

**NOVEL AND SUSTAINABLE INTEGRATION
OF R-152A HYDRATE-BASED DESALINATION
SYSTEM WITH A DOUBLE-EFFECT ABSORPTION
REFRIGERATION CYCLE**

BY

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A Thesis Presented to the
COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

MAY 2024

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

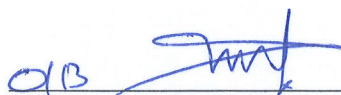
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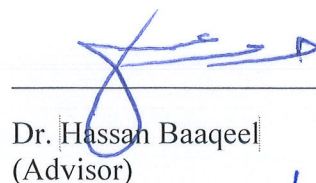
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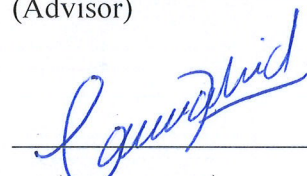
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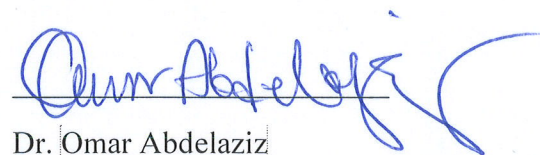
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2024

I dedicate this thesis to my wonderful parents, Ghassan Aldroubi and Omayma Aldroubi, and to my beloved twin sister, Farah. Without their unwavering support, I wouldn't be where I am today. I deeply appreciate the sacrifices they've made to see me succeed. I also acknowledge that my drive to succeed is fueled by the desire to provide them with a fraction of the love, care and opportunities they've generously given me throughout my life

ACKNOWLEDGMENTS

I begin by expressing my sincerest gratitude to Allah (God) for His blessings, guidance, and strength throughout this academic journey. Without His divine support, none of this would have been possible.

I am deeply indebted to my thesis advisor, Dr. Hassan Baaqeel, for his unwavering support, invaluable guidance, and encouragement. His expertise and mentorship have been pivotal in navigating the challenges of research and academic writing.

I am grateful to the members of my thesis committee, Dr. Umer Zahid and Dr. Omar Abdelaziz, for their insightful feedback, constructive criticism, and scholarly input. Their expertise has greatly contributed to the quality and rigor of this thesis.

Furthermore, I would like to thank my family, friends, and all those who have supported and encouraged me throughout this journey. Their belief in my abilities has been a constant source of motivation and inspiration.

At last, I extend my heartfelt appreciation to King Fahd University of Petroleum and Minerals (KFUPM) for providing me with the opportunity to pursue my Master's degree. The resources, facilities, and academic environment at KFUPM have played a crucial role in shaping my educational experience and facilitating the completion of this thesis.

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LIST OF ABBREVIATIONS

Nomenclature

Abbreviations

GHBD: Gas hydrate-based desalination

RHBD: Refrigerant hydrate-based desalination

AHRI: Air-conditioning, Heating, and Refrigeration Institution

COP: coefficient of performance

MSF: Multi-stage flash

MED: Multi-effect Distillation

VCR: Vapor Compression Cycle

DEAB: double-effect absorption

LiBr lithium bromide

LMTD: log-mean temperature difference

EES engineering equation solver

SEC: Specific energy consumption

HEX: Heat exchanger

Symbols

SS: Strong solution (Water/libr)

WS : weak solution

V: Vapor

LVM: Liquid-vapor mixture

P : Propane

EG : Ethylene glycol

HF: Hydrate former

SW: Sea water

B: Brine

PW: Pure water

HW: Hot water

T : Temperature

m mass flowrate, kg/s

ABSTRACT

Full Name : [SIEF ADDEEN GHASAN ALDROUBI]
Thesis Title : NOVEL AND SUSTAINABLE INTEGRATION OF R-152A
HYDRATE-BASED DESALINATION SYSTEM WITH A
DOUBLE-EFFECT ABSORPTION REFRIGERATION CYCLE
Major Field : CHEMICAL ENGINEERING
Date of Degree : May-2024

Innovative desalination technologies are emerging as critical solutions to address the escalating challenge of freshwater scarcity. Among these, gas hydrate-based desalination (GHBD) stands out as a promising approach due to its independence on water salinity and TDS. GHBD involves the formation of crystal ice-like structures from a hydrate former (typically gas) and water under specific conditions, separating pure water as crystals and leaving behind a concentrated brine solution. However, conventional hydrate formers often necessitate near-zero Celsius temperatures and high pressures, leading to high energy consumption and operational costs.

To address these challenges, this study proposes leveraging gas hydrate-based desalination with R-152a refrigerant as a hydrate former. The refrigerant hydrate-based desalination process (RHBD) proves exceptional, reducing specific energy consumption by 60% compared to propane. Comparative analysis while using the Vapor Compression Cycle (VCR) reveals significant energy consumption reductions compared to conventional fluids like methane and propane. However, energy analysis highlights the dominance of compressors and pumps in total energy consumption, emphasizing on the need for replacing the vapor compression cycle with a more sustainable integration.

Here comes the dual-effect absorption refrigeration cycle, running on heat dissipated from the exothermic reaction of hydrate formation. Integrating this cycle with RHBD not only decreases the energy requirement to almost zero but also reduces CO₂ emissions by 20%. Economic analysis results in a total annualized cost of 4.91 M\$, which is 20% less than using a vapor compression cycle as a refrigeration system to cool the feed.

ملخص الرسالة

الاسم الكامل: سيف الدين غسان الدروبي

عنوان الرسالة: التكامل الجديد والمستدام لنظام تحلية المياه المعتمد على الهيدرات باستخدام R-152a مع دورة تبريد مزدوجة التأثير بالامتصاص

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: أيار-2024

تظهر التقنيات المبتكرة لتحلية المياه المالحة كحلول حيوية لمعالجة التحدي المتزايد لندرة المياه العذبة. من بين هذه التقنيات، كنهج واعد بسبب استقلاليتها عن ملوحة المياه ومحتوى الأملاح (GHBD) تبرز تقنية تحلية المياه بناءً على الهيدرات الغازية تكوين هياكل شبيهة بالتلج، تعرف بالهيدرات الغازية، من مادة تكوينية للهيدرات (عادةً غاز) GHBD الذائبة. تتضمن تقنية والماء تحت ظروف معينة، مما يفصل الماء النقي على شكل بلورات ويترك الحل المركز من محلول الملح. ومع ذلك، غالبًا ما تتطلب المادة التكوينية التقليدية درجات حرارة تقريبًا قريبة من الصفر المئوي، مما يؤدي إلى استهلاك طاقة عالي وتكاليف تشغيلية.

لمعالجة هذه التحديات، يقترح هذا الدراسة الاستفادة من تقنية تحلية المياه بناءً على هيدرات الغاز مع مادة تكوينية هي استثنائية، حيث تقلل (RHBD) يثبت عملية تحلية المياه بناءً على هيدرات الريفريجرانت R-152a. الريفريجرانت (VCR) استهلاك الطاقة النوعية بنسبة 60٪ مقارنة بالبروبان. يكشف التحليل المقارن أثناء استخدام دورة الضغط البخاري عن تقليلات كبيرة في استهلاك الطاقة مقارنة بالسوائل التقليدية مثل الميثان والبروبان. ومع ذلك، يسلط التحليل الطاقوي الضوء على سيطرة الضواغط والمضخات على استهلاك الطاقة الإجمالي، مما يؤكد على الحاجة إلى استبدال دورة الضغط البخاري بتكامل أكثر استدامة.

يأتي هنا دور الدورة الثنائية لامتصاص التبريد، التي تعمل بواسطة الحرارة الناتجة عن التفاعل الحراري لتكوين الهيدرات. يخفض تكامل هذه الدورة مع RHBD ليس فقط متطلبات الطاقة تقريبًا إلى الصفر، ولكن أيضًا يقلل انبعاثات ثاني أكسيد الكربون بنسبة 20٪. يسفر التحليل الاقتصادي عن تكلفة سنوية مجمعة بقيمة 4.91 مليون دولار، وهو أقل بنسبة 20٪ من استخدام دورة الضغط البخاري كنظام تبريد لتبريد التغذية.

CHAPTER 1 INTRODUCTION

1.1 What are gas hydrates?

Gas hydrates, also known as clathrate hydrates, are crystalline substances that can be considered as ice. They form under specific temperature and pressure conditions when guest molecules, referred to as hydrate formers, are enclosed within a three-dimensional framework of water molecules, creating cavities or cages. These guest molecules, which must be of a certain size (no larger than 9 Å), are held in place by van der Waals interactions, ensuring the stability of the hydrate structure [1,2]. Hydrate formers encompass a range of substances, including light hydrocarbons etc. Notably, gas hydrates are often non-stoichiometric, meaning they can remain stable even if some cavities within their structure remain unoccupied. [3]. Figure 1 shows a schematic diagram of gas hydrate crystal showing the encapsulated hydrate former inside the crystal. Clathrates structures can be classified into three main types, sI, sII and sH hydrates. Both sI and sII are cubic structures, whereas sH represents a hexagonal structure.

