electricity generation capacity. Before 2010s, Singapore depended on its neighboring countries with natural gas reserves (Malaysia and Indonesia) for natural gas import via pipelines. Since 2013, liquefied natural gas (LNG) has become an alternative option after completion of Singapore's first LNG terminal for energy source security and diversification purpose [9]. In 2018, 4 LNG terminals have been completed in Singapore, with natural gas send-out capacity of 11 million tons per annum (MTPA).

Pipeline has been the safest, most reliable and convenient distribution option for natural gas, which is readily available in gas form. However, not every location in the world is

accessible or connectible to a natural gas resource through a pipeline. Such inaccessibility of pipelines can be due to border between countries, terrain between locations or simply the distance between the resource and demand.

Transporting natural gas across long distances, particularly across the continent, is a big problem due to its low density. Thus, LNG is developed as alternative transportation method for natural gas, which is proven to be a successful option for the past three decades [10]. Natural gas liquefies at -160°C under ambient pressure, and thus work needs to be supplied for the refrigeration process. Various refrigeration cycles for natural gas liquefaction have been developed, which can be divided into two main types: cascaded processes and mixed refrigerant processes [11]. For a real-life liquefaction process, up to 10% of feed natural gas is consumed to provide the required energy for compression work. LNG produced is then transported using cryogenic tankers or trucks to the destinations [10].

After being liquefied, the volume of natural gas is reduced by 600 times, with density of about 400 kg/m^3 . Its temperature is also reduced to below -162°C under atmospheric pressure. Due to LNG's ultra-low temperature, if handled properly, useful thermal energy can be retrieved in the form of sensible heat and latent heat (due to liquid-gas phase change), on top of its chemical energy. Losses incurred during the liquefaction process can thus be partially recovered and thereby improving the economy of LNG. When LNG reaches its destination, prior to its distribution to the end users, it must be regasified and heated to near ambient temperature. During the regasification process, about 860 kJ of cold energy is released [12], which includes the latent heat that LNG absorbs to vaporize from its liquid state to gaseous state and the sensible heat used to elevate the temperature of LNG from -160°C to ambient temperature. Amount of cold exergy released is estimated to be 370 kJ/kg [13].

Conventional regasification of LNG is carried out using specially designed heat exchangers. There are three most commonly used heat exchangers: (a) open-rack vaporizer (ORV), (b) submerged combustion vaporizer (SCV) and (c) ambient air vaporizer (AAV) [10]. An ORV uses water or seawater as heat source for the regasification. To receive LNG transported by cryogenic tankers, an LNG terminal is generally located close to the sea to facilitate the unloading process. Thus, ORV is most commonly used, as regasification can be carried out at the LNG terminal where seawater is readily available. ORVs are estimated to contribute to about 70% of all types of LNG vaporizers [10]. Figure 1.1(a) shows the schematic diagram of an ORV [10], where seawater is taken in via a pump and passed through the vaporizer, exchanging heat with LNG in the process.

An SCV combusts part of the vaporized LNG to generate required amount of heat energy for LNG regasification. This regasification process utilizes about 1.5% of the natural gas product, which increases the operating cost of the regasification facility. Figure 1.1(b) shows the schematic diagram of an SCV [10], where natural gas is burned to warm a water bath, which is subsequently used to vaporize the LNG passing through it. Despite its higher operating cost, an SCV is favourable only when natural heat sources such as seawater is not available for regasification process, which can be due to the geographical reason (e.g. in-land portable LNG regasification facilities) or environmental considerations (to prevent temperature fluctuation on seawater).

An AAV is another regasification option without needing to use seawater or combusting the vaporized natural gas. In this vaporizer, ambient air is used as heat source, and thus is more environmentally friendly than the ORV and SCV with no emission and minimal environmental impact. However, due to low volumetric energy

density of ambient air compared to seawater and natural gas, an AAV needs larger heat transfer area for regasification and thus larger space.

Figure 1.1: Schematic diagrams of (a) an ORV and (b) an SCV vaporizer [10]

All the three abovementioned commercially available LNG vaporizers share a same characteristic: the high-grade cold energy of LNG is not recovered but consumed internally or released into the atmosphere. Such wastage of energy is worsened with mechanical work consumed for the regasification process, such as work used to drive the LNG pumps, seawater pumps or ambient air fans.

In Singapore, the total import of natural gas has been increasing every year from 2014 to 2018, which the percentage of contribution by LNG grows from 11.0% in 2013 to

28.6% in 2018 [14]. Contract of a pipeline gas from neighboring countries are also subjected to the countries internal demands and contracts. Thus, Singapore is projected to rely more on LNG import to meet its gas demand, which marks a possible economy return for harvesting the cold energy due to larger-scale LNG regasification. LNG is not only traded in Singapore, and worldwide LNG trade is projected to increase from 153 gigatonnes¹ in 2012 to about 370 gigatonnes in 2040 [15]. Such trade amount in 2040 is equivalent to averagely 10.1 GW of cooling power released worldwide. Looking at the current trend of growth for LNG trade around the world, there is a need to recover the cold energy from LNG, especially in tropical countries like Singapore where the cold demand is high throughout the year. A case study is carried out (detailed in Chapter 3) to compare the performances of different energy carriers in transporting cold energy from LNG regasification terminal to the cold demands.

From the study, thermal energy storage (TES) and working fluids are the two best candidates as energy carriers. In both cases, usage of fossil fuel primary energy is greatly reduced as cold energy is now supplied with these energy carriers (from physical cold energy of LNG) instead of conventional refrigeration cycles. Reduction in fossil fuel consumed is translated to reduction in carbon emissions. Despite the investigated energy carriers may not be able to fully support some of the cold demands with high-grade cold requirement, dependency on electricity can be greatly reduced due to presence of lower-than-ambient cooling medium for more efficient intercooling and reduction in compression work. Conventional heat pump cooling systems which are used to provide intercooling are also replaced with the energy carriers.

¹ LNG density is assumed as 450kg/m³ or 12.74kg/ft³

Although TES system yields higher carbon emission than a district thermal network, TES system is chosen as the subject for the second stage of research because of their significantly lower infrastructure cost compared to the thermal network, where pipelines need to be built, insulated and overcome geographical and terrain factors between the cold energy supply and demands. Besides, using a TES system allows for choices from abundance of storage materials compared to thermal network where selection of working fluids is limited to fluidic type. Such selection ensures better temperature match between the storage and the processes at cold demand, which exergy destruction during the heat transfer process can be minimized.

1.2. Motivation and research gaps

The wasted cold energy during regasification process should be meaningfully reused and monetized by LNG terminal operators. There are some currently in-place cold recovery technologies, as demonstrated by most LNG regasification facilities in Japan. However, most of these facilities designed their cold demand during the planning of regasification facilities. However, in real life, different types of cold demands exist, with different requirements on the cold temperatures.

Besides, there exist different energy carriers which are able to distribute the cold energy released during LNG regasification. With the author's best knowledge, there is no proper case study which research about the best type of energy carrier which fits the usage of different cold demands. There is also no study which evaluates the performance at the cold demands' side when the demands are given different choices of energy carriers. Thus, it is unknown that which energy carrier is the best choice for such LNG cold utilization. This drives the first study carried out by the author, which

studies the performances of different energy carriers at different stages, from their generation or charge processes to their distributions, and finally their consumptions at the cold demands' sides. The performances are evaluated based on 2 main criteria: carbon emissions and exergy efficiencies.

TES systems have been widely studied from a few aspects, from the types of materials, applications of these systems as well as the numerical simulations of these systems. However, most systems focused on heat energy recovery, mainly generated by solar thermal. In contrast, study of storage of cold energy is limited, which most of them focus on building comfort. With expansion of LNG trade around the world, the amount of cold energy released every year from LNG regasification also increases significantly and can form an economy chain which is profitable. TES system can be used as energy carrier for cold transfer from the LNG regasification facility to other cold demand, and the performance of TES should be investigated and optimized.

Thus far, study on TES system based on high-grade cold storage is very scarce, with the only example demonstrated in a LAES system where quartzite rock is used [16], which is a sensible storage with limited storage density. Storage of energy using latent heat storage is more efficient due to higher energy density, however, is also non-existent to the point this study is carried out, despite commercial PCMs with phase change temperature as low as -114°C have been developed. Thus, there is a need to look into experimental investigation of such system to understand its performance, as well as allows for generation of experimental data for numerical validation purpose.

TES systems using cascaded materials have been investigated by a few researchers. However, a lot of the time, the cascaded TES materials are assigned similar capacity or volume, which improves the performance but the performance is not optimized. Thus,

a study is carried out to identify combination of different capacity of different TES materials in a cascaded TES system, to understand the optimize combination of each material.

TES systems using macro-encapsulated PCM materials have high energy density, but also possess problems such as high void fraction, which subsequently reduces the overall storage capacity. During the experimental study, it is found that using granular materials can effectively reduce the void space of the TES system. A numerical study is thus carried out to understand the change in performance of the TES system, when subjected to different types of granular materials under different operating conditions. Such bidisphere packing has been investigated mainly for optimization of packing, but the thermal performance investigation is never carried out.

1-dimensional numerical study is proven to be good enough for prediction of temperature in axial direction of a TES system when subjected to flow of HTF in the same direction. However, in a real-life system, temperature variation in the radial direction of a cylindrical TES tank often exists due to 2 main reasons: (1) thermal energy loss to the surroundings and (2) extra thermal load due to the tank wall material. Such temperature variation may delay charge of TES materials near the side wall, and design to solve the problem can only be done in numerical study of 2-dimensional and above. TES tanks are subjected to slower charging at the region near to tank wall due to energy loss, and auxiliary inlet, near to the tank wall, is investigated to try to overcome the abovementioned problem.

1.3. Objective and scopes

This study serve a few objectives, which are listed as below:

- i. To identify the performances of different cold demands when they are subjected to different energy carriers carrying cold from LNG regasification facility
- ii. To identify the best energy carrier that is able to serve multiple cold demands simultaneously, with reasonable investment and operational costs and operational performances
- iii. For the best energy carrier identified (TES), to understand the experimental behavior of the system under normal operations of charging and discharging
- iv. To identify possible improvement on cascaded TES, which assignment of TES capacity has been random and not optimized
- v. To identify possible design of generalized map for pre-selection of TES materials capacity for desired performances
- vi. To identify other enhancement of packed bed TES systems by reducing the void fractions using different granular materials
- vii. To identify possible improvements on thermal energy storage system based on geometrical aspects, especially auxiliary inlet on the thermal storage system

1.4. Structure of thesis

This thesis consists of a few chapters, which are detailed as follow:

- Chapter 2 reports the literature review carried out based on the cold recovery of LNG and thermal energy storages.
- Chapter 3 reports the case study carried out to identify the best choice of energy carrier to recover and transport the cold energy from LNG regasification terminal to different cold demands.

- Chapter 4 reports the numerical simulation on using liquid-type HTF to recover the LNG cold and store the cold energy in PCM. Cascaded PCMs configuration is investigated, to allow better understanding on the amount of PCM for each type of PCM and proposed a design map which allows designers to estimate the amount of each PCM during design stage.
- Chapter 5 reports the experimental investigation on vapour-type HTF system for recovery of cold energy as low as -160°C . An experimental setup utilizing PCM with -120°C phase change temperature is used, while nitrogen is used as the HTF. Transient temperature variation during charging and discharging operations are used to validate numerical models for cold charging at such low temperature.
- Chapter 6 investigates numerically the performance of a packed bed TES system after reducing its void space using granular materials. Void space is a common drawback for packed bed type storage and contributes to no thermal storage capacity. Different granular materials are used to fill in the void to provide extra storage capacity and better performances.
- Chapter 7 investigates numerically the probability of using auxiliary inlet on the side of TES tank wall to improve the performance using 3-dimensional simulation. Due to thermal losses on the side of the tank wall, and the low diffusivity of vapour-type HTF, the side of tank wall always suffer from prolonged charge time and lower the efficiency of the charge process. Thus, auxiliary inlet is investigated to improve the charge behaviour in this region.
- Chapter 8 concludes the thesis and provides some suggestions on possible future works.

Chapter 2. Literature Review

2.1. Utilization of LNG cold energy

Different utilization method of LNG cold has been implemented in several countries as summarized in Table 2.1. As the world's largest LNG importer, Japan demonstrates a large variety of LNG cold recovery technologies which are in-use. Between 20 to 30% of LNG cold energy is utilized in Japan, with Osaka Gas Co. setting up the first plant in Japan to achieve 100% utilization of LNG cold energy, by cascading a few applications with different temperature requirements for cold energy in series [17]. South Korea, as the world's second largest importer of LNG, has also utilized LNG cold for air separation and cryogenic comminution [18].

Table 2.1: Processes and countries where utilizations of LNG cold are reported [19-21]

Process	Temperature range (°C)	Country
Air separation	-191 to -130	China, France, Japan, South Korea
Electricity generation	-160 to 0	Japan
Hydrocarbon liquefaction	-120 to -60	Japan
Cryogenic comminution	-110 to -60	Japan, South Korea
Liquid CO ₂ / dry ice	-60	Japan
Refrigeration/cold storage	-30 to 0	Japan, South Korea
Seawater desalination	-10 to 10	United States
Gas turbine inlet air cooling	0 to 10	India, Japan

Among all the utilization methods for LNG cold, electricity generation is the most discussed in the literature due to its possibility to be implemented in different electricity generation cycles. For a Carnot's heat engine, it is straightforward that the cycle

efficiency increases in proportional to the temperature difference between the hot and cold reservoirs [22]. Other heat engines also behave similarly. When LNG cold replaces the conventional heat sinks in a heat engine (i.e. cooling water), the performance is expected to improve. Almost all well-known heat engines can be coupled with LNG cold to improve their performances, and are reviewed thoroughly by Gomez [13]. For example, compressor inlet temperature of Brayton cycles can be effectively reduced with LNG cold. For Rankine cycles, condensation temperature of working fluid can be reduced using LNG cold instead of cooling water, allowing for higher pressure ratio of working fluid. Combined cycles are able to combine both the abovementioned usages of LNG cold.

There are also power cycles that work on mechanical energy of LNG, such as direct expansion cycle [23]. LNG works as working fluid in this direct expansion cycle, which is pumped to a higher pressure before heated with environmental heat source such as seawater or solar thermal for vaporization into high-pressure vapor, which is subsequently used to power a turbine. LNG cold can also be used as exergy source to power an organic Rankine cycle (ORC) without high temperature heat source [24]. Such ORC uses organic fluid with low boiling temperature as working fluid. Operation of the ORC is similar to a Rankine cycle, but it uses environmental resources such as seawater as heat source and LNG cold as heat sink.

Power cycles utilizing LNG cold to improve their performances that are discussed in the literature are summarized in Table 2.2, together with their reported performances, thermal efficiency (η_{th}) and exergy efficiency (η_{ex}).

Table 2.2: Summary of power cycles utilizing LNG cold to improve their performances

T_{min} (°C)	T_{max} (°C)	Type of cycle	Heat source	Working fluid	Efficiencies	Ref.
-160	80	Rankine cycle + direct expansion cycle	Flue gas	Tetrafluoromethane or propane	η_{th} not reported $\eta_{ex} = 52.00\%$	[25]
-150	30	Rankine cycle + direct expansion cycle	Exhaust heat	Methane + ethylene + propane	η_{th} not reported $\eta_{ex} = 38.90\%$	[26]
-145.7	800	Brayton cycle	Fuel	Nitrogen	$\eta_{th} = 69.00\%$ η_{ex} not reported	[27]
-144	1000	Series of Brayton cycle + Rankine cycle	Fuel	Helium and steam	$\eta_{th} = 65.61\%$ $\eta_{ex} = 55.09\%$	[28]
-144	1000	Brayton cycle + Rankine cycle (combined cycle)	Fuel	Helium and carbon dioxide	$\eta_{th} = 65.07\%$ $\eta_{ex} = 53.70\%$	[29]
-141.9	10	Kalina cycle	Seawater	Tetrafluoromethane + propane	$\eta_{th} = 23.50\%$ η_{ex} not reported	[30]
-139.3	800	Brayton cycle	Fuel	Air	$\eta_{th} = 67.50\%$ η_{ex} not reported	[27]
-129	1290	Brayton cycle + direct expansion cycle	Fuel	Flue gas and Nitrogen	$\eta_{th} = 75.50\%$ $\eta_{ex} = 52.60\%$	[31]
-128	10	Rankine cycle + direct expansion cycle	Seawater	Argon/methane/ tetrafluoromethane	η_{th} not reported $\eta_{ex} = 85.60\%$	[32]

-122.6	10	Rankine cycle + direct expansion cycle	Seawater	Methane/argon	$\eta_{th} = 24.10\%$ $\eta_{ex} = 42.70\%$	[33]
-120.8	600	Brayton cycle	Fuel	Argon	$\eta_{th} = 58.00\%$ η_{ex} not reported	[27]
-120	1000	Brayton cycle	Fuel	Nitrogen	$\eta_{th} = 78.86\%$ η_{ex} not reported	[34]
-120	1000	Brayton cycle + Rankine cycle	Fuel	Nitrogen and carbon dioxide	$\eta_{th} = 67.90\%$ η_{ex} not reported	[34]
-115.6	10	Rankine cycle	Waste steam	Pentane + fluoromethane + tetrafluoromethane	$\eta_{th} = 23.70\%$ $\eta_{ex} = 27.00\%$	[24]
-103.4	108	Rankine cycle	Flue gas	Pentane + tetrafluoromethane + fluoromethane	$\eta_{th} = 30.30\%$ $\eta_{ex} = 46.20\%$	[35]
-76.2	90	Rankine cycle + direct expansion cycle	Solar	Ammonia/ethane	$\eta_{th} = 33.49\%$ η_{ex} not reported	[36]
-71	10	Rankine cycle + direct expansion cycle	Seawater	Ammonia	$\eta_{th} = 8.10\%$ η_{ex} not reported	[37]
-65	134	Kalina cycle + direct expansion cycle	Waste heat	Ammonia + water mixed	$\eta_{th} = 39.33\%$ $\eta_{ex} = 50.15\%$	[38]
-60	75	Rankine cycle + direct expansion cycle	Solar	Fluoromethane	$\eta_{th} = 25.25\%$ $\eta_{ex} = 12.20\%$	[39]

-55.8	900	Rankine cycle	Solar + Fuel	Carbon dioxide	$\eta_{th} = 61.00\%$ $\eta_{ex} = 61.30\%$	[40]
-54.4	150	Kalina cycle + direct expansion cycle	Waste heat	Ammonia + water	$\eta_{th} = 33.28\%$ $\eta_{ex} = 48.87\%$	[41]
-53	1200	Rankine cycle	Oxy-fuel	Carbon dioxide	$\eta_{th} = 71.04\%$ $\eta_{ex} = 50.53\%$	[42]
-50.4	400	Rankine cycle + direct expansion cycle	Waste heat	Steam/ammonia	$\eta_{th} = 34.20\%$ η_{ex} not reported	[43]
-50	700	Rankine cycle	Fuel	Carbon dioxide	$\eta_{th} = 59.00\%$ η_{ex} not reported	[44]
-50	900	Rankine cycle	Oxy-fuel	Carbon dioxide	$\eta_{th} = 59.06\%$ $\eta_{ex} = 39.79\%$	[45]
-46.9	190	Rankine cycle	Waste heat	Ammonia + water mixed	η_{th} not reported $\eta_{ex} = 25.88\%$	[46]
-42	10	Rankine cycle	Seawater	Propane	$\eta_{th} = 12.50\%$ $\eta_{ex} = 65.20\%$	[47]
-20	190	Rankine cycle + direct expansion cycle	Waste heat	Isobutane	$\eta_{th} = 21.00\%$ η_{ex} not reported	[48]
-10	65	Rankine cycle	Solar	Carbon dioxide	$\eta_{th} = 8.48\%$ η_{ex} not reported	[49]
9	1300	Brayton cycle + Rankine cycle (combined cycle)	Fuel	Flue gas/steam	$\eta_{th} = 59.30\%$ $\eta_{ex} = 54.98\%$	[50]

From Table 2.2, with correct choices of working fluid in the power cycle, LNG cold can be utilized at different temperature ranges well below the ambient temperature. For example, in an ORC, LNG cold can be used to condense the organic fluid at temperature down to -120°C , and just with low temperature heat source such as seawater or medium temperature heat source such as solar power or industrial waste heat, efficiencies between 12% and 34% can be obtained. For Rankine cycles using natural working fluid such as CO_2 , higher temperature heat sources such as fuel combustion heat can be used. In these cases, thermal efficiencies are reported between 59% and 71%.

Pure gases such as nitrogen, argon, air and helium have low triple point temperatures. Thus, compared to a Rankine cycle which can be restricted by the condensation temperature of working fluid, in a closed Brayton cycle, the only limitation to the temperature of heat sink is restricted only by the vaporization temperature of LNG and the amount of heat LNG is able to absorb at cryogenic temperature range. Simple closed Brayton cycles with compressor inlet temperature cooled to between -120°C and -145°C have been reported, with thermal efficiencies between 58% and 69%. In the study carried out by Morosuk [31] where an open air Brayton cycle (turbine inlet temperature of 1290°C) is coupled with a closed nitrogen Brayton cycle with compressor inlet temperature of -129°C and a direct expansion cycle, thermal efficiency of 75.5% is reported, which is the highest thermal efficiency reported thus far. A combined cycle which generally consists of both Brayton and Rankine cycle benefits from both compressor inlet temperature and working fluid condensation temperature. However, not much study has been carried out on performance improvement of combined cycle, and there is only one study which reported thermal efficiency of 65.07% with LNG cold [29]. There are also other cycles reported using LNG cold to improve the performance such as Kalina cycle, which uses the absorption of working fluids

during the heating process, and reported efficiencies between 23% and 39%, depending on the temperature of heat sources used.

Usage of LNG cold in electricity generation has been discussed thoroughly in the literature. However, utilization of LNG cold for cold-to-cold applications is generally less discussed, with the available case studies in the literature listed in Table 2.3. An energy carrier (generally a working fluid) is used for the transport of cold energy.

Depending on the final usage of LNG cold, suitable working fluids with working temperature matching the demand temperature are selected as energy carrier. In some cases, the working fluid itself is the final user of cold energy, such as in the case of solid or liquid CO₂ production and butane liquefaction [51]. Demonstrated by Osaka Gas CO. (Figure 2.1), in these cases, CO₂ and butane transport the cold energy at desired temperature from the LNG regasification terminal to the processing site, where the precooled materials are processed into the final products.

Table 2.3: Cold applications utilizing LNG cold with LNG carrier used

Energy carrier temperature (°C)	Usage	Energy carrier used	Ref.
-160	Air liquefaction/separation	Nitrogen	[51]
-150	Olefin (alkene) Separation	LNG	[52]
-115	Cryogenic comminution	R22	[53]
-60	Solid/liquid CO ₂ production	CO ₂	[51, 53, 54]
-43	Freezing and refrigeration	CO ₂	[55, 56]
-5	Butane liquefaction	Butane	[51]
5	Gas turbine inlet air cooling	Water	[51]

In some cases, LNG itself is used as energy carrier, which is the case demonstrated by Osaka Gas Co. and Mitsui Chemicals in Senboku Terminal, Japan [52]. LNG is transported to the ethylene liquefaction plant via a pipeline, and is regasified using warm ethylene, releasing its latent heat for maximum cold energy transfer. In this case, usage of LNG as energy carrier is feasible because both plants are neighboring to each other.

Figure 2.1: 100% utilization of LNG cold demonstrated by Osaka Gas Co. [51]

In the case of using LNG cold to assist in air separation or liquefaction, nitrogen is used as energy carrier [57] instead of air to reduce the risk when leakage occurs and results in mixing of air and natural gas, which can be highly combustible or even explosive. Nitrogen which carries the cold energy is not consumed by the demand directly and only recirculates between cold source and demand, thus is also known as intermediate working fluid. Intermediate working fluid is also used for refrigeration and deep-freezing purpose, including food preservation where CO₂ is used [55]. CO₂ is used because it is easier to obtain compared to nitrogen and argon, which to produce these air products, the air needs to go through an energy-intensive air separation process. As mentioned, air is not used as working fluid to minimize its contact with LNG. For the case of cryogenic diminution where a material is deep-frozen to below -100°C to increase brittleness, usage of chlorodifluoromethane (R22), which exists in liquid phase

between -170°C and -40°C under atmospheric pressure, is reported. However, phase out of such hydrochlorofluorocarbon (HCFC) is in progress due to their high ozone depleting potential (ODP) [58] and alternative working fluid has to be sourced for.

One of the well-known examples of real life LNG cold-to-cold applications is demonstrated by Osaka Gas Co., where the cold demands are cascaded (i.e. different demands with different temperature requirements) to utilize the different grades of cold energy from -160°C to ambient temperature [51], and the cascaded configuration is shown in Figure 2.1. Osaka Gas Co. has used hydrocarbons (HCs) and hydrofluorocarbons (HFCs) as energy carriers in some of the scenarios. These materials are deemed to have high global warming potential (GWP) or ODP. However, leakage of these potentially environmentally harmful materials can be controlled due to short distance between the cold demand and LNG regasification site (within 2 km).

However, in the design of any new system, usage of HCs or HFCs as energy carrier needs to be avoided to comply with policy changes and minimize the environmental effect. Instead, natural working fluids such as CO₂, water or hydrofluoroolefins (HFOs) should be considered, especially if the cold energy needs to be transported over a long distance [59, 60]. In a case study done for Geneva, Switzerland, CO₂, HFO 2,3,3,3-Tetrafluoropropene (R1234yf) and HFO 1,3,3,3-Tetrafluoropropene (R1234ze) are three candidates as working fluid for heat and cold energy transfer in a simulated district energy network. All three working fluids have 0 ODP and GWP less than 10, and are operated at a pressure where phase change of these working fluids occur at 15°C, utilizing their latent heat as heat storage medium.

District energy network has been demonstrated as a successful system on reducing the total energy consumption of a district cluster, especially that with similar demand on

energy such as building heating or cooling. Singapore itself has demonstrated a successful example on putting the system into operations, with cooling energy supplied to office buildings, hotels and shopping centers, and implementation of such system is estimated to achieve 40% energy savings [61]. Similar projects are also implemented in other countries and regions such as Japan, Canada, Qatar, United States and China [62]. In a study carried out for Singapore, when waste heat and cold energy are recovered and utilized in a district cooling system, by 2050, the scenario yields 19.5% lower in energy demand and 41.5% lower in carbon emissions [63]. In a district cooling system, chillers are used to produce cooling energy at a central plant, which the energy is then supplied to the district [62]. Cold energy released by LNG during regasification process can be distributed in a similar manner. With the low-temperature provided by LNG cold energy, such district thermal network can distribute cold energy at lower temperature and with minimal work input, while using chillers only as backup.

For transportation of cold energy from LNG regasification site to the demand, thermal energy storage (TES) system can also be considered as one option. A district thermal network which uses pipeline to connect the energy supply and demand can only use fluidic mediums as energy carriers, which is restricted by their operating temperatures (melting point and boiling point) and environmental impacts. In contrast, a TES system can utilize almost any material as storage medium, if the material can be contained properly. Two main types of thermal energy storage materials are commercially available: sensible heat thermal energy storage (SHTES) materials and latent heat thermal energy storage (LHTES) materials [64]. SHTES materials use their sensible temperature change as main storage method while LHTES materials use phase change process on top of sensible temperature change for energy storage purpose, and thus LHTES materials are also named as phase change materials (PCMs). In general, a PCM

is more favourable compared to an SHTES material due to the extra storage capacity contributed by latent heat and ability to maintain a near constant temperature during discharge process [65]. When a truck is used to transport the TES materials from LNG regasification facility to the cold demand, larger storage capacity is equivalent to less truck-hour. Such transportation method of thermal energy is found to be cost-effective when the transportation distance is within 10 km [66]. More detailed review on TES systems are included in Chapter 2.2.

Another novel energy carrier, liquid air energy storage (LAES) is also widely discussed in the literature. The main advantage of LAES over other energy carriers is that LAES is able to generate both mechanical and cold power during discharge, which the mechanical power can be converted to electricity with a carefully designed isothermal expanders or turbines [67]. Usage of LNG cold to assist in air separation process has been investigated in multiple studies. During a conventional air separation process, multiple compression and intercooling processes are needed on the inlet air before being separated in the distillation columns. When available, cold energy from LNG regasification can be fed into the cooling process, effectively lowering the compressor inlet temperature for the inlet air while eliminating work input into conventional refrigeration cycle used for intercooling purpose. Such reduction in compressor inlet temperature is able to reduce the compressor work, and thus improving the overall efficiency of the air separation process. LAES has been investigated as storage method in an LNG regasification facility with electricity power output [68]. During non-peak hours, extra electricity is used to compress inlet air to above 25 bars. The air is then liquefied and stored at -154.5 °C. When extra electrical energy is required, the liquid air is pumped, heated and expanded, generating extra electricity [68]. Such concept can

also be used using liquid air as energy carrier, where liquid air is generated at the LNG regasification facility, and distributed to cold demands to be consumed when needed.

When energy distribution is discussed, using electricity as energy carrier should not be left out due to the readiness of facility (i.e. electricity grid). However, when cold-to-cold application is desired, multiple conversions of energy maybe involved, which result in loss in efficiency.

2.2. Literature study on thermal energy storage

2.2.1. Energy storage systems and potential applications

Driven by governments' policies and advance in technologies [2], sources of primary energy consumption are slowly shifted from fossil fuels towards renewable energies to ensure energy sustainability. However, renewable energies sources are well-known with two major problems: time-dependency and intermittency. For example, solar energy is only available during day time and the amount of energy reaching the Earth surface can be subjected to cloud blockage and Sun angle at different time of a day, resulting in interrupted or fluctuating energy supply, which can create problem when renewable energy sources are to be integrated in a multi-energy system.

An example is demonstrated in a smart grid where electricity is supplied with solar photovoltaic (PV) and conventional power plant [69]. Solar irradiance peaks around noon time, which also indicates highest solar electrical power generated in a day. Large number of PV devices installed easily leads to over-generation of electricity during day time, drastically reducing the loads from the conventional power plants. However, during the peak period for electricity consumption within a day, which is estimated to be between 6pm and 9pm, the electricity load on conventional power plant increases

significantly due to two reasons: (1) no more solar electricity after sunset and (2) increase in electricity load from the community. The fluctuation in demand for electricity from power plants over a day is shown in Figure 2.2, which resembles the shape of a duck, and thus, also named as a duck curve. In the duck curve demonstrated for the case of California, after evening, power plants need to be ramped up over 13 GW in 3 hours period to meet the sudden surge in demand [69]. Besides, in the mid-day, there is a risk for over-generation of power, as power plants need to operate on a baseload. Besides, when a system is over-dependent on renewable energy sources, disruption occurs easily due to the intermittency.

Figure 2.2: A duck curve showing the electricity demand from power plant with large-scale integration of renewable energy sources [69]

Due to the above stated reasons, there is a need to shift the power generated by renewable energy sources during mid-day to be consumed during evening when there is limited power generated from renewables. Energy storage systems have been widely discussed topic in the literature to bridge the mismatches between energy supply and demand [70]. Such mismatches are widely seen in modern energy systems and can be

divided into two main types: (1) distance between energy supply and demand and (2) time gap between energy generation and consumption. The distance mismatch between energy supply and demand is generally overcome using energy distribution system such as electricity grid (for electrical energy) or working fluids (for thermal energy, such as district energy systems). Energy storage system can be used to tackle such distance gap as well, with trucks as the main transportation method.

Energy storage systems are more commonly used to bridge the time mismatch between energy generations and consumptions, which an example is demonstrated in the duck curve when using a PV system. Batteries are used in California to smooth the duck curve, while in Stuttgart, Germany, pumped hydroelectricity storage (PHES) is used [71]. These storage systems are found to be able to solve the duck curve problem, integrate more amount of renewable energies, as well as reduce carbon emissions [72].

Different energy storage systems have been investigated and can be divided into a few categories based on the targeted storage energies and storage methods. The main categories of energy storages include: (1) chemical energy storage systems, (2) electrochemical energy storage systems, (3) mechanical energy storage systems and (4) TES systems [73]. These systems are elaborated in the subsequent paragraphs.

Chemical energy storage systems store energy using a secondary chemical energy carrier, typically generated from chemical fuels such as coal and oil products or surplus electricity. Common examples of such energy carriers include hydrogen, synthetic natural gas and biofuels. Hydrogen acts as energy storage for both electricity (from electrolysis of water) or chemical fuel energy (from fossil fuel reforming) [73]. Synthetic natural gas can be generated from biomass or gasification of coal. Generally, the secondary energy carrier generated is cleaner (lower C-H ratio) than the original

chemical fuel. These energy carriers, including hydrogen, can be used in power cycles where the chemical energy is used to generate high pressure and high temperature working fluid to drive a turbine [74]. Hydrogen can also be used to power a fuel cell. The main advantage of a chemical energy storage medium is its high energy density per unit weight. However, the generation of the chemical energy carrier can be energy-intensive and has low round-trip efficiency.

Electrochemical storage system stores energy in form of chemical energy and convert the chemical energy into electricity when needed. One most commonly seen example with this storage method is batteries, which are now widely used with renewable energy sources such as PV or wind power [75]. Fuel cell is another form of electrochemical energy storage system, which does not have energy stored in the system but instead uses external chemical energy carrier (e.g. hydrogen) and converts it into electricity. However, a battery targeting large-scale energy storage still takes a lot of space, has high investment costs and shorter cycle life [76].

Electricity can also be stored in the form of mechanical storage systems, such as flywheels, PHES and compressed air energy storage (CAES) system. In these examples, electricity is converted into mechanical energy such as gravitational potential energy in PHES, where electricity is used to drive a pump to elevate mass amount of water to a higher altitude, and retrieving the potential energy using a turbine when electricity is needed. In a CAES system, extra electricity energy is used to drive a compressor which pressurizes air. The pressurized air is stored in an underground cavern. When electricity is needed, the pressurized air is used to drive a turbine which powers a generator. Both CAES and PHES are able to provide large storage capacity and has low investment cost. However, these storage technologies are highly dependent on geographical factors (elevated or underground storages needed) [76].

The last type of energy storage system is TES systems, which only deal with storage of thermal energy. TES systems can be divided into different types based on the materials used, such as SHTES materials that use sensible temperature changes to store energy, or LHTES materials, which on top of sensible heat, also uses the energy absorbed or released during its phase change for extra energy storage [77]. Thermal energy can also be stored using exothermic or endothermic chemical reactions in thermo-chemical energy storage systems. When only thermal energy is dealt with, TES system is more advantageous due to no conversion of energy to other forms required. Besides, a TES system has high availability of materials for selections and has low investment costs [76], especially when common materials such as rocks and ceramics are used as SHTES materials and salt or salt-water solutions are used as LHTES materials. Besides, compared to other energy storage system such as electrochemical and mechanical storage, TES system also possesses higher mobility and can be used as energy carrier between energy supply and demand. Thus, there is no doubt that TES system should be chosen, for bridging and recovery of cold energy released from LNG regasification.

2.2.2. Reported applications of TES systems

One main targeted energy source to be stored in a TES system is solar thermal energy. Solar energy is the most widely available energy source, where by average, 239 W/m^2 of solar energy is considered available to be captured [78]. The amount of solar energy potentially able to be captured per year is estimated at between 15,750 EJ and 49,837 EJ (or between 4,375 and 13,843 PWh) per year [78, 79], which is at least 15 times more than the projected worldwide energy consumption in year 2050 (267.0 PWh) [80]. Thus, recovering solar energy has a high potential for energy sustainability on Earth.

Solar thermal energy can be utilized directly for water heating, or concentrated solar power (CSP) plants can be used to generate high temperature working fluids which can be used to drive a heat engine. Similar to other renewable energy systems, solar thermal systems are also subjected to intermittency issues. To ensure consistent power output, it is important to employ a TES system. Coupling of TES systems to a CSP plant has been investigated by multiple researchers. For example, a 42-kWh lab scale TES storage with phase change temperature 575°C is analyzed experimentally and numerically for CSP applications [81]. Galione et. al. investigated numerically a TES system with operating temperature between 300°C and 380°C for CSP application [82, 83]. Bruch et. al. setup a rock bed as TES system to store the thermal energy from a CSP plant, with operation temperature between 200°C and 300°C [84]. Bellan et. al. also investigated a lab-scale TES system with phase change temperature of 306°C [85]. TES systems can be used not only with CSP plants, but also used alongside other solar thermal systems. Wu et. al. tried different TES materials with a simple solar collector system used for building heating purpose [86, 87]. Nallusamy et. al. investigated a TES coupled with solar flat plate collector experimentally [88]. In the setup, water is heated to 70°C and is used to charge the TES tank, with phase change temperature of 60°C . Karthikeyan et. al. also investigated numerically a solar air-heating system with TES, which the air is heated up to 80°C to charge the TES tank with phase change temperature of 55°C [89]. Similar setup is also achieved by Yang et. al., who investigated performances of using cascaded PCMs with different phase change temperatures for TES on similar working conditions of solar flat plate collector [90].

Solar cooker is a concept where cooking of food is carried out using solar thermal energy, eliminating usage of fuels. Such cooker is also subjected to intermittency and

requires TES system for more consistent output. Domanski et. al. investigated usage of PCM with phase change temperature of 79°C as TES material, as discharge temperature at this temperature level is enough for cooking of most food [91]. Nkhonjera et. al. reviewed different designs of solar cookers with TES employed, and found that oils and organic PCMs are most frequently used as TES materials [92].

TES systems are not only associated with storage of solar thermal energy. For example, TES systems can be used with CAES system [93], where TES materials are used to absorb the compression heat from pressurized air, such that pressurized air is stored under near-ambient condition, reducing heat loss from the storing process. Such energy recovery is crucial as temperature of compressed air can reach up to 600°C [94]. Due to the storage temperature and no heat loss from storage, the system is also named as adiabatic compressed air energy storage (A-CAES) system. During energy recovery from pressurized air, the air can be heated to above ambient condition with the stored compression heat, eliminating the use of fuel for heating while increasing energy output in the process. With TES employed, the roundtrip efficiency for the CAES system increases to up to 75% [95] or 74% [93].

TES systems are also used with combined heat and power (CHP) plants. A TES system consisting of SHTES materials is subjected to flow of flue gas from a CHP plant with temperature between 800°C and 1200°C to capture the waste heat [96]. The heat energy is then used to heat a stream of ambient air, which is subsequently used to superheat the steam generated from the same CHP plant. TES systems are also used to improve the performance of incineration process in waste-to-energy (WTE) plants. A WTE plant is normally subjected to corrosions due to contaminated gas products, and fluctuation on the steam production and temperature. Using PCM-based refractory brick solves the abovementioned problems, while improving the efficiency by up to 34% [97].

Most of the time, waste heat needs to be transported between the supply and demand. Li et. al. investigated usage of different type of TES materials for transport of waste heat over distance of between 10 and 50 km, and found that using mobilized TES system for waste heat transportation is more cost-effective than conventional heat generation methods such as heat pump [98]. Nomura et. al. investigated the possibility of waste heat transportation at 330°C for a distance of 10 km to generate hot oil at 250°C, and found out that such TES system uses only 9.5% of energy consumed by an on-site fossil fuel heat pump, while generating only 19.6% of carbon emissions [99]. Wang et. al. investigated two different configurations of TES for mobile waste heat transportation [100]. Deckert et. al. investigated economic efficiency of such TES system storing waste heat generated from a biogas plant [101], and found that storage size of the TES system has the largest influence on the system cost. Miro et. al. also reviewed the cases where industrial waste heat are recovered, including off-site waste heat utilization where TES system is used [102].

TES systems are also used to assist a pumped thermal electricity storage (PTES) system [103-105], which is another type of mechanical system targeted for electricity storage. When there is extra electricity, argon is pressurized. The compression heat is then stored in a TES tank. When electricity needs to be extracted, the compressed argon gas then retrieves the heat energy stored in the TES tank and drives a mechanical turbine to generate electricity.

Alongside heat energy, TES systems are also used for storage for cold energy. Li et. al. listed a number of potential usages of cold energy under different temperature requirement [106], which are summarized in Table 2.4.

Table 2.4: Potential usages of cold energy at different temperature ranges

Temperature range	Usages of cold energy
0°C to -10°C	Cold air for buildings
-10°C to -35°C	Frozen food transportation, propane liquefaction
-50°C to -75°C	Production of dry ice
-75°C to -125°C	Liquefaction of ethane and ethylene
-125°C to -175°C	Liquefaction of natural gas
-175°C to -225°C	Air liquefaction and separation

Storage of cold energy using TES materials, is widely investigated to achieve passive cooling for a building. PCMs can be impregnated into constructions materials (e.g. concrete and wallboards) or integrated into a building envelope (e.g. walls, roofs, windows or even PV panels) [107]. Impregnation of 5% microencapsulated PCM inside concrete is reported to achieve energy savings of 12% [108]. Concrete after PCM impregnation is shown to have up to 300% increase in its thermal storage capacity [109].

Integration of TES materials into building envelope is a more common approach, as impregnation of TES materials into construction materials may affect the structural integrity of the final products. Kong et. al. incorporated PCM panels on the inner wall of a room and found the installation yields lower temperature during daytime especially when natural ventilation is available [110]. Panayiotou also installed PCM materials at different locations on a wall (outer surface, in between walls and inner surface) and discovered that for a Mediterranean weather, locating PCM in the outer surface yields the maximum energy savings of 28.6%, compared to 21.6% in between walls and 21.8% on the inner surface [111]. Shi et. al. also investigated locations of PCM at different location of a wall, and finds that PCM located in between walls is the most effective in

reducing room temperature, while PCM on the inner side of a wall can remove larger amount of humidity [112].

TES materials can also be installed on the floor and ceiling of a building. Xu et. al. investigated integration of PCM onto floor tiles, which are used to absorb solar thermal during winter and release the energy at night [113]. Weinlader et. al. integrated PCM boards on a ceiling, which energy is discharged for cooling during daytime, and at night, ambient air is drawn to charge the PCM again [114]. Temperature drop of 2°C is observed in the room. Li et. al. investigated that using PCM roof is able to absorb temperature fluctuation due to solar energy absorption compared to a normal roof [115]. Pasupathy et. al. also discovered that using double PCM panels with thickness of 4 cm is able to absorb all temperature fluctuation on a typical sunny day in India [116].

TES systems can also be integrated into ventilation system of a building. For example, Erek et. al. investigated numerically encapsulated ice TES system targeted for cooling loads for buildings, which a chiller operates at night when the electricity cost is lower [117]. The cold energy is recovered with air flow during day time. Besides, Kang et. al. investigated a ventilation system equipped with PCM [118], which at night, outdoor cold air is ventilated through the PCM system and the cold energy is stored. During daytime, the cold energy is discharged into the building. Wang et. al. explored a similar concept but uses micro-encapsulated PCM as storage material, which is found to be more energy-efficient to a similar system using ice storage [119].