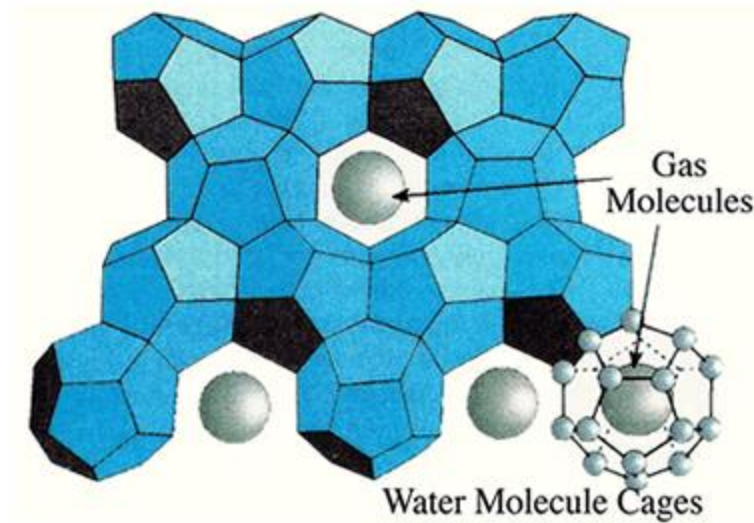


Figure 1 schematic diagram of gas hydrate crystal taken from [4]

The main difference between the hydrate crystal structure type can be summarized as follows:

Number of Cavities: The number of cavities in each unit cell varies, this number is proportional to the number of water molecules, the higher the number of cavities the more water molecules needed to form a unit cell of a gas hydrate crystal. The number of water molecules forming the unit cell differs between structures. sI consists of 46 water molecules; sII has 136 water molecules; and sH has 34 water molecules.

Guest Molecules: Different guest molecules are accommodated in each structure based on their sizes. For example, small molecules like methane, ethane, carbon dioxide, and hydrogen sulfide typically occupy sI hydrate, while larger molecules like propane and iso-butane occupy sII hydrate. sH hydrate can accommodate a mixture of small molecules (e.g., hydrogen sulfide, methane, nitrogen) and large ones (e.g., iso-pentane, neohexane).

Unit Cell Formulas: Each structure has a unique unit cell formula, indicating the arrangement of water molecules and cavities within the unit cell. These formulas provide a concise representation of the structural differences between the hydrate types.

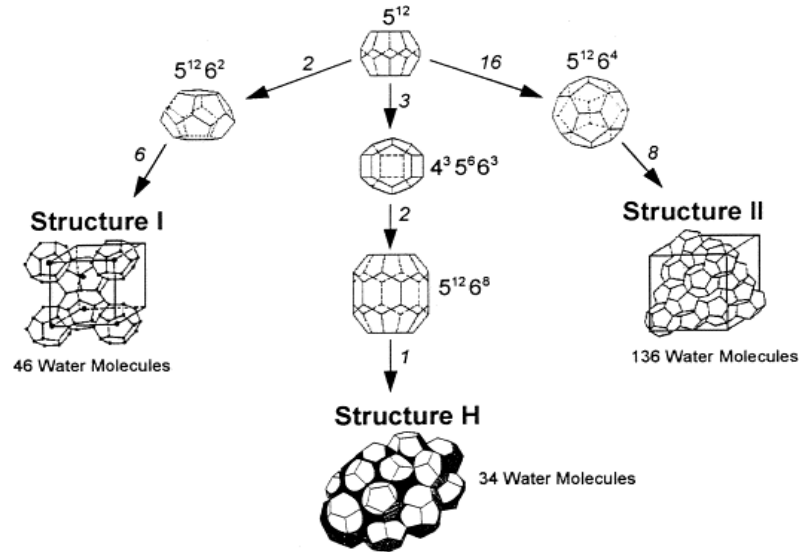


Figure 2 types of gas hydrates structures, taken from [5]

1.2 Types of Desalination

Accessing clean and reliable water sources is increasingly difficult, underscoring the importance of desalination. With only 3% of Earth's water being fresh, and much of that inaccessible in icecaps and glaciers, reliance solely on these sources is challenging [6]. The vast majority, 97%, of Earth's water is saline, making the exploration of diverse desalination techniques vital [7]. These methods fall into three main categories: Thermal-based, Membrane-based, and emerging technologies like Gas-hydrate and Capacitive Deionization (CDI). Currently, approximately 95 million cubic meters of fresh water are produced daily by nearly 16,000 desalination plants worldwide. Geographically, the Middle East, particularly Saudi Arabia and the UAE, dominate global desalination capacity, with thermal technologies prevalent due to abundant fossil fuel resources [8].

1.2.1 Thermal-Based Technologies

In thermal desalination, fossil fuels, predominantly natural gas, are burned to generate the necessary heat for boiling the brine solution. This process produces steam, which is then condensed to yield pure distilled water. The two most commonly used thermal-based technologies, Multistage Flash (MSF) and Multiple Effect Distillation (MED), contribute 23% and 8% respectively to the total production of fresh water. Despite their effectiveness in producing fresh water, these methods have limitations due to their high energy requirements associated with the phase change of water. Figure 1 and 2 below shows the Multi-stage flash distillation and multi effect distillation respectively. The multi-stage flash (MSF) process and the multi-effect distillation (MED) process are two prominent methods employed in desalination to convert seawater into freshwater. In the MSF process, seawater undergoes heating under high pressure within a sequence of chambers known as flashes. As the seawater enters each flash chamber, it experiences a decrease in pressure, causing a portion of it to instantly vaporize into steam. This steam is then condensed to yield freshwater, while the remaining seawater, now at a lower temperature, proceeds to the next stage for further treatment. MSF plants typically employ multiple stages to maximize freshwater production efficiency, albeit at the cost of substantial energy inputs for heating and pressurization.

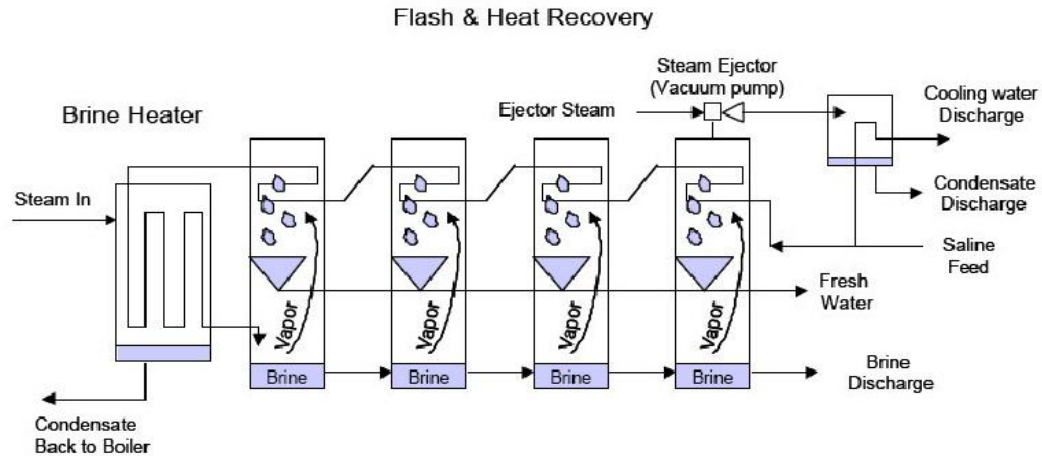


Figure 3 Multi-stage flash desalination taken from [9]

Conversely, the multi-effect distillation (MED) process utilizes a series of evaporator stages, or effects, to achieve desalination. Each effect operates at decreasing pressure and temperature levels. Seawater is heated in the initial effect, prompting evaporation, with the resulting vapor condensed in successive effects. The condensed vapor transfers its heat to evaporate more seawater in the upcoming effects, thus enhancing the distillation process. MED plants are known for their energy efficiency, as they effectively utilize the latent heat of vaporization across multiple stages. In a MED plant, evaporation occurs on the contact area between the sea water thin film and the hot surface. Whereas, in MSF, heat is transferred by convection along the tubes, flashing brine in each stage; hence producing vapor.

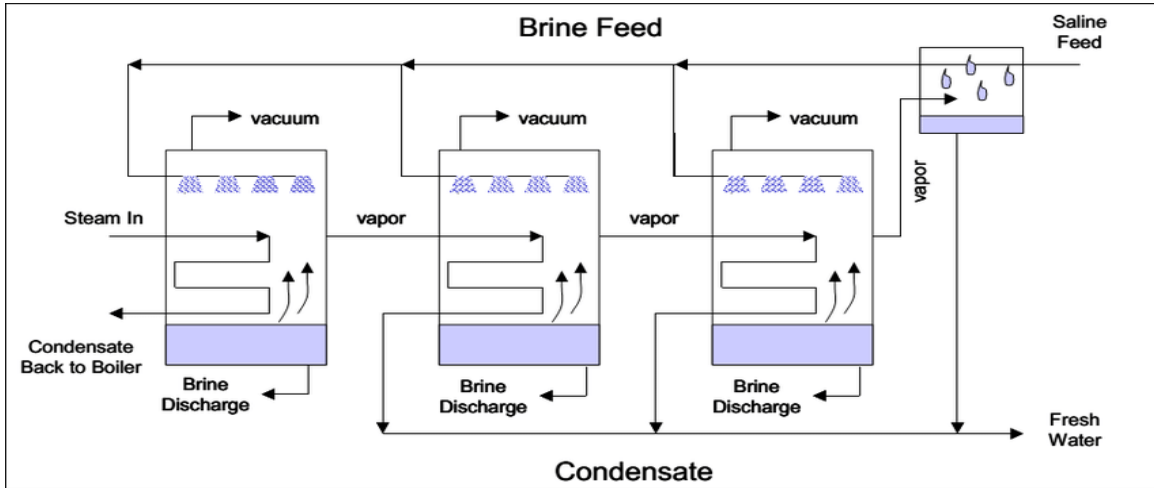


Figure 4 Multi-effect distillation

1.2.2 Membrane-based desalination

In reverse osmosis (RO) desalination, an external force is utilized to drive water molecules against their natural osmotic flow. This pressure prompts them to pass through a semi-permeable membrane, effectively separating them from dissolved salts and producing a less concentrated solution. However, RO technology is only suitable for water with low total dissolved solids (TDS). Furthermore, its feasibility is hindered by the need for a pre-treatment facility, where chemical additives are introduced into seawater, and the demand for high operating pressures, which can reach up to 80 bar.[10]. In addition, The RO system effluent requires a post-treatment process involving PH neutralization and removal any gases in the solution.