Besides being used to store cooling energy for a building either from ambient air available at night or off-peak electricity, TES system is also used for low temperature food storage. Azzouz et. al. incorporated PCMs on a household refrigerator, and discovered that under power interruption, the refrigerator maintains low temperature

for up to 9 hours [120]. Oro et. al. investigated using PCM to enhance performance of a freezer. When compared with freezer without PCM, the freezer with PCM maintains lower freezer temperature by up to 6°C, while product temperature lower by up to 2°C when subjected to 3 hours of power disruption [121]. Liu et. al. also investigated using PCM to maintain low temperature inside a refrigerated truck. Instead of using refrigeration system driven by diesel fuel, a containment with PCM is used to provide cold energy to the refrigerated truck. The PCM is charged using electricity when the truck is not operating and can be charged selectively based on off-peak tariff which brings a much lower cost. As such, the best case scenario yields up to 86.4% in energy cost saving compared to a conventional refrigerated truck [122].

LAES is a novel energy storage system which is capable to generate both mechanical and cold energy during the discharge stage. During discharge, liquid air is heated from cryogenic temperature (-194°C) towards ambient temperature. Although the cold energy can be captured for other cooling purpose such as building cooling, however, there can be large amount of exergy loss. The best utilization method for the high-grade cold energy is to store and reuse it during the next charging process of LAES, where ambient air needs to be cooled to near cryogenic temperature. Such concept has been used in study carried out by Hutterman et. al. [123] and Sciacovelli et. al. [16].

2.2.3. Type of TES materials

Almost any substance can be used as a TES material. TES materials can be divided into 3 main types according to the storage method. SHTES materials use only sensible temperature change as storage method, while LHTES materials use mainly latent heat absorbed or released during phase change process for storage, while chemical reactions

which are either exothermic or endothermic can also be used for TES inside a thermo-chemical type storage material [77].

SHTES materials can be divided into two main types according to the material state: solid or liquid [64]. Gaseous state materials are unsuitable because they are difficult to contain and exhibit low volumetric energy density. Liquid SHTES materials have been commonly used. Water, with its working temperature between 0°C and 100°C has been used as TES storage in conventional water heating systems or solar flat plate collector [88]. Molten salts and oils have higher operating temperature, and are used as TES materials in CSP plants [64]. Liquid state SHTES materials is more advantageous over other materials as they can also be used as working fluid for thermal energy transfer between supply and storage, and from storage to the demand.

Solid state SHTES materials are more commonly available, with examples of rocks sands, concretes, ceramics or even metals [64]. Due to high availability of these materials, solid state SHTES materials are lower in cost. Besides, most of these materials exhibit good thermal properties such as high energy density (metal oxides and ceramics) and exhibit large operating temperature range due to their high melting points. Table A.1 lists examples of SHTES materials reported in the literature.

LHTES materials or PCMs are commonly used as TES materials due to their higher energy density provided by latent heat. Besides, due to PCMs' near-constant temperature during phase change, constant discharge temperature can be achieved as pointed out by Mawire [65] and Zanganeh et. al. [124]. PCMs can be divided into different types according to the state before and after phase change [64], including solid-liquid type, solid-gas type, liquid-gas type or solid-solid type. However, rapid expansion when transition into gaseous state causes intensive pressure build-up, and

thus, PCM involving vapor state is not favourable. PCM with phase change between solid and liquid phase is the most common, which can be further divided into two main types: organic and inorganic PCMs. Examples of organic PCM include paraffins, hydrocarbons, alcohols, glycol solution, glycerol and fatty acids or eutectic mixtures of these materials [64, 106, 125], while for inorganic PCM, water, salts and eutectic salt-water solutions [64, 125] are commonly used. In some occasions, composite PCM made by mixing inorganic and organic compounds is used, such as mixture of ammonium chloride with glycol solution [106]. Despite multiple commercial PCMs commonly available in the market, PCMs exhibits a disadvantage compared to SHTES materials, which is its low thermal conductivity. Table A.2 lists PCMs that are reported use in TES systems in the literature.

A thermochemical type storage uses heat energy absorbed or released during chemical reactions for TES purpose. One example is ammonia, which decomposes into nitrogen and hydrogen molecules when heat energy is absorbed. When heat energy is needed, nitrogen is mixed with hydrogen with suitable catalysts (which reduce the activation energy) to form ammonia, releasing heat energy [64, 126]. Other examples of thermochemical type storage include carbonate compounds, which decompose on heat to form oxides and CO₂. Absorption or adsorption materials are also used for thermochemical energy storage [106, 127]. During absorption or adsorption process, heat energy is released due to attraction between the working pairs and vice versa during separation process. Widely used absorption working pairs are ammonia/water or lithium bromide/water. For adsorption process, working pairs of silica gel/water and carbon/methanol are commonly used.

Various requirements for the TES materials have been summarized in a number of review papers [64, 70, 128, 129]. One category is the chemical requirement, which the

TES materials must be stable and non-reactive (except for thermochemical type TES); non-corrosive; and non-hazardous in case of leakage. Other requirements are on the physical side, which the TES materials should exhibit high density (or high energy density); low density variation with temperature change or phase change; and minimal subcooling during solidification process. Thermal requirements are also crucial. The TES material must suit itself with the operating temperature (i.e. SHTES materials are stable within operation temperature and PCM to have suitable phase change temperature), exhibit high latent heat capacity, specific heat capacity and high thermal conductivity. The final requirement is on the economic side, which the TES materials should be inexpensive and abundant to obtain.

Multiple reviews have been carried out for TES materials. Gil et. al. reviewed solid and liquid SHTES materials used for CSP generation with operation temperature above 200°C and commercial and potential PCMs with phase change temperature above 100°C [64]. Zalba et. al. [130] reviewed inorganic PCMs including eutectic mixtures, and organic PCMs such as fatty acids with phase change temperature above 0°C. Similar reviews are carried out by Gasia et. al. for PCMs with phase change temperature above 150°C [128], Pereira da Cunha et. al. for PCMs with phase change temperature between 0°C and 250°C [131] and Kenisarin et. al. for PCMs with phase change temperature between 120°C and 1000°C [132].

Reviews on TES materials have also been carried out for cold energy storage. Oro et. al. listed commercial PCMs and non-commercialized PCMs with sub-ambient phase change temperature [125]. Li et. al. reviewed PCMs with sub-zero phase change temperature [106], including eutectic water-salt solutions, paraffins, alkanones and mixture of organic PCMs. In another work, Li et. al. summarized PCMs used for air-

conditioning, with phase change temperatures between 0°C and 15°C [127], including inorganic PCMs such as eutectic salt or hydrated salt, and organic PCMs such as paraffin waxes and fatty acids.

Commercial PCMs' market is also developing rapidly with more companies with ability to manufacture PCMs in bulk quantity, including those for cold energy storage purpose. The lowest phase change temperature for PCM available in the market is recorded at -114°C, while different types of materials are available including organic and inorganic PCMs. The commercialized PCMs for cold TES are listed in Table A.3.

Despite rapid development of materials and multiple reviews on cold TES, TES on cold energy is still less studied compared to heat storage which can be observed in Table A.1 and Table A.2. Similar observation can also be made in Chapter 2.2.2, where there are more studies for storage of heat energy. In contrast, the studies on cold energy storage are very limited, and focus on building comforts or food storage, where only lower-grade cold energy is required. The only study about storage of higher-grade cold energy is for LAES application. Such low number of research studies can be mainly attributed to the low availability of cold energy. Unlike heat energy which can be cheap due to presence of solar thermal energy and industrial waste heat, free cold energy is only available at night when cold air is present. Cheaper cold energy can also be generated with low-electricity tariff; however, such application is only limited to building comfort in the literature. A new promising source of “free” cold energy is available from LNG regasification process, however, utilization of cold-to-cold from LNG is seldom investigated compared to using the cold energy for electricity generation. There is generally low interest on investigation of cold TES, which render most development of cold TES materials unutilized.

2.2.4. Type of TES systems

A TES system generally consists of immobile TES materials, and HTF is used for thermal energy transfer from the source to the storage during charge and from storage to cold demand during discharge. A TES system can be divided into two types according to their configurations. The first type is modified from a shell-and-tube heat exchanger, which TES materials are accommodated in either the shell or tube section, while HTF is flowed through the other section, transferring heat energy. PCMs are commonly used as TES material in this configuration. The second TES system is a packed bed, which solid SHTES materials are packed in a column, then flushed with HTF for storage or recovery of energy. PCMs and liquid SHTES materials are also suitable for packed bed, however, extra encapsulation is needed for isolation of these materials from the HTF. Figure 2.3 shows illustrations of the TES systems.

Figure 2.3: Illustrations of (a) a simple shell-and-tube TES system and (b) a packed bed TES system

Both shell-and-tube and packed bed TES systems have been investigated. PCMs are well-known for their low thermal conductivities. When PCM is used as TES material

in a shell-and-tube system, heat transfer process can be long as thermal energy needs to propagate to every node of the PCM section. Thus, it takes longer time for a TES system to be fully charged or discharged, and risking a low efficiency as longer charge time taken simply means more HTF and energy needed to charge the TES system.

Due to the low heat transfer area for shell-and-tube storage, researchers turned to packed bed structure, which offers high heat transfer area due to individual encapsulation of PCMs. Spherical encapsulation is commonly used as encapsulation geometry. HTF then flows through the porosity of the packed bed and exchange heat energy with the PCMs. Due to the increase in heat transfer area compared to a shell-and-tube TES system, a packed bed TES system achieves up to 3.2 times faster charge and discharge rate [133]. Smaller encapsulation leads to larger surface area to volume ratio for the encapsulation, while effectively reduces the thermal propagation distance. Recent development in encapsulation methods have led to production of encapsulated PCM with the size of micrometers. Such PCM is named micro-encapsulated PCM and has encapsulation size from 1 μm to 1000 μm . In contrast, PCMs with encapsulation size larger than 1 mm are macro-encapsulated [134]. A macro-encapsulated PCM has PCM injected into the cavity of encapsulation, while in a micro-encapsulated PCM, PCM is embedded in a continuous film of polymeric film or shell using physical coating or chemical processes such as precipitation [106]. Despite large heat transfer area, such processes are expensive and can increase the cost of a TES system.

Fernandes listed a few requirements for a good TES system [129], including high storage capacity which can be contributed by the latent heat, specific heat capacity and density of the TES materials. Besides, the charge and discharge of TES system should be fast, which means high heat transfer rate between the HTF and the TES materials. The system and the materials should also be stable, both mechanically and chemically.

The thermal energy loss from the TES system should also be minimal. Gasia et. al. also listed a number of requirements [128] on economic factors such as affordable cost of the system, as well as environmental factor such as minimal carbon emissions.

2.2.5. Performance enhancement of TES systems using cascaded materials

Performance enhancements on PCM-based TES systems are widely researched due to the poor thermal conductivity of PCMs. Use of multiple PCMs with different phase change temperatures in a TES system has interesting potential due to its simplicity and ability for performance improvement [135]. This method ensures constant heat flux throughout the system, as temperature difference is more uniform between the HTF and PCMs at different locations along the flow direction. Advantages including higher utilization of latent heat, uniform discharge temperature [136], and shorter charge time [137] are observed. Elfeky et. al. also determined that for a CSP plant, with a three-stage PCM configuration in a packed bed TES system, higher heat transfer rate and efficiency are observed [138]. Table 2.5 lists research studies where the cascaded system is introduced. In most studies, the amount of PCM assigned for each cascaded section is random, mainly equal volume. Despite the improvement they are able to achieve compared to a single-PCM TES system, for the author, such system is not optimized. Shamsi has described the optimization of thermal capacity of different PCMs in a cascaded TES system using genetic algorithm, however the study was limited to four hours of a charge-discharge cycle [139].

Table 2.5: List of cascaded PCM TES systems reported in the literature

Authors	Phase change materials	Phase change temperature (°C)	Capacity of each PCM	Ref.
Aldoss et. al.	PCM40	43	Equal	[140]
	PCM60	61	distribution of system volume	
Elfeky et. al.	59.98 wt% MgCl ₂ – 20.42% KCl – 19.6% NaCl	382.1	Equal	[138]
	55 wt% MgCl ₂ – 45% NaCl	439.8	distribution of system volume	
	35 wt% Li ₂ CO ₃ – 65 wt% K ₂ CO ₃	505		
Sunku Prasad et. al.	KOH	360	Equal	[141]
	KNO ₃	335	distribution of system volume	
	NaNO ₃	306		
Wu et. al.	Mixed of molten salts	305	Equal	[142]
	Mixed of molten salts	340	distribution of system volume	
	Mixed of molten salts	375		
Yuan et. al.	PCM1 (34.83 wt% Li ₂ CO ₃ - 65.17 wt% K ₂ CO ₃)	499.7	44.05% total latent heat	[143]
	PCM2 (46.59 wt% Li ₂ CO ₃ - 53.41 wt% K ₂ CO ₃)	483.9	32.84% total latent heat	
	PCM3 (22.00 wt% Li ₂ CO ₃ - 62.00 wt% K ₂ CO ₃ - 16.00 wt% Na ₂ CO ₃)	422.0	24.02% total latent heat	

2.2.6. Numerical simulation of TES system

Experimental studies on TES system can be costly in terms of capital and operation costs, especially when cryogenic-grade cold energy is not readily available. As such, numerical studies are much preferred during design stage of a TES system, which allows prediction on performance of TES systems prior to real operations. Several numerical models have been developed to predict the temperature developments inside a TES system. Simulation for packed bed system is selected as the candidate for TES system. Thus, only numerical models developed for packed bed are introduced.

2.2.6.1. Simulation models for SHTES based TES systems

Ismail and Stuginsky listed four numerical models for simulation of packed bed TES system with SHTES materials [144]. For savings on computational resources, in all the models, TES material is assumed to behave like a continuous medium, instead of being treated as independent particles. The first model listed is continuous solid phase model, where energy equations are modelled for both HTF and TES material.

$$\begin{aligned} \varepsilon \rho_f c_{p,f} \left(\frac{\partial T_f}{\partial t} + v_\infty \frac{\partial T_f}{\partial x} \right) \\ = k_{f,x} \frac{\partial^2 T_f}{\partial x^2} + k_{f,r} \left(\frac{\partial^2 T_f}{\partial r^2} + \frac{1}{r} \frac{\partial T_f}{\partial r} \right) + h a_s (T_s - T_f) \\ - U_w a_w (T_f - T_\infty) \end{aligned} \quad (2.1) \quad [144]$$

$$(1 - \varepsilon) \rho_s c_{p,s} \frac{\partial T_s}{\partial t} = k_{s,x} \frac{\partial^2 T_s}{\partial x^2} + k_{s,r} \left(\frac{\partial^2 T_s}{\partial r^2} + \frac{1}{r} \frac{\partial T_s}{\partial r} \right) + h a_s (T_f - T_s) \quad (2.2) \quad [144]$$

Where ε – void fraction of the TES system, ρ – density, c_p – specific heat capacity, T – temperature, t – time, v_∞ - velocity of HTF, x – axial direction in TES system, k – thermal conductivity, r – radial direction in TES system, h – overall heat transfer

coefficient between HTF and TES materials, a – surface area to volume ratio for TES materials, U_w – heat loss coefficient, a_w – TES system area to volume ratio; while for subscript, f – HTF, s – TES materials.

For HTF energy equation demonstrated in equation (2.1), in the left-hand side of the equation, the first term represents the transient change of HTF's energy content, while the second term represents the energy flow associated with fluid advection movement. In the right-hand side of the equation, the first two terms represent the thermal energy transfer by conduction in both axial and radial direction. The third term represents thermal energy transfer due to convection between HTF and TES materials while the last term represents thermal energy losses to the surroundings.

For energy equations for the TES materials demonstrated in equation (2.2), the left-hand side term of the equation represents the transient change in energy content of TES materials. For the right-hand side of the equation, the first two terms represent the change in energy content by thermal conduction, while the last term represents thermal energy transfer by convection with HTF.

In the original form, 2-dimensional heat transfer is assumed – in axial direction and radial direction of a cylindrical coordinate, when a cylindrical storage is considered. The equations can be simplified into 1-dimensional form by assuming that there is no temperature variation in the radial direction, $\partial T / \partial r = 0$. Updated 1-dimensional energy equations for continuous solid phase model are shown below:

$$\begin{aligned} \varepsilon \rho_f c_{p,f} \left(\frac{\partial T_f}{\partial t} + v_\infty \frac{\partial T_f}{\partial x} \right) &= k_{f,x} \frac{\partial^2 T_f}{\partial x^2} + h a_s (T_s - T_f) - U_w a_w (T_f - T_\infty) \end{aligned} \quad (2.3) \quad [144]$$

$$(1 - \varepsilon) \rho_s c_{p,s} \frac{\partial T_s}{\partial t} = k_{s,x} \frac{\partial^2 T_s}{\partial x^2} + h a_s (T_f - T_s) \quad (2.4) \quad [144]$$

The second model listed by Ismail and Stuginsky is the Schumann's model, which is built based on further simplification of continuous solid phase model. In this model, it is assumed that heat conduction effect is negligible in both HTF and TES material. Energy equations for HTF and TES materials based on Schumann's model is displayed as equations (2.5) and (2.6).

$$\varepsilon \rho_f c_{p,f} \left(\frac{\partial T_f}{\partial t} + v_\infty \frac{\partial T_f}{\partial x} \right) = h a_s (T_s - T_f) - U_w a_w (T_f - T_\infty) \quad (2.5) \quad [144]$$

$$(1 - \varepsilon) \rho_s c_{p,s} \frac{\partial T_s}{\partial t} = h a_s (T_f - T_s) \quad (2.6) \quad [144]$$

The third model listed is single-phase model, which is applicable under specific conditions when TES materials have high thermal conductivity and low thermal energy capacity. In this case, the temperature of TES materials is similar to temperature of HTF and is represented by T_{eff} . The energy equations split for HTF and TES materials can be simplified into one, which is shown in equation (2.7). The equation can be reduced into 1-dimensional form by reducing thermal variation in the radial direction.

$$\begin{aligned} & [\varepsilon \rho_f c_{p,f} + (1 - \varepsilon) \rho_s c_{p,s}] \left(\frac{\partial T_{eff}}{\partial t} + v_\infty \frac{\partial T_{eff}}{\partial x} \right) \\ & = k_{eff,x} \frac{\partial^2 T_{eff}}{\partial x^2} + k_{eff,r} \left(\frac{\partial^2 T_{eff}}{\partial r^2} + \frac{1}{r} \frac{\partial T_{eff}}{\partial r} \right) \\ & - U_w a_w (T_{eff} - T_\infty) \end{aligned} \quad (2.7) \quad [144]$$

The last model listed is concentric dispersion model, which is different with the other three models listed. In the previously listed models, after discretization, TES material in a certain grid is assumed to exhibit uniform temperature. Such assumption is untrue especially when a TES material exhibits low thermal conductivity, which makes the lumped capacitance model invalid as Biot number, $Bi = hL/k$ can be larger than 0.1. Concentric dispersion model solves the problem by adding a heat conduction equation on top of the energy equations for HTF and TES materials, to predict the temperature

variation within a grid of TES material. Heat conduction equation is generally only modelled in radial direction in spherical coordinate (which sphere is the common shape of TES materials), and is presented in equation (2.8).

$$\rho_s c_{p,s} \frac{\partial T_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(k_s r^2 \frac{\partial T_s}{\partial r} \right) \quad (2.8) \quad [144]$$

2.2.6.2. Simulation models for PCM based TES systems

The abovementioned models listed by Ismail and Stuginsky are straightforward if only SHTES materials are involved. In a PCM based TES system, alongside sensible heat (which is modelled by term of $c_p \Delta T$), latent heat which is absorbed or released without temperature change needs to be incorporated into the energy equations. As such, equivalent specific heat capacity method is used, which incorporates the latent heat into representable format using specific heat capacity near the material's phase change temperature [145]. To prevent the specific heat capacity from reaching infinity at the phase change temperature, suitable range of mushy zone is provided for phase change. Equivalent specific heat capacity is represented in equation (2.9).

$$c_p = \begin{cases} c_{p,s} & T < T_m - \Delta T \\ \frac{L}{2\Delta T} + \frac{c_{p,s} + c_{p,l}}{2} & T_m - \Delta T < T < T_m + \Delta T \\ c_{p,l} & T > T_m + \Delta T \end{cases} \quad (2.9) \quad [145]$$

Where L – latent heat of PCM, T_m – phase change temperature, $2\Delta T$ – mushy zone of phase change. De Gracia and Cabeza also did a similar review on numerical models, focusing on PCM based TES system [146]. The four similar models are reviewed, and an enthalpy term, H is used to represent the total energy content of the TES materials. For example, the continuous solid phase is defined as follow:

$$\begin{aligned}
& \varepsilon \rho_f c_{p,f} \left(\frac{\partial T_f}{\partial t} + v_\infty \frac{\partial T_f}{\partial x} \right) \\
& = k_{f,x} \frac{\partial^2 T_f}{\partial x^2} + k_{f,r} \left(\frac{\partial^2 T_f}{\partial r^2} + \frac{1}{r} \frac{\partial T_f}{\partial r} \right) + h a_s (T_s - T_f) \quad (2.10) \quad [146] \\
& - U_w a_w (T_f - T_\infty)
\end{aligned}$$

$$(1 - \varepsilon) \rho_s \frac{\partial H_s}{\partial t} = k_{s,x} \frac{\partial^2 T_s}{\partial x^2} + k_{s,r} \left(\frac{\partial^2 T_s}{\partial r^2} + \frac{1}{r} \frac{\partial T_s}{\partial r} \right) + h a_s (T_f - T_s) \quad (2.11) \quad [146]$$

It can be noticed that the only change made for the model is replacement of sensible heat term, $c_{p,s} \Delta T$ in energy equation of TES materials with an enthalpy term, ΔH_s , equation (2.11). Similarly, Schumann's model can be modified as follow:

$$\varepsilon \rho_f c_{p,f} \left(\frac{\partial T_f}{\partial t} + v_\infty \frac{\partial T_f}{\partial x} \right) = h a_s (T_s - T_f) - U_w a_w (T_f - T_\infty) \quad (2.12) \quad [146]$$

$$(1 - \varepsilon) \rho_s \frac{\partial H_s}{\partial t} = h a_s (T_f - T_s) \quad (2.13) \quad [146]$$

For concentric dispersion model, the energy equations are taken from either continuous solid phase model or Schumann's model. The 1-dimensional heat conduction equation representing the PCM is also modified to into enthalpy format as follow:

$$\rho_s \frac{\partial H_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(k_s r^2 \frac{\partial T_s}{\partial r} \right) \quad (2.14) \quad [146]$$

It is also important to find the relationship between the enthalpy term, which is provided by Faghri in the following representation [145]:

$$H = \begin{cases} c_{p,s}(T - T_m) & T < T_m \\ c_{p,l}(T - T_m) + L & T > T_m \end{cases} \quad (2.15) \quad [145]$$

Using enthalpy method provides possibility for simulation of phase change without need to allocate a mushy zone which can be more realistic when simulating phase change in natural working fluid such as water, where mushy zone is almost undetectable.

For simulations for PCM with mushy zone during phase change, the enthalpy method can also be modified as follow:

$$H = \begin{cases} c_{p,s}(T - T_m) & T < T_m - \Delta T \\ \left(\frac{L}{2\Delta T} + \frac{c_{p,s} + c_{p,l}}{2} \right) (T - T_m) & T_m - \Delta T < T < T_m + \Delta T \\ c_{p,l}(T - T_m) + L & T > T_m + \Delta T \end{cases} \quad (2.16) \quad [145]$$

2.2.6.3. Other general coefficient terms available

The heat transfer coefficient, h is used in all numerical models to govern the convective heat transfer rate between HTF and TES materials. Nusselt correlations for packed bed has been provided by various researchers, which can be subsequently used to determine the heat transfer coefficient. Beek provided a Nusselt correlations (Nu_{HTF}) for Reynolds number, $Re > 40$, which is represented as follow:

$$Nu_{HTF} = 3.22 \cdot Re^{1/3} \cdot Pr^{1/3} + 0.177 \cdot Re^{0.8} \cdot Pr^{0.4} \quad (2.17) \quad [146]$$

Wakao et. al. also derived a Nusselt correlation suitable to be used with flow with Re between 15 and 8500 [147], which is listed as follow:

$$Nu_{HTF} = 2 + 1.1 \cdot [6 \cdot (1 - \varepsilon)]^{0.6} \cdot Re^{0.6} \cdot Pr^{1/3} \quad (2.18) \quad [147]$$

Micrometer-sized granular materials have very small particle diameter, d_p which results in extremely low Reynolds number, $Re = \rho v d_p / \mu$, beyond the Re ranges of the two Nusselt correlations mentioned in equations (2.17) and (2.18). De Gracia et. al. cited a Nusselt correlation for $Re < 40$ [146], which is listed as follow:

$$Nu_{HTF} = 18.1 \cdot Pr^{1/3} \quad (2.19) \quad [147]$$

Subsequently, Nu_{HTF} is used to derive the convective heat transfer coefficient, h_{conv} using the following correlation [148]:

$$h_{conv} = \frac{Nu_{HTF} \cdot k_{HTF}}{L_c} \quad (2.20) \quad [148]$$

Where L_c is the characteristic length of the TES material, which under non-uniform arrangement, can be derived as ratio of their total volume to their total surface area.

$$L_c = V_{TES} / A_{TES} \quad (2.21)$$

Natural convection is observed within the encapsulated PCM during its melting process due to the density difference observed between its solid and liquid phase. During melting, PCM turns from solid into liquid state, starting from the encapsulation surface and detaching the solid PCM from the surface. Natural convection is observed due to displacement on liquid PCM volume by solid-state PCM due to buoyancy force. Due to the natural convection effect, heat transfer rate is enhanced. Such enhancement is incorporated into thermal conductivity of PCM, which effective thermal conductivity, k_{eff} can be calculated using the equation below from thermal conductivity of liquid-state PCM [149]:

$$\frac{k_{eff}}{k_{l,PCM}} = 0.74 \left(\frac{Pr}{0.861 + Pr} \right)^{0.25} (Fra)^{0.25} \quad (2.22) \quad [149]$$

F represents the geometric factor, which is determined by encapsulation diameter, D_{outer} as well as solid state PCM diameter, D_{inner} , and can be represented using equation as follow [148]:

$$F = \frac{D_{outer} - D_{inner}}{(D_{outer}D_{inner})^4(D_{outer}^{-1.4} + D_{inner}^{-1.4})^5} \quad (2.23) \quad [148]$$

Ismail and Stuginsky simulated a stone-bed TES system with water as HTF with different models under similar time step and grid sizes [144]. In the study, 2-dimensional models are 20 to 25 times more time-consuming compared to 1-dimensional model. Indeed, as proven in different numerical studies which has been done in the literature [83, 86, 90, 94, 150], 1-dimensional study is able to provide close comparisons between numerical and experimental results and is widely used.

Chapter 3. Case study of cold energy flow from LNG regasification facility to consumption with cold demands

3.1. Methods

3.1.1. Energy carriers and cold demands

There is no study reported on investigating performance of different energy carriers in transporting LNG cold energy from regasification facility to the cold demands. Thus, it is important for such analysis to be carried out. In this chapter, the study carried out to understand the overall performances of cold energy flow, from generations of energy carriers in LNG regasification facility to consumptions at cold demands, is introduced. An LNG regasification facility of infinite size is assumed, which is able to generate as much cold energy as required by the demands. Four cold demands with different requirements on the cold energy are considered:

- a) Air separation unit which generates 1 kg/s liquid nitrogen (LN_2) at -196°C and 1 kg/s liquid oxygen (LO_2) at -184°C , both at atmospheric pressure,
- b) Production of dry ice at 1 kg/s at atmospheric pressure and -78°C ,
- c) Deep-freezing unit with constant cooling demand of 1 MW_t at -20°C , and
- d) District cooling central plant with constant demand of 1 MW_t and cool water output of 7°C .

All four cold demands are assumed to locate in a same industrial cluster located 5 km from the LNG regasification facility. Four energy carriers used to distribute the cold energy from LNG regasification facility to the cold demands are listed as below:

- a) Electricity generated in a cascaded Brayton cycle power plant utilizing LNG cold to improve the performance, distributed by electricity grid,

- b) Liquid CO₂ and chilled water cooled (or charged) using LNG cold, transported using pipelines connecting the LNG regasification facility and the industrial cluster,
- c) PCMs encapsulated and packed in a tank and charged using LNG cold, transported by truck, and
- d) LN₂ generated in an air separation plant utilizing LNG cold, transported by cryogenic truck to the industrial cluster.

Cold demands are able to retrofit their configurations to adapt with the different energy carriers. In high-grade cold-intensive processes not able to be sustained by an energy carrier, electricity energy generated by a conventional combined cycle power plant is obtained from the electricity grid to provide additional work input. For example, air separation process with lowest possible temperature -196°C is impossible to be sustained with sole presence of liquid CO₂, which has a lowest possible operating temperature of -56°C due to its triple point. In such case, a compression with intercooling system will be responsible for the for generation of high-grade cold energy.

The case study carried out is summarized as shown in Figure 3.1. The baseline case is the case where LNG cold is not recovered. LNG is regasified using an ORV with seawater as heat source. The natural gas is sent to a combined cycle power plant near to the regasification facility to generate electricity. The cold demands use conventional configurations, where the main energy input comes from electricity to drive refrigeration systems for generation of cold energy or cold products.

In the case where electricity is generated using LNG assisted Brayton cycle, electricity is transported using the same electricity grid. As there is no change on energy carrier, similar conventional configurations are used by cold demands.

District thermal network uses liquid CO₂ and cooled water as energy carrier and distributes them using pipelines. Supply and return of CO₂ are delivered at a constant pressure such that its phase change temperature is -50°C, and only its latent heat during phase change between liquid and vapor state is used as storage medium. At LNG regasification facility, the return CO₂ is liquefied from vapor phase to liquid phase. At the cold demands, liquid CO₂ supplied is vaporized in a heat exchanger, releasing cold energy at constant temperature. For cooling water, cold energy is supplied using its sensible heat between 4°C and up to 50°C. No phase change is involved for cooling water due to its high boiling point under atmospheric pressure.

Figure 3.1: Case study on utilization of LNG cold by cold demands

In the TES system, latent energy from liquid-solid phase change of PCMs is used to capture the cold energy released by LNG regasification. The PCMs selected have different phase change temperatures, chosen by matching these temperatures with the required temperatures of the cold demands. After being solidified or charged at the LNG regasification facility, the PCMs are distributed using a truck. After the latent

energy is consumed, the PCMs are brought back for another charge process with LNG cold.

LN₂ used as energy carrier is produced by an LNG assisted air separation unit. Alongside producing liquid air products to satisfy the market need (1 kg/s of LN₂ and 1 kg/s of LO₂), extra LN₂ is generated to be used as energy carrier. LN₂ is delivered by cryogenic trucks to the cold demands, where at the demand side, if mechanical work is needed, the work can be supplied using the expansion of LN₂. If no mechanical work is required, the mechanical work is converted into extra cold energy using a refrigeration system.

3.1.2. Assumptions used in the case study

In the case study, the assumptions used are listed as follow:

- a) Composition of LNG is assumed to be 100% methane,
- b) Composition of air is 79% nitrogen and 21% oxygen by volume,
- c) Thermal losses and friction losses in all the systems are negligible, and
- d) All processes are assumed to work under steady-state conditions.

3.1.3. Equations for efficiencies calculations

For heat engines, thermal efficiency, η_{th} and net efficiency, η_{net} are two commonly used key performance indices to analyze their performances. Both efficiencies are defined as the ratio of net work production, $\dot{W}_{net}$ to the heat addition to the system, $\dot{Q}$. Their definitions are listed as equations (3.1) and (3.2), where $\dot{Q}_{in}$ represents heat added to the working fluid, while $\dot{Q}_{fuel}$ represents the heat released by burning the fuel to supply the required $\dot{Q}_{in}$.

$$\eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} \quad (3.1)$$

$$\eta_{net} = \frac{\dot{W}_{net}}{\dot{Q}_{fuel}} \quad (3.2)$$

For most cases, thermal efficiency is not enough to define the real performance of a system, especially when cold energy is involved as the main or extra energy source. Exergy, which defines the amount of useful energy with respect to a reference condition, is more suitable to be used to define the performance of the system in this case. Specific physical exergy, e of a stream can be determined using Equation (3.3):

$$e = H - H_0 - T_0(s - s_0) \quad (3.3)$$

where H and s are specific enthalpy and entropy of a material, while H_0 and s_0 are these properties under reference conditions of temperature, T_0 at 15°C and pressure, p_0 at 1 atm. The rate of physical exergy, $\dot{E}$ transported by a stream with mass flow rate, $\dot{m}$ can be calculated as Equation (3.4):

$$\dot{E} = \dot{m}e \quad (3.4)$$

Exergy efficiency, η_{ex} can then be calculated using Equation (3.5) and is defined as the ratio of usable exergy to total exergy input into the system. All forms of exergy can be considered as input, $\dot{E}_{in}$ into the system, including chemical exergy (from fuels), which is subsequently converted into physical exergy for other materials (i.e. heated working fluids of thermal cycles) through combustion process. For streams of exergy loss $\dot{E}_L$ and exergy destroyed $\dot{E}_D$, only physical exergy is considered.

$$\eta_{ex} = 1 - \frac{\sum \dot{E}_L + \sum \dot{E}_D}{\sum \dot{E}_{in}} \quad (3.5)$$

3.2. Generations of energy carriers

Generations of the four introduced energy carriers are discussed. The layout of each system used to generate these energy carriers are introduced in detail.

3.2.1. Electricity generated using baseline case – combined cycle

Figure 3.2: Layout of combined cycle used to generate electricity in the baseline case

A combined cycle power plant composed of an open air Brayton cycle (topping cycle) and a closed steam Rankine cycle (bottoming cycle) is modelled. The energy carrier produced is electricity. The schematic diagram of the combined cycle power plant is shown in Figure 3.2. In the topping cycle represented by state points (1) to (6), the inlet air is compressed in a compressor (CP-1) before mixed with natural gas fuel and combusted to 1400°C in a combustion chamber (CC-1). The flue gas leaving the combustion chamber is then passed through an expander (EP-1) and a heat recovery steam generator (HRSG) where heat of the flue gas is utilized to boil the water of the

bottoming cycle before being released into the atmosphere. In the steam Rankine cycle represented by state points (11) to (14), liquid state water from the condenser (HX-1) is pressurized using a pump (PP-1) before sent to the HRSG to be boiled and superheated. The superheated steam is then passed through an expander (EP-2) and condensed in HX-1. The parameters used for the simulation and the results obtained are reported in Table 3.1.

Table 3.1: Main parameters and performance for the baseline case

OPERATING PARAMETERS	VALUES
Brayton cycle pressure ratio – [CP-1]	15
Brayton cycle turbine inlet temperature (°C) – [EP-1]	1400
Pressure drop across heat exchangers (%) – [HRSG & HX-1]	1-3
Compressor and pump isentropic efficiency (%) – [CP-1 & PP-1]	85.0
Turbine isentropic efficiency (%) – [EP-1 & EP-2]	90.0
Steam Rankine cycle pressure ratio – [PP-1]	550
Steam condensation temperature (°C) – [HX-1]	40
PERFORMANCE PARAMETERS	
Thermal efficiency (%)	53.5
Exergy efficiency (%)	50.5

Using dual-pressure or triple-pressure steam generator in the steam Rankine cycle is shown to yield a thermal efficiency increase of 0.8% and 1.0%, respectively [151]. However, in this study, for simplicity, combined cycle with single pressure steam generator is modelled. The exergy flow Sankey diagram (which explains the exergy efficiency) is relocated to Appendix chapter.

3.2.2. Electricity generation using LNG assisted Brayton cycles

The combination of an open air Brayton cycle with a closed nitrogen Brayton cycle and an LNG direct expansion cycle is modelled, with electricity as the energy carrier generated. Selection of such model is to utilize as much as possible the ultra-low temperature cold energy from LNG, as well as chemical energy from the fuel. In Table 2.2, a number of power cycles have been assessed with different ranges of maximum temperature (turbine inlet temperature) and minimum temperature (compressor / pump inlet temperature). Gas Brayton cycles, CO₂ Rankine cycles and combined cycles can achieve thermal efficiencies above 60%. Despite the high thermal efficiencies reported, closed real gas Brayton cycles have reported relatively lower net efficiencies than open air Brayton cycles. In an open air Brayton cycle, fuel is mixed with air and combusted to achieve high temperature in the flue gas, which is subsequently used as working fluid. In a closed Brayton cycle, heat addition to the working fluid is done using a heat transfer interface with another heat source maintained at a higher temperature than the working fluid. This results in more fuel burnt to achieve a same turbine inlet temperature with an open Brayton cycle and a large mismatch between $\dot{Q}_{fuel}$ and Q_{in} , which explain the main difference on its high thermal efficiency but low net efficiency.

An open air Brayton cycle is chosen as topping cycle due to the high net efficiency it is able to achieve. For the bottoming cycle, a closed nitrogen Brayton cycle is chosen because of its ability to be cooled to near the boiling temperature of LNG, thus effectively reducing the compression power required. An LNG direct expansion cycle is also included to harvest the mechanical exergy of LNG. The schematic diagram of the LNG assisted power cycle is shown in Figure 3.3.

Figure 3.3: Schematic diagram of an LNG assisted power cycles (2 Brayton cycles with a direct expansion cycle)

Table 3.2: Main parameters and performances for LNG assisted power cycle

OPERATING PARAMETERS	VALUES
Air BC pressure ratio – [CP-1]	21
Air turbine inlet temperature (°C) – [EP-1]	1400
Pressure drop across heat exchangers (%) – [HX-1, HX-2 & HX-3]	1-3
Compressor and pump isentropic efficiency (%) – [CP-1, CP-2 & PP-1]	85.0
Turbine isentropic efficiency (%) – [EP-1, EP-2 & EP-3]	90.0
Nitrogen BC pressure ratio – [CP-2]	8.7
PERFORMANCE PARAMETERS	
Thermal efficiency (%)	66.5
Exergy efficiency (%)	51.1

The open air Brayton cycle is indicated by state points (1) to (6). The inlet air is first pre-cooled to 5°C (HX-1) using 8.6% of LNG before being pressurized in the compressor (CP-1). Temperature of 5°C is selected because the inlet air is untreated and to prevent the water vapor from being solidified. The compressed air is then mixed

with $\approx 10\%$ of natural gas from expander of the LNG direct expansion cycle (EP-3) and heated to 1400°C in the combustion chamber (CC-1). The high temperature gas then drives an expander (EP-1) before rejects heat energy to the compressed nitrogen via a heat exchanger (HX-2). The untreated flue gas is then rejected to the atmosphere.

The closed nitrogen Brayton cycle is indicated by state points (11) to (14) where the cooled nitrogen at -130°C is compressed in a compressor (CP-2) and heated to 620°C utilizing the waste heat from the flue gas of the open air Brayton cycle via HX-2. The heated nitrogen is then used to drive an expander (EP-2) before being cooled in another heat exchanger (HX-3) by the LNG exiting the pump of direct expansion cycle.

LNG from the storage tank is split into two streams. Stream (22) to (23) is utilized to precool the inlet air of the open air Brayton cycle, and stream (24) to (28) represents the LNG direct expansion cycle. In this second stream, LNG from the storage tank is first pressurized using a pump (PP-1) before heated to about 250°C via HX-3 using the turbine exhaust of the closed nitrogen Brayton cycle. The heated natural gas is then used to drive an expander (EP-3) to generate electric energy. Part of the natural gas (27) is sent to the open air Brayton cycle, while the rest (28) together with stream (23) is supplied to the rest of the natural gas consumers. Table 3.2 lists the operating parameters of the LNG assisted power cycle and its performances under these criteria. The exergy flow Sankey diagram is relocated to the Appendix chapter.

3.2.3. Liquid CO_2 and chilled water charged by LNG cold

As shown in Table 2.3, various working fluids, including HFCs or HCs have been used to distribute cold energy from LNG regasification facility to different cold demands. However, the interest towards natural working fluids and HFOs as alternative working

fluids, especially for long distance distribution of cold energy, has recently increased because of concerns about the GWP of the HFCs and safety issues of the HCs.

Figure 3.4: Schematic diagram of thermal network for working fluid distribution

Table 3.3: Main parameters and performance for the thermal network

OPERATING PARAMETERS	CO ₂	Water
Required mass flow rate (kg/s)	13.0	15.0
Supply temperature (°C)	-50 (liquid)	5
Return temperature (°C)	-50 (vapor)	50
LNG flow rate (kg/s)	7.7	
PERFORMANCE PARAMETERS		
Exergy efficiency (%)	29.2	

In a case study done for Geneva, Switzerland [60], three working fluids are considered: water, CO₂ and HFO R1234yf; water is used to provide heating/cooling using its sensible heat, while CO₂ and R1234yf provide heating/cooling using their latent heat. All three working fluids show similar electricity consumption for operations. In another study, CO₂, R1234yf and HFO R1234ze are simulated as working fluid [59], where

CO₂ is found advantageous due to smaller pipeline diameter required. Both R1234yf and R1234ze are excluded from this study because of their high cost [60].

A dual-temperature thermal network is considered with liquid CO₂ and chilled water serving as energy carriers for high-grade and low-grade cold. These energy carriers are distributed using pipelines connecting the LNG regasification facility with the industrial cluster. Liquid CO₂ is pumped to the cold demands and returned in vapor state after the cold energy transfer. In a similar way, chilled water is pumped and returned as warm water. The schematic diagram is shown in Figure 3.4. In thermal network, the cold applications can choose the appropriate energy carrier that suits them the most. For example, deep freezing and district cooling applications only require cold from the liquid CO₂ when temperature of chilled water is above their demand. For air separation unit and dry ice generation, cold energy is taken from both chilled water and liquid CO₂. These two different types of cold demands are illustrated as cold applications X and Y.

The distribution parameters and required amounts of CO₂ and water are tabulated in Table 3.3. The exergy flow Sankey diagram is relocated to the Appendix chapter. For this thermal network, pressure of CO₂ working fluid is set at 6.8 bar, which corresponds to its boiling point at -50°C. This condition has been chosen as an optimum operating point, considering the triple point of CO₂ (-56.4°C) and the trade-off if higher operating temperature is selected (larger temperature mismatch and exergy destruction at the central plant).

3.2.4. Latent heat thermal storage charged by LNG cold

Figure 3.5: Schematic diagram for TES systems used to distribute LNG cold

Table 3.4: Main parameters and results for LNG assisted TES system

OPERATING PARAMETERS	PCM-A	PCM-B	PCM-C	PCM-D
Name / Composition	24.8 wt% HCl	24.0 wt% LiCl	SN33	AN03
Phase Change Temperature (°C)	-86	-67	-33	-3
Latent Heat (kJ/kg)	810	364	245	328
Mass Rate (kg/s)	1.7	2.2	12.1	3.1
LNG Flow Rate (kg/s)	7.4			
PERFORMANCE PARAMETERS				
Exergy Efficiency (%)	24.0			

Suitable PCMs are chosen from the work of Oro et al. [125] to recover the LNG cold and deliver the cold energy (Figure 3.5). At the central plant, the LNG is delivered through a set of heat exchangers, which enable heat transfer to different tanks

containing the four PCMs. The charged PCMs tanks are then delivered to their respective cold demands by truck. Upon unloading the charged tanks, the truck picks up the discharged tanks and returns to the central plant.

Four PCMs are chosen by matching their phase change temperature as close to the temperature requirements of the cold demands. The first PCM chosen is a eutectic water-salt solution: 24.8 wt% hydrochloric acid (HCl) solution with phase change temperature of -86°C . This PCM is chosen for air separation unit, as PCM with lower phase change temperature is not developed up to the point of the study. The second PCM chosen is another eutectic water-salt solution, 24 wt% lithium chloride (LiCl) solution with phase change temperature of -67°C . This PCM is targeted for the dry ice production. The last two PCMs chosen are two commercial PCM products dedicated for cold storage: SN33, which undergoes phase change at -33°C , and AN03, which undergoes phase change at -3°C . Thermo-physical properties of each PCM chosen, as well as performance of the system are reported in Table 3.4. The exergy flow Sankey diagram is relocated to the Appendix chapter.

3.2.5. LN_2 generated by LNG assisted air separation unit

Liquid air energy carrier can generate both mechanical and cooling power during its consumption. The mechanical power can be generated by pumping the liquid air to high pressure, vaporizing it with environmental heat source and finally using its pressure energy to operate different expanders such as reciprocating engines [67] and/or turbines [16, 152]. The cooling power can be harvested during vaporization of pressurized liquid air and from the cold air at exit of the expanders. In this study, liquid air products are involved as one of the desired cold products from the industrial cluster. Thus, it is not feasible to operate another plant for production of liquid air as energy carrier. Instead,

extra LN_2 is generated by the air separation unit on top of the desired air products, and is used as energy carrier for other cold demands.

With LNG cold, it is possible to avoid using the conventional setting of Linde's double separation column to produce liquid air products. In a conventional double column setup, the inlet air is compressed to a high pressure of ≈ 12 MPa [153]. There have been multiple papers discussing air separation operations with LNG cold. Innovative layouts have been considered, such as single-column producing liquid air products [154] and double column processes producing liquid air products [155] or vapor air products [156] aimed at reducing the level of compression required to below that of the typical air separation plants.

A modified double column process is used to generate the required amount of liquid air products. Schematic diagram of the process is shown in Figure 3.6. The inlet air stream (1) is first pressurized using a compressor (CP-1) to slightly above the pressure of high-pressure column (HPC) at ≈ 6 bar. The compressed air stream (2) is then precooled in a heat exchanger (HX-1) using cooling water before passed through a multi-stream heat exchanger (MSHE) where the air is cooled by streams of unwanted air products and cold released from LNG regasification. The cooled feed air (4) is then delivered to the HPC and separated into gaseous high-purity nitrogen (7) and an oxygen-enriched stream (5), which is delivered to the low-pressure column (LPC) (6). The gaseous nitrogen stream (7) is then compressed in compressor CP-2 to ≈ 3 MPa (8), before cooled to its liquid state (9) using LNG cold energy in another heat exchanger (HX-2). Required amount of high-pressure LN_2 is extracted at state point (10) and pressure-relieved before being separated into the liquid (12) and vapor nitrogen product (13). The amount of LN_2 produced depends on the total demand, which consists of the 1 kg/s market need and those required by the downstream cold demands. The vapor state

nitrogen generated is then sent to the MSHE for feed air cooling purpose. The rest of the high-pressure LN₂ stream (15) is pressure-relieved and delivered to the low-pressure column (LPC).

Figure 3.6: Schematic diagram of an LNG assisted air separation unit

Table 3.5: Main parameters and performance of LNG assisted air separation unit

MAIN PARAMETERS	Value
Pressure of HPC (bar)	5.5
Pressure of LPC (bar)	1.0
Compressor outlet pressure of CP-2 (bar)	30.0
Mass rate of LN ₂ produced (kg/s)	5.5
Mass rate of LO ₂ produced (kg/s)	1.0
LNG flow rate (kg/s)	5.3
PERFORMANCE PARAMETERS	
Exergy efficiency (%)	33.1

From the LPC, pure LO₂ stream (17) and purge nitrogen stream (21) is produced. 1 kg/s of LO₂ required is extracted (18) while the rest (19), together with the purge nitrogen stream is delivered to the MSHE for feed air cooling. Feed air cooling will also be carried out by the LNG regasification process which is represented by streams (25) to

(26). The parameters and the results of the abovementioned LNG assisted air separation unit is tabulated in Table 3.5. The exergy flow Sankey diagram is relocated to the Appendix chapter.

3.3. Distributions of energy carriers

In this section, distribution methods of the energy carriers are introduced. Electricity generated by both baseline case and LNG assisted power cycle is transmitted over the electricity grid, while liquid/vapor CO₂ and water are distributed through a pipeline network connecting the LNG regasification facility and the industrial cluster. PCMs and LN₂ are contained inside cryogenic containers and distributed by trucks.

3.3.1. Electricity grid

Distribution and transmission losses of electricity via electricity grid is obtained from averaged values over ten years from 2006 - 2015 [157]. The averaged transmission loss via electricity grid is about 5.5%, indicating the exergy efficiency for the electricity grid transmission is 94.5%.

3.3.2. Pipeline network for carbon dioxide and chilled water

Insulated pipelines are used to distribute liquid CO₂ at -50°C and water at 5°C. The pipes are insulated using fiber glass with thermal conductivity of 0.04 W/m·K [158]. The losses are divided into two main types: thermal and friction loss. Thermal power lost, $\dot{W}_{loss,thermal}$ can be deduced using Equation (3.6):

$$\dot{Q}_{loss,thermal} = \frac{\Delta T}{Res_{ov}} \quad (3.6)$$

where ΔT represents the temperature difference between the working fluid and environment and Res_{ov} represents the overall thermal resistance which can be deduced using Equation (3.7):

$$Res_{ov} = Res_{conv,in} + Res_{cond,pipe} + Res_{cond,ins} + Res_{conv,out} \quad (3.7)$$

where $R_{conv,in}$ is the convection resistance between working fluid and pipe, $R_{cond,pipe}$ is the conduction resistance of pipeline material, $R_{cond,ins}$ is the conduction resistance of pipeline insulation and $R_{conv,out}$ is the convection resistance between insulation and the ambient environment. Each resistance can be deduced using Equation (3.8) and (3.9):

$$Res_{conv} = 1/hA \quad (3.8)$$

$$Res_{cond} = \frac{\ln D_{outer}/D_{inner}}{2\pi kL} \quad (3.9)$$

where h represents the convective heat transfer coefficient, A represents the surface area for heat transfer, D represents the diameter of pipe, k represents the thermal conductivity of pipeline material or insulation and L represents the length of the pipe.

For insulation material with very small thermal conductivity and large thickness, it is expected that $R_{cond,ins}$ dominates other resistance terms and thus, Equation (3.7) can be simplified into Equation (3.10).

$$Res_{ov} \approx Res_{cond,ins} \quad (3.10)$$

The friction loss is calculated using Equation (3.11):

$$W_{loss,friction} = \frac{fL\rho v^2}{2D_{inner}} \quad (3.11)$$

where f is the friction factor that is obtained with information on a fluid flow's Reynold's number and pipe roughness, ρ represents the working fluid density and v represents the velocity of working fluid. Table 3.6 shows the main parameters and the performance of the liquid CO₂ and chilled water pipelines, respectively.

Table 3.6: Main parameters and results for the pipeline network

MAIN PARAMETERS	Liquid CO ₂ pipe	Water pipe
Velocity of working fluid (m/s)	0.8	1
Inner diameter of pipe (m)	0.134	0.138
Insulation thickness (m)	0.08	0.04
Temperature difference with ambient (K)	80	25
PERFORMANCE PARAMETERS		
Pressure loss per length (Pa/m)	52.4	68.7
Friction loss for 5 km pipe (kW)	2.9	5.2
Thermal loss for 5 km pipe (kW)	115.1	61.9

3.3.3. Trucks for PCMs and LN₂ distribution

Trucks are used to distribute the PCMs from the LNG regasification site to the cold demands, as it is not possible to pump solid-state PCMs through a pipeline. Besides, environmental issue can be minimized by carefully insulating the PCMs from ambient environment, minimizing the possibility of leakage.

For usage of LN_2 as energy carrier, trucks are used for distribution because pumping the LN_2 over long distances requires ultra-high-grade insulation to minimize thermal losses due to large temperature difference between LN_2 and environment. Such thermal loss is massive and raise environmental concern as fogging or icing can form over the pipelines due to leakage of ultra-cold energy.

A semi-trailer truck weighing 40 tons with 20 tons payload is selected. The road transport loss information is obtained from US Environmental Protection Agency [159] and is reported in Table 3.7.

Table 3.7: Road transport parameters and performances of a semi-trailer truck [159]

MAIN PARAMETERS	Value
Distance travelled (km)	5.0
Total weight (tons)	40.0
PERFORMANCE PARAMETERS	
Diesel consumed (liter)	7.0
CO_2 emissions (kg)	18.3

Specially designed tanks are used to accommodate the PCMs and the LN_2 . Details of LN_2 tanks are obtained from Linde Engineering [160], while the PCMs are transported using tanks with similar parameters. These parameters are reported in Table 3.8.

Table 3.8: LN_2 and PCM cryogenic containers information [160]

MAIN PARAMETERS	Value
Payload Weight (tonnes)	20.0
Boil off rate (% per day)	0.3

3.4. Configurations and performances of cold demands when subjected to different energy carriers

Cold demands that generate cold products (liquid nitrogen / oxygen and dry ice) or cold services (refrigeration and district cooling) are introduced. For the baseline case, conventional configurations are used. When alternative cold carrier is present, the cold demands can modify their configurations to adapt to the specific cold carrier. For a clear comparison, each application is assumed to stand-alone and do not use cold left over or degraded from other cold consumer.

3.4.1. Generation of liquid air products

As mentioned in Section 3.2.5, generation of LN_2 can be carried out in an air separation with assistance from LNG cold, with standard liquid air products demand met while generating extra LN_2 as energy carrier. Thus, there is no air separation plant required at a distance away which consumes LN_2 as energy carrier.

For liquid air products LN_2 and LO_2 obtained using electricity as exergy input, a modified Linde's double-column system, Heylandt's system is generally used [153]. As shown in Figure 3.7(a), as represented by streams (1) to (9), the inlet air is compressed to ≈ 12 MPa with intercooling and aftercooling by cooling water and a 1,1,1,2-tetrafluoroethane (R134a) heat pump (HX-5) to state (10). The compressed air is then split into two streams. Stream (11) is passed through an expander (EP-1) and delivered to the high-pressure column (HPC) while stream (13) is cooled with MSHE to state (14) using waste nitrogen stream (29) and oxygen stream (26) before being pressure-relieved (15). From the HPC, an oxygen-enriched stream (16) is produced and pressure-relieved to (17). Stream (15) then mixes with (17) and the mixed stream (18) is delivered to the low-pressure column (LPC). Another stream produced by the HPC is the high purity LN_2 stream (19), in which the market need of 1 kg/s is extracted as

— Pure N₂ stream
 - - - Purge N₂ stream
 - - - Pure O₂ stream
 - - - R134a from heat pump
 — Inlet air stream
 — Cooling water stream
 — O₂-enriched stream

Legend:

- Pure N_2 stream
- Purge N_2 stream
- Pure O_2 stream
- Liquid CO_2/HCl solution
- Inlet air stream
- Chilled water/SN-33
- O_2 -enriched stream

Figure 3.7: Schematic diagrams of air separation unit using energy input of (a) electricity only (b) electricity assisted by liquid CO₂/chilled water/PCMs

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with main changes in the four-stage compression and intercooling section. The energy carriers mentioned here can be chilled water/liquid CO₂ if cold is obtained from the thermal network or PCMs of SN-33 together with 24.8 wt% HCl if cold is obtained from the thermal storage.

Represented by stream (1) to (7), the inlet air is compressed and intercooled using chilled water in HX-1 and liquid CO₂ in HX-2 (SN-33 and HCl solution if energy carriers from thermal storage). Represented by stream (8) to (10), after the third stage of compression, intercooling is carried out using chilled water (or SN-33) in HX-5 and unwanted product streams from the air separation in MSHE-1 to further lower the stream temperature. Upon the last stage of compression, aftercooling represented with streams (11) to (13) is carried out using chilled water and liquid CO₂ (or SN-33 and HCl solution) again. The processes after stream (13) is exactly the same with processes after stream (10) for air separation process using only electricity exergy input.

Table 3.9: Input exergy and performance of air separation units utilizing different energy carriers to produce 1 kg/s LN₂ and 1 kg/s LO₂

Energy carrier	Electricity	Liquid CO ₂ /water	PCMs
SOURCE OF EXERGY INPUT (MW)			
Electricity Exergy, E_E	4.64	3.62	3.59
Exergy of Energy Carrier, $E_{CW}/E_{LCO_2}/E_{PCM}$	0.00	0.89	1.12
PERFORMANCE PARAMETERS			
Exergy Efficiency (%)	25.61	26.86	25.69

The results are tabulated in Table 3.9, which reports the performance of the air separation unit using different energy carriers as energy input. It is observed that with the existence of cold energy carriers, which replace conventional refrigeration systems

and lower the temperature for intercooling process, the amount of electricity required for compressor work is greatly reduced. The exergy flow Sankey diagram is relocated to the Appendix chapter.

3.4.2. Generation of dry ice

Four different configurations are considered according to the energy carriers utilized by the dry ice production processes. Figure 3.8(a) shows the setup of a conventional dry ice production using electricity as main energy input described by Arora [161]. First, inlet CO₂ stream (1) is mixed with recycled CO₂ stream (12) from the snow chamber to lower its temperature. The mixed stream (2) is then compressed to a pressure slightly above the triple point of CO₂ (3) before water-cooled to state (4). Afterwards, it is mixed with another recycled stream (13) from the separation column before being further compressed to ≈ 20 bar (6). The compressed CO₂ is cooled by a water cooler and an R134a heat pump (represented by (21)-(24)) to liquid state (8), before being pressure-relieved to state (9) with pressure slightly above its triple point. The liquid CO₂ is separated from its vapor state in a separation column (SC); the vapor stream is recycled (13) and liquid CO₂ (10) is sent to the snow chamber. In this specially designed snow chamber, the liquid CO₂ is pressure-relieved, and dry ice is collected as the output product as state (11).

The dry ice production using liquid CO₂/chilled water as assistive source of energy input is shown in Figure 3.8(b). The process is similar to the conventional dry ice production, but the cooling steps are modified to reduce the compressor work. Inlet CO₂ stream (1) is first precooled using liquid CO₂ from the thermal network to about -40°C. The precooled stream (2) is then mixed with recycled CO₂ stream (15) from the snow chamber to state (3) to further reduce its temperature. The mixed stream is then

compressed to state (4), slightly above the CO₂ triple point pressure, before being cooled by chilled water in HX-2 and liquid CO₂ in HX-3 to state (6). Next, it is mixed with the recycled CO₂ stream (13) from the separation column before being further compressed to ≈ 10 bar (8). Further cooling is done by chilled water and liquid CO₂ to state (10). The liquefied CO₂ is then pressure-relieved (11) and sent to the separation column. From the separation column, liquid CO₂ stream (12) is then delivered to the snow chamber to be processed into dry ice while the vapor stream (13) is recycled for cooling. This dry ice production mechanism still uses two stage compression, which is found to consume much less power compared to a single-stage configuration.

(a)

(b)

(c)

(d)

Figure 3.8: Schematic diagrams of dry ice production using energy input of (a) electricity only (b) electricity and liquid CO₂/chilled water (c) electricity and PCMs (d) LN₂ only

With availability of lower temperature cold sources such as PCMs, the CO₂ compressor outlet pressure can be further reduced, simplifying the whole setup into a single compression process as shown in Figure 3.8(c). In this setup, salt solution 24 wt% LiCl is used as the PCM with phase change temperature of -67°C. The input CO₂ stream (1) is first pre-cooled using cold released from the PCM to state (2), before mixed with recycled CO₂ (8) from the snow chamber. The mixed CO₂ stream (3) is then compressed to state (4) with pressure just above the triple point and is cooled using cooling water and PCM to its liquid state (6) before delivered to the snow chamber.

With LN₂ energy carrier, as shown in Figure 3.8(d), dry ice can be produced with single-stage compression process. Inlet CO₂ stream (1) is mixed with recycled CO₂ (7) from the snow chamber. The mixed stream (2) is then compressed to ≈ 8.5 bar using mechanical power generated during the expansion of LN₂. The compressed CO₂ stream (3) is then cooled to state (4) by using cooling water and state (5) using a mix of water-glycol and nitrogen gas (13) exiting the isothermal expander (EP-1), before being delivered to the snow chamber. In this case, the CO₂ compressor outlet pressure is set at 8.5 bar, which is optimized based on the amount of LN₂ needed and the availability of mechanical energy in the LN₂ supplied to the expander. Inside the isothermal expander (EP-1), the LN₂ stream (12) is mixed with water-glycol solution (11) and is evaporated, generating mechanical power. The mixed stream (13) is then delivered to HX-2 to liquefy the CO₂ prior to be discharged.

Table 3.10: Input exergy amounts and performance by utilizing different energy carriers to produce 1 kg/s dry ice

Energy carrier	Electricity	Liquid CO ₂ /water	PCM	LN ₂
SOURCE OF EXERGY INPUT (MW)				
Electricity Exergy, E_E	0.79	0.24	0.18	0.00
Exergy of Cold Carriers, $E_{CW}/E_{LCO2}/E_{PCM}/E_{LN2}$	0.00	0.49	0.32	1.22
PERFORMANCE PARAMETER				
Exergy Efficiency (%)	32.99	39.98	58.27	23.84

Table 3.10 shows the amount of exergy input and the exergy efficiencies of dry ice production processes using different energy carriers as their energy sources. With the cold energy carriers (liquid CO₂, chilled water and PCMs), the dependency on electrical exergy is reduced due to reduced compressor work as a result of reduction of

compressor inlet temperature, as well as elimination of refrigeration systems for cooling water. With usage of LN_2 energy carrier, the dependency on electricity in the dry ice production process is totally eliminated because of carrier's ability to provide mechanical work for compression of CO_2 . The exergy flow Sankey diagram is relocated to the Appendix chapter.

3.4.3. Deep freezing

For deep freezing purpose, 1 MW_t of cold is constantly supplied to air that is cooled from -10°C to -20°C . Conventional deep-freezing processes utilize an R134a heat pump to provide the cold energy, with a coefficient of performance (COP) of 2.0. Layout of the process is shown in Figure 3.9(a). The returned air (1) is cooled to -20°C (2) via HX-1 using R134a heat pump cycle, represented by streams (11) to (14). When energy carriers, such as liquid CO_2 or PCM SN33 with supply temperature of -50°C and -33°C are considered, single heat exchangers replace the refrigeration system as shown in Figure 3.9(b).

(a)

(b)

(c)

Figure 3.9: Schematic diagram for deep freezing process using energy input of (a) electricity only (b) liquid CO_2 /PCM (c) LN_2 only

Table 3.11: Input exergy amounts and performance of deep-freezing processes utilizing different energy carriers

Energy carrier	Electricity	Liquid CO_2	PCM	LN_2
SOURCE OF EXERGY INPUT (MW)				
Electricity Exergy, E_E	0.49	0.00	0.00	0.00
Exergy of Cold Carriers, $E_{CW}/E_{\text{LCO}_2}/E_{\text{PCM}}/E_{\text{LN}_2}$	0.00	0.61	0.34	0.81
PERFORMANCE PARAMETER				
Exergy Efficiency (%)	32.79	31.72	55.95	23.75

LN_2 is able to generate cold and mechanical power at the same time when used to drive an isothermal expander. Shown in Figure 3.9(c), in the isothermal expander (EP-1), LN_2 stream (22) is mixed with water-glycol solution (21) to be evaporated, generating

mechanical power in the process. The mechanical power is used to drive an R134a heat pump cycle, which is represented by streams (11) to (14), with COP of 2.0 for heat extraction from the inlet air stream (2) via HX-2. The mixture of LN₂ and water-glycol solution (23) exiting EP-1 at a low-temperature, is used for heat extraction from another stream of inlet air stream (4) via HX-1.

Table 3.11 tabulates the amount of exergy input for deep-freezing processes acquiring different energy carriers as energy source. For conventional deep freezing, the main energy source comes from electricity. For deep freezing processes using alternative cold carriers, the dependency on electricity is completely eliminated. The exergy flow diagrams are relocated to Appendix chapter.

3.4.4. District cooling

The industrial district is cooled using a district cooling system to achieve energy savings compared to stand-alone cooling system in each industrial facility. 1 MW_t of constant cooling power is assumed and is supplied using chilled water from a central plant to each facility via a pipeline system that is already in-place. In this scenario, it is assumed that this central plant receives the returned chilled water at 15°C and cool it to 5°C before supplying it to the district cooling network again.

In conventional district cooling process using electricity input, a heat pump with COP 4.2 is used to convert electricity to cooling energy to cool the return chilled water. The scenario is similar to the deep freezing process as shown in Figure 3.9(a), with streams (1) and (2) replaced with return water at 15°C and chilled water at 5°C respectively. With liquid CO₂ or PCM AN-03 energy carriers to supply cold energy for district cooling, due to their low temperatures, the heat pump cycle is replaced by a single heat

exchange process, similar to the deep-freezing process shown in Figure 3.9(b), where streams (1) and (2) are replaced with returned water and chilled water.

The district cooling can also be powered by LN₂. The setup is similar to the deep-freezing process shown in Figure 3.9(c), in which streams (1), (2) and (4) are replaced with returned water and streams (3), (5) and (6) replaced with chilled water. The heat pump cycle represented with streams (11) to (14) has a COP of 4.2 and utilize mechanical energy produced by LN₂ during the nitrogen evaporation process to drive the compressor. This heat pump cycle is used to cool the water through HX-2 while direct heat exchange occurs through HX-1 between the mixture of water-glycol with boiled nitrogen (23) and the returned water (4).

Table 3.12: Input exergy amounts and performance for cooling of returned water utilizing different energy carriers

Energy carrier	Electricity	Liquid CO ₂	PCM	LN ₂
SOURCE OF EXERGY INPUT (MW)				
Electricity Exergy, E_E	0.24	0.00	0.00	0.00
Exergy of Cold Carriers, $E_{CW}/E_{LCO2}/E_{PCM}/E_{LN2}$	0.00	0.61	0.07	0.49
PERFORMANCE PARAMETER				
Exergy Efficiency (%)	6.95	3.66	27.08	4.06

As shown in Table 3.12, the performance of district cooling using different energy carriers is similar to the performance of deep-freezing process, where only electricity is only required for the conventional process with only electricity exergy input choice. The exergy flow Sankey diagram is relocated to the Appendix chapter.

3.5. Exergy flow chain and performances from generation of energy carriers to individual cold consumer

This section explains the performance when the exergy flows are studied from generation of an energy carrier, its distribution and final consumption at different cold consumers, which is illustrated as the overall process in Figure 3.1. To understand the CO₂ emissions for the overall processes subjected to different energy carriers, all the electricity consumed are converted to amount of primary fuel consumed according to respective electricity generation method. Another source of CO₂ emission is the distribution of PCMs and LN₂ by trucks. Finally, efficiency of the overall flow chain is also considered.

3.5.1. Exergy flow chains ending at air separation unit

From Table 3.13, the air separation unit utilizing electricity generated by LNG assisted power cycle has the highest efficiency among all, with advantage over the air separation unit coupled to the baseline combined cycle by significantly reducing the amount of natural gas consumed. However, the overall advantage is not significant as it also consumes vast amount of exergy from the LNG physical exergy, which is wasted if not recovered. For air separation unit coupled to a thermal network or a thermal storage, the dependency on cold exergy contained in the LNG significantly increased, thus reducing the overall exergy efficiency of these setups. For the comparison of the overall CO₂ emissions for the different setups of air separation units, due to the large consumption of natural gas for electricity generation, an air separation unit coupled to the baseline combined cycle yields the highest overall CO₂ emissions, followed by an air separation unit coupled to the LNG thermal cycle. Due to similarity in the setups, air separation units coupled to the thermal storage and thermal network yield the least

CO₂ emissions due to their significantly reduced compression work, which is caused by the presence of the subzero temperature energy carriers for intercooling process.

Table 3.13: Exergy input and performances of air separation units coupled to different energy carriers

Source of Energy Carrier	Baseline	LNG	Thermal	Latent
		Thermal Cycle	Network	Thermal Storage
SOURCE OF EXERGY INPUT (MW)				
NG Chemical Exergy, $E_{C,NG}$	9.59	7.83	7.07	7.00
LNG Physical Exergy, $E_{P,LNG}$	0.00	1.79	3.59	4.41
Diesel Fuel Exergy, E_{fuel}	0.00	0.00	0.00	0.12
PERFORMACE PARAMETERS				
Overall Exergy Efficiency (%)	12.35	12.50	10.30	10.07
Overall CO ₂ Emissions (kTPA)	16.64	13.59	12.26	12.41

3.5.2. Exergy flow chain ending at dry ice generation facility

From Table 3.14, the cleanest and most exergy efficient energy carrier for dry ice production is the PCM thermal storage. This is because with suitable PCM to assist in the dry ice production, the dry ice production setup is simplified from two-stage compression to single-stage, significantly reducing the compression work required and increasing its efficiency. Usage of liquid CO₂ and chilled water as energy carriers, is the second cleanest option for dry ice production due to large reduction in compression work due to removal of extra heat pump used to provide intercooling (illustrated in the conventional dry ice production process). LN₂ as energy carrier has the lowest

performance despite only a single stage compression is required. Despite availability of LNG cold, air separation is still an energy-intensive process. Besides, the high-grade cold contained in the LN₂ cannot be utilized completely by the dry ice production, causing large amount of exergy destruction in the process, further reducing the overall exergy efficiency. The exergy flow for each energy carrier from their generations to consumptions in respective dry ice facility is relocated to Appendix chapter.

Table 3.14: Exergy input and performances of dry ice production downstream different energy carrier generation processes

Source of Energy Carrier	Baseline	LNG Power Cycle	Thermal Network	PCM Thermal Storage	LNG ASU
SOURCE OF EXERGY INPUT (MW)					
NG Chemical Exergy, $E_{C,NG}$	1.73	1.41	0.49	0.37	4.62
LNG Physical Exergy, $E_{P,LNG}$	0.00	0.32	1.46	1.18	2.08
Diesel Exergy, E_{fuel}	0.00	0.00	0.00	0.03	0.02
PERFORMANCE PARAMETERS					
Exergy Efficiency (%)	15.70	15.88	13.08	18.42	4.26
CO ₂ Emissions (kTPA)	3.00	2.45	0.85	0.71	8.07

3.5.3. Exergy flow chain ending at deep-freezing warehouse

The amount of exergy source consumed and the performance parameters are shown in Table 3.15. For overall exergy efficiency, deep freezing utilizing electricity (from both the baseline combined cycle and LNG assisted power cycle) as main energy input is

more advantageous because of the relatively smaller amounts of total exergy input needed due to high COP of refrigeration systems, as compared with deep freezing processes acquiring other energy carriers as exergy input, which experience large exergy destruction during heat exchange with LNG cold.

However, LNG cold energy is wasted if not utilized, and it is shown that with these cold energy carriers, natural gas chemical exergy input is totally eliminated due to ability of these energy carriers to sustain the deep-freezing process. Besides, deep freezing acquiring liquid CO₂ or PCM as cold energy carrier have been significantly simplified. However, for deep-freezing process utilizing LN₂, due to presence of both mechanical and cold energy, the setup becomes more complicated as two different loops are required to recover both types of energy. Besides, the exergy efficiency is extremely low due to the energy-intensive process for air separation. Besides, high-grade cold energy contained in LN₂ is unrecoverable by the deep-freezing process alone resulting in large exergy destructions. For the CO₂ emissions part, when using electricity as main source of exergy, the CO₂ emissions are 1.8 kTPA for deep-freezing downstream the baseline combined cycle and 1.4 kTPA for downstream the LNG assisted power cycle. For deep-freezing with liquid CO₂ as energy source, the CO₂ emissions are almost negligible, and the only cause of CO₂ emissions is the consumption of electricity to compensate the pressure loss during working fluid distribution. The deep freezing using cold input from the PCM yields 0.12 kTPA and is mainly caused by the truck emissions. For the deep freezing using LN₂ energy carrier, the CO₂ emissions are higher at 5.3 kTPA due to high amount of electricity consumed in the air separation process as well as the truck emissions.

Table 3.15: Exergy input and performances of deep-freezing warehouse downstream different energy carrier generation processes

Source of Energy Carrier	Baseline	LNG Thermal Cycle	Thermal Network	Thermal Storage	LNG ASU
SOURCE OF EXERGY INPUT (MW)					
NG Chemical Exergy, $E_{C,NG}$	1.02	0.83	0.00	0.00	3.06
LNG Physical Exergy, $E_{P,LNG}$	0.00	0.19	1.96	1.33	1.38
Diesel Exergy, E_{fuel}	0.00	0.00	0.00	0.05	0.02
PERFORMANCE PARAMETERS					
Exergy Efficiency (%)	18.57	18.75	9.49	15.96	4.94
CO ₂ Emissions (kTPA)	1.77	1.44	0.01	0.12	5.34

3.5.4. Exergy flow chain ending at district cooling central plant

Due to the similar setup with the deep-freezing processes, the exergy input into the district cooling systems with different energy carrier input and exergy flows as shown in Table 3.16 is very similar to that discussed in Section 3.5.3. The exergy flow Sankey diagrams are relocated to the Appendix chapter as Figure A.9.

Table 3.16: Exergy input and performances of dry ice production downstream different energy carrier generation processes

Source of Energy Carrier	LNG				
	Baseline	Thermal Cycle	Thermal Network	Thermal Storage	LNG ASU
SOURCE OF EXERGY INPUT (MW)					
NG Chemical Exergy, $E_{C,NG}$	0.49	0.40	0.00	0.00	1.87
LNG Physical Exergy, $E_{P,LNG}$	0.00	0.09	1.80	1.23	0.84
Diesel Exergy, E_{fuel}	0.00	0.00	0.00	0.04	0.01
PERFORMANCE PARAMETERS					
Exergy Efficiency (%)	3.87	3.91	1.06	1.77	0.80
CO ₂ Emissions (kTPA)	0.85	0.69	0.01	0.09	3.27

3.6. Overall exergy flow and performances using each energy vector for LNG cold distribution

Each of the energy carrier generation methods is analyzed by looking at the total exergy consumption, exergy efficiency and CO₂ emissions when each of them is connected to all the downstream cold applications which are listed in Table 3.17. The exergy flows from generation of energy carriers (with and without LNG cold) to their consumption at cluster of cold demands, which form a detailed flow chart, is shown in Figure 3.10.

Table 3.17: Overall performances for energy carriers to meet all cold demands

Source of energy carriers	Baseline	LNG	Thermal	Thermal	LNG
		Thermal	Network	Storage	ASU
		Cycle			
SOURCE OF EXERGY INPUT (MW)					
NG Chemical Exergy, $E_{C,NG}$	12.83	10.48	7.96	7.78	12.01
LNG Physical Exergy, $E_{P,LNG}$	0.00	2.39	7.77	7.50	5.40
Diesel Exergy, E_{fuel}	0.00	0.00	0.00	0.23	0.05
PERFORMANCE PARAMETERS					
Exergy Efficiency (%)	13.02	13.17	10.04	11.08	9.90
CO ₂ Emissions (kTPA)	22.26	18.18	13.81	14.03	20.93

(a)

(b)

(c)

(d)

(e)

Figure 3.10: Exergy flows from (a) baseline power cycle (b) LNG assisted power cycle (c) thermal network (d) thermal storage (e) LNG assisted air separation coupled to cluster of cold applications

As shown in Figure 3.10(a), for usage of electricity generated by the baseline combined cycle as main energy carrier, main exergy input comes from the chemical exergy of the natural gas consumed by the baseline combined cycle (95% of the total exergy input or 12.8 MW). 43.3% of total exergy destruction occurs in the combined cycle, mainly in the combustion chamber and in the heat exchangers. About 2.7% of the total exergy is lost during electricity distribution. Majority of electricity is supplied to the air separation unit, mainly due to the massive compressor work needed for generation of liquid air products at cryogenic temperatures. Thus, significant amounts of exergy loss and destruction are observed in the air separation unit (26.1% of the total exergy input). The exergy losses are due to large amounts of waste heat by the compressors and unused by-products, as well as the exergy destruction caused by heat exchangers, compressors and the distillation columns. For the other cold applications, the electricity input is much less compared with that of the air separation unit. The total amount of exergy loss and destruction in the three cold applications (i.e. dry ice production, deep freezing and district cooling) are between 3.9% and 6.6%. The overall exergy efficiency is 13%,

with carbon emissions of 22.3 kTPA, which is generated solely by the baseline combined cycle.

Figure 3.10(b) shows the exergy flows of electricity energy carrier from generation using the LNG assisted power cycle to its consumption at the cold demands. The main difference with the case of baseline combined cycle is the dependency on natural gas chemical exergy, which is reduced to 10.5 MW and represents 78.4% of the total exergy input to the LNG assisted power cycle exergy flow. The physical exergy of LNG to be regasified by the LNG assisted power cycle contributes to another 17.9% of the total exergy input. Exergy destruction occurs in the LNG assisted power cycle as well, mainly caused by the combustion chamber and the heat exchangers. The exergy flows of the electricity are almost the same as that obtained by using the electricity generated by the baseline combined cycle, and thus is not reiterated. The overall exergy efficiency has improved when compared with the baseline combined cycle (13.2%) and the carbon emission is reduced by 18.3% compared to the baseline case, mainly due to reduction of natural gas consumption in the power cycle.

Figure 3.10(c) shows the exergy flows for usage of thermal network with two selected working fluids, CO₂ and water as energy carriers to supply energy from LNG regasification to the cold demands. Whenever compressor work is required where high-grade cold is required (i.e. air separation and dry ice production), electricity is obtained from the baseline combined cycle. As cooling systems in most cold demands are replaced with cold carriers wherever possible, chemical exergy of natural gas consumed is reduced to 8 MW and represents 45.4% of total exergy input. The electricity is mainly supplied to the air separation unit. The central plant for the thermal network is where heat exchange between working fluids and LNG occurs. The physical exergy of LNG to be regasified is 44.3% of the total exergy input (7.8 MW). Due to the limited phase

change temperature of CO₂ (-50°C), high-grade cold of LNG is not utilized, causing large amount of exergy destruction in the thermal network central plant. At the cold demand, the exergy lost or destroyed is greatly reduced compared to that using electricity as main energy carrier, due to less components (eliminations of heat pump cycles) and presence of cold source closer to the product temperature. The overall exergy efficiency is 10%, which is less than the baseline case. However, almost half of the exergy input comes from the physical exergy of LNG, which can be considered as free exergy source. Due to largely reduced compressor work in the air separation unit and dry ice production, and elimination of heat pump cycle in the all the cold demands, the CO₂ emissions are significantly reduced by 38.0% when compared with the baseline case, and represents 13.8 kTPA.

Figure 3.10(d) shows the exergy flows for using PCM as energy carrier. The exergy flows are similar to that using liquid CO₂ and chilled water as energy carriers, except that the cold exergy is now distributed by the PCMs. The dependency on the natural gas chemical exergy input has further decreased to 7.8 MW, due to the further reduction of compressor work in air separation and dry ice production. This is due to the lower temperature intercooling between the compression stages because of the lower phase change temperature of the PCMs. Large amount of exergy is destroyed in the thermal storage central plant where heat exchange between LNG and the PCMs occurs. Due to the need of using trucks for distribution of the PCMs, there is a small amount of extra exergy input from chemical exergy of the fuel consumed by the trucks. The exergy flows and distribution in the cold demands are similar to that using other energy carrier inputs. The overall exergy efficiency is slightly lower when compared with the baseline case, due to larger amount of LNG physical exergy input. The CO₂ emissions are 14.0

kTPA which is 1.5% higher than the usage of liquid CO₂ and chilled water energy carrier, mainly due to the truck emissions during distribution of the PCMs.

Figure 3.10(e) shows the exergy flows for using LN₂ as energy carrier. Large amount of electricity is involved to drive the compressors in the air separation unit, thus the chemical exergy of the natural gas consumed by the baseline combined cycle makes the major exergy input at 66.8% (12 MW), resulting in exergy loss and destruction in the baseline combined cycle at 33.6% of the total exergy input. Another major exergy input is the physical exergy of LNG input to the air separation unit, at 30.1% (5.4 MW). The large amount of electricity and LNG physical exergy input to the air separation unit is due to the need to produce large amounts of LN₂ as energy carrier for the other cold demands alongside the required amount of LN₂ and LO₂ for the market. The exergy destroyed and exergy loss in the air separation unit is large, at 42.2% of the total exergy input. For subsequent cold demands with LN₂ input (i.e. dry ice production, deep freezing and returned water cooling process), the amount of exergy destruction is high when compared with cold applications using other energy carriers, largely due to the exergy destroyed since high-grade cold contained in the LN₂ is hardly utilized. The total exergy loss and destruction in these cold demands are 12.5% due to unutilized high-grade cold in the LN₂, resulting in an overall exergy efficiency of only 9.9%. High CO₂ emissions is mainly due to the large amount of natural gas consumption to produce electricity for the air separation unit, and it is only 6.0% less than that of the baseline combined cycle.

In general, Table 3.17 shows that the carbon emissions for all alternative energy carriers generated with LNG cold is effective in reducing the dependency of cold demands on electricity or primary fuel consumptions, which is also translated to reductions in CO₂ emissions. Figure 3.10 also shows that the amounts of exergy destroyed in the assumed

5 km distribution of the energy carriers (applied for any energy carrier and corresponded distribution method) are relatively small when compared to exergy destroyed and lost during the generation or charging of energy carriers. This implies that such energy carriers can be applied for most ranges of short to medium distances (i.e. less than 10 km).

3.7. Conclusions drawn from different energy carriers for transportation of LNG cold

With introduction of different cold energy carriers generated or charged using LNG cold energy, various cold demands can be modified and become more efficient and cleaner when compared with their conventional setups, mainly by reducing their dependency on the electricity through the means of increased intercooling effect (which reduces the amount of compressor work required and eliminates the need for a heat pump for generation of cooling water). These energy carriers can also act as the main exergy input to the lower grade cold demands, replacing heat pump cycles with simpler heat exchange processes. For usage of LN_2 as the main energy input to the cold applications, its mechanical energy can be used to drive the compressors for the medium-high grade cold applications, such as dry ice production; or used to drive a single heat pump cycle for lower-grade cold applications, while providing cold at the same time, thus eliminating the electricity input to these cold applications.

The following main results have been obtained when the cold applications are modelled as stand-alone cases:

- For an air separation unit producing LN_2 and LO_2 , the LNG-assisted air separation unit, which uses cold energy from LNG as the main energy source, is the cleanest and most exergy efficient solution.

- Dry ice production utilizing PCM as cold source has the highest efficiency and lowest CO₂ emissions due to significantly simplified setup.
- Deep freezing utilizing electricity has high exergy efficiency but high CO₂ emissions as well. The cleanest energy carrier for deep freezing is liquid CO₂ or PCM, which yields negligible CO₂ emissions.
- District cooling system has similar performance as the deep-freezing process, where electricity as energy carrier yields the highest exergy efficiency, while utilizing liquid CO₂ or PCM as energy carrier gives almost no CO₂ emissions.

When the considered cold demands are grouped as a cluster, and an individual energy carrier is considered to support all the cold applications, it is discovered that using working fluids energy carrier generated from a thermal network (i.e. liquid CO₂ and chilled water) or PCM as main/assistive energy input source to the cold applications cluster gives the cleanest overall process. The CO₂ emissions are reduced by 38% for liquid CO₂/chilled water energy carrier and reduced by 37% for PCM energy carrier, when compared with the baseline case. However, for these two energy carriers the exergy efficiency does not look attractive due to the large amount of exergy input from cold of LNG, which is wasted if not utilized. The usage of LN₂ as energy carrier demonstrated a high flexibility when coupled to different cold applications due to its ability to generate mechanical energy and cold energy at the same time. However, due to the energy-intensive air separation process, this cold energy carrier yields the highest CO₂ emissions amongst all the alternative energy carriers produced by the LNG cold recovery approach, which is only a 6% improvement compared with the baseline energy carrier.

3.8. Choice of next step of study

In the study carried out, it is found out that the carbon emissions are reduced by more than 35% for both usage of liquid CO₂ / chilled water and PCMs as cold carrier to assist or improve the configuration of cold demands for performance improvement and emission reduction purpose, due to their ability to greatly reduce the compressor power consumption (due to lower temperature intercooling) or eliminate the usage of heat pump. These two cold carriers also have similar performances on primary fuel and LNG cold consumption. Thus, they are further assessed for their compatibility for selection as subject for further studies.

First, the infrastructure required for both the thermal network and thermal storage systems are compared. The central plant for both setups could be based on the same size, as the flow rate for LNG is similar for both the setups (7.7 kg/s for thermal network and 7.4 kg/s for PCM storage). In both central plants, the configurations can be quite similar which consists of a series of shell-and-tube heat exchangers which allow heat exchange between LNG and working fluids, or between LNG and PCMs (enclosed in shell section of the heat exchanger).

However, it can make a big difference when the distribution of energy carriers is considered. For a thermal network system, pipelines are required to connect the LNG central plant with the cold demand cluster. It is estimated in the study carried out by Henchoz et. al. in 2015, for a network of CO₂ piping with length 1.84 km in Geneva, the estimated cost is €7.35 million including the piping and excavation cost, while the costs of supportive equipment such as booster pumps or compressors and other control or probing equipment have not been considered [59]. The pipeline diameter used in the Geneva study is similar to that used in this study, and the cost is used to provide estimation for the pipeline used, equivalent to almost €20 million. Such initial

investment cost can be high and unfavorable. Besides, installations of pipelines also need to go through careful urban planning to avoid possible alterations in any near future for other development purpose. The operation cost, which includes manpower cost and annual maintenance cost is estimated to be €105,000 per year [59].