From the fact that RO plants have been operating for more than 15 years, it has been deduced that the daily monitoring of the plant contributes the most when it comes to operational cost. In addition, the most concerning problem accompanied by such operation is clogging the membranes. This results in fouling of RO units; hence results in lower water

capacity. To prevent this, usually back wash or regular cleaning of the membranes is done, In addition , the cartridge should be replaced every two months. [11]

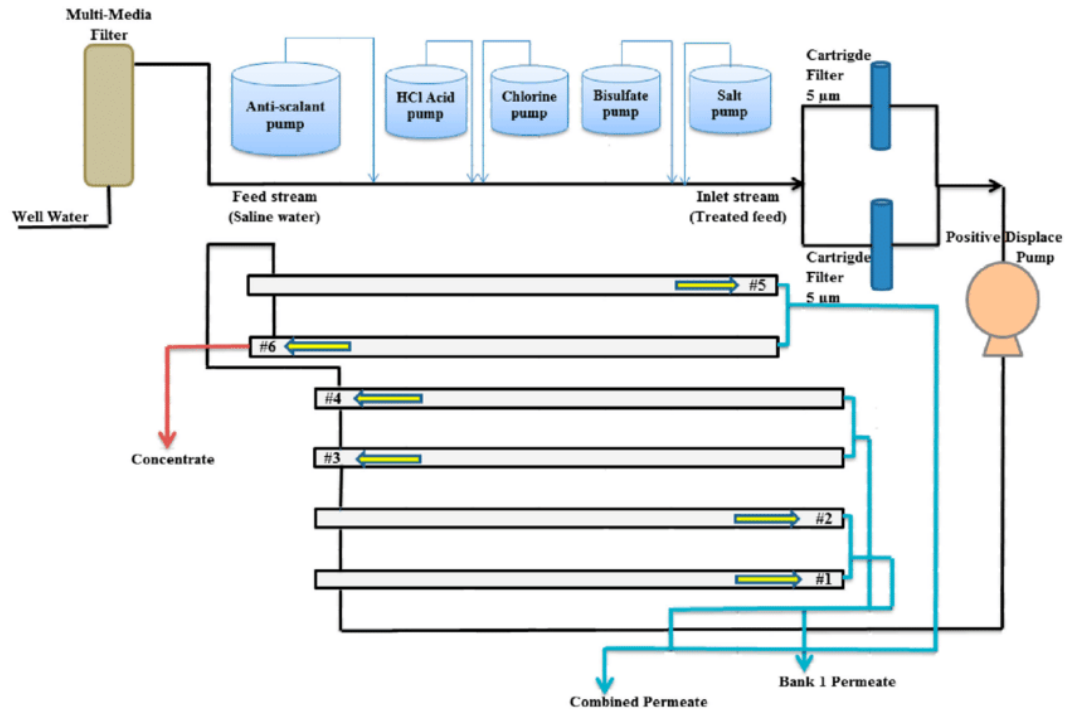


Figure 5 Reverse osmosis process outline, taken from[12]

1.2.3 Hydrate-based desalination

The concept of harnessing hydrate-based desalination for seawater purification dates back to its proposal in 1942 [13]. Hydrate-based desalination involves a unique process where pure water is coerced into forming a crystal-like structure called hydrate around a specific guest molecule at temperatures above the water's freezing point. By melting the hydrate, salt-free water is produced along with the former guest molecule, which can be recycled in the process. The temperatures at which hydrate formation and dissociation occur depend on the chosen hydrate former. These gas hydrates are not considered chemical compounds; rather, the enclosed guest interacts with water molecules through relatively weak van der Waals forces. The resulting hydrate crystal contains over 85% water, indicating a high degree of purity in the water produced [14]

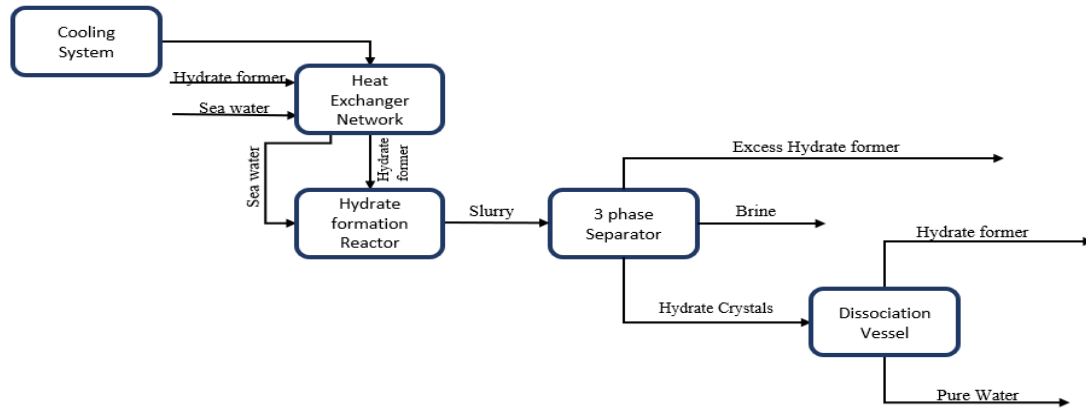


Figure 6 Block flow diagram of Hydrate-based desalination

1.3 Absorption refrigeration cycle

As mentioned previously, the feed conditions of hydrate formation reaction require cooling, usually the two main cooling systems that are widely used in plants are vapor compression cycles and absorption chillers. Because the novelty of this thesis is in integrating absorption refrigeration system to integrate, this work will mainly focus on it.

1.3.1 Overview

The global demand for energy is significantly increasing along with the requirement to reduce greenhouse gas emissions. This drives the need for exploring new and efficient cooling technologies. Speaking of conventional cooling systems like vapor compression cycles and chillers, they are typically driven by electricity, increasing the emissions to the atmosphere. As a result, Interests have been emerging investigating new environmentally friendly sources of energy for cooling systems. Here comes the absorption refrigeration cycle , a sustainable alternative which runs on low grade heat. It is evident that most of the industrial plants have waste heat which can be recovered using water streams to run the absorption refrigeration cycle; hence increasing the energy efficiency of the cooling process [15,16]. When comparing absorption refrigeration systems to compression refrigeration systems, several distinctions arise. Absorption refrigeration cycles run on

cheaper fuel associated with waste heat. In addition, they boast lower maintenance costs due to their minimal moving parts, contrasting with the higher maintenance demands of compression systems. Moreover, such systems maintain efficiency even at partial loads and may even enhance efficiency in such conditions, whereas compression systems may suffer efficiency losses. The absence of reciprocating parts in ARSs also translates to lower costs compared to compression systems, which typically rely on reciprocating compressors. Additionally, ARSs generally offer a longer service life. However, it's important to note that ARSs may have limitations in achieving very low temperatures compared to compression refrigeration systems. Another advantage of absorption refrigeration cycle over vapor compression cycle is the fact that it uses green refrigerants like ammonia and water/LiBr as working fluid which is environmentally friendly when compared to CFCs, HFCs and organic compounds [17]. Figure 1 shows general waste-heat temperature classifications [18]

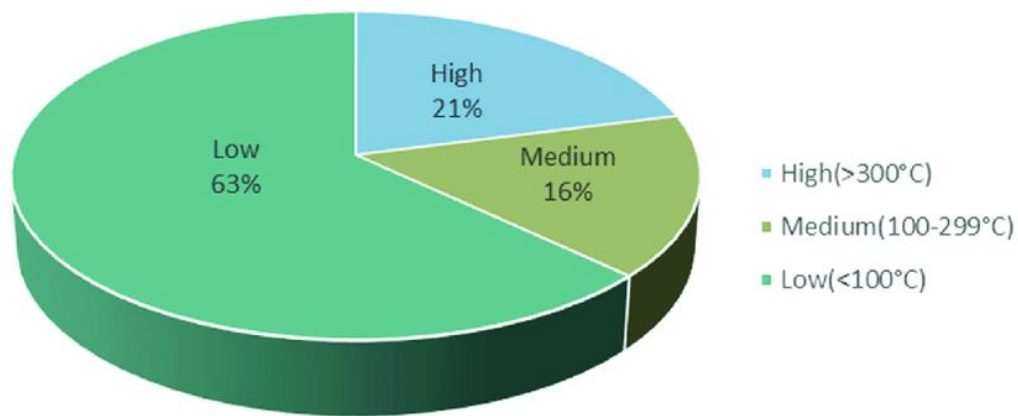


Figure 7 Waste-heat classifications

1.3.2 Types of Absorption refrigeration cycles

1.3.2.1 Single-effect absorption refrigeration cycle

This cycle consists of the basic components of the absorption refrigeration cycle: the absorber, evaporator, generator, and condenser. It relies on a low-pressure steam or hot water as a driving source. However, the overall thermal efficiency of this system is relatively low.

Before exploring another types of absorption refrigeration cycles, it is important to know how the basic working principles of each equipment as they are included in every type [19].