In contrast, for a TES system, a cryogenic truck is required for the distribution of PCMs from the LNG regasification site to the industrial cluster. Trucks specially designed for PCM transportation are not investigated in detail to the point of this study, thus, the cost of a truck used to transport LNG is used instead to provide suitable estimation as LNG truck needs heavier insulations and thus should be traded at a higher cost compared to a truck targeted for PCM storage. Kim et. al. have estimated cost of a truck with 48 m³ storage capacity is costs 0.5 million USD [162] while the operation for such a truck is merely 0.86 USD per km travelled, which is negligible in the case here. If assumed that a truck is targeted for a cold demand, at least 4 trucks and 8 trailers are needed. If 8 trucks are purchased, the initial investment cost for the distribution is simply US\$ 4 million, or equivalent to €3.6 million, which is just 18% the investment cost for a pipeline system. Besides, usage of truck for PCM transportation does not involve any alteration in urban development.

For the cold demand side, both usage of liquid CO₂ or water and PCMs involve similar alteration of configurations in air separation plants, deep-freezing facility and district cooling tower. The only obvious difference between alteration of configurations using these two energy carriers are only observed in dry ice production facility, where using PCMs as energy carrier leads to simpler setup (single-stage compression) compared to liquid CO₂ (two-stage compression), which also translate to higher savings in choice of PCM as energy carrier.

From the simple study on cost, it is found that choice of PCM thermal storage system is the more cost-effective option due to less infrastructure cost and involves less urban planning as well as less control equipment along the distribution process. The study is not carried out in a deeper manner due to the obvious differences found in the preliminary study. Thus, usage of PCM as thermal storage facility is chosen as the main subject for the further study.

Chapter 4. High-grade cold TES storage with cascaded PCM using liquid state HTF

4.1. Background information

It is determined in Chapter 3 that TES can be a good candidate for cold energy transfer from LNG regasification facility to different demands. It is important to understand how a TES system can work under extremely low temperature condition, especially for recovery of LNG cold. Thus, numerical studies are carried out to help understand the transient behaviors during charge and discharge operations for the TES system. The simulations are also important to help fixing design parameters when an experimental setup is being designed.

As reported by Li et. al., packed bed TES storage provides up to 3.2 times faster charge and discharge rate compared to a shell-and-tube system with PCM as TES material [133]. Thus, a packed bed TES (PBTES) system with PCM as TES material is selected as the main subject in this and the subsequent chapters. Liquid HTF is well-known for its high energy density when compared to gaseous HTF, resulting in smaller pipeline size and smaller HTF flow velocity for similar amount of thermal power transferred. However, when it comes to high-grade cold temperature range, very few working fluids are suitable (i.e. fluidic state, low viscosity and low hazard). Only a few short carbon-chain organic materials (i.e. hydrocarbons and alcohols) meet both the requirements of fluidic state below -100°C with low viscosity. However, these materials can be highly-flammable under room condition. After screening with balance between material safety and thermophysical requirements, a commercial HTF, Galden HT-55 (chemical name 1,1,2,3,3,3-hexafluoroprop-1-ene) is selected. This HTF has operating temperature as low as -85°C [163] and is non-corrosive and non-flammable.

4.2. Modelling and validation of model

4.2.1. Assumptions used in modelling

To simplify the modelling, a few assumptions are made and listed as below:

- Temperature for HTF is assumed to vary along the axial direction of PBTES system only (1-dimensional).
- All PCM domains along radial direction, but in the same axial location of TES tank are assumed to share the same temperature profile.
- Temperature variation within a PCM capsule is assumed to be 1-dimensional along the encapsulation radius.
- The TES tank is well-insulated and there is no heat loss.
- PCM properties are not temperature dependent in their respective solid/liquid phases.
- HTF flow is uniform along the whole TES tank.
- There is no viscous dissipation within HTF.

4.2.2. Concentric dispersion model

Concentric dispersion model is recommended when PCM is used as TES materials, where thermal conductivity is low. Transient variations of thermal energy content for both HTF and PCM are modelled using 1-dimensional energy equations for both the HTF and PCM domains are expressed as equations (2.10) and (2.11), while the concentric temperature-time profiles within a PCM capsule is modelled using a heat conduction equation as expressed in equation (2.14). TES tank's operations, as well as volume and encapsulation volume discretization are shown in Figure 4.1. The capsule's

inner radius is denoted as R_{PCM} , while the thickness of a capsule is denoted as p . The tank is discretized into uniform volumes along its axial direction with notation of i -th volume, while the capsule's volume is discretized into uniform volumes along its radial direction with notation of j -th volume.

(a)

(b)

Figure 4.1: (a) Indication of heat transfer and boundary/initial conditions; (b) Discretization of tank volume and encapsulation volume

The enthalpy method [145], shown in equation (2.16), is used to solve for the relationship between enthalpy and temperature for the PCM. Correlation of Wakao and Funazkri [147] is used to estimate Nusselt number for convective heat transfer between HTF and PCM capsule, Nu and is shown in equation (2.17). The Nusselt number is then used to estimate the convective heat transfer coefficient, h using equation (2.20) and (2.21). Thermal resistance for the encapsulation material is not negligible and is integrated into the convective heat transfer coefficient between HTF and PCM using total thermal resistance method.

For melting process, correlations of Raithby and Hollands, equation (2.22) and (2.23), are used to estimate the effective thermal conductivity of the PCM in liquid state, k_{eff} ,

as there is significant natural convection within the capsule. Initial and boundary conditions listed from equations (4.1) to (4.5) are used to solve the equations.

Initial conditions for the transient study:

$$\text{(charging)} \quad T_{HTF} = T_{PCM} = T_{ambient} \text{ for } t = 0 \quad (4.1)$$

$$\text{(discharging)} \quad T_{PCM} = T_{PCM,0} \quad (4.2)$$

$$\text{(discharging)} \quad T_{HTF} = T_{HTF,0} \quad (4.3)$$

Boundary conditions:

$$T_{HTF} = T_{inlet} \text{ for } x = 0 \quad (4.4)$$

$$\partial T_{HTF} / \partial x = 0 \text{ for } x = L \quad (4.5)$$

4.2.3. Validation of concentric dispersion model

At the time when this study was carried out, experimental setup for TES system in Nanyang Technological University had not been completed. Thus, to ensure validity of the simulation model, the model is validated using experimental results published by Nallusamy et al. [88] for melting and solidification of paraffin (phase change temperature of 60 °C) using water as HTF. The paraffin is enclosed in high-density polyethylene capsules with 55 mm outer diameter and 0.8 mm thickness. In order to charge the TES system (melting the paraffin), water as the HTF at a temperature of 70 °C, is flowed through the capsules at flow rate of 2 L/min and during discharge (solidification of paraffin), water of 32 °C with a flow rate of 2 L/min is used. The validations are shown in Figure 4.2 while the main parameters of PCM used in the study

(paraffin) are listed in Table 4.1. In the validation study, energy equations are discretized using upwind scheme for space due to convection-dominant flow while heat conduction equation within PCM is discretized using central differencing scheme. They are solved using explicit method for time with MATLAB as the simulation software.

(a)

(b)

Figure 4.2: Validation of numerical concentric dispersion model against experimental data by Nallusamy et al. for (a) melting and (b) solidification [88]

Grid sensitivity analysis is carried out to obtain a balance between the accuracy and the computational resources for different grid sizes. Discretization using 4, 8, 16 and 32

nodes per encapsulation diameter in the tank's axial direction, and discretization of 10, 20, 40 and 80 nodes per encapsulation volume are investigated using Richardson's extrapolation method [164]. With mesh size of 8 nodes per encapsulation diameter in the tank axial direction and 20 nodes per encapsulation radius, both melting and solidification studies yield error less than 2%, when compared with the asymptotic value calculated using Richardson extrapolation. The time step is refined to 0.0125 s for solidification case and 0.00625 s for melting, and further refining these time steps yields negligible difference on the results.

Table 4.1: PCM thermophysical properties used in [88]

Thermal properties of PCM		
Parameter	Values	
Melting temperature (°C)	60	
Latent heat of fusion (kJ/kg)	213	
	Solid	Liquid
Density (kg/m ³)	861	778
Specific heat capacity (J/kg·°C)	1850	2384
Thermal conductivity (W/m·°C)	0.40	0.15

4.2.4. Key performance indices for a packed bed TES system

Two main key performance indices are investigated: the time to complete operations (i.e. charge and discharge) and the operation efficiency. The charge time is defined as the time when all the PCMs complete phase change (i.e., latent heat fully utilized). In Figure 4.3, the legends, PCM-1, PCM-2 and PCM-3, describes the PCMs which store the highest grade (or coldest) thermal energy, medium-grade and lowest grade thermal

energy, respectively. In this case, PCM-3 completes phase change the latest among all PCMs, and its phase change time defines charge time required for the entire TES tank.

The discharge time is defined as the time which the HTF recover the cold energy as useful energy. The HTF's temperature leaving the TES tank begins to increase when the high-grade cold energy stored in the PCMs is depleted or when the discharge rate of the PCM cannot keep up with HTF thermal capacity. A threshold temperature that defines the cut-off time of discharge, is set at 0.1°C above the phase change temperature of PCM-1. When HTF at the TES outlet is unable to sustain this temperature, the discharge is deemed to complete. Such example is shown in Figure 4.4. It is worth noting that due to the low thermal conductivity of PCM, PCM-1 is not completely discharged when the HTF at the outlet is unable to sustain the discharge threshold temperature.

Figure 4.3: The completion of charge is defined at time when all the PCMs have completed phase change

The charge efficiency, η_{ch} is defined as the ratio of the total thermal energy stored by the TES materials to the total thermal energy of HTF supplied within the charging period. The discharge efficiency, η_{disch} is defined as the total thermal energy recovered

by HTF during the discharge period to the total amount of thermal energy stored in the system. The cyclic efficiency, η_{cyclic} is the products of both charge and discharge efficiencies. Equations for the efficiencies are defined in equations (4.6) to (4.8).

$$\eta_{ch} = \frac{E_{stored,PBTES}}{E_{HTF}} \quad (4.6)$$

$$\eta_{disch} = \frac{E_{recovered,HTF}}{E_{stored,PBTES}} \quad (4.7)$$

$$\eta_{cyclic} = \eta_{ch} \times \eta_{disch} \quad (4.8)$$

Figure 4.4: The completion of discharge phase is defined at time when the discharged HTF is unable to sustain a high-grade cold temperature

4.3. Introduction to a cascaded PCM system, and drawbacks of current system

Cascaded PCM method (using PCMs with different melting temperature in a single TES system) is reported with well-known behavior (Chapter 2.2.5). Thus, cascaded method is simulated to observe the performance of such system. Cascaded PCM

systems are well-investigated, however, it is not optimized and the mentioned advantage such as shorter charge time as well as higher efficiency is not fully utilized.

In Figure 4.5, an ideal PBTES tank for cold storage is illustrated. The storage tank is separated into PCM-1, PCM-2 and PCM-3 regions with the PCM of lowest phase change temperature (PCM-1) storing high-grade cold, PCM-2 storing medium-grade cold and PCM-3 for low-grade cold. x_1 , x_2 and x_3 denote the position of PCM capsule from the inlet of each PCM section (x_1 for PCM-1 and so-on), while L_1 , L_2 and L_3 denotes the length of each PCM section. x also denotes the position of a PCM capsule from the PBTES tank inlet while L_{tank} and D_{tank} represent the length and diameter of the TES tank. For this paper, D_{tank} is fixed at 1.0 m while the tank wall is assumed to be vacuumed and well insulated such that no heat loss occurs through the wall of the tank. L_{tank} , L_1 , L_2 and L_3 depend on the designated storage capacity of related PCMs, which will be varied in this study.

In an idealized scenario of charging a PBTES with cascaded PCMs, the high-grade cold energy carried by the HTF should transfer its thermal energy mainly to PCM-1 with the lowest phase change temperature. At the same time, medium-grade cold energy exchanges its thermal energy with PCM-2 and low-grade cold energy exchanges its thermal energy with PCM-3. This is illustrated with the colored arrows in Figure 4.5. For idealized discharge case, PCM-1 which stores the highest-grade thermal energy rejects the thermal energy stored to the medium-grade cold region of HTF (not to the highest-grade region) due to loss in the thermal energy quality because of temperature mismatch between PCM phase change temperature and cold source temperature; while PCM-2 to the low-grade cold energy region and PCM-3 to the cool grade.

During an actual operation, this idealized situation will not occur because of storage of part of the medium and low-grade cold energy as sensible heat in PCM-1, as well as part of low-grade cold energy in PCM-2. When charging the storage, PCM-2 and PCM-3 do not start their phase changes at the same time as PCM-1, causing a delay in these two PCM sections. A baseline case is conducted to evaluate a cascaded TES tank with equally distributed storage capacity among different TES materials and the result is shown in Figure 4.3. The temperature-time profiles are taken from last tier of each PCM section for PCM-1, PCM-2 and PCM-3, as they are the last to complete phase change among the same material. Charge time of each PCM is thus defined, and the overall charge time for the whole PBTES system is determined by the completion of phase change for PCM-3, which is the last to complete phase change among all three PCMs. It is observed that PCM-1 has a charge time of about 5.9 hours but PCM-3 has a charge time of about 8.1 hours. In these cases, it implies that the capacity allocated for PCM-1 is too low compared to PCM-2 and 3, which is defined as the first scenario of overcharging, where too low capacity is assigned for PCM-1. In this scenario, there is some loss of high-grade thermal energy towards the end of charging process (i.e. after PCM-1 completes phase change), as the energy is not stored as latent heat in PCM-1 but is degraded into the latent heat of PCM-2 and 3. Such degradation is irreversible, and the system is unable to recover the energy as higher-grade thermal energy during the discharge process.

Figure 4.5: Ideal charge and discharge of a packed bed TES system using cascaded PCMs as TES materials

There is also a second scenario of overcharging which occurs when too high capacity is allocated for PCM-1 when compared with of PCM-2 and PCM-3. This scenario also applies to packed bed TES system with a single type of PCM (i.e. 0 capacity for PCM-2 and PCM-3). During the charging process, much of the high-grade thermal energy from the charging HTF can be captured. However, the HTF has a broad sensible temperature change from ambient towards storage temperature, which also includes low-grade energy and medium-grade energy. During the discharge process, the high-grade thermal energy stored in PCM will be degraded to fulfil requirement of these lower-grade thermal energy. This results in lower storage efficiency when compared to an optimized cascaded system. In both overcharging cases, overcharging time is defined as the time difference between the charge time of the entire packed bed TES system and the time where the first PCM regions completes its phase change process.

In both scenarios of overcharging, the efficiencies are predicted to be lower than the optimized counterpart. Thus, a comprehensive study is carried out to study on sizing a PBTES system with cascaded PCMs. In particular, the storage capacity can be properly scaled to achieve as high thermal storage efficiency as possible, or shorter charge time and less PCMs can be allocated with similar thermal storage efficiency, where cost saving is achieved.

4.4. Material selections and methods

HTF Galden HT-55 is chosen due to its ability to work at temperature as low as -80°C with minimal risk. The main target of this study is to investigate the effect of capacity allocation for each PCM and the effects on performance of a PBTES system. With the author's best knowledge, there is no general relationship which can relate the

thermophysical properties (i.e. density, thermal conductivity and specific heat capacity) of different PCMs with their phase change temperature, as these properties can be highly dependent on the material type, structure or molecular interactions.

To study the sole effect of storage capacity of each PCM on PBTES performance, it is important to eliminate the effect of other thermophysical properties. Virtual PCMs, with similar density, thermal conductivity and specific heat capacity, are proposed. The other important thermophysical property, latent heat capacity for each PCM is decided using linear interpolation, which is introduced in the subsequent section.

4.4.1. Defining thermophysical properties of each PCM

From the review on commercial PCMs, inorganic PCMs (mainly eutectic salt solutions) have better properties when compared with organic PCMs (e.g. thermal conductivity of ≈ 0.6 compared to ≈ 0.2 for organic PCM and latent heat capacity of more than 200 kJ/kg compared to ≈ 100 kJ/kg for organic PCMs). Thus, these properties, which are to be assumed constant for all the virtual PCMs to be selected, are carefully chosen based on these values where thermal conductivity is assumed to be $0.6 \text{ W/m}\cdot^\circ\text{C}$ and specific heat capacity of $3000 \text{ J/kg}\cdot^\circ\text{C}$.

The specific heat capacity of HTF, Galden HT-55 is considered during the selection of phase change temperatures of PCMs. [163]. The charge temperature of HTF is set at -80°C and the discharge temperature is 30°C . This operating temperature range of HTF is further divided equally into four grades as shown in Figure 4.6, with each grade of cold has the same amount of thermal energy. Such division is to ensure that same amount of thermal energy is shared among each PCM during the charge and discharge phase, and this is illustrated in Figure 4.5 for an ideal case of charge and discharge of a cascaded TES system. The temperature which marks the boundary between different

grades of thermal energy is then chosen as the phase change temperature of each PCM and are listed in Table 4.2.

Figure 4.6: Division of the heat capacity of HTF into equal regions which corresponds to the phase change temperatures of the phase change materials

Latent heat of commercial inorganic and eutectic PCMs with sub-ambient phase change temperature are collected [165-172] and plotted against their phase change temperatures in Figure 4.7. It is observed that latent heat increases with phase change temperatures. Using the four regions (and desired phase change temperature) defined in Figure 4.6, latent heat capacities of the virtual PCMs are then determined from Figure 4.7. The thermo-physical properties of these virtual PCMs are listed in Table 4.2.

Table 4.2: List of material properties used

Material properties		
Material	Phase change temperature (°C)	Latent heat capacity (kJ/kg)
PCM-1 (high-grade PCM)	-49	225
PCM-2 (medium-grade PCM)	-19.5	262
PCM-3 (low-grade PCM)	6.5	290

Material properties that are assumed constant with materials	
Thermal conductivity (W/m·°C)	0.6
Specific heat capacity (J/kg·°C)	3000
Density (kg/m ³)	1100
Capsule thermal properties	
Thermal conductivity (W/m·°C)	0.5
Specific heat capacity (J/kg·°C)	2250
Density (kg/m ³)	950

Figure 4.7: Plot of latent heat capacity variation with phase change temperature for inorganic PCMs

4.4.2. Determining the capsules' packing structure

To ensure uniform PCM distribution in the PBTES tank, the PCMs are assumed to be stacked using tier-by-tier method, in which each tier contains similar number of capsules containing PCM. Such approach will also ensure simpler structural support for

PCM capsules. The number of capsules in each tier is decided using algorithm developed by Mueller [173].

4.5. Baseline case

The operating conditions of HTF for charge and discharge phases are listed in Table 4.3. In the TES tank, the tank-to-capsule diameter ratio is assumed to be 20. Such big diameter ratio is necessary as it is ideal to keep the height-to-diameter ratio at a sufficiently low level to minimize the parasitic loss on the HTF [174]. Geometrical parameters of the PBTES tank are listed in Table 4.4.

Table 4.3: Operating conditions of HTF under charge and discharge phases

Parameter	Values	
	Charge	Discharge
Inlet temperature (°C)	-80	30
Thermal power (kW)	20	20
Mass flow rate (kg/s)	0.221	0.221

For the baseline case, latent heat capacity of each cascaded PCM is set to be at least 15 kWh. 11 tiers of PCM-1, together with 9-tiers of PCM-2 and 9 tiers of PCM-3 are used, which results in the storage capacities of 15.6, 15.1 and 16.0 kWh, respectively. The total number of capsules is 9,483.

Under an idealized condition, the high-grade cold energy of HTF (with power of 5 kW) will charge PCM-1, while the medium-grade and low-grade regions charge PCM-2 and PCM-3, respectively. However, from Figure 4.3, such scenario is too idealized, and the cascaded PCMs start their phase change at different times, with PCM-2 delayed behind PCM-1 and PCM-3 behind PCM-2. For the baseline case, the charge and discharge

temperature profiles are shown in Figure 4.3 and Figure 4.4, respectively. The charge phase is completed after 8.1 hours with charge efficiency of 83.2%. However, after 5.88 hours, PCM-1 completes phase change, resulting in much of the high-grade cold converted to lower-grade cold energy, and stored as latent heat for PCM-2 and PCM-3. This conversion is irreversible as low-grade thermal energy is unable to be converted to higher-grade without addition of work. For the discharge stage, it is observed that the HTF is unable to sustain the threshold temperature after 7.0 hours, recording discharging efficiency of 88.7%. The cyclic efficiency is calculated as 73.8%.

Table 4.4: Geometrical parameters for packed bed TES tank used in simulation

Parameters	Values
TES tank diameter (m)	1.0
Encapsulation external diameter (m)	0.05
Encapsulation thickness (m)	0.001
Tank-to-capsule diameter ratio	20

4.6. Generalized map determined from numerical study

Multiple combinations of capacity allocated for PCM-1, PCM-2 and PCM-3 in the cascaded PBTES system are simulated. The operating conditions and tank geometries are same as the boundary conditions defined earlier. Performances on packed bed TES system based on different capacity combinations are analyzed.

These results provide the dependency of the system's cyclic efficiency and the charge and discharge times on storage capacity. Upon deeper analysis, it is understood that the results can be generalized into maps, which are able to provide comparisons without need of multiple line graphs. In the generalized maps, the results are normalized based

on two parameters: (1) storage capacities are normalized with the baseline capacity of PCM-1, 15.6 kWh and (2) the charge or discharge time is normalized with the charge time for 15.6 kWh of PCM-1, 5.88 hours. Numerical studies are done based on the range of each parameter provided in Table 4.5.

$$\text{Normalized capacity} = \frac{\text{Capacity}}{\text{Capacity}_{\text{PCM1,baseline}}} = \frac{\text{Capacity}}{15.6 \text{ [kWh]}} \quad (4.9)$$

$$\text{Normalized charge time} = \frac{\text{Charge time}}{\text{Charge time}_{\text{PCM1,baseline}}} = \frac{\text{Charge time}}{5.88 \text{ [hrs]}} \quad (4.10)$$

Table 4.5: Range for parameters used in numerical study

Parameters	Value-Range
Normalized PCM-1 capacity	1-2
Normalized PCM-2 capacity	0.5-2.8
Normalized PCM-3 capacity	0.5-2.8

4.6.1. Effect of varying storage capacity of PCM-1 and PCM-2 on charge time for these two sections

Figure 4.8 shows the effect of varying storage capacity of PCM-1 and PCM-2 on the charge time for these two sections in a packed bed TES tank. The normalized TES capacity of PCM-1 is plotted as the x-axis while normalized TES capacity of PCM-2 is plotted as isoline legend with 0.5 interval. Normalized charge time for the two PCM sections combined is plotted as y-axis. When TES capacity of PCM-1 is fixed while capacity of PCM-2 is increased, the normalized charge time of the whole section should increase, which can be read from the graph by fixing the x-value, while moving the point of interest according to the isoline to read the y-value on the plot. Similar

observation can also be observed when storage capacity of PCM-2 is fixed. In this case, the point of interest should move along the isoline, which has a positive gradient – meaning that for a fixed capacity of PCM-2, when TES capacity of PCM-1 is increased, the charge time for combined PCM-1 and PCM-2 sections also increases.

Figure 4.8: Effect of thermal capacity of PCM-1 and PCM-2 capacity on charge time for these two sections in the storage tank

There are two regions with empty plot – one on the top-left corner and another in the bottom-right corner. There is a limit on PCM-2 TES capacity in this study, which the region with PCM-2 TES capacity exceeded the limit not simulated as thus has no result. For the bottom-right corner, the zero-plot region is defined by charge time of PCM-1 section. The charge time of PCM-1 is defined by the boundary of the bottom-right zero-plot region and is unaffected by TES capacity of PCM-2. The charge time (y-axis) value increases with increase of PCM-1 capacity. When TES capacity of PCM-1 is increased further, if capacity of PCM-2 is too low, the charge time is decisive based on PCM-1 and PCM-1 is still charging while PCM-2 has completed charging.

The relationship between charge time of combined PCM-1 and PCM-2 region with TES capacity of PCM-1 and PCM-2 is linear. There is some optimal ratio of PCM-2 to PCM-

1 that can be deduced from the results, if no difference in charge time between PCM-1 and PCM-2 charge time is being looked for. To achieve this criterion, the capacity of PCM-2 should be selected such that it lies on boundary of the zero-plot region in the bottom-right corner, which is approximated to be 0.7 times the capacity of PCM-1.

4.6.2. Effect of combined storage capacity on the overall charge time of TES system

Figure 4.9 shows the effect for charge time for combined PCM-1 and PCM-2 section (derived in Section 4.6.1) and capacity of PCM-3 on overall charge time of the TES system. When charge time of PCM-1 and PCM-2 sections combined is known (from the y-axis), together when allocated PCM-3 TES capacity is known (from the isoline plots), the overall charge time for the TES tank is determined from the x-axis. Reversal of x-axis and y-axis is to facilitate the reading of generalized maps, which is introduced in section 4.6.5.

Figure 4.9: Effect of PCMs capacity to the PBTES system's charge time

Such plot also has two zero-plot regions, one at the top-left corner and another on the bottom-right corner. The top-left corner zero-plot region in Figure 4.9 is resulted when allocated TES capacity of PCM-3 is too few, until the charge time is determined by combined section of PCM-1 and PCM-2. The charge time of combined section of PCM-1 and PCM-2 is defined by the positive-gradient boundary of the top-left zero-plot region. The bottom-right zero-plot region is due to amount of allocated capacity for PCM-3 exceeded the threshold parameter value, and is not simulated.

When the capacity of PCM-3 is increased, the charge time also increases. When charge time for combined PCM-1 and PCM-2 sections are known (y-axis), when capacity of PCM-3 is increased, the isoline plot moves to the right of the plot, which indicates increase in x-axis value, the overall charge time for the TES system. Similar deduction can be made as done in Section 4.6.1, where to obtain the similar charge time between PCM-1, PCM-2 and PCM-3, the recommended TES capacity for PCM-3 should be approximately 0.5 times the capacity of PCM-1.

4.6.3. Effect of combined storage capacity on the overall discharge time of TES tank

Figure 4.10 shows the effect of the combination capacity for PCM-1, PCM-2 and PCM-3 on the discharge time. There are also two zero-plot regions, both attributed to the unbalanced TES capacity of PCM-2 and PCM-3. There is a limit for TES capacity for PCM-2 and PCM-3, as defined in Section 3.5, which is equivalent to ≈ 5.6 times the storage capacity of PCM-1. Cases with PCM capacity above the limit is not simulated resulting in zero-plot region on the top-left corner of the plot. The same condition also applies to the zero-plot region in the bottom-right corner, where the lower-limit for TES

capacity of PCM-2 and PCM-3 combined is 0.8 times the TES capacity of PCM-1. Combined TES capacity of PCM-2 and PCM-3 less than that value is not simulated.

Figure 4.10: Relationship of discharge time with TES capacity of PCM-1, PCM-2 and PCM-3

For a fixed capacity of PCM-1 (fixed x-axis value on the plot), the discharge time increases when the combined TES capacity of PCM-2 and PCM-3 is increased (isolines of the plot moves upwards when capacity is increased). Similarly, when combined capacity of PCM-2 and PCM-3 is fixed (moving along an isoline), when TES capacity of PCM-1 increases, and the discharge time increases.

4.6.4. Effect of combination of charge and discharge time on cyclic efficiency of TES system

The dependency of cyclic efficiency of the packed bed TES system on normalized charge time and discharge time is shown in Figure 4.11. Iso-efficiency regions are plotted based on the simulated charge and discharge time of the TES system. When the charge time for the PCM tank is determined from Section 4.6.2, with discharge time

determined from Section 4.6.3, x-axis value and y-axis value for the plot is available and the coordinate is used to obtain the cyclic efficiency of the TES system.

Figure 4.11: Dependency of TES system's cyclic efficiency on normalized charge and discharge time

If a diagonal line with gradient of 1 is drawn on the plot, which represents the line of *normalized discharge time = normalized charge time*, the highest efficiency region (>80%) is found to be the closest to this diagonal line, which identifies another important criterion of a cascaded PCM packed bed TES system: the charge and discharge time should be as close to each other as possible for the most efficient PBTES.

As all isolines have gradient less than 1, for cases with shorter charge time (i.e. smaller x-axis value), despite being optimized (with coordinate as close to the line with gradient 1), the efficiency will be lower than cases with longer charge time which are optimized. Such condition indicates that larger overall storage capacity leads to better performance, due to availability of larger heat transfer area due to increased amount of PCM capsules.

4.6.5. Putting together the generalized map and the applications

The four generalized maps introduced from previous sections are arranged in a 2 by 2 pattern such that for the maps located on the same row, their y-axes coincide each other while for the maps located on the same column, their x-axes coincide each other.

Two applications of the maps are presented. In the first application, which also serves as validation of the generalized maps, the charge and discharge time, including cyclic efficiency can be obtained based on selection of TES capacities of PCM-1, 2 and 3. In the second application, a preliminary scaling of a packed bed TES system is achieved with desired performance requirements and availability of PCM materials.

The first application which uses the TES capacity defined in the baseline case is illustrated in Figure 4.12 and has the following steps:

- (1) TES capacities of PCM-1 and PCM-2 are selected and used to determine the charge time for combined sections of PCM-1 and 2.
- (2) With charge time for combined sections of PCM-1 and 2, and with TES capacity of PCM-3, overall charge time of TES system is determined.
- (3) The overall charge time of TES is located on the cyclic efficiency plot.
- (4) TES capacities of all PCMs are used to determine the discharge time.
- (5) The overall charge time and discharge time of the PBTES system is used to determine its cyclic efficiency.

Prediction on performance using criteria from the baseline case (normalized capacity of ≈ 1 for each of the PCM) is compared with the numerical result to estimate the error of the generalized map method. For the charge time, the normalized charge time is determined as 1.38 (8.11 hours) while the simulated charge time is 8.06 hours. The normalized discharge time determined using the generalized map is 1.18 (6.94 hours)

while compared to simulated discharge time of 7.02 hours. Using generalized map method, the cyclic efficiency is estimated at $\approx 73.0\%$ which agrees with the simulated result. Each of the performance parameters records error of less than 1%.

For the second application where TES capacity of each PCM can be defined based on the desired performance of the TES system, three parameters are needed: cyclic efficiency, overall charge time and TES capacity of one of the PCM prior to working with the generalized map. For the example demonstrated in Figure 4.13, the cyclic efficiency is chosen as 80%, normalized charge time of 2.2 and normalized PCM-1 capacity of 1.75. The steps for using the generalized map are listed here:

- (1) Overall charge time and cyclic efficiency are used to locate the coordinate on the efficiency chart, and is then used to deduce the discharge time.
- (2) The normalized TES capacity of PCM-1 is used to determine the combined TES capacities of PCM-2 and PCM-3, which is 3.3.
- (3) The normalized charge time is used to obtain an allowed range of capacity for PCM-3, which is ranged from 1.3 to 2.8.
- (4) The normalized TES capacity of PCM-1 is used to determine an allowed range of TES capacity for PCM-2, which is ranged from 1.3 to 2.8.
- (5) With the determined range for the TES capacities of PCM-2 and PCM-3, a rectangular orange box can be drawn. The rectangular box must include only possible region of TES capacity for PCM-2 and PCM-3 (i.e., no zero-plot region). A horizontal bridge is then used as cursor (dashed line) which both ends of the bridge indicate possible values of capacity for PCM-2 and PCM-3. For example, when PCM-2 is chosen to has normalized TES capacity of 2.0, normalized TES capacity of PCM-3 is 1.3 by default.

Figure 4.12: Using generalized maps to obtain performance of packed bed TES tank with pre-determined storage capacity

Figure 4.13: Using generalized map for preliminary scaling of packed bed TES tank under performance requirements

4.7. Further discussions on numerical study for cascaded PCM capacities

4.7.1. Reducing overcharging of TES system by varying capacity of each PCM component

Effects of varying various alteration to reduce overcharging (mainly observed by improving efficiency performances of TES systems) are observed. Overcharging can occur on two situations: overly high, or overly low TES capacity for PCM-1. In the baseline case, TES capacity for PCM-1 is too low compared to that of PCM-2 and PCM-3, which is deduced from delay charge complete time for PCM-2 and PCM-3 compared to PCM-1. Thus, in this subsection, various improved cases using two different strategies are discussed. The strategies are: (1) reducing TES capacity of PCM-2 and PCM-3 and (2) increasing TES capacity of PCM-1 and PCM-2.

4.7.1.1. *Reducing TES capacities of PCM-2 and PCM-3*

Possibility of reducing TES capacities for both PCM-2 and PCM-3 is investigated to overcome the overcharging issue. TES capacity of PCM-1 is fixed at 15.6 kWh (values allocated in the baseline case). Various combinations of the TES capacities of PCM-2 and PCM-3 are simulated. Notable cases are listed in Table 4.6, and cases are arranged in the order of highest to lowest cyclic efficiencies.

When compared to the baseline case, when TES capacities of PCM-2 and PCM-3 are reduced, the charge time also reduces from 8.1 hours to as low as 5.9 hours. It is because PCM-2 and PCM-3 only start their phase change process after a time delay compared to PCM-1, due to PCM-1 absorbed some lower-grade thermal energy for its sensible temperature change. The lowest possible charge time observed is 5.9 hours, which is observed in cases ‘f’, ‘g’, ‘h’ and ‘i’, where further reduction in capacities for PCM-2

or PCM-3 is unable to further reduce the charge time. This charge time coincides the charge time of PCM-1, which its TES capacity is unchanged over all listed cases.

Table 4.6: Notable cases with fixed PCM-1 latent capacity at baseline value

Cases	PCM-1 capacity (kWh)	PCM-2 capacity (kWh)	PCM-3 capacity (kWh)	charge time (hrs)	discharge time (hr)	overcharging time (hrs)	η_{ch} (%)	η_{disch} (%)	η_{cyclic} (%)
baseline	15.6	15.1	16.0	8.1	7.0	2.2	83.2	88.7	73.8
a	15.6	11.8	12.5	6.9	6.2	1.0	82.6	91.7	75.7
b	15.6	11.8	10.7	6.5	5.9	0.7	82.5	91.7	75.7
c	15.6	13.5	10.7	6.8	6.1	0.9	82.7	91.5	75.7
d	15.6	10.1	10.7	6.3	5.7	0.4	82.3	91.9	75.7
e	15.6	13.5	12.5	7.2	6.4	1.3	82.8	91.3	75.6
f	15.6	8.4	10.7	5.9	5.4	0.4	82.2	91.7	75.3
g	15.6	6.7	10.7	5.9	5.3	0.9	79.1	91.2	72.2
h	15.6	6.7	8.9	5.9	5.1	0.9	75.7	91.9	69.6
i	15.6	5.1	8.9	5.9	5.1	1.4	72.6	91.1	66.2

Overcharging time is defined as the time difference between the time for any of PCM section to complete phase change and the overall charge time of the tank. Comparing case ‘a’ with case ‘d’², which the two cases have their cyclic efficiencies differ by less than 0.1%, the overcharging time decreases from maximum of 1.0 hour to 0.4 hour. Despite having very similar performances, TES capacities of PCM-2 and PCM-3 are

² Due to number of significant figures, cyclic efficiencies of case “a” to case “d” looks similar but they are arranged from high to low.

reduced by 14.4% each in case 'd' compared to case 'a', marking significant savings on TES materials. When compared to the baseline case, case 'a' with highest cyclic efficiency recorded has 1.9% improvement on the cyclic efficiency, while recorded 22.2% saving on materials for PCM-2 and PCM-3 combined. For comparison of case 'd' with the baseline case, up to 33.3% of PCM-2 and PCM-3 can be saved.

From Table 4.6, the baseline case represents the first scenario of overcharging, where high TES capacities are allocated to PCM-2 and PCM-3. Case 'a' has similar charge efficiency compared to the baseline case, which the difference in cyclic efficiency is caused by improvement of discharge efficiency from 88.7% to 91.7%. To explain the improvement of η_{disch} , the temperatures of all PCM nodes, along the axial direction of the PBTES systems during discharge cut-off time (when HTF leaving TES tank reaches threshold temperature) are tabulated in Figure 4.14.

Figure 4.14: Temperature along axial direction for PCMs during discharge cut-off time for baseline case and case 'a'

At the discharge cut-off, temperature of PCMs of the baseline case is lower than that of case 'a'. It shows higher amount of cold energy stored is not properly discharged, especially in the region of $x/L = 0.6$ to $x/L = 1.0$. This location is where PCM-1 is

located, and in this region, these PCMs still contains a vast amount of low-grade cold energy due to too-high amount of PCM-2, while HTF reaches the cut-off temperature. The capacity of PCM-1 is not enough to supply medium-grade cold energy to the HTF, resulting the discharge process to be cut-off early. Such improvement in discharge efficiency is observed in almost every case listed in Table 4.6 (when compared with baseline case), which shows that correct proportion of PCM-1, PCM-2 and PCM-3 is important to ensure high efficiency in the cascaded packed bed TES system.

In contrast, the charging efficiency maintains constant with variation of $< 1\%$ from the baseline case to case 'f'. However, from case 'f' to case 'i', there is a substantial drop in charge efficiency when TES capacity of PCM-2 and 3 are reduced further. In these cases, PCM-1 is the limiter which causes the delay in charge time for the whole packed bed TES system, and represent the second scenario of overcharging. The low charge efficiency can be explained with Figure 4.15, which indicate two temperature-time profiles of HTF leaving the PBTES system along the charging process: baseline case and case 'i'. Baseline case and case 'i' are chosen for better clarity due to the large difference for charge efficiency between these two cases. Area under each curve indicates the temperature region of the cold energy of HTF entering the TES system which is recovered for each case. For case 'i', after 65% of total charge time, the temperature of HTF at outlet of TES tank starts to decrease with large amount of cold energy in the temperature range of -40°C to 5°C not recovered, It is because PCM-2 and 3 are fully charged due to low capacities.

From all the cases listed, case 'a' has the most efficient configuration of PCM capacities combination, with 1.93% increase in cyclic efficiency and 22.2% less material of PCM-2 and PCM-3 used. In case 'd', similar efficiency with case 'a' is observed with 33.3%

less material of PCM-2 and PCM-3 used. Reducing TES capacity of PCM-2 and PCM3 to the level of case ‘f’ is 1.52% more efficient than the baseline case, with total materials of PCM-2 and PCM-3 reduced by 38.9%. It shows that having equal amount of capacity for all the PCMs in a cascaded PBTES system causes wastage on the material, as similar cyclic efficiency can be easily achieved with less capacity allocated for both PCM-2 and PCM-3.

Figure 4.15: Temperature-time profiles for HTF leaving TES tank for baseline case and case ‘i’

4.7.1.2. Increasing TES capacities of PCM-1 and PCM-2

Another method to overcome the first scenario of overcharging problem in the baseline case is by increasing the TES capacities of PCM-1 and PCM-2. Different combinations of TES capacities of PCM-1 and PCM-2, while fixing the TES capacity of PCM-3 are simulated, and the notable cases are listed in Table 4.7.

Table 4.7: Notable cases with fixed PCM-3 TES capacity at baseline value

Selected case	PCM-1 capacity (kWh)	PCM-2 capacity (kWh)	PCM-3 capacity (kWh)	charge time (hrs)	discharge time (hrs)	overcharge time (hrs)	η_{ch} (%)	η_{disch} (%)	η_{cyclic} (%)
baseline	15.6	15.1	16.0	8.1	7.0	2.2	83.2	88.7	73.8
Same PCM-2 capacity with baseline case									
A	26.9	15.1	16.0	9.6	9.4	0.5	84.5	95.7	80.8
B	25.5	15.1	16.0	9.4	9.2	0.5	84.5	95.3	80.5
C	24.1	15.1	16.0	9.3	8.9	0.6	84.3	94.9	80.0
D	28.3	15.1	16.0	10.1	9.8	0.8	83.0	96.0	79.7
E*	22.7	15.1	16.0	9.1	8.6	0.9	84.1	94.6	79.5
F*	21.2	15.1	16.0	8.9	8.4	1.2	83.9	94.1	78.9
G*	19.8	15.1	16.0	8.7	8.1	1.5	83.7	93.4	78.1
H*	18.4	15.1	16.0	8.5	7.8	1.7	83.5	92.4	77.2
I*	17.0	15.1	16.0	8.3	7.7	2.0	83.3	91.0	75.8
Other PCM-2 capacity for higher cyclic efficiency									
J*	29.8	18.5	16.0	10.6	10.4	0.1	84.7	96.1	81.4
K*	28.3	18.5	16.0	10.3	10.1	0.2	84.9	95.8	81.3
L*	31.2	20.2	16.0	11.2	10.9	0.4	84.1	96.2	80.9
M*	26.9	16.8	16.0	9.9	9.6	0.3	84.7	95.7	81.1
N*	25.5	16.8	16.0	9.7	9.4	0.6	84.5	95.2	80.5
O*	24.1	16.8	16.0	9.6	9.1	0.9	84.4	94.9	80.1

*Cases with highest cyclic efficiency for the specific PCM-1 capacity when PCM-3 capacity is fixed

In Table 4.7, cases ‘A’ to ‘I’ indicate the cases in which the TES capacity of PCM-1 is varied from 15.6 kWh to 28.3 kWh, while TES capacity of PCM-2 is kept constant at 15.1 kWh (value same as the baseline case). For cases ‘J’ to ‘R’, similar to case ‘A’ to ‘I’, TES capacity of PCM-1 is varied from 15.6 kWh to 28.3 kWh, but the TES capacity of PCM-2 are also varied to have higher TES capacity for PCM-2 compared to the baseline case, which for some of the cases also lead to higher cyclic efficiencies. Cases marked with asterisks indicate the cases which the TES capacity of PCM-2 is optimized for the cyclic efficiency, based on the specified TES capacity of PCM-1 and fixed TES capacity for PCM-3.

The results from Table 4.7 are also tabulated in Figure 4.16. In the plot, the blue dashed line indicates the case with varying TES capacity for PCM-1 while keeping TES capacity of PCM-2 and PCM-3 at the baseline values, which represents cases ‘A’ to ‘I’. The orange dashed line indicates the maximum achievable cyclic efficiency under specified TES capacity for PCM-1, which represents cases marked with asterisk in Table 4.7. The charge time for these optimum scenarios is also plotted, and is observed to increase with cyclic efficiency and with capacity of PCM-1. Such trend is explained in Chapter 4.6, which the cyclic efficiency should increase with charge time (increase with TES capacity of PCM-1) due to larger heat transfer area. However, as TES capacity of PCM-1 increases beyond 26.9 kWh (also shown as case ‘I’ and ‘P’), the cyclic efficiency drops due to overly high TES capacity of PCM-1 compared to PCM-3 (second scenario of overcharging). Such indication again shows that correct proportion between TES capacities of PCM-1, PCM-2 and PCM-3 are important to ensure high performance of a TES system.

In Table 4.7, by varying the TES capacity of PCM-1, cyclic efficiency can be increased by up to 7.0%, which is demonstrated in case ‘A’. Case ‘A’ has also demonstrated a reduction of overcharge time to 0.5 hour. Similar improvement is also observed on case ‘J’, where overcharge time is reduced to merely 0.1 hour, with cyclic efficiency improved by 7.6%. The improvement on cyclic efficiency is also attributed to the more efficient discharge process, which can be explained using Figure 4.14. The cyclic efficiency is also shown to have an inversely proportional relationship for overcharge time, which again signals the importance of having proper TES capacity for each component in a cascaded PCM TES system.

Despite the increase in cyclic efficiency, the time taken for the TES system to complete charging has increased from 8.1 hours to 10.6 hours for the optimized efficiency case (case ‘J’) which marks significant increment of $\approx 30\%$. Thus, increasing TES capacity of PCM-1 is not always feasible, especially when the charging time is a constraint (i.e. thermal energy is only available at a certain time of a day).

Figure 4.16: Cyclic efficiency for fixed PCM-3 TES capacity with varying PCM-1 TES capacity and charge time for optimized cases

4.7.1.3. Tabulating cases with similar charge time

In the two previous subsections, the charge time can be greatly altered in the trial to reduce the overcharge time (i.e. in Table 4.6 charge time is reduced while in Table 4.7 charge time is increased). This section lists notable cases in which the charge time is within ± 0.8 hours (10%) with the baseline case to check the effect of overcharge time on the cyclic efficiency. In Table 4.8, it shows that up to 4.6% improvement on cyclic efficiency can be achieved when the overcharge time decreases from 2.2 hours to 0.5 hours in case ‘i’. Correct proportion between capacity for PCM-1, 2 and 3 is needed to avoid any scenario of overcharging and maintain high cyclic efficiency of the system.

Table 4.8: Effect of overcharging time on cases with similar charging time

Selected case	PCM-1 capacity (kWh)	PCM-2 capacity (kWh)	PCM-3 capacity (kWh)	charge time (hrs)	discharge time (hrs)	overcharge time (hrs)	η_{ch} (%)	η_{disch} (%)	η_{cyclic} (%)
i	21.2	15.1	12.5	8.2	7.7	0.5	83.3	94.1	78.4
ii	19.8	15.1	12.5	8.0	7.5	0.7	83.6	93.6	78.2
iii	18.4	11.8	16.0	7.9	7.3	1.2	83.3	92.5	77.0
iv	21.2	8.4	19.6	8.3	7.5	2.0	83.8	90.4	75.8
v	17.0	18.5	12.5	8.1	7.2	1.7	83.5	90.1	75.2
vi	19.8	8.4	19.6	8.1	7.2	2.0	83.6	89.7	75.0
vii	17.0	11.8	19.6	8.3	7.3	2.0	83.4	89.4	74.5
viii	19.9	15.1	8.9	8.0	7.0	1.1	79.1	94.0	74.3
ix	18.5	8.4	19.6	7.9	7.0	2.0	83.4	88.8	74.1
baseline	15.6	15.1	16.0	8.1	7.0	2.2	83.2	88.7	73.8
x	17.0	18.5	8.9	8.1	7.0	1.7	79.1	92.4	73.0

xi	21.3	5.0	23.2	8.3	7.1	3.1	83.9	85.8	72.0
xii	19.9	5.1	23.2	8.1	6.8	3.1	83.7	85.0	71.2
xiii	21.3	15.2	5.4	8.3	6.8	2.3	74.3	94.2	69.9

4.7.2. Parametric studies on capacity

4.7.2.1. Variation of optimized cyclic efficiency with TES capacity of PCM-1

Figure 4.17: Variation of optimum cyclic efficiency with TES capacity of PCM-1

The optimum cyclic efficiency against each TES capacity of PCM-1 is plotted in Figure 4.17. The cyclic efficiency increases with storage capacity of PCM-1, which coincides the observation made in Section 4.7.1.2, which system with larger PCM-1 TES capacity leads to longer charge time, and higher cyclic efficiency under correct capacity of PCM-2 and 3. The high efficiency is due to the longer travel distance for HTF within the TES tank (increase in TES length for all PCM capsules) and larger heat transfer area for more complete heat exchange between HTF and TES. However, this cyclic efficiency is saturating as the capacity increases, and is projected to saturate at $\approx 85\%$.

4.7.2.2. Variation of cyclic efficiency with charge-to-discharge time ratio

TES tank cyclic efficiency can also be plotted against its charge-to-discharge time ratio. With more cases with different combinations of TES capacities simulated, a general relationship between cyclic efficiency and the time ratio can be plotted. Such plot is shown in Figure 4.18, where cyclic efficiency is almost inversely proportional to the charge-to-discharge time ratio. However, there can be multiple values of cyclic efficiency that can be read when one charge-to-discharge time ratio is chosen (multiple y-coordinates are corresponded to an x-coordinate). This is due to the different TES capacity for PCM-1, which larger capacity leads to higher efficiency as discussed in previous section and Section 4.7.1.2.

Figure 4.18: Variation of cyclic efficiency with charge-to-discharge time ratio

4.7.3. Effect of PCM encapsulation diameter on cyclic efficiency

In the baseline case, more than 9,400 capsules are used to achieve the designed TES capacity while for the simulated numerical case with the highest cyclic efficiency, more than 15,000 capsules are required. Encapsulation can occupy a large portion of the capital cost in a TES system, while almost 50% of the encapsulation cost is attributed

to the encapsulation material and its manufacturing process [175]. To maintain the competitive cost of a TES system, number of capsules should be reduced.

The encapsulation diameter is varied for a range between 0.05 and 0.10 m and the effects on the charge and discharge efficiencies are investigated. Case of TES combinations with highest efficiency found in the mapping in Section 4.7.2.1 (30 kWh of PCM-1; 22 kWh of PCM-2 and 18 kWh of PCM-3) is used. The diameter of the packed bed TES system is kept at a constant 1.0 m, and the only varying factor is diameter of the PCM encapsulation, which subsequently affects the diameter ratio between the TES tank and PCM particles. The effect of such variations on charge, discharge and cyclic efficiencies as well as number of capsules are shown in Figure 4.19 while the effect on charge and discharge time are shown in Figure 4.20.

Figure 4.19: Effect of encapsulation diameter on efficiencies and number of capsules

Figure 4.20: Effect of encapsulation diameter on charge and discharge time of PBTES system with similar capacity

From Figure 4.19, as encapsulation diameter increases from 0.05 to 0.10 m, the number of encapsulated PCMs required decreases drastically from more than 15,000 to about 1,800. However, the cyclic efficiency of TES system also reduces from 82.1% to 69.2%. This decrease in cyclic efficiency is contributed by a decrease in both charge and discharge efficiencies. For larger encapsulation radius, longer charge time is expected as thermal energy takes longer time to reach the innermost node of encapsulation discretization (due to low thermal conductivity of PCM), which means longer time taken to charge and discharge a PCM capsule. In Figure 4.15, the charge efficiency of TES system can be related to the HTF temperature leaving the system, which lower temperature equals to more thermal energy unrecovered and lower charge efficiency. In cases with large PCM encapsulation diameter, similar thermal gradient exists along radial direction of PCM, but larger diameter leads to larger temperature difference between the innermost and outermost node of a PCM capsule. Temperature of HTF generally mirrors the temperature of outermost node of PCM capsule, and thus the HTF temperature at outlet of TES tank during charge depends on the surface temperature of last tier of capsules in PCM-3. When this capsule has a large temperature difference along the radius, the temperature of the surface is lowered when charge time progress

to charge its innermost node. HTF leaving the TES tank is at lower temperature than the case with smaller encapsulation diameter, and thus lower charge efficiency.

For packed bed TES system with a larger encapsulation diameter, during the discharge stage, the efficiency is lower due to earlier cut-off. Similarly, under the same thermal gradient, a large diameter results in a larger temperature difference between the outermost and innermost node of the PCM capsule. The HTF which mirrors the outermost temperature of a PCM encapsulation is then unable to maintain a temperature below the threshold while substantial amount of energy is still trapped in innermost node of the PCM encapsulation, and the discharge process ends and resulting in a lower discharge efficiency. Combination of both lower charge and discharge efficiencies lead to a lower cyclic efficiency which is reflected in Figure 4.19

However, from Figure 4.19, the cyclic efficiency has only dropped by $\approx 4.7\%$ when the encapsulation diameter increases from 0.05 to 0.07 m, while the number of capsules is decreased by more than half from more than 15,000 to about 5,300 capsules. This finding is important as for the operation of a packed bed TES system, it is likely the cost-efficiency will play a key role and a large diameter ratio of tank-to-capsule is not always a necessity.

4.8. Conclusions for liquid HTF study

Several main conclusions have been drawn and are listed below:

- Overcharging of a packed bed TES system is mainly due to two reasons:
 - Excessive high-grade PCM, which causes loss of low-grade thermal energy during the charging process.

- Insufficient high-grade PCM, which causes degradation of high-grade energy in the charging phase; and lower-grade thermal energy not recovered during the discharging stage.
- The charge times of different PCMs cascaded in a packed bed TES system should be made as close to each other as possible for higher cyclic efficiency with material savings.
- Efficiency is inversely related to the ratio between charge and discharge time.
- Higher cyclic efficiency is achievable with higher TES capacity of PCM which stores the highest-grade of thermal energy.
- To achieve a TES system with cascaded PCM of higher efficiency, PCM-2 should be allocated capacity of approximately 0.7 times the capacity of PCM-1 while PCM-3 approximately 0.5 times the capacity of PCM-1.
- Larger encapsulation diameter would result in less capsules used for a similar thermal capacity, and encapsulation diameter of 0.07 m should be used for tank diameter of 1.0 m, where cyclic efficiency decreases by $< 5\%$ compared to the usage of 0.05 m encapsulation diameter.

A generalized map is also provided for the study, which can serve as guideline for sizing a packed bed TES system under same operating or material conditions for HTF and PCMs. From the map, different combinations of capacity for each cascaded PCMs, information about charge time, discharge time and cyclic efficiency can be devised. The map would also allow preliminary scaling to be carried out if desired performance criteria such as charge time, efficiency and storage capacity of one PCM are known.

4.9. Future work for TES study

Some rooms of improvement are identified. The first is that liquid HTF may not be the best choice for high-grade cold distribution. LNG is regasified at -160°C under ambient pressure. The HTF selected under compromise of operating conditions and safety or environment concern, can only work at lowest temperature -80°C . Such limitation results in loss of high-grade cold energy (or exergy) from the cold source to the storage. Thus, gaseous HTF may need to be considered in the subsequent study.

Another room of improvement is observed from the model validation. The validation carried out using literature data is less promising, which can be due to fluctuation of inlet conditions, due to pipes before TES tank also starting from an initial temperature and captured some thermal energy, which is not reported in the literature study. As such, setting up a TES storage facility allows for capture of clearer information and allows for more experimental results for model validation purpose.

Chapter 5. Experimental setup and investigations

Experimental results available in the literature may exhibit losses of information, particularly for the boundary conditions of fluid flow, where most real-life systems are subjected to transient boundary conditions between system start up and steady-state boundary condition. Thus, it incurs difficulties for validation of simulation model, which inaccuracies may arise. Besides, there is no experimental study using vapor-type HTF to transport cold energy. Thus, to overcome the abovementioned problems, an experimental setup is setup to investigate on these issues.

5.1. TES System 1

An experimental setup for TES system is built in Thermal Energy Systems Lab (TESLAB) in Nanyang Technological University (NTU). The experimental setup is targeted to investigate the operations of TES system near regasification temperature of LNG. There is no “safe” liquid HTF which is able to recover the cold energy at temperature as low as the LNG regasification, resulting in losses of high-grade cold energy prior to energy storage. Thus, in the experimental setup, gaseous HTF is considered as the first choice.

The experimental setup is designed around a TES tank as the main subject, followed by supporting equipment for the charge and discharge operations of the TES tank. As discussed in the literature and section 2.2.4, a PBTES system is selected due to its larger heat transfer area and thus shorter charge and discharge time compared to a shell-and-tube system. An in-house-developed PCM with phase change temperature of -118°C has been pre-developed and is used as TES material. Thermophysical properties of the materials are listed in Table 5.1. The in-house-developed PCM has undergone cyclic test between cryogenic temperature and room temperature for more than 90 cycles, and any significant change on thermophysical properties is not observed.

Table 5.1: Thermophysical properties of in-house-developed PCM used in TESLAB

Properties	Values
Phase change temperature	-118 °C
Thermal conductivity	0.20 W/m·°C
Volumetric specific heat capacity	1.499 MJ/m ³ ·°C
Volumetric latent heat capacity	67.88 MJ/m ³

Nitrogen (N₂) is chosen as HTF because it is cheap and easily available due to its abundancy in the atmosphere, as well as zero environmental concern. Liquid nitrogen (LN₂) with temperature of -196°C is commercially available, and such LN₂ can be used not only as HTF, but also cold energy source as its pressure and temperature can be easily tuned to the designated boundary conditions of the TES system. Thus, heat exchange between cold source and HTF is unnecessary, simplifying the configuration.

In Singapore, commercial LN₂ is available in standardized cylinders with tank volume of 165 liters. Thus, the PBTES system must be scaled properly to ensure smooth operations during charge and discharge, such that LN₂ is not used up and no change of LN₂ cylinder is required during operation. For usage of LN₂ as HTF, prior to entering the TES tank, LN₂ must be fully vaporized to avoid fluctuation on thermal energy entering the TES tank due to fluctuation on liquid fraction. When only vaporized N₂ is used, an 80% filled LN₂ cylinder (to accommodate the boil-off) with usable temperature as low as -160°C (to mimic LNG regasification temperature) is estimated to be able to supply cold energy for 55 liters of in-house-developed PCM, assuming that all cold energy is recovered.

However, additional loss factor such as lower charge efficiency of HTF needs to be accounted when there are less PCM capsules, where smaller heat transfer area exists as

discussed in section 4.7.2. Besides, when the TES system is small, the tank surface area to volume ratio is high and the system is more prone to thermal energy loss to the surroundings. A conservative numerical simulation is carried out using setup with 200 capsules of 50 mm encapsulation diameter and estimated the charge efficiency can be as low as 30% under no thermal loss condition. Such low thermal efficiency can be due to two reasons: (1) small heat transfer area between HTF and PCM for cold energy transfer to be stored and (2) the phase change temperature of single-PCM used is too low (-118°C) with initial condition of 20°C , which approximated the second scenario of overcharging a TES system. In the first design of the TES system, it is decided that cascaded PCM is not used for two reasons: (1) the tank scale can be too small for allocation of enough capacity for each PCM and (2) to ensure simplicity of the system for troubleshooting in the first phase of experiment.

If charge efficiency is as low as 30%, it is estimated that without any energy loss, an LN_2 cylinder is only enough to charge ≈ 16.5 liters of PCM. 50% allowance is allocated for thermal loss through the tank wall, thus, in the finalized TES system, only 8.3 liters of PCM is used. For a PCM capsule with encapsulation with 50 mm outer diameter and 1 mm encapsulation thickness, the inner cavity is 58 ml. To avoid pressure buildup within the capsule due during phase change especially during melting, only 85% of the capsule inner volume, which is approximated to be 50 ml is filled with PCM. Thus, 166 capsules are needed for 8.3 liters of PCM volume.

A packed bed setup with tank-to-particle diameter ratio of 5 is used. For this diameter ratio, 19 PCM particles can be packed on the same height in a single layer. The layout of 19 capsules in a single layer is shown as Figure 5.1. Layer-by-layer approach is chosen for the PCM packing, to prevent overly high pressure exerted on the base of

TES tank as well as to prevent capsules from exerting pressure on the thermocouples. Support is welded to the tank wall after every layer of PCM, and a mesh is used to hold all PCM capsules in place. Altogether 9 layers of PCM capsules are allocated which sums at 171 capsules.

Figure 5.1: Layout of encapsulated PCM arranged in the TES tank

Temperature distribution within a TES tank is one important criterion to investigate the charge and discharge process as well as thermal losses to the surroundings. In total, 26 resistance temperature detectors (RTDs) Omega PT-100 are used with class A accuracy which provides maximum deviation of $\pm 0.45^{\circ}\text{C}$ under the most extreme temperature reachable by the setup. Locations of RTDs are plotted in Figure 5.2. At least one temperature measurement is taken in the HTF region at every interval between each tier, at the center of the tank to obtain the development of HTF temperature along the axial direction. For certain intervals, temperature measurements are taken at 5 locations along the radial direction: for the inlet, outlet and at 1/3rd and 2/3th length of the tank. At these intervals, each RTD is placed 60 mm apart from each other and positioning of the RTDs is shown in Figure 5.3. The RTDs are inserted to the TES tank along the radial direction and are attached to the mesh used to support the PCM capsules for

additional support. Temperature within PCM capsule is not taken due to safety concern (i.e. prevent leakage from contaminating the TES system).

Figure 5.2: Locations of RTDs within the TES system

Figure 5.3: 5 RTDs configuration for a specific layer interval in TES tank

7.5 mm gap is allocated between each tier to accommodate the mesh, which is 2 mm thick and RTDs which have 3 mm diameter. The tank thus has inner diameter of 250 mm and height of 520 mm, resulting in inner cavity of 25 liters. The tank is made of 2 mm thick SS316-grade stainless steel. To minimize thermal energy losses to the surroundings, the TES system is insulated using Armaflex Class 0 with thermal conductivity of 0.032 W/m·K [176], with thickness of 18 mm.

Supporting equipment to ensure proper HTF flow during charge and discharge is built alongside the TES system. Complete layout for the system setup in TESLAB is shown as Figure 5.4. The photographic view of the experimental setup is shown in Figure 5.5. During charge and discharge operations, the whole system is enclosed in a stainless-steel built structure, which is partially vacuumed to isolate the tank from ambient environment, that is otherwise subjected to ambient air with high humidity. The stainless-steel structure is shown in Figure 5.6.

A commercially available LN₂ cylinder serves as HTF source as well as cold source throughout the experiment during the charge process. LN₂ flows from the cylinder and enters the system through the inlet tube of the setup. LN₂ is then vaporized using an electrical heater to the desired boundary condition temperature. The vaporized N₂ is then sent into the PBTES tank to charge the PCMs. Upon leaving the TES tank, N₂ gas flows through a Brook's 5850E mass flow controller designed to maintain constant N₂ flow rate between 100 and 400 L/min. The maximum error of measurement is 1%. Prior to entering the mass flow controller, N₂ gas is warmed using another heater to a constant temperature to ensure no temperature fluctuation, which could otherwise affect the flow density and measurement accuracy of the mass flow controller. Gaseous N₂ is then vented to the ambient through a fume hood of the room where the experimental setup is located.

Figure 5.4: Layout for the TES system setup in TESLAB, NTU

During discharge studies of the TES tank, gaseous N_2 is delivered from an N_2 tank, which is passed through a compressor to ensure a steady flow rate and pressure. The N_2 is warmed using a heater to maintain a constant discharge boundary condition temperature at the inlet of the TES tank. A buffer tank is used to absorb any excessive pressure at the compressor outlet to avoid any flow fluctuations towards the mass flow controller. N_2 is then passed through the TES tank to discharge the cryogenic energy stored. Similar to the charge process, upon leaving the TES tank, gaseous N_2 is redirected to the loop of the heater and mass flow controller before being vented out to the ambient.

Figure 5.5: Photographic view of the TES experimental setup

Figure 5.6: TES setup enclosed in vacuum enclosure for ambient condition control

To allow communication between user and the TES system as well as for experimental data logging purpose, a graphical user interface (GUI) is built using National Instrument

(NI) LabVIEW (Figure A.14). Temperature, pressure, and flow rate measurements taken at different locations of the TES setup are monitored to allow the user to react to the system conditions. Solenoid valves are used to control the flow path of HTF, whether through the TES tank or to bypass it, and can be controlled via the same interface. Temperature measurements within the TES tank are displayed on another individual layout due to the large numbers of measurements, which is shown in Figure A.15. Locations and temperature measured by the 26 RTDs are displayed. All measurements on the system layout and within TES tank are transmitted to a data logger, and is logged every 1 second interval.

Multiple experiments have been carried out under different boundary conditions, with the boundary conditions subjected to changes most of the time is the flow rate, which subsequently varies the thermal power carried by HTF into the TES tank. In general, a higher flow rate means higher charge rate or discharge rate, which leads to shorter charge and discharge time.

(a)

(b)

Figure 5.7: Validation of charge of TES tank in (a) axial direction and (b) radial direction using flow rate of 200 liter/min

(a)

(b)

Figure 5.8: Validation of discharge of TES tank in (a) axial direction and (b) radial direction using flow rate of 125 liter/min

Different flow rates have been used for charging and discharging the TES system. For charge, flow rates of 175, 200, 225 and 250 liter/min have been used (with flow rate of 200 liter/min demonstrated as Figure 5.7) and discharge flow rates of 125 and 150 liter/min have been used (flow rate of 125 liter/min is shown in Figure 5.8). In both sets of figures, two plots are shown which plots (a) show the temperature development along the axial direction and plots (b) show the temperature development along radial directions for different layers of interest. From the radial temperature plot, thermal energy losses in the TES system is found to not negligible. However, from the experimental, it was unable to estimate clearly the amount of energy losses via tank wall. It is because of the lack of proper measurements which can be explained with the followings: (1) lack of measurements on TES materials energy content, (2) lack of measurements on the heat flux via the tank wall. Thus, measurement of energy loss is omitted for the time-being and is revisited during simulation (where the heat loss coefficient can be estimated) to allow calculation of the energy loss amount.

Performances of the TES system are measured based on their charge and discharge time, as well as the corresponding charge and discharge efficiencies. During the experiment, the charge time is defined as the time where the HTF at the TES system outlet ($x/L = 1$) reaches at least 5°C below the phase change temperature of the PCM allocated. Discharge time is however defined as the time where the HTF at the TES system outlet ($x/L = 0$) reaches 0°C, which the cold energy recovered is not useful for most cold demands. The efficiencies are estimated as follow: Charge efficiency is defined as ratio of thermal energy captured by TES materials to thermal energy supplied by HTF, while discharge efficiency is defined as ratio of thermal energy recovered by HTF to thermal energy stored by TES materials.

Despite understanding of such performance indices, such performances are not evaluated for each experiment as the main purpose of the experimental setup is to obtain a credible transient data for validation of numerical simulation models. Instead, charge and discharge time are more often used as the gauging parameters to decide whether an experiment is complete.

5.2. Improvement on TES System 1

The TES setup introduced in Section 5.1 is found to has large void space due to its extra height allowance for each PCM capsule layer to accommodate the structural mesh and RTDs. The void fraction of the TES system is calculated to be 0.559, more than half the volume of the tank. Such void space does not contribute to any TES capacity. Thus, after obtaining enough sets of experimental results from the original configuration for simulation model validation, the TES system is upgraded.

Energy performance of a packed bed system can be improved by reducing its void fraction. According to Ismail and Stuginsky [177], when smaller void fraction is assumed in the numerical model, higher energy density is resulted. Besides, due to increase in heat transfer area, faster charge or discharge rate is also expected. In fact, reducing the particle size is one way to decrease the void fraction of packed bed system. Löf and Hawley [178] suggests that such reduction results in heat transfer enhancement between the packed bed and HTF. On the other hand, reducing the particle size may result in larger number of encapsulated PCM particles to achieve similar TES capacity. In the study conducted by Hohlein et al. [175], the cost of capsules, due to its material amount and manufacturing expenses, contributed to almost 50% of the total cost of encapsulated PCM. Thus, reducing void fraction of a TES system by using PCM capsules with smaller encapsulation size may be favourable for performance but not for the overall cost.

Other than reducing the encapsulation size of PCM, another way to decrease the void fraction of packed beds is to use smaller-sized granular TES materials to fill the void space between PCM capsules. Due to the defined size of macro-encapsulation, void space in packed bed TES can go up to 50% of tank volume (55.9% in experimental setup due to extra allowance allocated). If such void space is properly utilized using additional filler materials, packed bed TES system can provide higher storage capacity and efficiency. There are only a few studies up to now. Vallejo used both larger-sized rocks and smaller-sized sand to fill a cylindrical container [179]. With correct ratio between these two packing materials and application of slight compressive force (13.9 kPa), the void fraction was reduced to 0.24 from 0.35 where if only rocks were used. Odenthal et al. [180] suggested that the combination of large and small particles, known as bidisperse packing, can achieve higher packing density. The bidisperse packed bed

was numerically simulated using quartzite and sand, and the model was verified with experimental results. In these examples, using packing materials with multiple sizes led to significant decrease in the void fraction.

Moreover, introducing a secondary storage material to packed bed TES can improve its performance. Many researches have used both sensible heat materials and encapsulated PCM in a packed bed TES, or tested cascaded TES with more than one PCM. However, in these papers, newly introduced materials are not placed homogeneously with the primary storage material. Okello et al. [181] inserted copper tubes containing a PCM into the packed bed of rocks. Zanganeh et al. [124], Geissbühler et al. [182], and Becattini et al. [183] applied encapsulated PCMs on top or at bottom section of sensible heat materials with the purpose of increasing energy density of TES tank and stabilizing the outflow temperature of HTF. This concept is also used for other types of TES than packed bed. Dabiri et al. [184] introduced a PCM into bricks, which is designed as sensible heat materials. Ahmed et al. [185] inserted PCM encapsulated in tubes between rod-structured sensible heat materials to provide stable outlet temperature for the HTF.

The approach of filling the void space around the macro-encapsulated PCM tiers with granular material is taken. The space is filled with quartzite pebbles as illustrated in Figure 5.9. The distribution of pebbles is thoroughly controlled during the insertion process, and adding in 1.7 kg of pebbles per tier reduces the void fraction from 55.9% to 33.2%. The charge and discharge of the TES tank filled with both granular and macro-encapsulated materials are identical with the procedures described in Section 4.1. Properties of the quartzite pebbles are provided in Table 5.2.

Experimental studies are carried out by using the updated TES configuration with granular materials. Experiments are repeated under different flow rates (charge: 225,

250, 275, 300 and 350 liter/min and discharge: 150, 200 and 250 liter/min). In this configuration, the flow rate is slightly elevated compared to the setup without inserting granular material. It is because in the setup with granular materials, the pressure drop is more significant, and thus low velocity HTF is unable to sustain the flow across the much-reduced void space. Experimental results for charge at 225 liter/min and discharge at 150 liter/min are shown in Figure 5.10 and Figure 5.11 respectively.

Table 5.2: Thermophysical properties of quartzite pebbles used to fill void space

Material	Quartzite pebbles [186]
Density (kg/m^3)	2600
Thermal conductivity ($\text{W/m}\cdot^\circ\text{C}$)	5.0
Specific heat capacity ($\text{J/kg}\cdot^\circ\text{C}$)	690

Figure 5.9: Filling void space around macro-encapsulated PCM with granular pebbles

(a)

(b)

Figure 5.10: Temperature-time profile of charge of TES tank with granular pebbles using flow rate of 225 liter/min in (a) axial direction and (b) radial direction

(a)

(b)

Figure 5.11: Temperature-time profile for discharge of TES tank with granular pebbles using flow rate of 150 liter/min in (a) axial direction (b) radial direction

Using a single PCM with high-grade cold phase change temperature in a TES system leads to the second scenario of overcharging, which sacrifices the overall efficiency of the TES system. Using cascaded PCM in a TES system has been investigated in various

literature, including in detail for allocation of TES capacities between different PCMs for optimum system performance.

Table 5.3: Thermophysical properties of PureTemp -37X

Material	PureTemp -37X [187]
Density (kg/m^3)	880
Thermal conductivity ($\text{W/m}\cdot^\circ\text{C}$)	0.15
Specific heat capacity ($\text{J/kg}\cdot^\circ\text{C}$)	1990
Phase change temperature ($^\circ\text{C}$)	-37
Latent heat (J/kg)	145000

Thus, in the most recent upgrade of the TES system (end of March 2020), 4 tiers (out of 9) of in-house-developed PCM in the TES setup are removed and replaced with PureTemp -37X, which has a phase change temperature of -37°C . Thermophysical properties of PureTemp -37X is shown in Table 5.3.

(a)

(b)

Figure 5.12: Temperature-time profile of charge of TES tank with cascaded PCMs using flow rate of 250 liter/min in (a) axial direction and (b) radial direction

Experimental studies are also carried out using different flow rates for this updated configuration, including charge (flow rates: 250, 300, 350 and 400 liter/min) and discharge (flow rate: 150, 200, 225 and 250 liter/min). Selected results are plotted in Figure 5.12 and Figure 5.13.

(a)

(b)

Figure 5.13: Temperature-time profile of discharge of TES tank with granular pebbles using flow rate of 225 liter/min in (a) axial direction and (b) radial direction

5.3. TES System 2

TES system 1 introduced in Section 5.1 is well-controlled and uses one-time HTF (which does not circulate itself and vented after used) for cold energy distribution. The system is more targeted for experimental purpose as a real system is subjected to ambient conditions such as air convection and recirculates the HTF to minimize the operating cost. Besides, latent heat of LN_2 is wasted in the setup, resulting in a smaller size of designed system. Thus, a second TES system is setup in TESLAB. However, to the date this section is written, the TES system is still under progress of being set-up, and only minor testing has been carried out on the system.

Figure 5.14: Schematic diagram of TES system under charge condition

Schematic diagram of the TES system under charge condition is shown as Figure 5.14.

In this system, LN₂ is used as cold source to supply cold energy to the HTF via an evaporator (EVA). N₂ gas is used as HTF, and to ensure the purity of HTF, before every operation the system is purged using boil-off N₂ gas from an LN₂ cylinder. During charging of TES system, the N₂ gas is pressurized using a blower to overcome any

possible pressure drop, then sent to the EVA for cooling to cryogenic temperature. After the EVA, the temperature of N₂ gas can be adjusted using an electric heater (EH3) before sent into the TES tank cluster (REG1 and REG2) before being sent back to the blower. Before entering the blower, the N₂ gas is heated in another electric heater, EH1 to near ambient temperature to avoid condensation of water on the blower surface. In this setup, two TES tanks are used, with each of them containing different TES materials. In REG1, SHTES material (quartzite) is used while in REG2, in-house-developed PCM is used. The N₂ gas HTF can choose to charge any of the tank, combination of both or bypass both tanks by adjusting the 3-way valves to the correct settings.

The layout used for discharge process is demonstrated in Figure 5.15. During discharge process, N₂ HTF is passed through the heater and blower to suitable boundary condition before recovering thermal energy stored inside REG1 and REG2. Then, the N₂ gas at low temperature is passed through a heater EH4 which is the temperature is slightly adjusted to around -50°C. The cold energy of N₂ gas is then rejected into a heat exchanger HEX1 before the N₂ gas is returned to EH1 and blower. The HEX1 links the N₂ HTF with another liquid HTF, which is 60% glycol solution. The glycol solution then carries the lower-grade cold energy to be stored in another TES system REG3, which uses PCM PureTemp -37X as TES material.

Photographic view of the TES system under construction is shown in Figure 5.16. Multiple valves can be observed for control of the HTF flow direction to ensure the correct TES is charged and to prevent wastage of thermal energy.

Figure 5.15: Schematic diagram of TES system under discharge condition

TES system 2 is used to study performance and operation of TES system under real-life condition, which is subjected to ambient air convection and higher amount of thermal loss to the surroundings. Besides, HTF in TES system 2 is recirculated all the time. The parameters of the TES tanks are calculated using standard size of an LN₂ cylinder, which is approximated to contain 130 liters of usable LN₂. As latent heat of

LN₂ is now utilized by N₂ HTF in the evaporator, the size of REG2 (which contains in-house-developed PCM) is also scaled up. Assuming 80% heat exchanger effectiveness, the in-house-developed PCM volume able to be charged using cold energy from an LN₂ cylinder is estimated to be 12.8 liters after considering the charge efficiency and 50% allowance of energy of thermal losses, which is equivalent to 256 PCM capsules. Tank-to-particle diameter of 6 is selected, which is equivalent to 27 capsules per layer and 243 capsules are allocated for 9 layers. REG1 uses quartzite pebbles as SHTES material. The volume of REG1 is set at 35 liters. With approximated of 50% porosity after filled with SHTES materials, it is assumed that 45 kg of quartzite can be inserted into the tank.

Another liquid HTF based TES system is built, mainly charged by thermal energy recovered from REG1 and REG2. In this system, PureTemp -37X of 13.5 liters is used, and is encapsulated in 270 capsules. Slightly over-scaled system is used here to allow for further upgrade when external cold source (e.g. from a chiller) is used to charge the system. The setup is estimated to commission by September 2020.

In thermodynamic points of view, TES system 2 has a higher TES capacity due to the bigger size and larger number of capsules (all capsules have same geometry). However, TES system 2 with recirculating HTF, particularly gaseous HTF such as nitrogen also creates some potential problem such as pressure built-up and need for consistent heat sink to ensure similar boundary conditions to the TES system. Besides, TES system 2 is subjected to larger extent of thermal losses, particularly due to the exposed tank wall to the ambient and is subjected to ambient air flow, due to the increased convective heat transfer coefficient due to more vigorous ambient air movement.

Figure 5.16: Photographic view of TES system 2

With obtain of experimental data, it is now possible to proceed to develop simulation models TES system with vapour HTF with higher confidence level. Experimental data is used to validate these models, which will be introduced in detail in the next two chapters.

Chapter 6. 1-dimensional numerical study on TES system using vapor HTF

In this chapter, to utilize the full sensible temperature range of LNG, vapor HTF, nitrogen which is able to cover larger temperature range compared to liquid HTF is chosen. In this chapter, the improvement on TES system is based on reduction of void ratio, without cascading PCMs to investigate to potential improvements achievable.

Reducing void fraction of a TES system increases the TES capacity of the system, especially for systems equipped with macro-encapsulated PCM with large encapsulation diameters. Large void within a TES system is unfavorable as it reduces TES capacity and performances of the system. Despite many papers for PBTES system using encapsulated PCM, investigation on improvement due to reduction of void fraction is still absent. While bidisperse packings have been primarily considered for an optimization of packing density, their impact on the thermal performance of TES system is seldom investigated. Thus, a study is carried out to focus on using homogeneously distributed granular materials within void space of a TES, initially containing macro-encapsulated PCM, to reduce its void fraction and enhance its performance. Experimentally validated 1D numerical model is used. Parametric analysis is carried out, which includes four parameters: types of macro-encapsulated PCMs, encapsulation sizes, types of granular materials and HTF flow rates. The results are evaluated and compared in terms of charge/discharge time and efficiency.

6.1. Concentric dispersion model

Despite has been introduced in Section 4.2.2, concentric dispersion model is slightly modified here due to introduction of second TES material: the granular materials. The

encapsulation size of PCM is set to vary between 50-100 mm, where these upper and lower bounds are based on commonly used sizes of macro-encapsulated PCMs [188]. For these encapsulation sizes, their Biot number is higher than 0.1 and temperature variation within the encapsulated PCM volume is expected to be significant. Therefore, concentric dispersion model is used to predict the temperature development in macro-encapsulated PCMs. Similar assumptions introduced in section 4.2.1 are used.

Discretization of the TES tank is also similar to Figure 4.1, which is discretized into equal volumes in its axial direction, x with the notation of i^{th} volume, where in each node the HTF is considered to have a same temperature. Within each axial node of the tank, an encapsulated PCM is discretized into equal volumes along its radial direction, r with the notation of j^{th} volume where in each node the PCM is considered to have a same temperature. Energy equations for HTF and PCM are demonstrated in equations (2.10) and (2.11). To obtain temperature of each radial node of the PCM, heat conduction equation represented in spherical coordinates is used as equation (2.14). Latent heat involved in the process is included using enthalpy method as equations (2.16).

Effective size of the granular materials is less than 10 mm for sensible heat materials, and about 20 μm for micro-encapsulated PCM. Under these dimensions, the Biot number for the materials is less than 0.1, indicating the applicability of lumped capacitance method. Corresponding energy equation (2.4) is taken and temperature variation within the granular material is not considered. For the micro-encapsulated PCM, the same energy equation is used as in the macro-encapsulated PCM, but equation (2.14) is omitted as there is no radial temperature variation. The energy equation for granular materials is slightly modified due to difference in void fraction:

$$(\varepsilon - \varepsilon_{PCM})\rho_{granular}c_{p,granular}\frac{\partial T_{granular}}{\partial t} = ha(T_{HTF} - T_{granular}) \quad (6.1)$$

Nusselt correlation for HTF-PCM heat transfer is adapted from equation (2.17) while for HTF-granular material heat transfer is adapted from equation (2.19).

For granular materials where no encapsulation is involved, h_{conv} is taken as final heat transfer coefficient between HTF and the granular material, h . For macro-encapsulated PCM, thermal resistance due to its encapsulation is included in the final heat transfer coefficient between HTF and PCM, h using the total resistance method.

The initial and boundary conditions are listed as equations (6.2)-(6.4) and equations (6.5)-(6.6) respectively:

$$(\text{charge}) \quad T_{HTF} = T_{PCM} = T_{ambient} \quad (6.2)$$

$$(\text{discharge}) \quad T_{PCM} = T_{PCM,complete \ charging} \quad (6.3)$$

$$(\text{discharge}) \quad T_{HTF} = T_{HTF,complete \ charging} \quad (6.4)$$

$$T_{HTF} = T_{inlet} \text{ for } x = 0 \quad (6.5)$$

$$\frac{\partial T_{HTF}}{\partial x} = 0 \text{ for } x = L \quad (6.6)$$

6.2. Validation of model with experimental data

Experiments are carried out using different flow rates of N₂ during charge and discharge processes. The numerical model is then validated using the experimental results by comparing temperature values recorded at different locations of the TES tank.

In Section 4.2.1, thermal energy losses from TES tank is excluded in numerical studies. However, during the experiment, despite the usage of vacuumed enclosure and significant amount of insulation, thermal loss is observed. The thermal loss must be considered to minimize the deviation of numerical results from experimental studies. The loss mainly takes place from the HTF through the tank walls. Therefore, the energy equation related to HTF is modified to consider the thermal energy loss. Thus, equation (2.10) is updated into the following expression

$$\begin{aligned}
& \varepsilon \rho_{HTF} c_{p,HTF} \left(\frac{\partial T_{HTF}}{\partial t} + u \frac{\partial T_{HTF}}{\partial x} \right) \\
& = \varepsilon k_{HTF} \frac{\partial^2 T_{HTF}}{\partial x^2} + ha \left(T_{PCM}|_{r=r_{capsule}} - T_{HTF} \right) \\
& + ha (T_{granular} - T_{HTF}) + h_{loss} \frac{A_{tank}}{V_{tank}} (T_{amb} - T_{HTF})
\end{aligned} \tag{6.7}$$

The heat loss coefficient, h_{loss} is estimated using the total thermal resistance between HTF and the enclosed environment, which includes two most significant heat resistance components thorough the TES tank wall: conduction resistance of Armaflex insulation and natural convection resistance to the enclosed environment. The natural convection is estimated using vertical plate approximation [148] using dimensions of the insulated TES tank, while the conduction resistance is calculated based on the heat transfer through a cylindrical geometry. As a result, h_{loss} is estimated to be $0.9 \text{ W/m}^2 \cdot ^\circ\text{C}$.

Figure 6.1: Validation of charge of macro-encapsulated PCM filled TES tank using flow rate of 200 liter/min

Figure 6.2: Validation of discharge of macro-encapsulated PCM filled TES tank using flow rate of 125 liter/min

For the numerical model, all energy equations are discretized using upwind scheme to take into account the convection-dominant flow regimes. Heat conduction equation is discretized using central differencing scheme. The equations are solved using explicit method with MATLAB software. The numerical model is validated with different charge and discharge conditions. Validation of numerical model of TES system without granular is shown in Figure 6.1 and Figure 6.2. Validation of numerical model for TES system with granular is shown in Figure 6.3 and Figure 6.4.

Figure 6.3: Validation of charge of macro-encapsulated PCM filled TES tank with granular pebbles using flow rate of 225 liter/min

Figure 6.4: Validation of charge of macro-encapsulated PCM filled TES tank with granular pebbles using flow rate of 150 liter/min

The validated numerical models are tested for grid sensitivity. Grid sensitivity analysis is carried out under three different criteria, mainly the TES tank axial mesh volume, encapsulation radial mesh volume and time step, with the time for all PCMs to complete phase change as the decisive parameter. The tank volume is divided into equal volumes with 1/40, 1/80, 1/160 and 1/320 m length respectively while for the encapsulation volume is divided into 10, 20, 40 and 80 equal volumes along the radial direction. Simulations are carried out with time steps of 0.02, 0.01, 0.005 and 0.0025 s. Convergence of the simulation results is noticed with smaller mesh size and time step. Once Richardson extrapolation is carried out, the time step of 0.005 s, the axial mesh

size of 1/160 m and 40 equal volumes for the encapsulation have been accepted since they can provide less than 4% error compared to the calculated asymptotic values.

6.3. Key performance indices

Two main key performance indices are investigated: charge and discharge time and their corresponded efficiency. The charge time is defined as the time when the PCM completes phase change. The discharge time is defined as the time which the HTF recover the cold energy as useful energy. As explained in Section 4.2.4, the HTF's temperature leaving the TES tank increases with time due to depletion of high-grade cold energy in the PCMs. A threshold temperature that defines the cut-off time of discharge, is set at 50°C. This temperature is chosen based on the phase change temperature of in-house-developed PCM (-120°C). When subjected to discharge temperature of 20°C, the averaged value of operational temperature is identified as -50°C. When HTF at the TES outlet is unable to sustain this temperature, the discharge is deemed to complete.

The charge efficiency, η_{ch} is defined as the ratio of the thermal energy stored by the TES materials to the thermal energy supplied by HTF within the charging period. The discharge efficiency, η_{disch} is defined as the total thermal energy recovered by HTF during the discharge period to the total amount of thermal energy stored in the system. The cyclic efficiency, η_{cyclic} is the products of both charge and discharge efficiencies. Equations for the efficiencies are defined in equations (6.8) to (6.10).

$$\eta_{ch} = \frac{E_{stored,PBTES}}{E_{HTF}} \quad (6.8)$$

$$\eta_{disch} = \frac{E_{recovered,HTF}}{E_{stored,PBTES}} \quad (6.9)$$

$$\eta_{cyclic} = \eta_{ch} \times \eta_{disch} \quad (6.10)$$

6.4. Baseline case and parametric analysis

6.4.1. Baseline case

A scaled-up TES tank for real-life application is simulated as the baseline case. The in-house-developed PCM used in the experimental setup is simulated. The diameter and height of the scaled-up TES tank are taken to be 1 m and 0.9 m respectively. The height-to-diameter ratio of the tank is kept low to minimize parasitic heat losses from the HTF near the wall [174]. Same stainless-steel encapsulation with 50 mm outer diameter and 1 mm thickness is used to fill the scaled-up TES tank. The tank is filled with capsules on a tier-by-tier basis, with the amount of capsules placed on each tier determined using an algorithm developed by Mueller [173]. Thus, there are 18 tiers and each tier contains 327 capsules. Thus, using in-house-developed PCM supplies ≈ 5.5 MWh of latent heat. The void fraction of the TES tank is 0.46.