- **GENERATOR:** The generator or reboiler is where the absorbent solution is heated, typically through a heat source like natural gas, steam, or electricity. This heat causes the refrigerant to be released from the absorbent, creating a high-pressure refrigerant vapor.
- **CONDENSER:** The condenser is where the high-pressure refrigerant vapor from the generator is cooled down, causing it to condense into a high-pressure liquid. This process releases heat, which is usually dissipated to the surroundings or utilized for other purpose.
- **EVAPORATOR:** The evaporator is the cooling space of the refrigeration cycle, it is the place where the refrigerant absorbs heat from the substance to be cooled, turning into vapor. Typically it consists of coils through which the substance to be cooled passes.
- **ABSORBER:** The absorber is where the regeneration of the strong solution takes place, the refrigerant evaporated is absorbed in the absorbent (weak solution).

1.3.2.1 Dual-effect absorption refrigeration cycle

This type stands among the single-effect type due to it having an extra generator and condenser. The extra condenser is responsible for condensing the refrigerant vapor, this given-off heat energy is utilized to boil off more refrigerant from the absorbent solution in the second generator. [20]

1.3.2.2 Triple-effect and Multi-effect absorption refrigeration cycle.

In this setup, there are three generators: one operates on low temperatures, another on medium temperatures, and a third on high temperatures. The vapor from the high and medium temperature generators is condensed, with the released heat utilized to warm the next lower temperature generator. Compared to double-effect chillers, triple-effect systems can achieve even greater efficiency. However, operating this system requires higher temperatures, leading to higher costs compared to double-effect systems. It is evident that the efficiency increases with increasing number of effects. The main focus of this thesis will be on double effect absorption refrigeration cycle, due to it being the targeted configuration for our sustainable integration.

1.3.2.3- Process description of dual-effect absorption refrigeration cycle

There are two types of dual-effect absorption cycles: parallel and series. The key distinction lies in the flow of the solution from the absorber to the desorber. In the parallel configuration, the weak solution initially enters the low-temperature desorber before proceeding to the high temperature, whereas the opposite occurs in the series configuration. The series configuration, known for its higher cooling capacity, will be the focus of this investigation.

In the double-effect absorption refrigeration cycle, as depicted in Figure 2, there are two different temperature generators (one high and one low) and three heat exchangers for recovering heat. The process begins with a concentrated (strong) solution leaving the absorber. This solution is pressurized by passing through a pump and then splits into two streams to optimize energy recovery.

One stream undergoes preheating by absorbing heat from the diluted solution in a low-temperature heat exchanger (LHX). This preheated stream further splits into two streams through a splitter. One enters a generator operating at low temperature (LTG), while the other enters a high-temperature heat exchanger. This allows the concentrated solution to absorb heat from the returning solution, raising its temperature higher than that of the unsplit stream. The concentrated solution then enters a generator operating at high temperature (HTG), which is driven directly by a heat source, typically hot water. The purpose of the heat source is to facilitate the decomposition of the concentrated solution into weak solution and refrigerant vapor.

The vapor exits the HTG and enters the LTG, where it dissipates heat to the upcoming concentrated solution. This heat exchange contributes to the breakdown of the concentrated solution into vapor, leaving a diluted solution behind. The refrigerated vapor produced in the LTG exits to a condenser.

The cycle continues with the refrigerant entering the CHX, releasing heat to the concentrated solution. Consequently, it exits at a lower temperature. The concentrated solution leaving the condenser merges with another stream to enter the LTG. Within the condenser, the refrigerant vapor releases heat, exiting at a relatively lower temperature. It

then flows through an expansion, experiencing a sudden pressure drop before entering the evaporator.

In the evaporator, the low-pressure refrigerant absorbs heat from the cooling space entering the absorber. Simultaneously, the diluted solution leaving the HTG passes through another heat exchanger, releasing heat to the concentrated solution. It is then mixed with the diluted solution from the LTG, where it loses heat to the concentrated solution, leaving at a lower temperature to the expansion valve. The expansion valve depressurizes the mixed diluted solution to the absorber operating pressure. The expansion valve depressurizes the mixed diluted solution to the absorber operating pressure.

The depressurized absorber feed absorbs the refrigerant from the evaporator, releasing heat and exiting as a concentrated solution.[21]

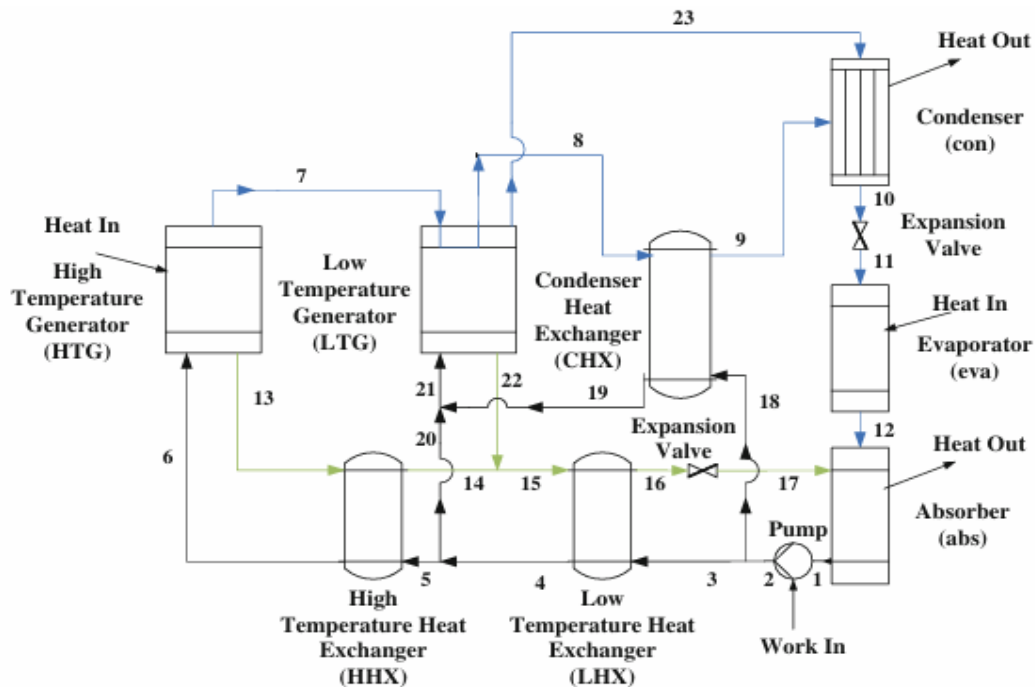


Figure 8 Dual-effect absorption refrigeration cycle

1.3.2 Working fluids

1.3.2.1 Common Working fluids

Aided by its thermodynamic properties, the working fluid has a great effect on the performance of absorption refrigeration cycle. One of the basic fundamentals to take into account when choosing a working fluid combination is that they have to be miscible (can be mixed) especially under the system's operating conditions [22]. In addition to the stated requirements, certain desirable characteristics further enhance the effectiveness of a refrigerant-absorbent system. Maximizing the boiling point elevation, ensuring a significant difference between the pure refrigerant and the mixture at the same pressure, is crucial.[23].

Out of 200 absorbents and refrigerants mixtures, the most common working fluids tends to be Water/ammonia and LiBr/water systems. For ammonia systems, NH_3 act as a refrigerant and water is the absorbent, where as in LiBr (Lithium-bromide) systems, water is the refrigerant. For ammonia systems, both ammonia and water are stable over wide ranges of operating conditions. In addition, the high latent heat of vaporization make ammonia a strong candidate for the efficient performance of the system.

The main advantage of the ammonia/water systems is that they can cool to low temperatures However, this results in a high input temperature requirement in the generator. In addition, both NH_3 and H_2O are volatile which make the presence of a rectifier important to strip away the water vapor that might evaporate with the ammonia. This prevents the accumulation of water in the evaporator, increasing the refrigeration performance. [24]

The use of water/lithium-bromide for absorption refrigeration goes back to 1930, what really makes this solution a great choice is the fact that LiBr (lithium-bromide) is non-volatile which makes the rectification process unnecessary. However, using water as a refrigerant has an operational constraint which is the cooling temperature must be above zero degree Celsius. In addition, this system has to be operated under-vacuum. Since the solution is salt, so it is prone to both crystallization and corrosion. Usually, Lithium chromate is added to the solution to prevent corrosion occurrence. [25,26]

Water/LiBr is used in this work because it has numerous benefits when compared to ammonia/water systems. As mentioned previously, no rectifier is needed because LiBr is non-volatile(boiling point 1265 °C) whereas water boils at 100°C; hence require less components. In addition, (very low vapor pressures) vacuum pressure is a must to ensure smooth refrigerant (water vapor) flow in the system. Furthermore, Unlike NH₃/water system which has toxic ammonia as a refrigerant, no risk is associated with the leakage of the refrigerant vapor (water) in Water/LiBr system.

1.3.2.2 New trends in working fluids

In recent years, there has been a growing interest in exploring alternative working fluids for absorption refrigeration systems, alongside the traditionally used lithium bromide-water and water/ammonia solutions. Among these alternatives, fluorocarbon-based refrigerants like R22 and R21 have gained attention due to their favorable solubility with various organic solvents. However, challenges such as crystallization at high concentrations and temperatures have been encountered when using inorganic salt absorbents like LiBr-water or NaOH-water. To address these challenges, researchers have

explored ternary mixtures such as LiBr + CHO₂/water, which have shown potential in improving the overall performance. [27]

Ionic liquids have a unique property of remaining liquid at room temperature or even below 100°C. Unlike regular salts, their molecules are not tightly packed, allowing them to flow easily. In an ionic liquid, at least one ion has a spread-out charge, and there's also an organic part that prevents the formation of crystals. Important characteristics such as viscosity and solubility depend on the organic components and the ions they contain. These characteristics enable customization for specific applications, making them valid in several applications. A focus is placed on water-soluble ionic liquids due to their enhanced efficiency and reduced environmental impact. These ionic liquids are categorized based on their solubility in water, with examples including those fully soluble, partially soluble, and those chemically interacting with CO₂. By exploring these alternative working fluids, researchers aim to develop more sustainable and efficient refrigeration systems for variety of applications.[28]

1.3 Thesis Objectives

Because hydrate based desalination comes with challenges in terms of energy requirements, a new integrated system of double effect absorption refrigeration and refrigerant hydrate based desalination is to be investigated the main tasks to be done is to be summarized as follows:

- Investigate the use of R-152a refrigerant as a hydrate former, conducting a comparative analysis with conventional hydrate formers to assess its impact on reaction conditions and energy consumption.
- Propose a new integrated system wherein cooling is provided by a double-effect absorption refrigeration cycle instead of a vapor compression cycle.
- Perform techno-economic evaluation and environmental analysis to evaluate the integrated system's impact and potential for easing the commercialization of hydrate-based desalination.

1.4 Thesis Scope

The 1st chapter summarized the importance of desalination and its categories. Also, discussed the types of absorption refrigeration cycles and the introduces the term gas hydrates and how water is desalinated using this technology. In addition, an extensive literature review about the hydrate-based desalination process, the absorption refrigeration cycles and the integrated systems is to be done in Chapter2. Chapter 3 highlights the proposed processes by describing them in detail, Also it mentions the equilibrium conditions of hydrates that might help in understanding the phase equilibria. Chapter 4 discusses the methodology, which implies the simulation details, the models used in Aspen custom modeler, and their validations. The fifth chapter highlights the impact of our proposal by delving into energy analysis, economic analysis and environmental analysis. The sixth chapter presents the key findings and highlights of our study and recommends what type of advancements to be done to build on this research. |

CHAPTER 2

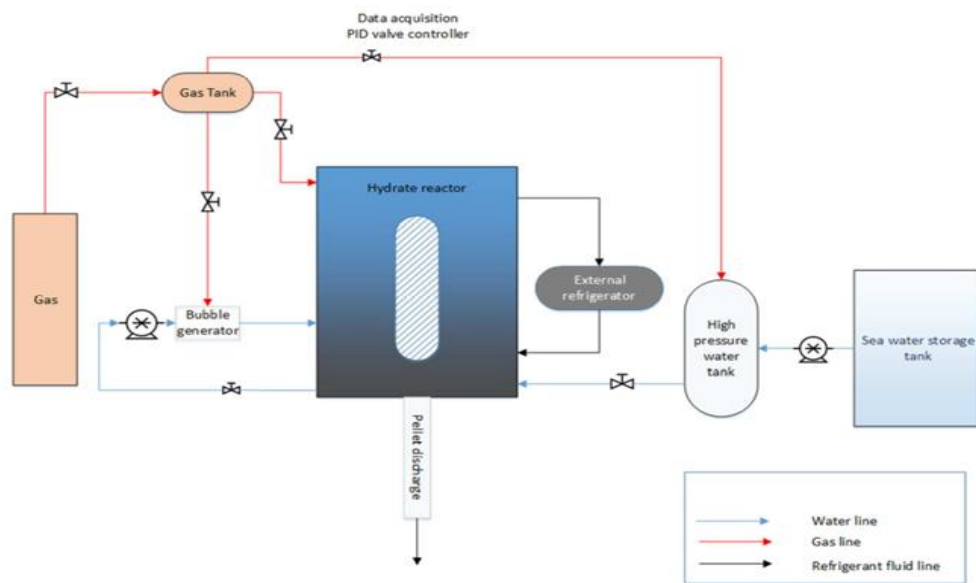
LITERATURE REVIEW

2.1 Hydrate-based desalination

2.1.1 Process configuration

Forming hydrates as a technique to remove water molecules from salts goes back to 1942 and the research continued reaching its prime in 1960s and 70s. A few process configurations were proposed for hydrate-based desalination. For example, Park et al[29], proposed a process including a novel apparatus which can form both carbon dioxide hydrates and hydrate pellets. Referring to figure 3 below, it can be shown that the novel apparatus has a hydrate formation vessel with two cylinders and specific feed lines for water and gas. In addition, the circulation pump which is responsible for bubble generation enhances the contact between the feed water and gas and hence increases the hydrate-forming rate. Squeezing of the reaction slurry(outlet) occurs by the double cylinders along with the piston, producing hydrate pellets which would overcome the difficulty of separating hydrate lattice from the leftover brine. Although the apparatus resulted in 80%

salt removal, but its energy intensive due to both the gas-liquid mixing process which generates bubbles and the double cylinder piston.



[Figure 9 The proposed hydrate pelleting apparatus [7]]

Recently, there has been a contribution concerning the accelerated kinetics of forming hydrates in a fixed-bed reactor having silicas as a porous media, particularly when the hydrate is generated from a gas mixture containing propane as a co-guest [30]. After conducting kinetic studies at microscopic levels, propane proved to be a great hydrate forming promoter. Such studies revealed that propane demonstrates the ability to attract and transfer dispersed water from silicas into the gaseous phase, facilitating hydrate growth. Building upon such observation, a novel clathrate hydrate-based desalination process was proposed, employing a fixed-bed reactor in conjunction with a hybrid process involving hydrate formation through gas separation for CO₂ capture and seawater

desalination, as illustrated in Figure 10. While the conceptual process appears promising, its viability requires validation through experimentation with seawater

Additionally, the conditions at which carbon dioxide's hydrates forms and dissociates were explored in a 3 wt% NaCl solution [31]. To broaden the scope, experiments were conducted with silica gel saturated with both deionized water and a 3 wt% NaCl solution. Notably shown, in 3wt% NaCl solution, hydrate forms faster when compared to deionized water. [31]

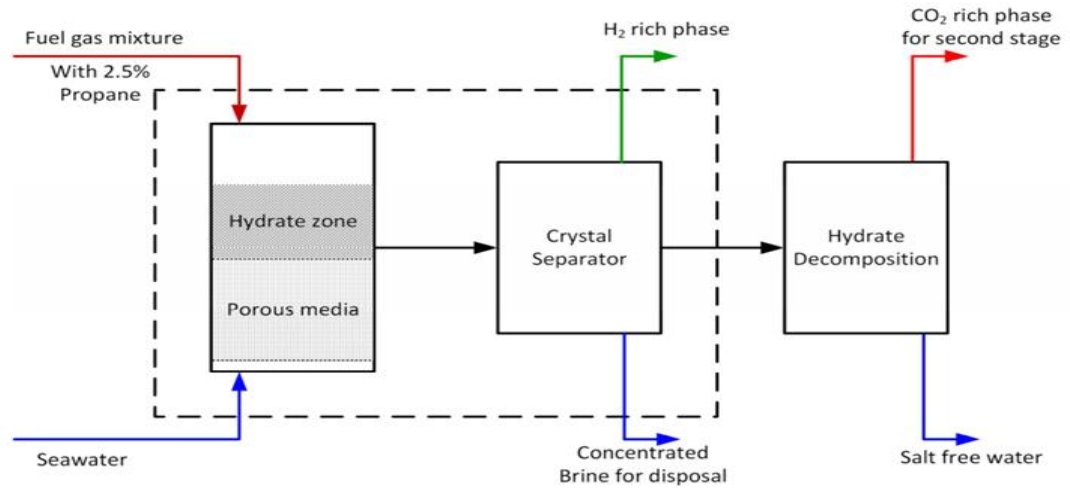


Figure 10 Hybrid gas separation integrated with hydrate-based desalination process

2.1.2 Process design

A range of studies have explored gas hydrate-based desalination process design. He et al. [32] proposed a process where cyclopentane was used as a hydrate-forming agent to increase temperature at which crystal form to 280.25 K. However, during the hydrate dissociation cyclopentane tends to form a cyclo-pentane water emulsion requiring further liquid-liquid separation. He et al. [33] focused on improving the process efficiency of hydrate-based desalination. They developed a novel conceptual design for a hydrate-based

desalination process that utilizes LNG cold energy, significantly reducing energy consumption. It was reported that the resulting specific energy consumption (SEC) of the process was reduced from 65.14 kWh/m³ when using an external refrigeration cycle to 0.84 kWh/m³ when using LNG cold energy to cool the process. The hydrate-based desalination process not only showed great performance when operating solely but also acted as a great precursor for RO systems. Lee et al [34] proposed an approach towards optimally designing a hybrid system containing both gas hydrate and reverse osmosis. Given that, the pretreatment stage in any RO system is costly. The main idea of the proposed process was to deal with gas hydrate based desalination as a pretreatment unit to reverse osmosis. It aimed to reduce the SEC of the overall simultaneous process and make it close to the performance of a standalone sea water RO unit. The results indicated that the total SEC of the hybrid process was 2.1 kWh/m³, and the gas hydrate based desalination process successfully excluded 90% of the salts in the feed water acting as a great pre-treatment unit [34]. Later, LNG was utilized to supply energy to same hybrid RO-gas hydrate based desalination plant. This resulted in yielding a profit from generating an excess of 25.4 kWh electricity/ ton pure water. The profit was calculated to be \$0.521/ ton pure water [35].