The flow rate at the inlet is set to $3.2 \text{ m}^3/\text{min}$, to maintain similar Reynolds number from the validated numerical model. During the charge process, the inlet temperature is fixed at -160°C , corresponds to regasification temperature of LNG. The temperature development along the TES tank is simulated and shown in Figure 6.5. Two temperature profiles of the innermost volume-node of the PCM at different locations are shown, respectively at the middle ($x/L = 0.5$) and outlet ($x/L = 1.0$) of the tank. The innermost node of the PCM capsule at the outlet of the tank is the last node to receive thermal energy. Therefore, when phase change is completed at this node, phase

change is completed with the TES tank. The defined charge time is 309.9 minutes, with charge efficiency of 48.4%. The total amount of thermal energy stored in the TES tank contributed by both sensible and latent heats of PCM is 36.4 MWh.

Figure 6.5: Temperature-time profile for charge of baseline case and indication of charge complete point

For the discharge regime of the baseline case, a similar flow rate of $3.2 \text{ m}^3/\text{min}$ is simulated, and the inlet boundary condition 25°C . Temperature profiles simulated over the discharge duration at the same locations are shown in Figure 6.6. The threshold temperature is prescribed to -50°C , above which the HTF leaving the TES tank is no longer useful, hence the discharge is completed. The discharge time is determined to be 164.5 minutes, with discharge efficiency of 93.0%. Consequently, the calculated cyclic efficiency is 45.0%.

Figure 6.6: Temperature-time profile for discharge of baseline case and indication of discharge complete point

6.4.2. Parametric analysis

Parametric analysis is studied based on four parameters: (1) type of granular materials, (2) type of macro-encapsulated PCM, (3) HTF flow rate and (4) encapsulation size of TES materials. The geometry of the TES tank, as well as the inlet temperature of HTF to the TES tank are fixed.

6.4.2.1. Type of granular materials used to fill the void space

Large void space is left over when macro-encapsulated PCM is used as TES materials in a PBTES tank. This void space can be filled with different granular materials, which bidisperse packing is proven to be able to reduce the void fraction. 4 materials, quartzite pebbles, alumina (Al_2O_3) particles, aluminum (Al) particles and micro-encapsulated n-decane powders are shortlisted to fill the void space. These materials have been actively used as TES materials. The materials and their properties [106, 186, 189-191] are listed in Table 6.1. The final void fraction of the TES tank after filled with granular materials is assumed to be 0.30, which is close to 0.33 achieved in TESLAB. The granular material is assumed to be evenly distributed among the void space.

Table 6.1: List of granular materials and their thermal properties

Material	Quartzite pebbles [186]	Alumina (Al ₂ O ₃) particles [189]	Aluminum (Al) particles [190]	Micro- encapsulated n- decane [106, 191]
Density (kg/m ³)	2600	2900	2700	900
Thermal conductivity (W/m·°C)	5.0	29.0	210.0	0.13
Specific heat capacity (J/kg·°C)	690	790	900	2200
Phase change temperature (°C)	N/A	N/A	N/A	-30
Latent heat (kJ/kg)	N/A	N/A	N/A	145

6.4.2.2. Type of macro-encapsulated PCMs

Type of macro-encapsulated PCMs is another factor to be investigated. As phase change temperature is lowered towards cryogenic temperature region, the choice of PCMs becomes few and it is more difficult to search for materials with properties as good as most inorganic materials (i.e. moderately high thermal conductivity and high latent heat capacity). Unpreferable thermal properties are among the reasons to low cyclic efficiency in the baseline case.

In this section, two commercially available macro-encapsulated PCMs other than that used in the experimental studies are considered. Both PCMs are eutectic materials manufactured by PCM Products Ltd [171, 172]. The first PCM, PlusIce E-75 (abbreviated as E-75) has different phase change temperature, but similar properties

with the in-house-developed PCM, while the other PCM, PlusIce E-65 (abbreviated as E-65) has similar phase change temperature with E-75, but much distinctive thermal properties. Thermal properties of these two PCMs are listed in Table 6.2.

Table 6.2: List of macro-encapsulated PCMs and their thermal properties

Material	PlusIce E-75 [171]	PlusIce E-65 [172]
Phase change temperature ($^{\circ}\text{C}$)	-75	-65
Density (kg/m^3)	902	1180
Thermal conductivity ($\text{W/m}\cdot^{\circ}\text{C}$)	0.17	0.56
Specific heat capacity ($\text{J/kg}\cdot^{\circ}\text{C}$)	2430	3280
Latent heat (kJ/kg)	102	240

6.4.2.3. Encapsulation size

Manufacturing cost is one of the main criteria considered when designing a TES tank, and manufacturing of the capsules can contribute up to 50% to the total cost [175]. Thus, it is desirable to reduce the number of capsules to reduce the manufacturing cost, while maintaining the efficiency and capacity of the TES system. The encapsulation size is varied between 50 mm and 100 mm to study the effect on storage time and efficiencies.

6.4.2.4. Flow rate

Flow rate is responsible in supplying the right amount of thermal power into the TES. For example, in the regasification process of LNG, the amount of thermal energy released depends on the demand for natural gas. When large amount of thermal energy is released, the flow rate of HTF has to be increased to capture and transport the energy. A large increment in flow rate may not always be desired as it changes the flow characteristics such as Re and subsequently affects the Nu and heat transfer

characteristics. The flow rate of the HTF is varied between 3.2 and 16.0 m³/min and its effect on charge and discharge is studied.

6.5. Results and discussions

6.5.1. Effect of granular materials with different macro-encapsulated PCMs

Here the results are divided into two sections: the first section discusses the effect of varying the type of macro-encapsulated PCM without any granular material, while the second discusses the effect of filling the void space of different TES tanks with granular materials.

6.5.1.1. *Without granular materials*

Two commercially available macro-encapsulated PCMs are compared with the in-house-developed PCM. Temperature-time profiles for charge / discharge simulations on the scaled-up TES tank filled with different PCMs – are displayed in Figure 6.7 and Figure 6.8. For in-house-developed PCM, the charge time is 309.9 minutes, while PCM E-75 and E-65 filled TES tanks have charge time of 293.2 minutes and 564.4 minutes respectively. The charge time of PCM E-75 is shorter than the in-house-developed PCM. It is because when compared to the in-house-developed PCM, E-75 has larger temperature difference between the HTF boundary condition temperature and the average temperature-time profile of PCM mainly due to its higher phase change temperature. Such temperature difference enhances the heat transfer between the HTF and PCM. Such phenomenon is dominant as the TES based on E-75 has larger capacity (47.9 kWh) compared to TES based on the in-house-developed PCM (36.7 kWh). The charge time of E-65 filled TES tank is significantly longer (around 564.4 minutes) due to its high TES capacity of 88.6 kWh.

Figure 6.7: Temperature-time profiles at TES tank outlet using different macro-encapsulated PCM during charge

Figure 6.8: Temperature-time profiles at TES tank outlet using different macro-encapsulated PCM during discharge

Charge efficiency for the TES tank using in-house-developed PCM is 48.4%, while for the TES tank using E-75 and E-65, the charge efficiencies are 70.9% and 75.2% respectively. The low efficiency for the in-house-developed PCM can be explained from the temperature-time profile of the HTF at the tank outlet in Figure 6.7. The area under the curve for this temperature-time profile indicates the temperature region where energy is captured and stored by the PCM, while area above the curve indicates the region where energy is lost with HTF leaving the TES. Due to low phase change

temperature of the PCM (-118 °C), the temperature of HTF leaving the TES tank decreases from initial condition until reaching its constant temperature plateau near -120°C before further decreases towards its inlet boundary condition. Such profile results in much smaller area below curve for in-house-developed PCM and explains why its charge efficiency is lower.

The discharge time of the TES tank filled with the in-house-developed PCM is 164.6 minutes, compared to 314.7 minutes of the TES tank filled with E-75. Shorter discharge time for the in-house-developed PCM can be explained by its larger temperature difference between temperature-time profile and inlet boundary condition compared to E-75, which enhances the heat transfer between PCM and HTF and the discharge rate. Besides, the TES containing macro-encapsulated E-75, is about 30% higher in the storage capacity. However, the cold energy stored in the TES tank containing E-75 has lower exergy value (temperature is closer to ambient) compared to in-house-developed PCM. If the HTF outlet threshold temperature is migrated to a higher-grade-cold region, for instance, to -100°C, the difference in discharge time for both PCMs is significantly reduced. The TES tank using E-65 can sustain the longest discharge time due to its highest phase change temperature and its highest thermal storage capacity. For the discharge efficiency, all three TES tanks show similar performance. In-house-developed PCM based TES has discharge efficiency of 93.0% while the TES tanks using E-75 and E-65 have discharge efficiency of 95.1% and 97.9% respectively.

6.5.1.2. With granular material filling the void space

This section investigates the effect of using various granular materials to reduce the void space of TES tank containing different macro-encapsulated PCMs. Their effect on

charge and discharge time, charge and discharge efficiency, and energy storage performance are illustrated in Figure 6.9. These results are normalized according to their respective values from the baseline studies without granular materials.

Figure 6.9(a) shows the charge time of the TES tank added with different granular materials. For in-house-developed PCM, the charge time increases by 18.6% when the void space is filled with quartzite pebbles, 24.5% when filled with aluminum particles, 29.9% when filled with alumina particles and 21.9% when filled with micro-encapsulated n-decane. Quartzite, aluminum and alumina particles are SHTES materials and increase in the charge time is almost proportional to the change in the thermal energy stored, reflected in Figure 6.9(f). For the TES using micro-encapsulated n-decane, as shown in Figure 6.9(f), the increase in the thermal storage capacity is just lower than that of using alumina particles. The thermal energy stored in this tank configuration is larger compared to the one using aluminum and quartzite particles to fill the void space, yet the charge time is the shortest. It is because of the presence of constant temperature plateau due to the phase change of the micro-encapsulated n-decane at about -30°C . Such temperature plateau creates a gap with large temperature difference between the HTF and micro-encapsulated n-decane and as a result, heat transfer is enhanced and charge time is reduced.

The normalized discharge time is shown in Figure 6.9(b). For the TES tank containing macro-encapsulated in-house-developed PCM, the discharge time is almost proportional to the total thermal energy stored in the TES tank as shown in Figure 6.9(f), without regarding the type of granular materials whether it is an SHTES material or a PCM. Using alumina particles as a granular material contributes to the largest increase in thermal storage capacity and the largest increase in discharge time (56.8%). Micro-encapsulated n-decane is the second-best granular material to sustain discharge (53.3%),

followed by aluminum (46.0%) and quartzite particles (34.5%). When both charge and discharge time are compared, increase in charge time is significantly less than the increase of discharge time. It means that using granular material to fill the void space left by macro-encapsulated in-house-developed PCM does not only increase thermal storage capacity of the TES tank, but also improves the performance when the thermal energy stored becomes more usable and recoverable.

Figure 6.9(c) shows the normalized charge efficiency. For the case of the TES tank primarily containing macro-encapsulated in-house-developed PCM, using micro-encapsulated n-decane as a granular filler yields the largest improvement on the charge efficiency. This is due to the large increase in the TES capacity (only behind alumina particles as granular material) and significantly shorter charge time compared to other granular materials. Such condition interprets a larger charge efficiency where in simple words, shorter time is needed to charge similar capacity. For other SHTES materials, improvement on charge efficiency is almost proportional to the increase in the storage capacity of the TES tank. Such trend implies that using granular material yields better recovery of cold energy at the sensible-heat region, and granular materials with higher energy density is more advantageous.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 6.9: Normalized performance for filling the void space of TES tank with different macro-encapsulated PCM using different granular materials

The normalized discharge efficiency is shown in Figure 6.9(d). For the TES tank equipped with macro-encapsulated in-house-developed PCM, the improvement on the discharge efficiency is less significant compared to the improvement in the charge efficiency. Such difference is mainly due to the original high discharge efficiency without granular material (93.0%) when compared with charge efficiency (48.4%). For SHTES materials as granular material, the improvement on discharge efficiency is again proportional to the increase on storage capacity. However, using micro-encapsulated n-decane as granular material has the lowest improvement on discharge

efficiency. This is due to the phase change temperature of n-decane at -30°C , which is above the stated threshold temperature for discharge. As such, thermal energy stored in micro-encapsulated n-decane as latent heat is not discharged effectively and thus the lowest improvement on discharge efficiency. Combining both changes on charge and discharge efficiency yields the change in overall cyclic efficiency of the TES tank filled with granular materials, and it is shown in Figure 6.9(e). Using micro-encapsulated n-decane as granular material yields the largest improvement on cyclic efficiency which is mainly contributed by the improvement on charge efficiency, followed by alumina particles, aluminum particles and quartzite particles.

For TES tanks equipped with macro-encapsulated E-65 and E-75, the effects of filling the void space with different granular materials are similar to that of equipped with in-house-developed PCM. In case of the TES tank filled with the in-house-developed PCM, the increase in the total stored thermal energy is between 28.0% and 46.2%, while the increment is only between 11.3% and 18.8% for tank filled with macro-encapsulated E-65, and between 21.3% and 35.2% for that with E-75. Same amount of granular materials is used for TES tanks equipped with different macro-encapsulated PCMs resulting in similar increment in amount of thermal energy stored. Due to the originally high storage capacity for E-65 and E-75 compared to the in-house-developed PCM, the percentage improvement on storage capacity when granular materials are used to fill the void space in TES tanks equipped with these two PCMs looks less significant.

For the charge time shown in Figure 6.9(a), for the TES tank equipped with the macro-encapsulated E-75, the increment in charge time (increased between 19.1% and 30.8%) is comparable to the TES tank using in-house-developed PCM (between 18.6% and 29.9%). It is due to the similarly short charge time for both macro-encapsulated E-75 and in-house-developed PCM without any granular material. The total storage capacity

increases by the same amount, due to the same amount of granular material filled into the void space. As in-house-developed PCM has similar charge time to E-75, the addition of same granular materials into these TES tank results in similar increase on their charge times and thus similar percentage increment on the charge time. Furthermore, the TES tank equipped with macro-encapsulated E-65 sees slighter increase in charge time (between 10.3% and 16.4%), which can be due to similar extra amount of time needed for charging the TES, but the percentage increment looks insignificant due to its originally long charge time without granular materials.

Shown in Figure 6.9(b), after filling the void space with granular materials, the TES tanks equipped with macro-encapsulated E-75 and E-65 show less increase in their discharge times (between 22.3% and 36.7% for E-75, and between 13.7% and 23.0% for E-65) compared to the TES tank with in-house-developed PCM (between 34.5% and 56.8%). Similar enhancement on discharge time is yielded when same amount of granular material is used in all cases. Due to originally longer discharge time for the cases of macro-encapsulated E-75 and E-65, the percentage improvement on discharge time looks less significant. For the TES tanks equipped with macro-encapsulated E-65 and E-75, using micro-encapsulated n-decane as granular material is the best option for discharge time improvement where in these two PCMs, their latent heat capacities have higher weightage compared to sensible heat components. In TES tanks containing only macro-encapsulated PCM, at their final stage of discharge process, when sensible heat stored in the PCMs can no longer sustain the uptake in low-grade cold region, latent heat stored in PCMs starts to degrade into the low-grade cold. The presence of micro-encapsulated n-decane solves the problem with its high latent heat capacity at the low-grade cold region, which is able to fill in the place for sensible heat region for these PCMs, thus significantly improves the discharge time of the TES tanks.

Similar observations can be obtained for charge efficiency when granular materials are used for TES tank filled with any macro-encapsulated PCM, where micro-encapsulated n-decane is the best candidate. Using micro-encapsulated n-decane as granular material results in moderately high increase in total storage capacity, but less increment in charge time of the TES tank. Thus, this granular material has the highest increase in charge efficiency, followed by sensible heat materials in order of their storage capacity. When TES tanks equipped with different macro-encapsulated PCMs are compared, using in-house-developed PCM has the highest extent of improvement on charge efficiency (up to 11.6%), while E-75 (up to 5.8%) and E-65 (up to 3.6%) show less improvement due to their originally high efficiencies.

For discharge efficiency, as compared to the TES tank equipped with macro-encapsulated in-house-developed PCM, the TES tanks equipped with macro-encapsulated E-75 and E-65 show minimal improvement of up to 1%. For the TES tanks equipped with these two PCMs, using granular materials to fill the void space yields similar increase on their discharge time compared to the increase in their storage capacity. Such improvement is further suppressed by their originally high discharge efficiencies (more than 95%) when no granular material is used.

For cyclic efficiency, the effect of using granular materials to fill the void space of TES tanks with different macro-encapsulated PCMs shows the same trend, where micro-encapsulated n-decane is the best granular material largely due to its contribution on charge efficiency improvement, followed by sensible heat granular materials in order of their storage capacity. The extent of improvement on cyclic efficiency of TES tanks additionally filed with granular materials largely follows their charge efficiency, where the TES tank with in-house-developed PCM shows the highest increment due to its originally bad performance, where its cyclic efficiency increases between range of 7.0%

to 11.2% (from 45.0%). For the TES tank filled with E-75 the cyclic efficiency increased between 3.9% to 7.1% from 67.4% while with E-65, cyclic efficiency increases only between 1.3% to 3.7% from 73.6%. This implies that the filling the void space in the TES tank is critical for the efficient storage of the high-grade thermal storage, where PCMs with good thermo-physical properties are not yet developed.

Granular materials are very useful in improving performance of the TES tank, especially for lengthening the discharge time and to improve the storage capacity and efficiencies of a TES system. Alumina particles are the best choice as granular material when the increase on storage capacity is the main target for TES tank performance improvements. The usage of micro-encapsulated n-decane as granular material suits best in improving efficiencies of the TES tank. However, using micro-encapsulated n-decane may increase the cost of the system due to its complexity during manufacturing process. Besides, the effect of using granular materials is the most significant when the TES tank is equipped with a PCM aimed for high-grade-cold storage or low phase change temperature, where PCM with good thermal properties is not yet developed.

6.5.2. Effect of granular materials under different encapsulation size

Figure 6.10 shows the effect of the encapsulation size and addition of different granular materials on the performance of different TES systems. The performance is normalized with the baseline case where in-house-developed PCM and no granular material is used.

Figure 6.10(a) shows the effect on charge time. The increment on charge time with usage of different granular materials is explained in the previous section. Due to the PCMs' low thermal conductivities and high Biot numbers, the larger the encapsulation size, the longer the time taken for thermal energy to reach the innermost node to be

stored. Thus, the charge time increases almost linearly with the encapsulation size from 50 mm to 100 mm. In the case of 80 mm encapsulation diameter, due to the defined geometry constraints (TES tank with length 0.9 m), only 11 tiers of PCM capsules are allocated. In other words, the tank volume is not fully utilized. As a result, less thermal energy is stored within the TES tank with this configuration and it is reflected in Figure 6.10(f), resulting in slight drop of charge time when encapsulation is 80 mm.

The effect on discharge time is shown in Figure 6.10(b). As compared with the charge time, the effect of encapsulation size on the discharge time is less significant. With increase in encapsulation size, although thermal energy stored in TES tank decreases, the discharge time for TES tank is still extended slightly. For larger encapsulation sizes, the discharge of the thermal energy is less effective due to PCMs' low thermal conductivity and results in longer discharge time where the HTF can sustain below the threshold temperature. However, the HTF discharged is generally higher in temperature, or at a lower grade of cold. Similar almost linear trend can be observed for the discharge except at encapsulation size of 80 mm due to presence of slightly lower storage capacity.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 6.10: Effect of granular materials on TES tank filled with macro-encapsulated in-house-developed PCM at different encapsulation diameters

From Figure 6.10(f), the total amount of the stored thermal energy is reduced with the increment of the encapsulation size. It is due to decrease in the volume of macro-encapsulated PCM. Larger encapsulation size means lower diameter ratio between TES tank and encapsulations, and results in larger void fraction for the TES tank. However, when granular materials are used to fill the void space, the extent of decrease for the thermal storage capacity is reduced when encapsulation size increases. It is because when granular material is used, the resulted void fraction is set to be constant at 0.30 no matter the original void fraction. Thus, for the TES tank using macro-encapsulated

PCM at larger encapsulation size, more granular materials are used. However, with granular materials, the total storage capacity still decreases with increase in encapsulation size due to the reduction of macro-encapsulation PCM.

The effect on charge efficiency due to encapsulation size is shown in Figure 6.10(c). The charge efficiency decreases with increase on encapsulation size, which can be explained by the changes in storage capacity and charge time. For cases without granular material, when encapsulation size is increased, longer charge time is needed to charge lower storage capacity. Thus, the charge efficiency becomes lower than the baseline case. Usage of granular materials to fill the void space of TES tank elevates the charge efficiency, where much higher TES energy charged with slightly longer charge time. For encapsulation size of 60 and 70 mm, using any granular material maintains higher charge efficiencies than the baseline case. When encapsulation size is increased to 80 mm, using alumina particles and micro-encapsulated n-decane can maintain corresponding charge efficiencies above that of baseline case. The latter observation is significant, as similar performance can be maintained with larger encapsulation size (smaller number of capsules), which is its highest cost component. Using encapsulation size of 70 mm reduces the number of capsules required by 63.6% while using size 80 mm reduces number of capsules by 76.5% and is shown in Figure 6.11.

Figure 6.10(d) shows the effect of encapsulation size and granular materials on the discharge efficiency of TES tanks. For cases with granular materials, the discharge efficiency decreases with increase of encapsulation size, but the extent of decrease is less than the case without granular material. It is due to the slighter change in total storage capacity for cases with granular materials which is shown in Figure 6.10(f). The discharge time also increases with increase of encapsulation size, but still the discharge

efficiency decreases, meaning less amount of thermal energy stored is recovered due to ineffective discharge (averagely higher discharge temperature, HTF contains less thermal energy). Again, using granular materials allows utilizing larger encapsulation size without sacrificing much on the discharge efficiency, where aluminum particles, alumina particles and micro-encapsulated n-decane can be used for encapsulation size of 60 mm while maintaining higher discharge efficiency than the baseline case, while when alumina particle is used, encapsulation size up to 70 mm can be used.

Figure 6.11: number of macro-encapsulated PCM capsules in fixed size TES tank with different encapsulation diameter

Figure 6.10(e) shows the cyclic efficiency of the TES tank filled with macro-encapsulated in-house-developed PCM with different encapsulation diameters and the void space filled with different granular materials. For each encapsulation diameter, the cyclic efficiency of the resultant TES tank filled with micro-encapsulated n-decane is comparable with that of filled with alumina particles, followed by aluminum particles and quartzite pebbles. The downward trend of cyclic efficiency with increase of encapsulation size is due to decrease of storage capacity, charge efficiency and discharge efficiency. However, it can be observed that encapsulation size of up to 80 mm can be used for TES tank when alumina particles and micro-encapsulated n-decane

is used as granular materials, while being able to maintain comparable cyclic efficiency with the baseline case. Such indication means more than 75% cut on the amount of macro-encapsulated capsule. Using any granular material permits to utilize capsules with diameter of 70 mm, without compensating any efficiency of the tank.

6.5.3. Effect of granular material under different flow rate

The effect of HTF flow rate at the inlet on the storage performances of TES tank filled with macro-encapsulated in-house-developed PCM having 50 mm encapsulation diameter as well as various granular materials distributed into the void space is shown as Figure 6.12. Since variation of the inlet flow rate does not affect the amount of the total thermal energy stored in the tank, the effect is discussed mainly on the charge and discharge time, and their respective efficiencies.

Figure 6.12(a) shows the charge time for the TES tank subjected to different flow rates. For all granular materials, despite the flow rate is manipulated from two to five folds the baseline value ($3.2 \text{ m}^3/\text{min}$), the charge time did not decrease inversely proportionally. For example, when the flow rate is increased from $3.2 \text{ m}^3/\text{min}$ to $16.0 \text{ m}^3/\text{min}$, the charge time is not reduced to 20% but $\approx 28\%$ of the charge time of $3.2 \text{ m}^3/\text{min}$. It is because heat transfer between TES and HTF does not purely depend on the Reynolds number, and can be limited by thermal conductivity of the PCM.

As illustrated in Figure 6.12(b), the discharge time is almost inversely proportional to the HTF flow rate at the tank inlet. For example, when alumina material is used as granular material and the flow rate is increased from $3.2 \text{ m}^3/\text{min}$ to $16.0 \text{ m}^3/\text{min}$, the discharge time is reduced to 19.9% while the charge time is reduced to $3.2 \text{ m}^3/\text{min}$. This contradicts the condition for charge process and is probably due to higher effective

thermal conductivity, which is contributed by natural convection of the macro-encapsulated PCM during melting.

Figure 6.12(c) shows the impact of the HTF flow rate on the charge efficiency. The charge efficiency decreases with the increase of the HTF flow rate, due to the prolonged charge time (which is not inversely proportional to increment of flow rate) but similar thermal storage capacity. However, such decrease in charge efficiency can be recovered with the presence of granular materials. For example, the usage of any granular material allows the charge efficiency to be maintained above the baseline case when the flow rate is increased to $6.4 \text{ m}^3/\text{min}$. Using alumina particles and micro-encapsulated n-decane allows the flow rate to be increased to $9.6 \text{ m}^3/\text{min}$ without compensating on the charge efficiency. It is also worth noting that at less vigorous flow rate, the micro-encapsulated n-decane has the highest charge efficiency, however the advantage of this material deteriorates with higher flow rates. The advantage of micro-encapsulated PCM, the presence of its constant temperature plateau based on the latent heat, is diminished as the thermal energy rate is too high for the development of the plateau.

(a)

(b)

(c)

(d)

(e)

Figure 6.12: Effect of granular materials on TES tank subjected to different flow rates

Figure 6.12(d) shows that the discharge efficiency decreases with increasing flow rate despite the discharge time, which is almost inversely proportional to the flow rate. This can be due to the variation of the discharge temperature of HTF at the tank outlet, as the discharge is deemed to continue if the discharge temperature is lower than the set threshold temperature. For TES tanks subjected to lower discharge flow rates, the HTF extracts more amount of thermal energy, and thus larger amount of thermal energy at the high-grade cold region is extracted as the residual time of HTF in the TES tank is significantly longer. Similarly, using granular material is able to improve the discharge efficiency. However, the improvement is not as effective as in the charge process and only alumina particles as granular material can maintain the similar discharge efficiency as the baseline case when the flow rate is increased to $6.4 \text{ m}^3/\text{min}$.

Similar to charge and discharge efficiencies, cyclic efficiency – the product of the two aforementioned efficiencies – also decreases with increase of HTF flow rate. According to Figure 6.12(e), filling up the void space of the TES tank with alumina particles or micro-encapsulated n-decane provides the best cyclic efficiency. In fact, filling up the TES tank with micro-encapsulated n-decane gives better performance when the flow

rate is low due to low thermal power from HTF to develop its constant temperature latent heat plateau. As a product of the plateau, larger amount of thermal energy is transferred between HTF and micro-encapsulated n-decane in a shorter period compared to other granular materials. However, when the flow rate is high ($> 6.4 \text{ m}^3/\text{min}$), such constant temperature plateau cannot be developed and micro-encapsulated n-decane is regarded as “sensible-heat” TES materials, and the performance depends on the amount of extra thermal storage capacity supplied by granular materials. Thus, alumina particles perform better in terms of cyclic efficiency when the flow rate is high, therefore, they are recommended as granular material.

The performance of TES systems with various PCM and granular materials, especially charge and discharge time, and their respective efficiencies are deteriorated with the increase of HTF flow rate. Using any granular material allows to maintain the cyclic efficiency of the TES system above the baseline case level when flow rate is increased by two-fold, although when flow rate is further increased, only alumina particles can be considered as suitable granular material.

6.6. Conclusions

The large void fractions of PBTES system using macro-encapsulated PCM can be reduced effectively by inserting granular materials into the void space, reducing void fraction values to as low as 0.30. Based on the simulation results and parametric analysis, several conclusions can be drawn and they are listed below:

1. TES capacity of the tank is increased up to 46.2%, especially when macro-encapsulated in-house-developed PCM is used as the main TES material.

2. Cyclic efficiency is increased by up to 25.0%. Granular materials effectively improve the charge and discharge efficiencies by storing extra thermal energy in the form of their sensible heat and effectively prolong the charge and discharge time.
3. Increasing the encapsulation size of macro-encapsulated PCMs decreases the efficiencies of the TES tank. However, such decrement can be surmounted by insertion of granular materials. When alumina particles and micro-encapsulated n-decane are used, the encapsulation size can be increased by 60%, reducing the capsule amount by more than 75% without compensating on the performances of the system.
4. Increasing the HTF flow rate decreases the cyclic efficiency of the TES tank. It is not recommended to increase the flow rate by more than two times as the loss of the cyclic efficiency is not recoverable with granular materials.
5. Alumina particles is the best candidate as granular materials if the improvement of the thermal energy storage capacity of the TES tank is the main consideration.
6. Micro-encapsulated n-decane has the highest improvement over the cyclic efficiency of the TES tank under moderate operating conditions. However, under rigorous working conditions with high flow rate, alumina particles are better recommended compared to other granular materials.

Chapter 7. 3-dimensional modelling and simulation of TES

7.1. Introduction

For numerical studies carried out in Chapters 4 and 6, 1-dimensional concentric dispersion model is used. This model is proven to be accurate for predicting the temperature development of HTF and TES materials in the axial-direction. However, temperature gradient can develop in the radial direction of a TES tank due to two reasons: (1) thermal energy losses and (2) thermal energy absorbed by tank wall materials. These losses of thermal energy result in temperature measured at the regions near to tank wall is always higher than the temperature measured at the regions near to tank center, which is obvious even in a TES system operated under well-controlled environment. Such temperature variation in radial direction can be observed in Figure 5.7, Figure 5.8, Figure 5.10 and Figure 5.11. Besides, for 1-dimensional study, the HTF is assumed to travel in uniform velocity only along the axial direction of TES tank, limiting study of flow behavior development such as development of flow or mixing of flow from auxiliary inlets other than the main inlet. To simulate the abovementioned behaviors, 3-dimensional simulation model is inevitable.

As discussed in Chapter 6, inserting granular materials into the void space of a TES system with encapsulated PCM is proven to be beneficial for its performance. Thus, such configuration will continue to be used in this section. First, the TES system is filled with PCM capsules in layer-by-layer pattern, and granular materials are assumed to be distributed uniformly in the void space with resulted void fraction reduced to 0.30. In-house-developed PCM and granular quartzite pebbles are used as TES materials, with their properties are introduced in Table 5.1 and Table 5.2 respectively.

In this chapter, the abovementioned uneven temperature distribution of TES temperature in radial direction is investigated in detail, which is achieved through a 3-

dimensional simulation. Despite such simulation may take a longer time, the value added on investigation of auxiliary inlet is important for improving the charging a TES. Besides, 3D modeling may also create additional instabilities during simulations due to balance of flow and energy transfer in all x, y and z-coordinates. However, such 3-dimensional model is crucial to investigate the enhancement due to auxiliary inlets via the tank side, to allow the near-tank wall region, which always suffer from effect of thermal energy losses and reduced flow speed due to friction with tank wall. Different types of auxiliary inlets are investigated, and their effects on the charging speed are studied.

7.2. 3-dimensional simulation model

COMSOL Multiphysics 5.5 is used to simulate the 3-dimensional TES model. The models used in the numerical studies are introduced in this section.

7.2.1. Introduction of geometrical structure

A 3-dimensional geometry for the TES system is built in COMSOL. Geometry for the TES system which mirrors the experimental setup is demonstrated as example. Two TES materials are involved: the macro-encapsulated PCMs and the granular quartzite pebbles.

Macro-encapsulated PCM has large encapsulation diameter (50 mm) and low thermal conductivity, thus does not have low Biot number $\ll 0.1$. Temperature distribution within the encapsulation volume needs to be modelled, and specified volume domains are allocated for the PCM such that the volume can be discretized during numerical studies. However, size of quartzite pebbles is small (≤ 10 mm) and has higher thermal conductivity, thus has low Biot number. Due to the small size and large numbers of

pebbles inserted into the TES system, it is impractical to model the granular pebbles as separated domain. Instead, the granular quartzite pebble can be assumed to be packed in a uniform monodisperse pattern, enabling it to be simulated as porous medium in the HTF domain.

Layer-by-layer approach is used for macro-encapsulated PCM in the experimental setup, where the diameter ratio between tank and particle is equal to 5, with 19 PCM capsules per layer. The packing structure can be modelled easily with equal distance between all capsules. PCM particles are modelled with a shrunk particle size, due to its simplicity to operate compared with other methods. This method has been used by Lee et. al. [192] where 1 mm gap is left in between particles with 57 mm diameter in a packed bed reactor. The encapsulation layer is thus omitted to cater for the space required between PCM particles, which also resembles the shrinkage of particles. Removal of this encapsulation layer is after careful thought and validation of model, as the encapsulation layer is re-included into the heat transfer study in form of thin layer between the PCM and HTF domains. Figure 7.1 demonstrates the geometry of the PCM capsules in a single layer for the experimental setup, where dotted lines circulating the capsules represent the encapsulation layer, which is omitted in the geometry.

After a layer of PCM capsules is built, the layer is then duplicated with rotations of a fixed angle to prevent unobstructed flow of HTF through multiple PCM layers, to maximize the travel distance of a stream of HTF in the TES system and to ensure maximum heat transfer of thermal energy between HTF and the TES materials. Completed geometry of the experimental setup is shown in Figure 7.2, which contains altogether 9 layers of capsules.

Figure 7.1: Demonstration of packing of PCM in the baseline case where diameter ratio = 5

Figure 7.2: 3-dimensional layout of packed bed TES system, simulating the experimental setup in TESLAB

Tank wall structure is also omitted for minimal consumption of computational resource. Similar to the approach applied for encapsulation layer, similar thin layer is also simulated for the tank wall in the heat transfer study.

7.2.2. Key performance indices

So far, only charging of the 3-dimensional tank is considered. Thus, the only performance indices evaluated here is the charge time and charge efficiency only. The phase change time is defined as the time when all the PCMs complete phase change (i.e., with temperature below mushy zone of phase change temperature), while charge time is defined as the time when every node reaches -155°C , which is at 5°C proximity to the boundary temperature of -160°C . Charge efficiency is defined as the ratio of thermal energy captured by PCMs to total thermal energy delivered by HTF over the charging period (i.e. from time 0 to the charge time).

$$\eta_{ch} = \frac{E_{stored,PBTES}}{E_{HTF}} \quad (7.1)$$

7.2.3. Governing equations

In 3-dimensional numerical studies, TES system volume is discretized and the governing equations are solved numerically. Transient temperature and fluid flow profiles are two main parameters to investigate, and the equations are explained as below.

7.2.3.1. Mass transport simulation

Mass transport is observed only on the HTF domain, which is part of the porous medium region. Darcy's Law is one of the most well-known models for modelling a porous medium, which relationship between flow rate, $Q = vA$ and pressure difference, ∇P applied on the HTF is assumed to be proportional. The equation is demonstrated in equation (7.2). In the case where permeability, $\mathbf{K}$ is assumed to be isotropic, it can be

reduced to a scalar term, K and Darcy's equation can be rewritten as equation (7.3) [193].

$$\mathbf{v} = -\frac{1}{\mu} \mathbf{K} \cdot \nabla P \quad (7.2)$$

$$\mathbf{v} = -\frac{K}{\mu} \nabla P \quad (7.3)$$

According to Oro et. al., in the Darcy model it is assumed that the fluid is not subjected to any strain due to viscous stresses which can be unrealistic for high permeability porous media [194]. Besides, in Darcy's Law, the flow is subjected to pressure-driven boundary conditions, which can be inaccurate for large porosity case where velocity boundary conditions are more suitable. Besides, in Darcy's equation, perfect slip wall boundary condition is assumed, and the fluid flow is driven by the pressure gradient applied on the HTF. However, in the case where fluid is mainly driven by its inertia force, no-slip wall effect on the flow regime can be significant and discrepancies can occur if Darcy's equation is used [193, 195]. Such flow condition is applied for flow within porous regimes with high permeability such as in the case of packed bed. Brinkman equation, which accounts for the transition of fluid regime between Darcy flow and viscous free flow, should be used [195]. Such statement is in agreement with [193], which the momentum equation for Brinkman equation is listed as equation (7.4).

$$\rho \left[\frac{1}{\varepsilon} \frac{\partial \mathbf{v}}{\partial t} + \frac{1}{\varepsilon^2} (\mathbf{v} \cdot \nabla) \mathbf{v} \right] = -\nabla P - \frac{\mu}{K} \mathbf{v} + \tilde{\mu} \nabla^2 \mathbf{v} \quad (7.4)$$

Kozeny-Carman correlation can be used to predict the permeability of a packed bed using its geometrical parameters. The correlation which is related to the hydraulic radius of particles [193] is normally used and is listed as equation (7.5).

$$K = \frac{d_p^2}{180} \frac{\varepsilon^3}{(1 - \varepsilon)^2} \quad (7.5)$$

The TES system is subjected to a few boundary conditions which control the mass transport environment, which are listed as follow:

- A uniform velocity inlet is assumed
- The outlet has no backflow and is subjected to zero gauge pressure
- No slip condition at the TES tank wall as well as encapsulation boundaries.

For the initial condition, it is assumed that the system is under atmospheric condition and no HTF flow before the system is started.

To simplify the mass transport simulation, several assumptions are made and listed as follow:

- Due to low velocity flow of HTF within the TES tank (Mach number < 0.1), incompressible flow is assumed;
- HTF's temperature-dependent thermophysical properties are assumed to have negligible effect on the mass transport profile;
- HTF is assumed to be a Newtonian fluid;
- Transient variation of mass transport profile from the initial condition to steady-state condition is short compared to the transient temperature profile, and steady-state mass transport is assumed throughout the simulation.

7.2.3.2. *Heat transport simulation*

Heat transfer is considered for (1) between HTF and granular materials and (2) between HTF and macro-encapsulated PCMs. Due to different domains allocated for PCMs and

porous medium consisting of HTF and granular materials, different heat transfer theories are used for these different heat transfer scenarios.

In the porous media, it can be assumed that HTF and granular materials have temperature in proximity to each other, allowing their temperature to be solved using a single temperature, which is the single-phase model. Single-phase model is selected based on observation obtained from study carried out in Section 5, when extremely close temperatures are observed between HTF and granular materials in the same discretized volume grid. In COMSOL, physics of “heat transfer in porous media” is used to model the temperature of the porous media domain, and the energy equation is listed as equation (7.6). The effective thermophysical properties are obtained using combination of thermophysical properties of both the HTF and granular quartzite pebbles using equations (7.7) and (7.8). Physics “heat transfer in fluids” is used to model the temperature transfer between porous medium and the PCM, as well as the conduction within a PCM capsule. The energy equation is listed as equation (7.9). In COMSOL, equivalent specific heat capacity method is used to include the latent heat of PCM into the energy equation.

$$(\rho c_p)_{eff} \frac{\partial T_{eff}}{\partial t} + (\rho c_p)_{HTF} u \nabla T_{eff} = k_{eff} \nabla^2 T_{eff} + Q_{conv} \quad (7.6)$$

$$(\rho c_p)_{eff} = \frac{\varepsilon \rho_{HTF} c_{p,HTF} + (\varepsilon_{PCM} - \varepsilon) \rho_{granular} c_{p,granular}}{\varepsilon_{PCM}} \quad (7.7)$$

$$k_{eff} = \frac{\varepsilon k_{HTF} + (\varepsilon_{PCM} - \varepsilon) k_{granular}}{\varepsilon_{PCM}} \quad (7.8)$$

$$\rho_{PCM} c_{p,PCM} \frac{\partial T_{PCM}}{\partial t} = k_{PCM} \nabla^2 T_{PCM} + Q_{conv} \quad (7.9)$$

Boundary conditions of the TES system defined during heat transfer are listed as follow:

- A uniform inlet velocity in normal direction to the inlet surface is assumed, and upstream temperature is defined
- Outflow is assumed to have no temperature gradient.
- TES tank wall is subjected to thermal losses with constant heat transfer coefficient (only for the validation of experimental setup) and no thermal loss for other numerical studies.

To facilitate the heat transfer simulation, a few assumptions are also made and listed as follow:

- To prevent highly skewed mesh and solution inaccuracy, PCM encapsulation material which is not modelled in the geometry is simulated as thin layers, with equations listed as equation (7.10), and temperature of encapsulation layer is denoted as T_{enc}
- TES tank wall is assumed as thin layer as well for simplicity.
- Heat transfer between HTF and granular materials, and between HTF and PCMs are assumed to occur with method of forced convection only and free convection is not considered [194]

$$\mathbf{n} \cdot \mathbf{q} = d_s \rho_{enc} c_{p,enc} \frac{\partial T_{enc}}{\partial t} - d_s k_{enc} \nabla^2 T_{enc} \quad 7.10$$

From equation (80), the internal energy retained by the encapsulation layer (represented by the first term in right-hand-side of the equation) is equal to the difference in the heat flux received by the encapsulation layer from the external boundary (left-hand-side of equation) and the heat flux conducted by the encapsulation layer between its inner and outer boundaries (right-hand-side, second term).

7.3. Validation of model with experimental result

The 3-dimensional model is then validated with experimental results. Validation is carried out with TES system using in-house-developed PCM, and with quartzite granular materials, subjected to charge flow rate of 250 L/min. Comparisons are made between the numerically modelled temperature profiles and the experimentally obtained data. Figure 7.3 shows the comparison for temperature nodes taken near the center of tank ($r/R = 0$); while Figure 7.4 shows the comparison for temperature nodes taken near the tank wall ($r/R = 1$). There is another temperature taken at $r/R = 0.5$, but the temperature is similar to that taken at $r/R = 0$, hence for clarity of the graph, this temperature profile is not shown. Comparison at three locations, $\frac{x}{L} = \frac{1}{3}, \frac{2}{3}$ and 1 are shown for each graph, which also represents the temperature development in the axial direction. Accurate temperature profile modelling can be observed from both comparisons.

Figure 7.3: Comparisons between temperature profiles between experimental and numerical results for tank centre region

Figure 7.4: Comparisons between temperature profiles between experimental and numerical results for region near to tank wall

7.4. Baseline case and parametric studies

7.4.1. Baseline case and problem statement

A TES system with thermal storage capacity closer to a real-life application is simulated as the baseline case. For this case, a packed bed system using macro-encapsulated in-house-developed PCM with latent heat TES capacity of 5 kWh is simulated. Quartzite pebbles are used as granular material to fill the void space in between PCM capsules. The TES system is thus scaled up accordingly, to diameter ratio of tank to encapsulation of 20 (ratio of 5 for experimental setup), where the tank internal diameter is 1.0 m and the encapsulation external diameter is 50 mm. For this diameter ratio, it is estimated that about 322 capsules can be allocated in a single layer, which the top view of arrangement is shown in Figure 7.5(b). To fulfill latent heat capacity of 5 kWh, 15 layers of PCMs are needed, resulting in 4,830 PCM capsules in total with latent heat capacity of 5.27 kWh. The geometry of such tank configuration is shown in Figure 7.5(a).

(a)

(b)

Figure 7.5: (a) Isometric view of the TES system of the baseline case and (b) the top view of PCM arrangement for a layer with diameter ratio of 20

From the inlet to the PCM section of the TES system, an expansion of 10 times in cross-sectional diameter is observed. A diffuser simulated using porous media is used to develop the flow according to the permeability, uniformly in all directions. In the mass

transfer simulation, it is proven that sufficient diffusion occurs up to the boundary for the PCM section with the porous media flow. Such extra diffusion region is also more realistic for heat flow simulation as the extra length contributes to flow and temperature development of the HTF, such as no flow regime near to tank walls as well as thermal energy consumed by the tank structure along the expansion section.

The baseline case is subjected to nitrogen flow with flow rate of 4 m³/min, which is scaled up from flow rate of 250 L/min from TES system with diameter ratio of 5 to maintain similar flow velocity and Reynolds number. The TES system is subjected to boundary temperature of -160°C, assuming that there is a cold source with unlimited supply of cold energy at this cryogenic temperature.

Thermal energy losses to the surroundings is assumed to be negligible. However, such big temperature difference between center and near-wall region of tank is still contributed by two main factors: flow stagnation near to tank wall region and thermal energy absorbed by the TES tank wall structure.

For the baseline case, for all PCMs to complete phase change, 388 minutes are taken while for all the PCMs to reach cryogenic temperature, 439 minutes are taken. The development of temperature profile at different axial locations of the TES tank is shown in Figure 7.6.

Location

Height = 225 mm; 5th layer PCM from bottom

Height = 475 mm; 10th layer PCM from bottom

Height = 725 mm; 15th (last) layer PCM from bottom

Time = 100

mins

$T_{max} = -31.5^{\circ}\text{C}$; $T_{min} = -160^{\circ}\text{C}$

$T_{max} = 16.8^{\circ}\text{C}$; $T_{min} = -160^{\circ}\text{C}$

$T_{max} = 20^{\circ}\text{C}$; $T_{min} = -160^{\circ}\text{C}$

Time = 200

mins

$T_{max} = -121^{\circ}\text{C}$; $T_{min} = -160^{\circ}\text{C}$

$T_{max} = -90.9^{\circ}\text{C}$; $T_{min} = -160^{\circ}\text{C}$

$T_{max} = -0.7^{\circ}\text{C}$; $T_{min} = -160^{\circ}\text{C}$

Time = 300
mins

$T_{max} = -160^{\circ}\text{C}; T_{min} = -160^{\circ}\text{C}$

$T_{max} = -146^{\circ}\text{C}; T_{min} = -160^{\circ}\text{C}$

$T_{max} = -100^{\circ}\text{C}; T_{min} = -160^{\circ}\text{C}$

Time = 400
mins

$T_{max} = -160^{\circ}\text{C}; T_{min} = -160^{\circ}\text{C}$

$T_{max} = -160^{\circ}\text{C}; T_{min} = -160^{\circ}\text{C}$

$T_{max} = -139^{\circ}\text{C}; T_{min} = -160^{\circ}\text{C}$

Figure 7.6: Development of temperature profile in the baseline TES system at various z -locations and time

From Figure 7.6, temperature profiles on different axial-locations and different time in the TES system is demonstrated. The development of temperature difference within same axial location gets more significant with further distance of PCM layer from the inlet. For example, at the 100th minutes into charging process (which is shown as the first row), for height of 225 mm or the 5th layer of PCM, the temperature difference is 128.5°C, which increases to 176.8°C and 180°C at 10th layer and 15th layer (last layer) of PCM respectively. Similar observations are also made for temperature profile at 200, 300 and 400 minutes where the regions near the tank wall suffers a delay of temperature development compared to the region near the center of the tank. Such condition can be due to less PCM density or larger void fraction of PCM near the tank center region, as well as shorter propagation distance of HTF from inlet to the outlet. At the tank wall, the HTF does not only suffer from no-flow condition where temperature boundary layer can develop, as well as absorption of thermal energy by the tank wall stainless steel materials. Besides, the diffuser region from the pipe towards the tank section may also be subjected to a too large angle, which the diffusion of flow may not develop enough momentum to propagate to the side of the system. Such challenges and the resultant temperature profile can be some obstacles when designing a real-life TES system, which needs to be overcome.

Usage of side inlet as auxiliary inlet is proposed here to overcome the development of temperature profile within the same axial location in the TES system, as well as to overcome the condition where the flow rate is less diffused to the region near the tank wall. A parametric study is developed for the study and is introduced in the subsequent sub-section.

7.4.2. Parametric studies

Parametric studies are carried out to study the influence of different parameters and the possible parameters to be altered to optimize the TES system. The parameters are listed as follows.

7.4.2.1. Type of side inlet

Different types of side inlet are configured, which contributes to different flow profiles into the TES system. There are three types of side inlet assumed, which are (a) radial side inlet, (b) elbowed type side inlet and (c) cyclone side inlet. The different side inlets are demonstrated as Figure 7.7. Cross sections on the TES system across the side inlets are shown for better clarification on the inlet structure. As the flow is assumed to be in normal direction to the flow inlet plane, the different direction each inlet is facing means different directions for the flow at the inlet, where radial type inlet generates flow in radial direction to the TES tank axial cross-section, while elbowed type inlet generates flow in parallel to the TES axial direction and cyclone type inlet generates flow in tangential direction to the TES tank circumference of axial cross-section.

(a)

(b)

(c)

Figure 7.7: Different type of side inlets: (a) radial type, (b) cyclone type and (c) elbowed type with their inlet flow directions

7.4.2.2. Numbers of side inlet

It is unsure that how many side inlets are required to fully cover the regions near the tank wall. From a preliminary check (which is not disclosed here), 4 side inlets are far from enough to cover the tank wall region. Thus, at least 8 inlets are configured, which parametric analysis of 8, 12 and 16 inlets for each inlet type are simulated.

7.4.2.3. *Split of flow rate to the side inlet*

It is necessary to determine the amount of flow that is split between the main and side inlet to investigate the optimum ratio for amount of HTF split to enter via different inlet. The flow rate is split such that 0%, 25%, and 50% of the flow is entered via the side inlet. In this case, the total flow rate of HTF entering the TES system via all inlet is 4 m³/min. It should be noted that 0% split to the side inlet means the baseline case, where no side inlet is used.

7.4.2.4. *Time when side inlet is started*

After several studies into the utilization of side inlet, it is also discovered that time when side inlet starts operation is another important parameter which determines the final operation time of the system for charging. Starting the side inlet from the beginning also does not guarantee a saving on the charge time nor improvement on efficiencies. Thus, a few timings on when the side inlet is started is investigated, including 0 min (which is from the beginning of charge stage), 100, 125, 150, 175 and 200 mins.

7.4.2.5. *Fixed parameters*

A few parameters are controlled to include some constraints for the parametric study, including the latent heat capacity of in-house-developed PCM which is fixed at 5 kWh. The diameter ratio is fixed at 20. Encapsulation size for the PCM is also fixed. Type of PCM and granular material used is also fixed. In-house-developed PCM which has been discussed in both Section 4 and 5 are used, while quartzite granular material with size of 10 mm is continued to be used.

7.4.3. *Grid sensitivity analysis*

Due to the large size of the TES system to be simulated, it is important to run a grid sensitivity analysis to ensure a balance between grid size and accuracy of the numerical

studies. Three numerical grid sizes are simulated for the baseline TES system, and the effect on the time taken for all the PCMs of the system to complete phase change is studied. Using averaged grid size of 3.311 grids per cm^3 of domain yields almost constant results with 2.636 grids per cm^3 , compared to the coarsest grid density of 1,932 grids per cm^3 . Grid density of 3.311 grids per cm^3 is then chosen and subsequent meshes are ensured to have similar grid density.

7.5. Geometrical and operational parameters improvement

7.5.1. With different types and number of side inlet

The results for TES tanks equipped with different types and numbers of side inlet, with side inlet starts operation at $t=0$ with flow rate split of 50%, are tabulated in Table 7.1, which tabulates the time taken for all PCM nodes to complete phase change and Table 7.2, which tabulates the time taken for all PCM nodes to complete charge (reach cryogenic temperature $\leq -155^\circ\text{C}$). The time taken to achieve each criterion, as well as changes compared to the baseline case are tabulated. For the baseline case where no side inlet is used, for all PCM nodes to complete phase change, the time taken is 388 minutes while for all PCM nodes to charge, the time taken is 439 minutes.

None of the side inlet is advantageous compared to the baseline case when the side inlet starts at $t=0$. Such phenomenon can be explained using Figure 7.8, which tabulates the HTF temperature just after the side inlet. This temperature is significantly higher than the HTF temperature just after the main inlet, which is due to flow mixing with the flow from the main inlet. However, the flow from the main inlet is at ambient temperature, after storing the thermal energy in the PCM domains that the HTF flows through. This results in high temperature for the HTF from side inlet, which is above the phase change

temperature of in-house-developed PCM (-118°C). It means that the high-grade cold energy to be stored as latent heat of PCM is now lost due to internal mixing of HTF, and such loss results in longer time for all PCMs to complete phase change, as more HTF with high-grade cold is needed for phase change and compensate for the loss. Such loss of high-grade cold energy lasts for more than 120 minutes.

Table 7.1: Time taken for all PCMs to complete phase change in TES tank subjected to different numbers and types of side inlets

		Radial		Elbowed		Cyclone	
No	of	Charge	Change	Charge	Change	Charge	Change
inlet		time	w.r.t.	time	w.r.t.	time	w.r.t.
		(min)	baseline	(min)	baseline	(min)	baseline
8		487	+25.2%	532	+37.1%	448	+15.5%
12		452	+16.5%	504	+29.9%	423	+9.0%
16		433	+11.6%	473	+21.9%	430	+10.8%

Table 7.2: Time taken for all PCMs to reach cryogenic temperature in TES tank subjected to different numbers and types of side inlets

		Radial		Elbowed		Cyclone	
No	of	Charge	Change	Charge	Change	Charge	Change
inlet		time	w.r.t.	time	w.r.t.	time	w.r.t.
		(min)	baseline	(min)	baseline	(min)	baseline
8		585	+33.3%	600+	+36.7%	563	+28.2%
12		576	+31.2%	600+	+36.7%	543	+23.7%
16		576	+31.2%	594	+35.3%	554	+26.2%

Figure 7.8: Temperature of HTF at side inlet and main inlet – temperature of side inlet is higher due to mixing with HTF flowed from main inlet

7.5.2. Time when flow rate is started

To prevent the loss of high-grade cold PCM on HTF that enters the TES tank via side inlet due to mixing with HTF of high temperature, there is a need to start the side inlet later to allow the lower region of TES tank to be charged, resulting in lower temperature for HTF leaving the lower region, minimizing the loss of high-grade cold energy of fresh HTF entering via side inlet. 5 timings where HTF flow is started on side inlet are simulated, and the effect is shown in Figure 7.9 for using PCM phase change time as charge criterion, and shown in Figure 7.10 for using cryogenic temperature reached as charge criterion. When the side inlet is started, the HTF flow rate via main inlet is reduced to 50% ($2 \text{ m}^3/\text{min}$) while another 50% of flow rate is delivered averagely via all the side inlets. The time when side inlet is started is tabulated on the x-axis, where the limit on the x-axis is defined by the charge time defined in baseline

case (388 minutes and 439 minutes) respectively. It is because if the side inlet is not started beyond this point, the TES system has already met the charge criteria.

Figure 7.9(a) shows the time taken for TES tank to complete phase change for using radial-type inlet configuration with different start time for the side inlets. When the time to start the side inlet is increased from 0 minute, the overall phase change time for TES tank decreases to reach an optimum (shortest) charge time, before the phase change time increases again towards the baseline case value located at the far side of the x-axis. Using larger number of side inlets yielded shorter phase change time, which the shortest phase change time achieved by this configuration is 359 minutes, or 7.5% reduction when the side inlet is started at the 125th minute. Using 8 or 12 side inlets does not achieve high reduction on the phase change time, due to inefficient distribution of cold energy entered via the small number of side inlet. The shortest possible phase change time achieved by these two configurations is 374 minutes, or 3.6% reduction compared to the baseline case.

Using a cyclone-type side inlet (Figure 7.9(b)) yields better results compared to radial-type side inlet, where the configuration of 16 side inlets managed to yield shortest possible phase change time of 336 minutes, or reduction of 13.4%. In this scenario, using 12 or 16 side inlets yield significant reductions on phase change time of the TES tank, where using 12 side inlets yielded shortest phase change time of 342 minutes or 11.9% reduction compared to baseline case when side inlet is started at the 150th minute. Such result infers that 16-inlet configuration is near-optimum where further increasing the number of side inlet may not yield better result. The shortest phase change time achieved when 8-inlet-configuration is used is 370 minutes, which is merely 4.6% reduction.

Using elbowed type side inlet (Figure 7.9(c)) yields the slightest reduction in phase change time, where from the all simulations carried out on different number of side inlet, the shortest possible phase change time achieved is 375 minutes (3.4% reduction), and the performances observed on different number of inlets are similar to each other.

It is observed that using a cyclone type side inlet yields better performance than radial type side inlet, while using elbowed type side inlet yields the most insignificant improvement. Such difference is due to the flow direction of HTF via the side inlet, where in cyclone type side inlet the HTF entered via the side reaches the region nearest to the tank wall, which is the highest temperature region. Using radial type side inlet is better than elbowed type due to the inlet direction, where HTF entered via radial type inlet has momentum in the direction normal to axial flow direction of TES tank, yielding better convection of HTF towards the near tank wall region of TES tank.

Similar observation can be made on Figure 7.10, which indicates the time taken for the TES tank to reach a uniform cryogenic temperature. Using radial and elbowed type side inlet (Figure 7.10(a) and (c)) yields very similar performances, in which the number of inlets does not influence the results and minimal improvement on charge time is achieved. For both cases, the minimum charge time achieved is 426 minutes, which is 3.0% reduction from the baseline case. For cyclone type side inlet, using 16 inlets yield minimum charge time of 394 minutes, which is 10.3% reduction from the baseline case. Using 12 side inlets yield minimum charge time of 403 minutes, or 8.2% reduction while using 8 cyclone type side inlets yield similar performance as radial and elbowed type, which is 424 minutes for minimum charge time. The reasons for the differences in performance for different inlet are similar to the explanations made for the phase change time.

(a)

(b)

(c)

Figure 7.9: Time taken for phase change under different side inlet configurations (a – radial, b – cyclone and c – elbowed) with different side inlet start time

(a)

(b)

(c)

Figure 7.10: Time taken to reach cryogenic state under different side inlets (*a* – radial, *b* – cyclone and *c* – elbowed) with different side inlet start time

There is an optimum time where the side inlet should be started, to achieve as short charge time as possible. When the side inlet is started too early, mixing of HTF destroys the high-grade cold in the fresh HTF enters via side inlet (long charge time demonstrated on left-hand side of graphs), while when the side inlet is started too late, the HTF from side inlet is too slow to supply cold energy to the side region of tank wall,

which partly resembles the baseline case when there is a delay in charging the side region of TES tank (long charge time demonstrated on right-hand side of graphs).

7.5.3. Split of flow rates

Cases where 25% of total HTF flow enters via the side inlet is demonstrated as Figure 7.11 and Figure 7.12, where Figure 7.11 uses phase change of PCMs as charge completion criterion while Figure 7.12 uses cryogenic temperature as the criterion. The results shown in this section is in similar fashion as that discussed in Section 6.4.2, but the extent of improvement on performances is reduced.

From Figure 7.11(a), for radial side inlet, minimum phase change time of 373 minutes (4.0% reduction) is achieved when 16 side inlets are used. The extent of phase change time reduction increases with the number of side inlet. Cyclone type side inlets (Figure 7.11(b)) have much better performance where minimum phase change time of 355 minutes can be achieved (8.5% reduction), and the minimum phase change time increases to 366 minutes and 378 minutes, for usage of 12 and 8 side inlets respectively.

(a)

(b)

(c)

Figure 7.11: Time taken to complete phase change under different side inlets (a – radial, b – cyclone and c – elbowed) with different side inlet start time

Using elbowed type side inlet yields similar performances between different number of side inlet, where the minimum phase change time is 376 minutes, which is merely 3.1% reduction compared to the baseline case.

(a)

(b)

(c)

Figure 7.12: Time taken to reach cryogenic state under different side inlets (a – radial, b – cyclone and c – elbowed) with different side inlet start time

Observations on Figure 7.12 are very similar to those in Figure 7.11. For radial and side inlet, the effect on reduction for charge time is minimal, where in both configurations, the minimum charge time achieved is 426 minutes, which only 3.0% of charge time is reduced. Using cyclone type side inlet yields much better performance, where minimum charge time achieved is 405 minutes, which is 73.7% reduction compared to baseline case when 16 side inlets are used.

From comparison between Figure 7.11 and Figure 7.12, it can be deduced that using 25% flow rate entered via side inlet may have reduced effect on the phase change time, and thus, using 50% flow rate entered via side inlet is more recommended.

7.6. Conclusions of study

Effect of using different types of side inlet to tackle the problem of temperature difference between tank center and tank wall regions is investigated. A few key observations are summarized as follow:

- Using cyclone type inlets yields the largest possible reduction on both phase change time (13.4%) and charge time (10.3%), where in such inlet, the fresh HTF entered via side inlets directly enters the near tank-wall region compared to radial and elbowed type side inlets.
- In cyclone type side inlets, using more than 12 side inlets is necessary for tank-to-capsule diameter ratio of 20 to allow HTF via side inlet to be distributed evenly into every region near the tank wall.
- Radial and elbowed type inlet do not yield significant reduction in phase change time or charge time due to the difficulty for HTF via side inlet to reach the near tank wall region due to different flow configurations.
- The side inlets should not start at the same time as the main inlet where due to internal mixing between fresh HTF from side inlet and HTF flows from main inlet, high-grade cold energy is destroyed and wasted, leading to longer phase change / charge time compared to baseline case.
- Start time for side inlet after 150 minutes main inlet started is recommended for cyclone type inlet, where maximum reduction in charge time and phase change time is achieved.
- Splitting of 50% HTF flow rate to enter via side inlet is more recommended than using 25% flow rate due to larger amount of fresh energy reaching near the tank wall region.

Chapter 8. Conclusions and future works

8.1. Conclusions

LNG still exhibits high level of importance in the coming 20 to 30 years, with the total cold power to be released via regasification of LNG reaching an average value of 10 GW by 2040. A study on the potential of cold energy recovery from LNG regasification is carried out using different energy carriers – electricity, cold working fluids, PCM TES systems and LN₂ for distributing the cold energy to cold demands with different temperature requirements.

Using liquid type working fluids via pipelines and using PCMs via trucks are the two cleanest methods for cold distribution compared to using the cold energy to generate extra electricity or liquid air energy carrier. Using these energy carriers, consumption on primary energy by the cold demands are greatly reduced, due to a few points of improvements: (1) reduction of compression work during intercooling processes, (2) elimination of chillers as heat sink and compressor work involved, and (3) simplifications of systems. For both energy carriers, up to 38% of carbon emissions is reduced, which is translated to same amount of reduction on fossil fuels consumption as primary energy. PCMs are chosen as the next subject of study because of the low capital and operation costs compared to liquid working fluids where pipelines are required to be built, which the cost can be elevated when pipelines with thick insulation are to build across urban area.

A TES system is selected for the next subject of study. In the literature, TES systems are investigated as assistive components to another thermal applications to improve their performances or to eliminate their intermittent properties. However, these studies seldom investigate the performance of the TES system, nor optimization of these

systems. Thus a few possible improvement methods for PCM-based TES systems are studied to investigate their effect on the performance of a TES system.

The first improvement method that was studied is the cascade of different PCMs with different phase change temperatures in a PBTES system to improve the system efficiency. Despite there are some studies which investigate such cascaded system, however, in these studies, the allocation of TES capacity or volume between different PCMs is too straightforward (i.e., similar capacity or volume allocated for all PCMs) and needs to be optimized. A study is carried out to sweep across different combinations on TES capacity of each of the PCM used. A generalized map is derived based on all the simulated cases which assists the user during the design stage. The generalized map derives the performance of a TES system with predefined PCM capacity, and helps the user define the required TES capacity of each PCM when certain performance such as efficiencies and operation times are defined. From the study, two possibilities of overcharging are identified, which the first scenario is due to too low allocation of PCM with storage of the highest-grade energy (which also applies to cases with same TES capacity allocated for all PCMs), where during charging process, after the PCM for high-grade storage is fully charged, high grade energy carried by HTF is degraded into lower grade thermal energy to be stored in other PCMs. The second scenario occurs when too high TES capacity is allocated for PCM which stores the highest-grade thermal energy. During the discharge stage, the highest-grade thermal energy is degraded, to fulfill the thermal requirement of the HTF. In any scenario of overcharging, the cyclic efficiency is lowered, and to ensure the cascaded system works at the highest possible cyclic efficiency, the second PCM in such cascaded system should have TES capacity at 70% the first PCM (PCM used to store highest grade thermal energy) while the third PCM should have TES capacity at 50% the first PCM.

Another analysis is carried out to investigate on using smaller-diameter granular materials for void space reduction in a packed bed TES system using PCM with large encapsulation diameter as TES materials. In a TES tank using macro-encapsulated PCM, large void fraction is usually observed. For example, with diameter ratio of 20, void fraction of 0.46 is observed. With incorporation of granular materials and reduction of final void ratio to 0.30, TES capacity of system using in-house-developed PCM is increased by up to 46.2% and efficiency is improved by up to 25.0%. Although such improvement diminishes when PCMs with better thermophysical properties are chosen, however, phase change temperatures of these materials are also high, losing lots of exergy at the storage stage of cold energy. The improvement on performance of TES system when granular material is used to fill the void space can also be used to offset the drops in performance in occasions when PCM with larger encapsulation size is used. Using granular material allows for 40% increase in encapsulation size in certain cases, decreasing the number of encapsulations by more than 70%.

1-dimensional numerical analysis has been popularly used by researchers due to their simplicity and promising accuracy. However, for investigation of change in geometrical structures on the TES system, 1-dimensional numerical analysis is not enough. A 3-dimensional numerical analysis for a TES system is also carried out. It is found out that when large expansion is involved on the HTF during transition between the HTF pipeline and the tank storage section, large temperature differences can be observed between tank center and tank wall regions in the storage region, which result in longer charge time and lower efficiency for the TES tank. Thus, side inlet concept is proposed to tackle the temperature difference, and it is found that cyclone-type side inlet, with more than 12 side inlets in total, is useful to overcome the temperature difference as well as achieve up to 13.4% reduction in phase change time or 10.3% reduction in

charge time. In this type of side inlet, the HTF is flowed in tangential direction to the circumference of the TES tank, which achieved maximum contact between fresh HTF and the near tank wall region of TES tank compared to radial type (where HTF flows in radial direction) and elbowed type (where HTF flows in parallel direction to axial direction of tank) side inlets. Besides, it is also observed that if the side inlet starts at the same time as the main inlet, not only there will be no improvement on charge time, instead, the charge time is more delayed due to internal consumption of high-grade energy of HTF due to internal mixing. It is recommended that the HTF entering via the side inlet is started only after more than 150 minutes the HTF flows via the main inlet.

Besides the numerical studies carried out, experimental assessments are also carried out on packed bed TES systems to obtain experimental data for validations of numerical models. Two TES systems have been designed, and one of them has started operation. The first TES system is designed to has diameter ratio between TES tank and macro-encapsulated PCM of 5, and PCM volume of 8.3 litres which allows for 2 MJ of thermal storage capacity. In the system, an in-house-developed PCM is used as TES material, which undergoes phase change at -118°C . The TES system can operate under HTF flow rate of up to 400 litres/min and is subjected to HTF with -160°C temperature during charge and 20°C during discharge. From the first design of the TES system, large void fraction of 0.559 is observed due to its small diameter ratio as well as layer-by-layer structure of PCMs for structural integrity. The void fraction is reduced by inserting quartzite pebbles as granular materials into the void space to 0.332. The TES setup is also upgraded into a cascaded manner, where half of the in-house-developed PCM capsules are replaced with PCM PureTemp -37X with -37°C phase change temperature.

8.2. Future works

This work has investigated three main methods for optimization for a packed bed TES system using PCM as storage materials, which are cascading the PCMs, using granular materials to fill a void space and using geometrical changes such as multiple injection inlets to distribute the HTF. This work mainly discusses about proof of concepts and preliminary identifying on the effects brought by each enhancement method. There are still a lot left to be studied in these enhancement methods.

For example, in a case where the cascaded PCM configuration is used, the generalized map should be expanded to also consider on different operating conditions, which can be achieved by producing multiple generalized maps and trying to link between performances and the change of operating parameters. Besides, in the study carried out, variation of latent heat on PCMs is set as the only thermophysical properties which change with PCM to study the effect of thermal storage capacity without being influenced by other properties of PCMs. In the future, the study can also be expanded to real-life materials with varying thermal properties, or even limit the material selections into commercialized PCM available in the market for a more realistic study.

For the case of using granular materials to fill the void space, the study can also be expanded to more parameters, including combination with the idea with cascaded PCM in a packed bed. In the study, micro-encapsulated PCM is the most promising materials, however the only micro-encapsulated n-decane that was found with subzero phase change temperature is high cost, and still exhibit overly high phase change temperature (-30°C) compared to macro-encapsulated PCM such as in-house-developed PCM (-118°C), PlusIce E-75 (-75°C) and PlusIce E-65 (-65°C). Such study may need to be reexamined when micro-encapsulated PCM with lower phase change temperature is developed.

For optimization of TES system from the geometry point of view, in the study carried out only the side injection inlet is investigated. The study can be expanded to include more parameters including using different PCMs or even cascaded PCMs. The parameters can also include variation in TES capacity, variation of granular materials as well as other geometrical shape design on the TES tank, including conical design or radial flow design packed bed TES storage.

Experimental studies and constructions of TES systems are stopped after April 2020 until mid-July 2020. However, a few activities are identified upon resume of activities in TESLAB, including investigating TES system with more cascaded PCM. For the current system, 2 types of PCM are used, with potential to be expanded to 3 types. Different granular materials are also set to replace quartzite pebbles, such as alumina particles or micro-encapsulated PCM. Packed bed system can also be replaced with shell-and-tube storage to investigate the difference in performance and allows numerical modelling of shell-and-tube system.

Appendix

A.1. Literature review on materials

Table A.1: List of SHTES materials reported in the literature

SHTES materials	State	Working temperature	Usage	Reference
α -alumina beads	Solid	20°C to 700°C	Solar receiver	[196]
Gravels and sands	Solid	$\leq 300^\circ\text{C}$	CSP plant	[84]
Granite pebbles	Solid	-195°C to 20°C	Air liquefaction plant	[197]
Alumina	Solid	50°C to 700°C	CHP flue gas heat to superheat steam	[96]
Quartzite	Solid	290°C to 390°C	CSP plant	[82, 83, 198]
Rocks	Solid	298K – 700K	A-CAES	[199]
Magnetite (Fe_3O_4)	Solid	-170°C to 37°C; 25°C to 500°C	PTES	[103, 200]
Quartzite	Solid	Up to 600°C	CSP plant	[201]
Water	Liquid	32°C to 70°C	Solar flat plate collector	[88]
Quartzite	Solid	n.a.	LAES	[16]
River pebbles and pea pebbles	Solid	26.1°C to 136.1°C	CSP plant	[202]
Fe_2O_3 . SiO_2 , TiO_2	Solid	25°C to 500°C; -150°C to 25°C	PTES	[103]

Gravels	Solid	300K to 773K; 123K to 300K	PTES	[104]
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Table A.2: List of PCMs used in TES systems reported

PCM	Type	Phase change temperature	Operating temperature	Usage	Ref.
Sodium nitrate	Inorganic	305°C - 307°C	286°C - 326°C	n.a.	[85]
Mixture of capric acid / lauric acid with oleic acid	Organic	8.1°C - 13.2°C	7°C - 12°C	Solar generated cold	[150]
Ice	Inorganic	0°C	n.a.	n.a.	[117]
Potassium hydroxide	Inorganic	360°C	290°C - 390°C	CSP	[82, 83]
Eutectic mixture of ammonium alum and ammonium nitrate	Inorganic	48°C - 53°C	30°C - 65°C	Solar space-heating	[203]
Sodium nitrate (NaNO ₃)	Inorganic	583 K	298 K - 700 K	A-CAES	[199]
Rubitherm GR50	Organic	42°C - 50°C	Ambient to 65°C	n.a.	[204]
Paraffin wax	Organic	55°C - 66.5°C	Up to 80°C	Solar air heating	[89]
Erythritol (C ₄ H ₁₀ O ₄)	Organic	390 K	Up to 400 K	Solar powered ORC	[205]

NaNO ₃	Inorganic	306°C			
KNO ₃	Inorganic	335°C	285°C - 391°C	Parabolic trough solar	[136]
Eutectic MgCl ₂ /KCl/NaCl	Inorganic	380°C			
NaNO ₂	Inorganic	550 K - 577 K	450K - 600K	CAES	[206]
Dodecanoic acid	Organic	41°C	32°C - 65°C	Solar thermal	[207]
Rubitherm GR27	Organic	21°C - 29°C	n.a.	n.a.	[208, 209]
Rubitherm GR41	Organic	31°C - 45°C	n.a.	n.a.	[208, 209]
Paraffin wax	Organic	59.9°C	50°C - 70°C	n.a.	[210]
Ice	Inorganic	0°C	-30°C - 10°C	Refrigerated vehicles	[211]
PlusIce-H280	Inorganic	282°C	n.a.	ORC	[212]
Lithium carbonate (Li ₂ CO ₃)	Inorganic	723°C	600°C - 850°C	CSP plant	[213]
Mixture of lithium chloride, barium chloride and potassium chloride	Inorganic mixture	320°C	290°C - 390°C	CSP plant	[142]
Paraffin	Organic	60°C	50°C - 70°C	Solar heat storage	[86]
Myristic acid	Organic	58°C	50°C - 66°C	Solar heat storage	[87]

Alloy AlSi ₁₂	Inorganic	573°C - 577°C	25°C - 650°C	n.a.	[81]
Mixture of sodium fluoride and sodium bromide	Inorganic mixture	642°C	150°C - 650°C	Solar parabolic trough collector	[124]
n-tetradecane	Organic	4.45°C	-7°C - 10°C	n.a.	[214]
Mixture of n-tetradecane and n-hexadecane	Organic	7.62°C	-7°C - 10°C	n.a.	[214]
Merck P42-44	Organic	38°C - 44°C	Up to 75°C	n.a.	[215]
Merck P46-48	Organic	40°C - 47°C	Up to 75°C	n.a.	[215]
Merck P56-58	Organic	49°C - 58°C	Up to 85°C	n.a.	[215]
Stearic acid	Organic	69°C	n.a.	Solar cooking	[91]

Table A.3: List of commercial PCM for cold TES

Producer	Name	Phase change temp [C]	Latent heat [kJ/kg]	Materials	Ref.
PlusIce	E-114	-114	107	Eutectic salt solution	[171]
PlusIce	E-90	-90	90	Eutectic salt solution	[171]
PlusIce	E-78	-78	115	Eutectic salt solution	[171]
PlusIce	E-75	-75	102	Eutectic salt solution	[171]
PlusIce	E-62	-62	180	Eutectic salt solution	[172]
PlusIce	E-60	-60	172	Eutectic salt solution	[172]
Rubitherm	SP -50	-50	200	water-salt mixtures and additives	[167]
PlusIce	E-50	-50	175	Eutectic salt solution	[171]
PlusIce	E-46	-46	240	Eutectic salt solution	[172]

Va-Q-Tec	va-Q-accu-37G	-37	213	Solution of inorganic salts, nucleators and stabilisers	[169]
PlusIce	E-37	-37	225	Eutectic salt solution	[171]
Puretemp	-37X	-37	145	Fully hydrogenated fats and oils	[187]
PlusIce	E-34	-34	200	Eutectic salt solution	[171]
Va-Q-Tec	va-Q-accu -32G	-32	243	Solution of inorganic salts, nucleators and stabilisers	[169]
PlusIce	E-32	-32	225	Eutectic salt solution	[171]
Pluss	HS 33N	-30.5	224	Inorganic salt	[168]
Microtek	PCM -30	-30	150	Paraffin	[216]
PlusIce	E-29	-29	250	Eutectic salt solution	[171]
Rubitherm	SP -30	-28.5	250	water-salt mixtures and additives	[167]
Rubitherm	SP -28	-28.5	260	water-salt mixtures and additives	[167]
PlusIce	E-26	-26	265	Eutectic salt solution	[171]
Pluss	HS 26N	-25	272	Inorganic salt	[168]
Rubitherm	SP -24	-22.5	250	water-salt mixtures and additives	[167]
Climator	Climsel C-21	-22.5	285	salt hydrate based PCM	[165]
PlusIce	E-22	-22	305	Eutectic salt solution	[171]
Pluss	HS 23N	-22	262	Inorganic salt	[168]
Croda	CrodaTherm™ -22	-22	157	water insoluble organic PCM	[217]
Va-Q-Tec	va-Q-accu -21G	-21	234	Aqueous solution of NaCl (22%)	[169]
PlusIce	E-21	-21	285	Eutectic salt solution	[171]
Puretemp	-21X	-21	239	Fully hydrogenated fats and oils	[187]
Climator	Climsel C-18	-20.5	288	salt hydrate based PCM	[165]
Rubitherm	SP -21	-20	285	water-salt mixtures and additives	[167]
PlusIce	E-19	-19	300	Eutectic salt solution	[171]

Pluss	HS 18N	-18	242	Inorganic salt	[168]
Rubitherm	SP -17	-17.5	300	water-salt mixtures and additives	[167]
Pluss	HS 15N	-15.5	308	Inorganic salt	[168]
PlusIce	E-15	-15	320	Eutectic salt solution	[171]
Puretemp	-15X	-15	301	Fully hydrogenated fats and oils	[187]
PlusIce	E-14	-14.8	243	Eutectic salt solution	[171]
PlusIce	E-12	-12.3	250	Eutectic salt solution	[171]
PlusIce	E-11	-12	310	Eutectic salt solution	[171]
Rubitherm	SP -11 UK	-11.5	330	water-salt mixtures and additives	[167]
Rubitherm	SP -11	-11.5	240	water-salt mixtures and additives	[167]
Microtek	PCM -10	-10	180	Paraffin	[216]
PlusIce	E-10	-10	286	Eutectic salt solution	[171]
Pluss	HS 10N	-10	290	Inorganic salt	[168]
Rubitherm	RT -9 HC	-9	250	Organic PCMs	[167]
Rubitherm	SP -7_2	-6	290	water-salt mixtures and additives	[167]
PlusIce	E-6	-6	300	Eutectic salt solution	[171]
Pluss	HS 7N	-6	296	Inorganic salt	[168]
Rubitherm	RT -4	-4	180	Organic PCMs	[167]
PlusIce	E-3	-4	330	Eutectic salt solution	[171]
PlusIce	E-4	-3.9	282	Eutectic salt solution	[172]
Pluss	HS 3N	-2.5	346	Inorganic salt	[168]
PlusIce	E-2	-2	325	Eutectic salt solution	[171]
Puretemp	-2X	-2	277	Fully hydrogenated fats and oils	[187]

A.2. Cold energy distribution with energy carriers

In this section, the exergy flow diagrams tabulated here are for the examination of exergy efficiencies while recording the amount of exergy consumed, lost or destroyed.

A.2.1. Generation of energy carriers

A.2.1.1. Baseline combined cycle

Figure A.1: Exergy flow within baseline combined cycle for electricity generation

This section is an expansion from Section 3.2.1. Exergy flows between each component in the baseline combined cycle is shown in Figure A.1. The exergy input mainly comes from the chemical exergy of the natural gas fuel ($E_{C,NG}$), which accounts for 98.5% of total exergy input. The rest of exergy is contributed by the physical exergy of the materials entering the baseline combined cycle ($E_{M,BCC}$), such as air, fuel and cooling water. The exergy content of electricity is assumed to be the same as its energy content, as electricity is fully convertible into other forms of energy. The exergy efficiency for this baseline combined cycle is 50.5%, which is the ratio of electricity delivered to the grid ($E_{E,grid}$) to total exergy input into the system. Waste stream exergy ($E_{L,BCC}$) is 4.6%, which accounts for exergy streams leaving the cycle contributed by flue gas and cooling water. Exergy destruction ($E_{D,BCC}$) accounts for 44.9% of the total exergy input, which the main exergy loss comes from the combustion chamber ($E_{D,CC}$) due to chemical reaction and large temperature mismatch between the burner gases and the

inlet air in the chamber. Other sources of irreversibilities include exergy destructions in the turbomachineries (i.e. compressor, pump, heat exchangers and expanders), which accounts for 8.8% of the total exergy input.

A.2.1.2. LNG assisted power cycle

This section is an expansion from section 3.2.2. Figure A.2 shows the exergy flows and exergy destruction during operation of the LNG assisted power cycle. The physical exergy (i.e. cold and mechanical exergy) of LNG ($E_{P,LNG}$) makes a significant contribution to the exergy input (18.6%) alongside the chemical exergy of the consumed natural gas ($E_{C,NG}$). Physical exergy contributed by other material input into the power cycle (i.e. air) is negligible. The exergy efficiency of the LNG assisted power plant is 51.1%. The waste streams ($E_{L,LAPC}$), which mainly consist of the flue gas and regasified LNG, contain exergy amounts to 2.3% of the total exergy input. The exergy destroyed in this LNG assisted power cycle ($E_{D,LAPC}$) is 46.6%. Similar to the baseline combined cycle, the main exergy destruction occurs in the combustion chamber, due to the chemical reactions and temperature mismatch. Compared with the baseline combined cycle, the exergy destruction inside the heat exchangers is more significant (9.0%) due to presence of more heat exchangers, including HX-1, where LNG precools the inlet air with large temperature mismatch.

Compared to the baseline combined cycle, an LNG assisted power cycle demonstrates much higher thermal efficiency (66.5% vs 53.5%) due to higher amount of electrical energy generated by the bottoming cycle and lower compression inlet temperature for the bottoming cycle with LNG cold. Besides, additional electrical energy is also generated with the LNG direct expansion cycle.

Figure A.2: Exergy flow during operation of LNG assisted power cycle

A.2.1.3. Thermal network

Figure A.3: Exergy flows for the thermal network central plant

This section is an expansion from section 3.2.3. The exergy flow inside the thermal network is shown in Figure A.3. LNG physical exergy ($E_{P,LNG}$) is the main exergy source, accounting for 83.3% of the total exergy input. The physical exergy of material streams, $E_{M,TN}$ (i.e. returned vapor CO₂ and warm water) accounts for 16.7% of the total exergy input to the thermal network central plant. Physical exergy $E_{M,TN}$ is high because of low temperature of CO₂ vapor at -50°C. The exergy efficiency of the thermal network central plant is 29.2%, which represents the ratio of exergy recovered in the charged energy carriers leaving the thermal network central plant, $E_{R,TN}$ (i.e. liquid CO₂ and chilled water) to the total exergy input. Among the energy carriers, liquid CO₂ accounts for over 99.5% of exergy recovered due to its latent energy and low temperature at -50°C. Waste streams, $E_{L,TN}$ which consists of only the regasified LNG,

accounts for 0.6% of the total exergy input. The amount of waste stream is low because of near-ambient temperature of LNG. Almost all exergy destruction $E_{D,TN}$ (70.2%) comes from the heat exchangers, which are the only components inside the thermal network central plant. Here, large temperature mismatch occurs during heat exchange between LNG (-160°C) and the energy carriers (minimum temperature -50°C), leaving large amount of LNG exergy unutilized.

A.2.1.4. Thermal storage

Figure A.4: Exergy flows within LNG assisted TES central plant

This section is an expansion from section 3.2.4. Shown in Figure A.4, largest portion of the exergy input (98.5%) to the TES central plant comes from the physical exergy of LNG ($E_{P,LNG}$). The rest of exergy input comes from material stream, $E_{M,TS}$ contributed by the discharged PCMs. Due to the limited operating range of temperatures for the PCMs (lowest possible temperature -86°C), 75.3% of the exergy input is destroyed in the heat exchangers ($E_{D,HX}$) as high-grade cold exergy available in LNG is not fully utilized due to mismatch in phase change temperature between LNG and PCMs. The waste stream leaving the central plant, $E_{L,TS}$ mainly consists of the regasified LNG delivered to consumers and takes about 0.7% of total exergy input. The rest of the exergy (24.0%) is recovered by the PCMs.

A.2.1.5. Liquid air productions

This section is an expansion from section 3.2.5. Electricity ($E_{E,ASU}$) is the main source of exergy input to drive the two compressors (CP-1 and CP-2), accounting for 51.4% of the total exergy input. LNG physical exergy ($E_{P,LNG}$) is the second largest exergy source at 47.8%, which its thermal exergy is used for cooling in the MSHE and nitrogen liquefaction in HX-2. Material exergy (cooling water and inlet air), $E_{M,ASU}$ accounts for the rest of exergy input at 0.8%. The exergy efficiency, E_R is evaluated as 33.1%, and represents the exergy recovered by the LN_2 (28.0%) and LO_2 (5.1%) products. Waste stream exergy (E_L), which includes the exergy of cooling water, regasified LNG and side products (gaseous nitrogen and gaseous oxygen), accounts for 14.1% of the total exergy input. The total exergy destruction (E_D) of the process is 52.8%, where a substantial amount of 31.4% occurs in heat exchangers, $E_{D,HX}$ (i.e. MSHE, HX-1 and HX-2) due to large temperature mismatches. Exergy destruction in the separation columns, $E_{D,column}$ amounts to 11.4%, due to exergy destruction in the distillation columns where there is an exchange of heat in trays, the reflux sections and the distillation sections; exergy destruction in other components, such as compressors and Joule-Thompson valves is 10.0%.

Figure A.5: Exergy flows within an LNG assisted air separation unit

A.2.2. Performances of cold demand with different energy carriers

A.2.2.1. For liquid air products production

This section is an expansion from section 3.4.1. The exergy flows within the air separation process subjected to different energy carriers are shown in Figure A.6, which the values of exergy inputs correspond to that listed in Table 3.9. Figure A.6(a) shows that to produce 1 kg/s of LN₂ and LO₂ each by using an air separation unit with mainly electricity input, the major exergy input source comes from the electricity, E_E which corresponds with 97.9% of the total exergy input (4.64 MW) to the air separation unit. Exergy of the waste stream, $E_{L,ASU}$ is 23.6%, which mainly consists of the heated cooling water from intercooling and by-products of the air separation process. The total amount of exergy destruction in the air separation unit, $E_{D,ASU}$ is 50.8%, which is mainly contributed by the heat exchangers (including MSHE), compressors and distillation columns. The exergy recovered for the air separation process, $E_{R,ASU}$, which are exergy contained in the liquid air products, is 25.6% of the total exergy input.