2.1.3 Hydrate formers

The majority of the studies focused on identifying effective hydrate formers to enhance the kinetics of hydrate formation. In 1960s, Barduhn's group [36] established a criteria for selecting an ideal gas hydrate former for desalinating sea water. An ideal former should be eco-friendly, non-toxic, non-flammable, stable, be cost-effective, possess a transition temperature between 5.6 to 29.4°C. Several hydrate formers meeting the criteria were

tested as guest molecules. Both ethane and propane were identified candidates for this purpose[30,37,38], while both pure cyclopentane and cyclohexane were utilized as secondary hydrate guests to increase gas hydrate formation [39] . Pure Cyclopentane increased the hydrate formation temperature when compared to other hydrate formers [40,41] . Both cyclopentane and cyclohexane are highly volatile and toxic. This necessitates further liquid-liquid separation to separate cyclopentane and cyclohexane from the pure water produces, this extra separation step adds on the capital investment. Methane [42,43] , CO₂ [31,44–47] and Refrigerants [48,49] were all tested in different studies on a lab basis. Although a lot of effort was exerted, it was difficult to find an exceptional hydrate former that stands out. Both CO₂ and methane tend to contribute for global warming. In addition, excessive use of chlorofluorocarbons (CFCs) was restricted because of it promoting ozone depletion, this resulted in their substitution by Hydrofluorocarbons (HFCs) which are to be used in this work.

Thermal Energy Systems pioneered the use of R-141b refrigerant as a hydrate former in two Hydrate-based desalination pilot plants in the US. Using R-141b as a guest molecule increased the hydrate formation temperature to 278.5 K producing pure desalinated water at a price range of \$0.46–0.52 /ton which can be compared to both reverse osmosis (RO) systems (\$0.45 - \$0.92/m³) and Multistage flash (MSF) (\$1.10 - \$1.50/m³). This outcome showed promise, enabling further exploration into utilizing refrigerants as hydrate formers. HFCs or refrigerants, when employed in this role, tend to decrease energy consumption because they typically form at higher temperatures and lower pressures. Recent studies by Mok et al. [50] and Dongre et al. [51] compared the effectiveness of various refrigerants as hydrate formers, highlighting R-152a as the top choice due to its superior kinetics,

lowest Global Warming Potential (GWP) and conversion rates. According to their studies, R-152a forms hydrates at higher temperatures and lower pressures compared to propane and other refrigerants like R-22. Moreover, the kinetics of R-152a remains unaffected by seawater salt concentration, making it a strong contender for optimizing hydrate-based desalination processes, particularly in countries without LNG imports.

The main aim of this thesis is to attract the commercialization of this emerging method of desalination, as it can be shown that this process suffers from a high energy consumption, and the only way it is reduced is by utilizing the cold energy of LNG, so it has been decided based on thermodynamic analysis and phase equilibria comparison to decide which refrigerant to be used[52,53]. As it was previously stated, R-152a is used as a hydrate former for this process.

As far as the author knows, there is no available research that analyzed the performance of an integrated dual-effect absorption refrigeration system with hydrate-based desalination. The aim of this thesis can be summarized in the following points:

2.2 Absorption refrigeration cycle

2.2.1 Overview

The performance of the double effect absorption refrigeration cycle has been extensively studied, with various improvements and applications identified. An experimental study was conducted on a single-effect absorption refrigeration cycle with Water/LiBr solution. The proposed system operates on a different temperature range in the generator, condenser and evaporator. The results showed that using a solution heat exchanger increased the Coefficient Of Performance (COP) by 60%. This increase in performance is because of the

fact that the solution heat exchanger reduce the heat requirement in the generator (desorber). It was concluded that the generator (desorber) of the single effect system can operate on temperatures as low as 65 °C with a quite good performance [54].

Kurem and Horuz [55] analyzed the effect of altering the working fluid on the performance of a standard single-effect vapor absorption cycles. In this study, the two working fluids to be studied are Water/LiBr and Water/NH₃. Several operating parameters like COP, the evaporator duty and temperature constraints of the working fluids were investigated and compared. It was shown that the system with LiBr as a working fluid has high COP and lower equipment requirements. Also, increasing the generation temperature results in higher vapor production rate from the solution; hence increases the COP. A group of researchers [56] studied the performance of a commercially available refrigeration cycle powered by natural gas. The studies showed that the lesser the flue gases produced the lower the coefficient of performance since lower generation temperature is achieved. Furthermore, they observed that higher inlet temperatures of chilled water corresponded to increased cooling capacity

A recent study examined the energy and exergy aspects of two configurations of the dual-effect absorption cycle: series and parallel flow setups with Water/LiBr solution as the working fluid. The findings revealed noteworthy differences between single-stage and two-stage configurations. In the single-stage absorption system, the highest observed coefficients of performance (COP) and exergy efficiencies were 0.78 and 11.48%, respectively. Conversely, the two-stage absorption system demonstrated superior performance, with a COP of 1.373 and an exergy efficiency of 11.576%. Interestingly, an observed trend related to the evaporator temperature indicated that as it increased, the COP

of both systems also rose. However, this increase in COP was accompanied by a decrease in exergy efficiency [57].

Kaushik and Arora [58] evaluated the COP of both single and series dual-effect absorption cycle, both of them incorporate Water/LiBr as the working fluid. COP results ranged from 0.6-0.75. It is worth highlighting that the series flow two-stage system enhanced the Coefficient of performance of the system by 60-70%. Moreover, optimal generator temperatures were identified for both single and double-stage systems, set at 91°C and 150°C respectively, with a constant condenser and absorber temperature of 37.8°C.

Romero et.al [59] compared the COP between the H₂O-LiBr system and a ternary hydroxide mixture of NaOH, CsOH, and KOH (40:24:36). The ternary solution exhibited a high COP range of 1.2 to 2.2, surpassing the simple LiBr system. It allowed generator and absorber temperatures up to 170°C and 100°C, respectively.. Despite its promising performance, this new ternary solution presented challenges such as lower mass and heat transfer coefficients due to its lower density and viscosity, as well as the potential tendency of corrosion at high temperatures.

Manu [60] highlighted the negative impact of increasing approaching temperatures on performance and conductance. It was concluded that increasing the approaching temperature in the condenser, evaporator, absorber, and generator of a water/lithium bromide absorption refrigeration cycle results in decreased performance and conductance.

2.2.2 Simulation studies

A lot of literature has been published when it comes to simulating the process using several software packages like ANSYS, ASPEN, Engineering Equation Solver (EES), FORTRAN. In this thesis, only simulations focused on Water/LiBr solution will be presented because it is used in to provide cooling for the process of gas hydrate based desalination.

The performance differences between single and double-effect vapor absorption systems was investigated, focusing on their Coefficient of Performance (COP) and exergy efficiency[61]. The thermodynamic analysis was done within Fortran software, consistent cooling load of 300 kW was maintained to assess the behaviors of the systems. The study revealed that the maximum COP ranged from 0.74 to 0.79 for single-effect systems and from 1.22 to 1.42 for dual-effect systems. Similarly, a variation was observed in the exergy efficiency, with single-effect systems ranging from 12.5% to 23.2% and double-effect systems from 14.3% to 25%.

Bolcan et.al [62] designed a prototype of an aqueous ammonia absorption refrigeration system utilizing low-grade heat. Simulation was done using EES software to evaluate the performance of the system. Large deviation was observed between the predicted value and the real experimental value(prototype). This is because of a fault detected in the design of the rectifier and also the absence of insulation which resulted in leakage.

Somers et al.[63] simulated both single and dual effect LiBr-water absorption system using Aspen Plus simulation, the results were compared with the output of EES software for validation. The Aspen software modelling was considered successful as its results showed an error of less than 3 and 5 percent for single and dual effect cycles respectively. Singh and Mashhawri [64] used an artificial neural network (ANN) to conduct energy analysis of

a single-stage LiBr-water vapor absorption refrigeration system, achieving acceptable results.. The use of artificial neural networks for energy analysis was proven to provide faster and simpler solutions.

Additionally, Kayankli & Kilic [65] conducted a comprehensive parametric study on the COP of LiBr-water systems across varying operating parameters. Their findings highlighted a significant 44% increase in COP with the utilization of a solution heat exchanger, contrasting with only a 2.8% increase when using a refrigerant heat exchanger. In their investigation, a thorough analysis of the first and second law thermodynamics concerning LiBr-water absorption chillers was conducted. Their findings stated that the generator is the primary contributor to exergy loss, accounting for 45.6% of the total exergy loss within the cycle, regardless of operating conditions. On the other hand, the pump and refrigerant heat exchanger were identified as the components with the lowest exergy loss in the chiller. A study aiming to conduct a exergo-economic analysis of a dual effect cycle indicated that lower cost is obtained when the temperatures of both evaporator and generator are high and the condenser's temperature is low [66]. A group of researchers [67] further emphasized the importance of heating water (to power the generator (desorber)) and cooled water temperatures in enhancing cooling performance. They found out that enhanced cooling performance is achieved with higher temperatures of the heating water and the water to be cooled, yet it decreases as the temperature of the cooling water rises. Sofyan et.al. [68] also noted the influence of temperature on the system's coefficient of performance, with the absorber, condenser, and evaporator temperatures positively impacting performance, while the generator temperature had a negative effect.

2.3 Integrated systems

Integration of absorption refrigeration systems with desalination processes has garnered significant attention in research. Studies have explored different approaches to enhance performance and reduce energy consumption in desalination through such integration. For instance, Li et al. [69] investigated integrating an ammonia-water absorption heat pump with a multi-effect distillation system, which is driven by heat generated from ammonia vaporization, showing promising returns on investment. Similarly, Jian introduced a seawater desalination system that integrates a low temperature multi-effect desalination system with a double-effect parallel LiBr-water absorption heat pump, reducing energy consumption by 35.6%. These studies collectively demonstrate the potential of integrating double-effect absorption refrigeration with desalination systems to improve performance and reduce energy consumption.[70] A study proposed suggested utilizing the rejected heat from absorbers of Vapor absorption cycle to desalinate sea water by heat [71].

Another study utilized heat rejected from absorbers and compressors to run a humidification-dehumidification (HDH) desalination system. The waste heat from the DEAB system heats the HDH inlet, reducing the energy required for desalination. The proposed system produced pure water at a rate of 2100 L/h and provided a cooling effect of 350 kW [72]. Innovative integration systems have been developed to serve as both air conditioners and heaters. These systems leverage vapor absorption refrigeration to power direct-contact membrane systems, with the cooling water produced serving as a coolant in the air conditioning cycle. Such integrated approaches demonstrate significant performance improvements compared to standalone systems.[73] . Anand et al. [74] designed a system that integrates a VCR with

humidification-dehumidification desalination (HDH), achieving high desalination yield and cooling output. The proposed system achieved a maximum desalination yield of 7.35 liters per hour and a cooling output of 1.89 kW. The annual average desalination output was 25.884 m³/year, the cooling output was 4.26 MWh/year. Salins found that integrating vapor compression refrigeration in a multistage reciprocating dehumidifier test rig improved dehumidification efficiency and moisture removal rate[75] . A group of researchers used a water-lithium bromide absorption cycle for air conditioning and thermal desalination, driven by solar energy. These studies collectively demonstrate the potential for improved performance and energy efficiency in desalination systems through the integration of refrigeration cycles.[76]

CHAPTER 3

METHODOLOGY & SIMULATION DETAILS

3.1 Selecting a suitable hydrate former

As mentioned previously, R-152a refrigerant is chosen as a hydrate former, due to its exceptional hydrate forming abilities when compared to other refrigerants and conventional hydrate promoters. The hydrate formation behavior involves a phase change which turns liquid water into a crystalline structure that encapsulates around a guest molecule, leaving a concentrated brine solution behind. In reference to the phase equilibria data [36,37] of R-152a hydrates plotted in Fig. 11, it is measured that hydrate forms at our chosen operating pressure of 300 kPa at temperatures below 284 K.

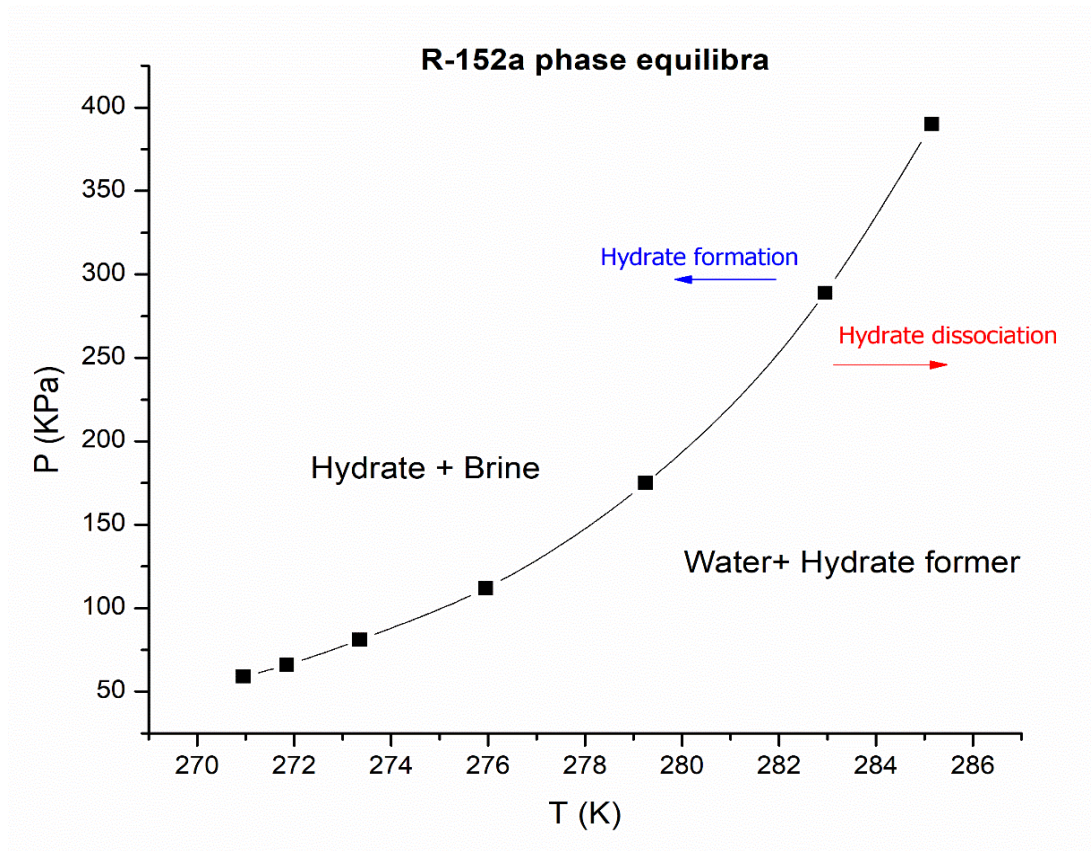


Figure 11 R-152a hydrate phase diagram

In this work, the vapor compression cycle, absorption refrigeration cycle and the hydrate formation process are simulated using Aspen software packages.

3.1 Refrigeration cycle

3.1.1 Vapor compression cycle

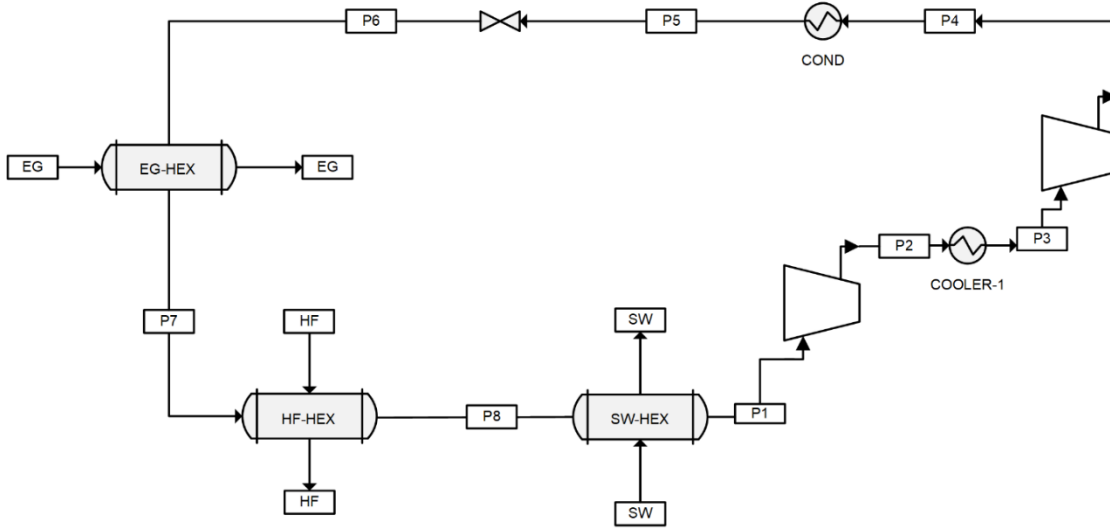


Figure 12 Schematic diagram of vapor compression cycle

The same configuration (Figure 12) of the vapor compression cycle and working fluid done previously in the literature is utilized in this work to maintain a fair comparison. However, the flow rate of the working fluid is different since lower cooling rate is required because the hydrate former R-152a forms hydrates at much higher temperatures and lower pressures when compared to conventional hydrate forming agents used in the literature like methane and propane. 187 kmol/hr of propane at 284K is input. it is cooled twice in a condenser after each compression stage, the delta T is -10. The compression stages have an isentropic efficiency of 75%.

3.1.2 Absorption refrigeration cycle

As previously mentioned Absorption refrigeration system was modelled and simulated using a simulation software used mainly for steady state modelling known as Aspen Plus.

3.1.2.1 Property Package

The most crucial step is to select a property method when dealing with such working fluid like Water/LiBr. The most widely used approach for simulating working fluids are the equation of state and the activity coefficient. Activity coefficient approach is proven to be better than activity coefficient in representing highly non-linear mixtures [63]. It is recommended by ASPEN to utilize the activity coefficient method (Redlich–Kwong equation of state) [77] for all vapor phase properties, alongside the non-random two liquid (NRTL) model for liquid solution properties [78]. In ASPEN, the activity coefficient property method (ELECNRTL) is suggested for the water/LiBr solution, as it dissociates to Lithium and bromide ions when in aqueous form [79]. Additionally, for states consisting of pure water, the built-in steam tables in aspen plus are employed for accurate representation.

3.1.2.2 Assumptions and Block details.

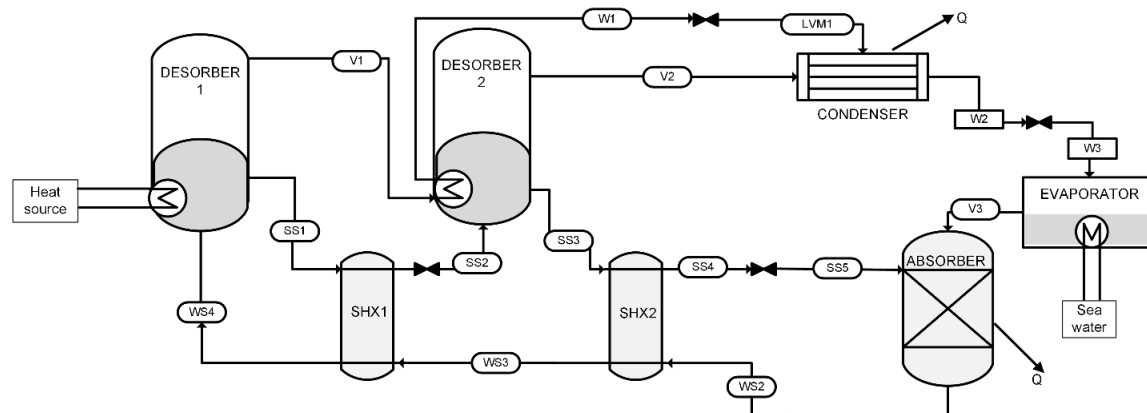


Figure 13 Standalone double-effect absorption refrigeration cycle

When modelling the absorption refrigeration cycle, a certain assumptions are followed which are mentioned in previous studies associated with absorption refrigeration cycles. Table1 shows the associated assumptions [21,25,63] The same assumptions were employed in this work to create a ground for validating our results.