(a)

Figure A.6: Exergy flows for air separation process using (a) electricity input (b) electricity and cold from liquid CO₂/chilled water (c) electricity and cold from PCMs

Figure A.6(b) shows the exergy flows inside the air separation unit using electricity assisted by cold from liquid CO₂/chilled water. Electricity is still needed to drive the compressors; however, the dependency on electricity is significantly reduced to 3.6 MW. The reduction of electricity input is due to more efficient intercooling process using liquid CO₂/chilled water at a lower temperature than cooling water, allowing compression work to be reduced. Besides, work input for refrigeration process used to generate cooling water is eliminated. Around 19.7% (0.89 MW) of the total exergy input now comes from the physical exergy contained in the liquid CO₂, E_{CO2} and chilled water, E_{CW} . Exergy of the waste stream, $E_{L,ASU}$ is 26.8% and is contributed by the heated energy carriers and unused by-products. The total exergy destruction, $E_{D,ASU}$ is 46.3%, and is mainly contributed by the heat exchangers, compressors and the distillation column; the exergy recovered by the liquid air products, $E_{R,ASU}$ is 26.9%.

Figure A.6(c) shows the exergy flows inside the air separation unit using cold from PCMs as part of the exergy input. 75.8% (3.59 MW) of the total exergy input comes from electricity which is used to drive the compressors, while 23.8% (1.12 MW) of the total exergy input comes from the physical exergy of PCMs, E_{PCM} which provide cold for intercooling. The amount exergy lost via waste streams is 13.5% of the total exergy

input. The amount of exergy destruction is 60.8%, and is mainly contributed by the heat exchangers, the separation column and the compressors. The percentage of exergy recovered by the liquid air products is 25.7%.

A.2.2.2. For dry ice production

(a)

(b)

(c)

(d)

Figure A.7: Exergy flows for the dry ice production using (a) electricity input (b) electricity assisted by cold from liquid CO₂/chilled water (c) electricity assisted by cold from PCM (d) energy from LN₂

This section is an expansion from section 3.4.2. To produce 1 kg/s of dry ice, from Figure A.7(a) and Table 3.10, the main source of exergy input (0.79 MW) comes from the electricity, E_E used to drive the compressors and contributes to 89.8% of the total exergy input. The rest of exergy input comes from material going into the system, $E_{M,DI}$, which is contributed mainly by cooling water. Exergy of the waste stream (mainly the heated cooling water), $E_{L,DI}$ makes 20.4% of the total exergy input. The total exergy destruction in the process, $E_{D,DI}$ is 46.6%, with the main location of exergy destruction in the compressors, heat exchangers and the Joule-Thompson valves.

Figure A.7(b) shows the exergy flows for dry ice production assisted by cold exergy from liquid CO₂ and chilled water. With liquid CO₂ and chilled water used for the intercooling process, the electricity required to drive the compressors is significantly reduced to 0.24 MW which is equivalent to 32.4% of the total exergy input. The major exergy input comes from the physical exergy of the liquid CO₂, E_{LCO_2} which contributes to 67.5% of total exergy input to the system. Waste streams leaving the dry ice production process are mainly contributed by heated water and vapor CO₂ that represents 36.1% of the total exergy input. The exergy recovered by the dry ice produced is 40.0% of the total exergy input. The total exergy destroyed is 23.9%, and

is mainly contributed by heat exchangers and Joule-Thompson valves. Compared with the case with electricity as main exergy input, the exergy destruction in the compressors is less due to the reduced pressure ratio.

Figure A.7(c) shows the exergy flows in the dry ice production utilizing cold from PCM as part of the exergy input together with electricity. Similar to the dry ice production process with liquid CO₂/chilled water input, the electricity input is 36.0% (0.18 MW) of the total exergy input. The compressor power is further reduced due to further suppression of CO₂ temperature at compressor inlet as well as smaller pressure ratio on CO₂ due to presence of low temperature cold source. Physical exergy of the PCM, E_{PCM} contributes 63.7% of the total exergy input. The exergy recovered by the dry ice is 58.3%, while the exergy destruction is 40.9%, mainly due to the heat exchangers and the Joule-Thompson valves.

The exergy flows for the dry ice production using LN₂ as energy carrier are shown in Figure A.7 (d). The mechanical power, which is part of the physical exergy of the LN₂ energy carrier, is used to drive the compressor. The physical exergy of LN₂, E_{LN2} , which also includes the cold exergy, contributes to about 99.6% of the total exergy input. The waste stream leaving the dry ice production, which mainly consists of the vapor nitrogen, contains exergy of 8.1% of the total exergy input. The exergy recovered by the dry ice is 23.8%. The exergy destruction in the process is 68.1%, and is mainly due to the heat exchangers operating with temperature mismatch between LN₂ and CO₂, which the high-grade exergy of LN₂ is not utilized.

A.2.2.3. For deep freezing -20C

(a)

(b)

(c)

(d)

Figure A.8: Exergy flows for the deep-freezing process using (a) electricity input (b) cold from liquid CO_2 (c) cold from PCM (d) energy from liquid nitrogen

This section is an expansion from section 3.4.3. Figure A.8 (a) shows the exergy flows of the deep-freezing process using a heat pump. Electricity, E_E represents 69.9% of the total exergy input (0.5 MW) and is mainly used to drive the compressor of the heat pump to generate cooling power. The rest of exergy input mainly comes from the exergy contained in the return inlet air, which are labelled as the material streams, $E_{M,DF}$. The waste stream, $E_{L,DF}$ which mainly consists of the heated cooling water leaving the heat pump, contains 26.1% of the total exergy input. Exergy recovered by the cooled air for the deep-freezing process, $E_{R,DF}$ is 32.8% of the total exergy input. Exergy destruction, $E_{D,DF}$ occurs evenly in all the major components of the setup, and account for 41.1% of the total exergy input.

Figure A.8 (b) and Figure A.8(c) show the deep-freezing process using liquid CO₂ and PCM SN33 as the main energy source for cold energy input. The main exergy input source is now the physical exergy from these energy carriers, E_{LCO_2} and E_{PCM} . The waste stream mainly consists of the energy carriers leaving the setup after exchanging heat with the inlet air (i.e. vapor CO₂ and melted PCM). The main location of exergy destruction is in the heat exchangers, where the heat transfer and temperature mismatch occur. The portion of exergy destroyed is reduced compared with the case with using electricity as the main exergy input due to the reduced number of components, particularly the extra refrigeration system. When the setup using liquid CO₂ as the main exergy input is compared with that using PCM as energy carrier, the analysis shows that the setup with PCM has significantly higher exergy efficiency (55.9% compared to 31.7%) due to good selection of material and thus better temperature profile match and less amount of waste of high-grade cold exergy.

Figure A.8(d) shows the exergy flows of the deep-freezing process using LN₂ as energy carrier; the physical exergy of LN₂ (i.e. cold and mechanical exergy) makes 82.6% of the total exergy input. The waste streams mainly consist of the used nitrogen and the cooling water leaving the heat pump, with their physical exergy values at 29.5% of the total exergy input. The exergy recovered by the cooled air is 23.8%, while the exergy destruction of the process is 46.7%. The exergy destruction in the heat exchangers for this deep-freezing setup is higher when compared with the deep-freezing process using other exergy input (i.e. electricity, liquid CO₂ and PCM) because of the extra refrigeration system in the overall setup and also the unutilized ultra-high-grade cold of LN₂.

A.2.2.4. For district cooling

(a)

(b)

(c)

(d)

Figure A.9: Exergy flows for cooling of returned water using (a) electricity input (b) cold from liquid CO_2 (c) cold from PCM (d) energy from LN_2

This section is an expansion from section 3.4.4. Figure A.9 shows the exergy flows for cooling the return water after district cooling process, before redistributing the cooled water to the district again. The exergy flows are similar to that of the deep-freezing processes shown in Figure A.9(a) shows the exergy flows for the district cooling using electricity, E_E as the main exergy input to cool the water returned from the district cooling process. Around 0.24 MW electricity (72.5% of the total exergy input) is consumed by the heat pump to generate the required 1 MW_t cooling power. The waste stream, $E_{L,DCS}$ mainly consists of the cooling water leaving HX-2 of the heat pump and contributes to exergy loss of 48.5% of the total exergy input. Due to the low-grade cold acquired by the cooled water to be distributed to the district, the exergy efficiency (equivalent to exergy recovered, $E_{R,DCS}$) is reduced to 6.9%, compared with the deep-freezing process where 32.79% exergy efficiency is achieved. The exergy destruction, $E_{D,DCS}$ is 44.6%, and is contributed mainly by heat exchangers HX-1 and HX-2.

Figure A.9(b) and (c) show the exergy flows for cooling of the returned water from district cooling via single heat exchange process using liquid CO₂ and PCM AN-03. For usage of liquid CO₂, the main exergy input comes from the physical exergy of the liquid CO₂, E_{LCO_2} (99.5% of the total exergy input or 0.61 MW). The exergy efficiency is low, at 3.7%, which is mainly affected by the high loss of exergy (52.3% of the total exergy input) through the waste streams contributed by vapor CO₂ at a below-ambient temperature and the large amount of exergy destruction (44.0%) in the heat exchanger. For cooling of returned water using PCM, the main exergy input source also comes from the physical exergy of the PCM (96.2% of the total exergy input) but at a far lower amount of 0.07 MW compared to that using liquid CO₂. Thus, this process yields higher exergy efficiency of 27.1%, with a much lower amount of exergy loss via waste streams (16.5% of the total exergy input), which mainly consist of the PCM at a closer-to-ambient condition.

Figure A.9(d) shows the exergy flows of the cooling process using LN₂ as energy carrier. The physical exergy of LN₂ is 88.4% of the total exergy input. The waste streams of the process consist of the physical exergy of the cooling water leaving the condenser HX-3 of the heat pump cycle as well as the used nitrogen, which is at 49.2% of the total exergy input. The exergy efficiency of this process is 4.1% while the total exergy destruction is 55.7% (mainly due to three heat exchangers).

A.2.3. Performances of single energy carrier coupled to all cold demands

A.2.3.1. For liquid air production

This section is an expansion from section 3.5.1. Figure A.10 (a) shows the overall exergy flows for an air separation unit coupled to the baseline combined cycle for the required liquid air products. 97.5% (9.6 MW) of the total exergy input (including

combined cycle and air separation unit), comes from the chemical exergy contained in the natural gas fuel, $E_{C,NG}$ while 1.5% comes from the physical exergy of material streams (i.e. inlet air and cooling water) into the combined cycle, $E_{M,BCC}$ and the rest comes from the physical exergy of material streams to the air separation unit, $E_{M,ASU}$.

As discussed in Section 3.2.1, the exergy efficiency of the baseline combined cycle is 50.5%, generating electricity amounts to 50.0% of the total exergy input which is subsequently delivered to the grid, $E_{E,grid}$. Exergy of the waste streams in the combined cycle, $E_{L,BCC}$ accounts for 4.5% of total exergy input while the total exergy destruction in the combined cycle, $E_{D,BCC}$ accounts for 44.5%, with the main source of exergy destruction from the combustion chamber. Exergy destruction due to transmission losses in the grid, $E_{D,grid}$ accounts for 2.7% of the total exergy input to the system. Thus, the electricity exergy that reaches the air separation unit is 47.3%. Inside the air separation unit, all the exergy destructions, $E_{D,ASU}$ account for 24.5% of the total exergy input, with the main sources of exergy destruction in the heat exchangers and the MSHE. The waste streams leaving the air separation unit, $E_{L,ASU}$ account for 11.4% of the total exergy input, while exergy of the liquid air products (i.e. LN_2 and LO_2), E_R accounts for 12.4%.

For an air separation unit coupled to the LNG assisted power cycle, as shown in Figure A.10(b), 18.4% (1.8 MW) of the total exergy comes from the physical exergy of LNG entering the LNG assisted power cycle, $E_{P,LNG}$. Exergy contained in material streams entering the power cycle, $E_{M,LAPC}$ (i.e. inlet air) is too small to be shown in the exergy diagram. Around 80.6% (7.8 MW) of the total exergy input to the system comes from the chemical exergy of the natural gas consumed by the power cycle, $E_{C,NG}$. 50.6% total exergy input is converted to electricity delivered to the grid, $E_{E,grid}$. Total exergy

destruction in the power cycle, $E_{D,LAPC}$ is 46.2% of total input, with majority of destruction occurs in the combustion chamber. Exergy destruction in heat exchangers is higher (8.9%) than the baseline case (3.2%), particularly due to existence of large temperature mismatch between LNG and inlet air stream and increased number of heat exchangers. Exergy destruction for the rest of the components in the LNG assisted power cycle accounts for 7.2% of the total exergy input. Due to similar configurations, the exergy distribution and destruction/losses in the air separation unit are very similar to the air separation unit discussed in the baseline case, and thus is not reiterated here.

For an air separation unit coupled to the thermal network, alongside the cold energy obtained from the thermal network, electricity from the baseline combined cycle is consumed as energy input to drive the compressors. Thus, shown in Figure A.10 (c), the source of exergy (left-hand side of exergy flow diagram) is divided into two parts, one from the baseline combined cycle and another from the thermal network central plant. 63.4% (7.1 MW) of the total exergy input is obtained from the chemical exergy of the natural gas consumed in the baseline combined cycle to generate electricity, $E_{C,NG}$. Exergy losses and exergy destruction in the combined cycle can be scaled from that discussed from Figure A.1(a), in the earlier paragraph of this section. Amount of electricity entering the air separation unit, $E_{E,ASU}$ accounts for 30.7% of the total exergy input. Around 30.5% (3.6 MW) of the total exergy input comes from the physical exergy of LNG, $E_{P,LNG}$ in the thermal network central plant. The rest of the exergy input comes from the returned material streams into the thermal network, $E_{M,TN}$ (i.e. vapor CO_2 and warm water). Inside the thermal network central plant, due to the large temperature mismatch between energy carriers and LNG, the amount of exergy destruction in the heat exchangers, $E_{D,HX,TN}$ is high and accounts for 24.6% of the total exergy input. Exergy of the waste stream leaving the thermal network, $E_{L,TN}$ is 3.2%

and is contributed mainly by the physical exergy contained in the regasified LNG. The exergy contained in the liquid CO₂, E_{LCO_2} and chilled water, E_{CW} leaving the thermal network central plant and entering the pipeline accounts for 7.8% of the total exergy input. During the pipeline distribution, the exergy destruction due to thermal and friction losses accounts for 0.1% of the total exergy input each. Inside the air separation unit, the total exergy destruction, $E_{D,ASU}$ is 17.8%, mainly contributed by the heat exchangers and MSHEs. Exergy of the waste streams leaving the air separation unit, $E_{L,ASU}$ is 10.3% of the total exergy input, in which 5.1% is contained in the consumed energy carriers (i.e. vapor CO₂ and warm water) which will be returned to the thermal network central plant as material stream. The exergy contained in the useful air products (i.e. LO₂ and LN₂), E_R accounts for 10.3% of the total exergy input, equivalent to the overall exergy efficiency.

(a)

(b)

(c)

(d)

Figure A.10: Overall exergy flows for air separation process downstream (a) baseline combined cycle (b) LNG assisted power cycle (c) thermal network (d) PCM storage

Figure A.10(d) shows the exergy flows of an air separation unit coupled to PCMs. Electricity is obtained from the baseline combined cycle to drive the compressors. Around 61.3% (7.0 MW) of the total exergy input comes from the chemical exergy of natural gas consumed by the combined cycle, while 36.6% (4.4 MW) of the total exergy input to the system comes from the physical energy contained in the LNG entering the thermal storage central plant, $E_{P,LNG}$. Exergy of the waste stream leaving the thermal storage central plant, $E_{L,TS}$ which is mainly contributed by the regasified LNG, amounts to 0.7% of the total exergy input. 26.6% of total exergy input into the system is destroyed in the heat exchangers between LNG and PCMs, $E_{D,HX,TS}$. The PCMs leaving the thermal storage, E_{HCl} and E_{SN33} contain 9.3% of the total exergy input. For distribution of the PCMs by truck, 1.0% of the total exergy is destroyed due to transport loss, $E_{D,road}$, and is compensated by the chemical exergy of the diesel fuel consumed by trucks, E_{fuel} . Due to good thermal insulating properties of cryogenic tanks, the thermal loss during distribution is negligible. Inside the air separation unit, the total exergy destruction, $E_{D,ASU}$ accounts for 23.8% of the total exergy input, with the main source of exergy destruction from the heat exchangers and separation columns. Exergy of waste stream leaving the air separation unit amounts to 5.3% of the total exergy input, while the useful air products accounts for 10.1% of the total exergy input.

A.2.3.2. For dry ice production

This section is an expansion from section 3.5.2. As shown in *Figure A.11(a)*, for conventional dry ice production downstream the baseline combined cycle, the main source of exergy input (93.3% of total or 1.7 MW) is the chemical exergy in the natural gas consumed by the combined cycle, $E_{C,NG}$. The exergy flows and destruction inside

the baseline combined cycle can be scaled according to exergy flow diagrams in Section 3.2.1. Upon grid distribution, the electricity that reaches the dry ice production amounts to 45.2% of the total exergy input to the system. Material stream entering the dry ice production process, $E_{M,DI}$ accounts for about 5.3% the total exergy input, which is contributed by the large mass flow of cooling water and CO₂. Dry ice is produced at an overall exergy efficiency of 15.7%, which is equivalent to exergy recovered in the dry ice, $E_{R,DI}$ to overall exergy input. The exergy of waste stream leaving the dry ice production process, $E_{L,DI}$ amounts to 10.2%, and is contributed mainly by the heated cooling water. The main occurrences of exergy destruction, $E_{D,DI}$ are in the valves, which included JV-1, JV-2 and the snow chamber where liquid CO₂ is pressure-relieved to atmospheric pressure to facilitate the production of dry ice. The exergy destruction in the heat exchangers amounts to 7.3%, while the exergy destruction due to the isentropic efficiency of the compressors amounts to 6.6%.

For dry ice production coupled to the LNG assisted power cycle, the exergy flows are shown in *Figure A.11(b)*. Compared with the dry ice production using electricity from the baseline combined cycle, the chemical exergy of the natural gas consumed, $E_{C,NG}$ is reduced to 1.4 MW, which is equivalent to 77.1% of the total exergy input due to improvement on the thermal efficiency. Around 17.6% (0.3 MW) of the total exergy comes from the physical exergy of the LNG going into the power cycle, $E_{P,LNG}$. The exergy of other material streams is too small to be included in the exergy flow diagram. The exergy flows inside the LNG assisted power cycle are similar to that discussed in Section 3.2.2, which can be scaled for the exergy losses and destructions. After the transmission loss, electricity reaching the dry ice production amounts to 45.7% of the total exergy input. In this overall process, dry ice is produced with exergy recovery percentage, $E_{R,DI}$ of 15.9%. The exergy flows and destructions in the dry ice production

process are similar to that shown in Figure A.10(a) and discussed in the previous paragraph.

Exergy flows for dry ice production coupled to the thermal network are shown in *Figure A.11(c)*. The electricity used to drive the CO₂ compressor is obtained from the baseline combined cycle. Chemical exergy of the natural gas consumed in the baseline combined cycle, $E_{C,NG}$ amounts to 22.0% (0.5 MW) of the total exergy input to the system, with exergy flows can be scaled with in Section 3.3.1. The amount of electricity that enters the dry ice production process upon grid distribution amounts to 10.6%. Around 65.7% (1.5 MW) of the total exergy input to the system comes from the physical exergy of LNG, $E_{P,LNG}$ which acts as the cold source to charge the liquid CO₂ and chilled water. The remaining 12.0% of the total exergy input is contributed by the material streams entering the thermal network central plant (returned water and CO₂), $E_{M,TN}$. Due to large temperature mismatches in the heat exchangers, the exergy destruction in the thermal network central plant, $E_{D,HX,TN}$ is 47.2%. Around 8.1% of the total exergy input is lost in the waste streams leaving the thermal network central plant, $E_{L,TN}$ which mainly consist of the regasified LNG. Around 22.4% of the total exergy input is converted into liquid CO₂ in the thermal network central plant, while the exergy of chilled water is too negligible to be displayed. Along the pipeline, the exergy destruction due to the thermal loss, $E_{D,T}$ is 0.3%, while the exergy destroyed due to friction loss, $E_{D,F}$ (0.1% of total exergy input) is covered by the electricity input to the pump. With electricity and the cold from liquid CO₂ and chilled water as main exergy sources for dry ice production, dry ice is produced with an overall exergy efficiency, $E_{R,DI}$ of 13.1%. Waste streams exiting the dry ice production process, $E_{L,DI}$ which mainly consist of the warm water and vapor CO₂ that will be returned to the thermal network central plant as $E_{M,TN}$, account for 11.8% of the total exergy input. Compared

with the dry ice production coupled to electricity as the sole exergy input, the exergy destruction in the dry ice production process is significantly reduced and only accounts for 7.8% of the total exergy input, which is due to more efficient dry ice production and also large proportion of exergy destruction in the central plant upstream.

Figure A.11(d) shows the exergy flows for dry ice production coupled to the thermal storage. Electricity is obtained from the baseline combined cycle to drive the compressors. Thus, 23.5% (0.37 MW) of the total exergy input is the chemical exergy of natural gas consumed by the combined cycle, $E_{C,NG}$ producing electricity (11.4% of total exergy input) entering the dry ice production. The main source of exergy input to the system (74.5% of the total exergy input or 1.18 MW) comes from the physical exergy of LNG entering the thermal storage central plant, $E_{P,LNG}$. However, the exergy destruction in the heat exchangers of the central plant, $E_{D,HX,TS}$ is large (50.9% of the total exergy input) due to large mass flow of LNG and temperature mismatch resulting in high waste of exergy. For the dry ice production, the total exergy destruction in the process, $E_{D,DI}$ is 12.9%, with the main source of exergy destruction in the heat exchangers. The overall exergy efficiency of the process, $E_{R,DI}$ is 18.4%.

Exergy flows for the dry ice production process coupled to the LN_2 are shown in *Figure A.11(e)*. LN_2 is produced using the LNG assisted air separation process, where electricity is assumed to be obtained from the baseline combined cycle, thus the main source of exergy input coming from the chemical exergy of natural gas consumed by the combined cycle, $E_{C,NG}$ (67.6% of the total exergy input or 4.6 MW). The exergy flows inside the combined cycle can be scaled according to that described earlier. Electricity produced and delivered to the air separation unit is 32.8% of the total exergy input. Another major exergy source is the physical exergy of LNG to be regasified in

the air separation unit, $E_{P,LNG}$ (30.5% of the total exergy input or 2.1 MW), providing cold energy for the air separation process. For the air separation process, the exergy contained in the waste streams, $E_{L,ASU}$ (i.e. the cooling water and unused side-product) is around 12.2% of the total exergy input. The total amount of exergy destruction in the air separation process, $E_{D,ASU}$ is 33.7%, with the main sources of exergy destruction in the MSHE and heat exchangers. After considering the road transport loss caused by fuel consumption (which is compensated by fuel exergy), the LN_2 reaching the dry ice production contains 17.9% of the total exergy input. The thermal loss is negligible due to the short transport time and assumption of minimal storage period. For the dry ice production process, due to the large temperature mismatch in heat exchangers, the exergy destruction in the heat exchangers, $E_{D,HX,DI}$ is the most significant and amounts to 10.6% of the total exergy input. The exergy destruction in the rest of the components (i.e. valves, compressor and separation column) amounts to 1.5%. The waste streams leaving the dry ice production, $E_{L,DI}$ mainly consisting of the physical exergy of glycol solution leaving the process and unused mechanical work, contain 1.5% of the total input exergy. Due to the large amount of exergy destruction in the baseline combined cycle, in the air separation process and in the heat exchangers during dry ice production, the overall exergy efficiency is only 4.3%.

(a)

(b)

(c)

(d)

(e)

Figure A.11: Overall exergy flows for dry ice production downstream of (a) baseline power plant (b) LNG assisted power plant (c) thermal network (d) thermal storage (e) LNG assisted air separation

A.2.3.3. Deep freezing

This section is an expansion from section 3.5.3. Figure A.12(a) shows the overall exergy flows from a baseline combined cycle to the deep-freezing process. The main source of exergy input (81.7% of total or 1.0 MW) is the chemical exergy contained in the natural gas consumed by the combined cycle, $E_{C,NG}$. Exergy flows within the combined cycle can be scaled with cases previously discussed. After considering the electricity distribution loss, the electricity reaching the deep-freezing process makes 39.6% of the total exergy input. For the deep-freezing process, the exergy destruction, $E_{D,DF}$ is 23.3% of the total exergy input and is mainly contributed by the heat pump. Exergy loss, $E_{L,DF}$ is mainly contributed by the cooling water leaving the heat pump, while the overall exergy efficiency, $E_{R,DF}$ is 18.6%.

Figure A.12(b) shows the exergy flows from an LNG assisted power cycle to the deep-freezing process. Amount of natural gas chemical exergy input, $E_{C,NG}$ is reduced to 0.83 MW (or 67.4% of the total exergy input) due to higher thermal efficiency of power cycle. Around 15.4% (0.2 MW) of the total exergy input comes from the physical exergy of LNG, $E_{P,LNG}$. After the transmission, the electricity reaching the deep-freezing process is 40.0% of the total exergy input. In the deep-freezing process, the amount of exergy destruction, $E_{D,DF}$ is 23.6% contributed by the heat pump cycle and the amount of exergy for the waste streams, $E_{L,DF}$ is 14.9%; the overall exergy efficiency, $E_{R,DF}$ is 18.7%.

(a)

(b)

(c)

(d)

(e)

Figure A.12: Overall exergy flows for the deep-freezing process downstream of (a) baseline power plant (b) LNG assisted power plant (c) thermal network (d) thermal storage (e) LNG assisted air separation unit

Figure A.12(c) shows the exergy flows from the thermal network central plant to the deep-freezing process. The main exergy input comes from the physical exergy of LNG entering the central plant, $E_{P,LNG}$ (80.4% of total exergy input or 2.0 MW). Other main

exergy input to the thermal network central plant comes from the material stream (returned CO₂ and water). The exergy destruction is large at the central plant where the heat exchange between LNG and the working fluids occur due to the large amount of unutilized high-grade cold energy from LNG. The exergy of liquid CO₂ distributed to the network is 28.1% of the total exergy input. The pressure loss in the pipelines is almost negligible, and the exergy destruction due to the thermal loss, $E_{D,T}$ is 0.3% of the total exergy input, yielding liquid CO₂ entering the deep-freezing process with an exergy of 27.8% of the total exergy input. Large amount of exergy is lost through the waste stream, $E_{L,DF}$ which is due to low temperature of CO₂ leaving the deep-freezing process to fulfill the requirement on the operating condition of CO₂ pipeline. The amount of exergy destruction during the heat exchange for deep freezing process is low at 1.8%, due to a better temperature profile matching during heat exchanger between CO₂ and air for deep-freezing. This yields the overall exergy efficiency, $E_{R,DF}$ of 9.5%.

The exergy flows from the thermal storage to the deep-freezing process, as shown in Figure A.12(d), are very similar to the deep-freezing process downstream the thermal network. Around 80.1% of the exergy input comes from the LNG physical exergy, $E_{P,LNG}$ in which large amount is destroyed in the thermal storage central plant. The heat exchange between LNG and PCM has poor temperature profile match and thus loss of high-grade cold exergy, resulting in 66.5% of total exergy input destroyed ($E_{D,HX,TS}$). The PCM selected has a good temperature match with the deep-freezing process, resulting in significantly reduced exergy destruction in the heat exchanger, $E_{D,HX,DF}$ at the cold demand. Exergy loss due to the waste stream (which mainly consist of the PCM leaving the heat exchange process), $E_{L,DF}$ is 6.8% while the overall exergy efficiency, $E_{R,DF}$ is 16.0%.

For the deep freezing process using LN₂ energy carrier shown in Figure A.12(e), the main exergy input comes from the chemical exergy of the natural gas, $E_{C,NG}$ consumed by the baseline combined cycle to produce electricity, which is subsequently used to drive the compressors in the LNG assisted air separation unit. The amount of chemical exergy consumed is 65.2% of the total exergy input (or 3.1 MW), and the exergy flows in the baseline combined cycle are similar to those discussed in Section 1.2.3.1. The electricity entering the air separation unit has 31.6% amount of the total exergy input. At the air separation process, another 29.4% of total exergy input is acquired from physical exergy of LNG, $E_{P,LNG}$. With exergy loss, $E_{L,ASU}$ of 11.8% total input and exergy destructions, $E_{D,ASU}$ of 32.5% total input, LN₂ is produced and contains exergy amounts to 17.5% of the total exergy input. The distribution loss of LN₂ is 0.3% the total exergy input, which is mainly contributed by the road transport loss; the thermal loss is negligible due to the good tank insulation and short distribution distance. The exergy destruction due to road transport loss is compensated from the diesel fuel input to the truck. For the deep-freezing process, the main cause of exergy destruction is in the heat exchangers, $E_{D,HX,DF}$ which amounts to 7.5% of total exergy input. The total amount of exergy lost and destroyed is 6.2% and 9.7% respectively in the deep-freezing process. Due to low efficiency in the baseline case, air separation and deep-freezing process, the overall efficiency, $E_{R,DF}$ is merely 4.9%.

A.2.3.4. District cooling

This section is an expansion from section 3.5.4. For Figure A.13(a) and (b), which show exergy flows for cooling of the returned water from district cooling using electricity, the main exergy source comes from the chemical exergy of the natural gas, $E_{C,NG}$ consumed by the power cycles to produce electricity. With the main exergy destruction

occurring in the combustion chamber of the power cycles and various components of the heat pump cycle, the overall exergy efficiency of the water cooling process, $E_{R,DCS}$ using electricity from both baseline combined cycle and the LNG assisted power cycle is low, at 3.9%, which is caused by the low exergy content in the product cooling water.

(a)

(b)

(c)

(d)

(e)

Figure A.13: Overall exergy flows for cooling of returned water using energy carriers generated from (a) baseline combined cycle (b) LNG assisted power cycle (c) thermal network (d) thermal storage (e) LNG assisted air separation unit

Figure A.13(c) and (d) show the exergy flows for using energy carriers produced by the thermal network and thermal storage respectively for the similar water cooling process. In both cases, the main exergy input comes from the physical exergy of the LNG, $E_{P,LNG}$, which is the main cold source. Due to the temperature mismatch between LNG and the energy carriers and thus unutilized high-grade cold, the exergy destruction inside the heat exchangers of the central plant for both the thermal network and the thermal storage, $E_{D,HX,TN}$ and $E_{D,HX,TS}$ is high. This causes the low overall exergy

efficiency, $E_{R,DCS}$ which is 1.1% for that using liquid CO₂ energy carrier and 1.8% for that using PCM.

Figure A.13(e) shows the exergy flows from the LNG assisted air separation unit to the cooling of return water. The main exergy input (66% of total) is the chemical exergy of the natural gas, $E_{C,NG}$ consumed by the baseline combined cycle, which is used to produce electricity to drive the compressors in the air separation unit. Another main exergy input is the physical exergy of the LNG, $E_{P,LNG}$ fed into the air separation process. The total amount of exergy lost and destruction in the baseline combined cycle and air separation unit is totaled at 33.2% and 44.9% respectively. Due to the large amounts of exergy destruction and lost, the overall exergy efficiency of the return water cooling process, $E_{R,DCS}$ using LN2 as energy carrier is only 0.8%.

A.3. Experimental setup – graphical user interface

Figure A.14: GUI showing real-time pressure, temperature and mass flow at various points and control panel for solenoid valves

Figure A.15: RTD locations and temperature distributions

This section is an expansion from section 5.1. The GUI for the general layout for user to understand the HTF flow conditions is shown in Figure A.14. Temperature distributions display are also available for each TES tank, with example of temperature distribution for REG2 is demonstrated in Figure A.15.

A.4. 1-dimensional TES study with granular materials

A.4.1. Granular materials under different encapsulation size for PCM E-75 and E-65

This section is an expansion from section 6.5.2. Granular materials are shown to be able to maintain the performance of a TES tank when cost effectiveness is preferred and the encapsulation with larger size is chosen. Using properly chosen granular materials with good thermophysical properties, such as alumina particles and micro-encapsulated n-decane, it is possible to maintain the cyclic efficiencies, while increasing the encapsulation size by 60%. Such increase in encapsulation size cuts the total number of capsules used by more than 75% and is an effective measure in cost cutting of a TES system.

Figure A.16 shows the effect of filling the void space of TES tank equipped with macro-encapsulated E-75 under different encapsulation size from 50 mm to 100 mm, with HTF flow rate of $3.2 \text{ m}^3/\text{min}$. Generally, the effects of different granular materials on the performances, such as storage capacity, charge / discharge time and their respective efficiencies are similar to that discussed for in-house-developed PCM. Alumina particle as granular material is the best candidate when increasing tank storage capacity is the priority, while using micro-encapsulated n-decane as granular material is the best choice to improve the efficiency during both charge and discharge. The efficiency of using other sensible heat granular materials can be sorted according to their heat capacity, where alumina particles give the best performances, followed by aluminum particles and quartz pebbles.

Figure A.16(a) shows the effect on TES tank charge time due to different encapsulation size for E-75. Using alumina particles as granular materials yields largest increase on charge time, followed by micro-encapsulated n-decane and aluminum particles which

share similar performance while quartz pebbles have the smallest increase on charge time. For SHTES granular materials, the increase in charge time is proportional to increase in storage capacity. Despite yielding larger increase in storage capacity than aluminum particles, using micro-encapsulated n-decane as granular material is advantageous due to shorter charge time, which is contributed by constant temperature plateau at -30°C because of phase change. Due to low thermal conductivity of E-75, when encapsulation size is increased, longer time is needed for thermal energy to reach the innermost node of E-75 to be stored and for PCM at the innermost node to complete phase change. The thermal energy by heat conduction within a PCM is the limiting factor and is much slower than the convective heat transfer between HTF and PCM. Thus, charge time increases. Slight drop in charge time for encapsulation size of 80 mm has been explained in Figure 6.10(a).

(a)

(b)

(c)

(d)

(e)

(f)

Figure A.16: Effect of filling the void space of TES tank filled with macro-encapsulated E-75 under different encapsulation sizes

Figure A.16(b) shows the effect of encapsulation size of E-75 on the discharge time. Using alumina particles and micro-encapsulated n-decane as granular materials yield similar increase in discharge time, despite alumina particles gives the largest amount of increase on the total thermal energy stored. Such observation on discharge time is slightly different compared to TES tank using macro-encapsulated in-house-developed PCM as primary TES material. In-house-developed PCM has major amount of thermal energy stored as latent heat at -118°C while micro-encapsulated n-decane has vast amount of thermal energy stored as latent heat at -30°C . For the HTF to reach the discharge temperature, there is a lack of thermal energy with temperature range between

-30°C and -118°C. Major amount of latent heat stored in in-house-developed PCM needs to be degraded into lower-grade cold energy to cover the big temperature gap between phase change temperatures of micro-encapsulated n-decane and in-house-developed PCM. Additional of micro-encapsulated n-decane cannot effectively cover the large sensible heat region between -30°C and -118°C, thus the improvement on discharge time using n-decane as granular material does not yield higher impact than using alumina. The condition is different when micro-encapsulated n-decane is used as granular material for TES tank equipped with macro-encapsulated E-75 PCM. Major amount of thermal energy is stored as latent heat in E-75 at -75°C. During discharge, micro-encapsulated n-decane effectively covers the sensible region of HTF from inlet boundary temperature down to -30°C, while the rest of sensible heat region during discharge can be effectively covered by latent heat of E-75 at -75°C. Thus, the discharge performance of micro-encapsulated n-decane as granular material is boosted in this case, where improvement on discharge time is similar to that of using alumina as granular material. Effect of other sensible heat granular materials can be sorted based on their effect on thermal storage capacity. Similar to TES tank using macro-encapsulated in-house-developed PCM, the discharge time increases with PCM encapsulation size, mainly due to ineffective discharge of thermal energy and degradation of high-grade thermal energy to lower-grade region, which has been discussed in the main manuscript.

The effect on charge efficiency is shown in Figure A.16(c). The charge efficiency shows a downward trend when encapsulation size increases, when increased amount of time is needed (Figure A.16(a)) to charge a lower storage capacity (Figure A.16(f)). The performance of different granular materials is similar to that discussed in previous section, where micro-encapsulated n-decane yields highest increment on charge efficiency, followed by alumina particles, aluminum particles and quartzite pebbles. To

maintain similar charge efficiency above the base case where no granular material is used while increasing the encapsulation size to 60 mm, any granular material can be used to fill the void space. To increase the encapsulation size to 70 mm, the only material suitable to maintain the charge efficiency is micro-encapsulated n-decane alone.

For effect on discharge efficiency (Figure A.16(d)), micro-encapsulated n-decane is the best candidate, mainly due to its superior performance in prolonging the discharge time as discussed. Improvement is followed by alumina particles, aluminum particles and quartzite pebbles based on the amount of increase in thermal energy stored. Similar to macro-encapsulated in-house-developed PCM, there is a downward trend on discharge efficiency when encapsulation size is increased. To increase the encapsulation size to 60 mm while maintaining discharge efficiency above the level where no granular material is used, micro-encapsulated n-decane and alumina particles are the only two suitable granular materials. No granular material is able to sustain encapsulation size of E-75 at 70 mm.

Effect of granular materials on cyclic efficiency is shown in Figure A.16(e). As a product of charge and discharge efficiency, cyclic efficiency also shows a downward trend when encapsulation size of E-75 increases, with micro-encapsulated n-decane as best granular material to improve cyclic efficiency, followed by alumina particles, aluminum particles and quartzite pebbles. When encapsulation size is increased to 60 mm, to maintain the cyclic efficiency, any granular material can be used. When encapsulation size is increased to 70 mm, only micro-encapsulated n-decane is left as the sole suitable granular material. Usage of alumina particles yields the largest increase on the amount of thermal energy stored as shown in Figure A.16(f). From cyclic

efficiency point of view, micro-encapsulated n-decane is a better choice as a granular filler material mainly because of its high charge efficiency.

For TES tank using E-65 as macro-encapsulated PCM, the effect of encapsulation size changes on charge time is similar to that of using E-75 as macro-encapsulated PCM, and is shown in Figure A.17(a). Using alumina particles as granular material yields the largest increment on charge time, followed by aluminum particles, micro-encapsulated n-decane and quartzite pebbles.

Figure A.17(b) shows effect on discharge time. The discharge time increases when encapsulation size is increased from 50 mm to 70 mm, then become almost constant from 80 mm to 100 mm. The decreases in discharge time at 80 mm encapsulation size is due to the reduction of thermal energy stored due to improper packing of macro-encapsulated PCM. Such trend is very different compared with TES tanks equipped with in-house-developed PCM and E-75 where discharge time shows increasing trend with encapsulation size. For E-65, the amount of latent heat (more than 2 times of E-65) which has minimal change in temperature on PCM when being utilized is too much to be discharged when encapsulation size is too large. Besides, the phase change temperature is too close to the threshold temperature where the discharge is cutoff. These reasons result in ineffective discharge of thermal energy for encapsulation size larger than 80 mm.

(a)

(b)

(c)

(d)

(e)

(f)

Figure A.17: Effect of filling the void space of TES tank filled with macro-encapsulated E-65 under different encapsulation sizes

Effect on charge efficiency is shown in Figure A.17(c). The effect is very similar to that discussed for TES tank equipped with E-75, where downward trend on charge efficiency is shown with increase of encapsulation size, and micro-encapsulated n-decane is the best candidate for increment on charge efficiency, followed by alumina particles, aluminum particles and quartzite pebbles. When encapsulation size is increased to 60 mm, only micro-encapsulated n-decane and alumina particles are suitable granular materials to maintain the charge efficiency, while when encapsulation size is increased to 70 mm, only micro-encapsulated n-decane is suitable. Similar trend is also observed on discharge efficiency where the discharge efficiency shows downward trend with increase on encapsulation size as shown in Figure A.17(d). Such trend is because of reduction of discharge time when encapsulation size is increased beyond 80 mm, where threshold temperature reaches early, retaining much stored thermal energy not discharged. In the case of TES tank equipped with E-65, no granular material is usable to maintain the discharge efficiency when encapsulation size is increased, showing that increasing encapsulation size is totally unfavorable for TES tank equipped with PCM of high latent heat capacity.

Figure A.17(e) shows the cyclic efficiency, under effect of granular materials and encapsulation size. As a product of charge and discharge efficiency, cyclic efficiency also shows a downward trend with increasing encapsulation size. To maintain the cyclic efficiency while increasing encapsulation size to 60 mm, micro-encapsulated n-decane and alumina particles are suitable to be used as granular materials. When encapsulation size is increased to 70 mm, no granular material is suitable, where the best option for granular material is micro-encapsulated n-decane.

In a nutshell, micro-encapsulated n-decane is the best candidate for improving efficiencies of TES tank with any PCM, where the encapsulation size can be increased

to 70 mm for most PCM, while 80 mm for in-house-developed PCM. For case of in-house-developed PCM, due to mismatch of phase change temperature between in-house-developed PCM and n-decane, the improvement is not as significant and using alumina particles as granular materials yield similar efficiencies. However, effect of inserting granular material on efficiencies of TES tank diminished for PCM of high phase change temperature (or close to threshold temperature). Such effect is further suppressed when the PCM has superior performance (i.e. high latent heat capacity).

A.4.2 Effect of granular material under different flow rate

This section is an expansion from section 6.5.3. Figure A.18 shows the effect of filling the void space of the TES tank made up of macro-encapsulated E-65 of 50 mm encapsulation diameter with granular materials under different flow rate condition. The effect on charge time is similar to those discussed in the earlier part of this section. As shown in Figure A.18(a), when the flow rate increases by 5 folds, despite not showing an inversely proportional response for the charge time, the charge time is reduced to $\approx 24\%$ the charge time at $3.2 \text{ m}^3/\text{min}$. This improvement is likely to be contributed by the higher thermal conductivity on E-65 compared to in-house-developed PCM. Performance of different granular materials are close to each other. For discharge time shown in Figure A.18(b), the effect is similar to that of in-house-developed PCM, where the discharge time is almost inversely proportional to the increase of flow rate.

The charge efficiency (Figure A.18(c)) shows similar trend to the in-house-developed PCM as well, where downward trend is observed when flow rate increases. Similarly, micro-encapsulated n-decane is the best granular material to improve on charge efficiency, followed by alumina particles, aluminum particles and quartzite pebbles.

However, on TES tank equipped with macro-encapsulated E-65, the improvement brought by granular materials is not significant mainly due to the originally high TES capacity contributed by E-65 and its high efficiency. Thus, when flow rate is increased to 6.4 m³/min, only n-decane is the suitable granular material to maintain the charge efficiency. Similar trend is also observed on discharge efficiency and cyclic efficiency, demonstrated in Figure A.18(d) and Figure A.18(e).

(a)

(b)

(c)

(d)

(e)

Figure A.18: Effect of filling the void space of TES tank filled with macro-encapsulated E-65 with 50 mm encapsulation size under different flow rate

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