Referring to the figure above representing the absorption refrigeration cycle simulated using Aspen. As mentioned previously, the double effect absorption refrigeration cycle consists of two desorbers (generators) , three throttling valves, an absorber and an evaporator. Regarding the purpose of using Aspen plus is to find a block that simulates the working principles of the aforementioned main equipments. The two desorbers were simulated using a Flash 2 separator which aims on conducting flash calculations to find the mole fraction of refrigerant (water) in both the liquid and the vapor phase. As mentioned previously, that the vapor phase which is generated from the first Desorber (DESORB-1) is used to preheat the liquid in the second generator (desorber) to increase the effectiveness and generate mor vapor. For this purpose, the UP-COND is present which aims to condense the vapor and utilize the heat dissipated as a source to power the second desorber (DESORB-2). The condensed vapor is depressurized with the throttling valve, this cause a vapor liquid mixture to form. Here comes the LOW-COND where all the vapors are condensed to enter the evaporator which is the cooling space of the cycle. The evaporator, condenser and absorber are simulated as a heater block, and the heat needed for evaporation is supplied by cooling water. The main function of the absorber is to regenerate the strong solution SS into weak solution WS by absorbing the water vapor into the concentrated solution and the cycle continues. On the other hand both absorber and condenser requires

a cooling utility as they dissipates heat to the surrounding. source which drive the whole absorption cycle (in our case it is hot water at 134C)

Table 1 Simulation assumptions

STREAM	Assumption
W1	Vapor quality is zero
W2	Vapor quality is zero
V1	Saturated vapor (Vapor quality set to 1 as assumption)
SS1	Liquid is saturated but vapor quality is set to zero as assumption
SS2	Depressurized at the saturation pressure
V2	Saturated vapor (Vapor quality set to 1 as assumption)
SS3	Liquid is saturated but vapor quality is set to zero as assumption
SS4	The temperature is determined by the heat exchange process
WS1-A/WS1	Saturated liquid (Vapor quality is set to zero as an assumption)
LVM1	Liquid vapor mixture, composition determined by the valve model
WS2	Subcooled liquid
WS3	Subcooled liquid
WS4	Subcooled liquid
V3	Vapor quality is 1
SS5	Determined by the valve model

3.1.2.3 Model validation

The simulation of the standalone series dual effect refrigeration cycle is compared with values in the literature to ensure that the results are validated.

Table 2 Model validation with existing literature

The data is validated upon the same conditions, $Q_{\text{DESORB1}} = 300\text{kW}$; $T_{\text{source}} = 139^\circ\text{C}$; $T_{\text{COND}} = T_{\text{ABS}} = 30^\circ\text{C}$; $m_{\text{LiBr}} = 1\text{kg/s}$			
Main component	HEROLD et .al [25]	This simulation	ERROR (%)
DESORB1	300	300	0.00
DESORB2	185.5	190.6	2.75
LOWER-CONDENSER	213.8	220.2	2.99
EVAPORATOR	372.5	380	2.01
ABSORBER	458.8	455.7	-0.68
SHX1	35.6	36.5	2.53
SHX2	91.5	92.8	1.42
COP	1.242	1.2667	1.99

3.2 Hydrate formation and dissociation

After going through the simulation details of both the absorption refrigeration cycle and the vapor compressions cycle, hydrate formation was simulated using aspen custom modeler. As mentioned in the previous section, the temperature = 283 K and pressure of hydrate formation are taken to be 283K and 300 kPa respectively. The molar ratio of hydrate formation is 7.7 ($\text{H}_2\text{O/R-152a}$ mol./mol.) [50] and the water transfer

rate is taken from the literature as 60% [53]. The feed basis are taken as of the hydrate former (R-152a) , implying a 100 kmol/ hr molar flow rate entering the reactor. 770 kmol/hr at 293 K and 101.3 kPa are required for each 100kmol/hr hydrate former.

The hydrate formation reactor was modelled using Aspen Custom modeler. The following reactions are hydrate formation and dissociation reactions respectively.



$$\text{Mass balance: } V_{in}y_i + L_{in}x_i = L_{out}x_i + Hx_i^H + V_{out}y_i \quad (3)$$

$$\text{Water transfer rate: } \frac{L_{in}x_i}{L_{out}x_i} \quad (4)$$

3.2.1 Thermodynamics of hydrate formation

A previously employed hydrate model [80] was utilized in Aspen Custom modeller to analyze the composition of the refrigerant R-152a within the hydrate structure. Before starting with the validation it is worth mentioning that gas hydrates generally exists in two structures , sI and sII. sII hydrates holds more water molecule per lattice, but they require extensive energy to be produced. R-152a , the hydrate former used in the process, forms sI hydrates. As mentioned previously, the temperature and the pressure should be fixed at condition in the hydrate formation region in the phase equilibria hence preventing hydrate dissociation.

$$T = T_0$$

$$P = P_0$$

Because the liquid and vapor phase are at equilibrium , the fugacity at the two phases tends to be the same

$$f_j^L = f_j^V$$

The fugacity of the components was obtained from Peng-rob equation of state was used as the fluid package.

The given thermodynamic correlations are used for model validation only , this help us know the composition of the refrigerant (hydrate former) in both the liquid and the vapor phase. If the hydrate former composition in the vapor phase is very high; this implies that R-152a is barely soluble in water.

$$\text{For small cages: } \theta_j = \frac{f_j^V c_j}{1 + \sum_i f_i^V c_i} \quad (5)$$

(R-152a only occupy larges cages[81]; this make , $\theta_j = 0$)

$$C_j = X_j \cdot \exp \left[\frac{Y_j}{T - Z_j} \right]; C_j \text{ is the Langmuir constant.} \quad (6)$$

$$z_j^* = \frac{f_j^V}{f_j^0 [1 - \sum_i \theta_i]^\alpha}; \sum_j z_j^* = 1 \quad (7)$$

$$f_j^0 = f_{Tj}^0 \cdot \exp \left[\frac{\beta P}{T} \right] \cdot a_w^{-\frac{1}{\lambda_2}} \quad (8)$$

$$f_{Tj}^0 = \exp \left[\frac{-\sum_j A_{ij} \theta_j}{T} \right] \cdot \left[A'_j \exp \left(\frac{B'_j}{T - C'_j} \right) \right] \quad (9)$$

$$\alpha = \frac{\lambda_1}{\lambda_2}$$

$$\alpha \text{ for sI hydrates} = 1/3$$

A_{ij} were considered zeros with no interaction parameters

z_j represents the molar composition of component j (R-152a) in hydrate phase. f_j^V is the fugacity of the refrigerant (R-152a) in vapor phase. f_j^0 stands for the hydrate-phase fugacity of the refrigerant when the small cavities are not occupied by R-152a. f_{Tj}^0 accounts for temperature effect on the hydrate phases fugacity f_j^0 . a_w denotes the activity of water and it is was denoted as 1. $A'_i, B'_i, C'_i, X_i, Y_i, Z_i$ were taken from the literature. [82,83]

3.2.2 Model Validation

The outcome revealed R-152a composition of 0.004 in the liquid (water) phase, indicating its limited solubility in water. Consequently, no flash calculation was deemed necessary for assessing gas/liquid interactions. This finding aligns with existing literature and serves to validate the model's accuracy[84]. Additionally, both mass and energy balances were conducted to ensure the precision of the process simulation. Validation of the model was also achieved by comparing the calculated enthalpy of hydrate formation, which measured at -84 kJ/mol, which is considered close to the value of -82.2 kJ/mol reported in the literature [53].

3.3 Economic Analysis

The cost estimates of the proposed processes depends on operating, capital investments and the costs associated with management , labor and equipment installation, the following assumptions are made:

Table 3 Assumptions of economic analysis

ASSUMPTIONS		Reference
Installation cost	20% of total purchasing cost	[85]
P & ID	18% of equipment's total purchasing cost	[85]
Land	4% of total purchasing cost	[86]
Emergency fund and Contingencies	15% of total (indirect + direct)	[87]
Operating labor cost	\$0.1/m ³ and 20% of it is dedicated to manage them	[73,88]
Annual maintenance cost	1.5% of capital cost	[72]
Working capital	15% of total purchasing cost	[89]
Operating life	30 years (with 90% availability)	[89]
Perfect insulation and fittings are assumed to prevent material leakage.		

The purchased cost of each equipment in the two proposed processes are presented in Table 3 and 4. The current purchasing cost is calculated based on the CEPCI inflation index by using the equation below. CEPCI for this year is considered to be 796. [90]

$$Z_{\text{Base}} = Z_{\text{Ref}} \cdot \frac{CEPCI_{\text{Base}}}{CEPCI_{\text{Ref}}}$$

Where Area is required, it is calculated using the following equation:

$$A = \frac{Q}{UA T_{LMTD}}$$

The overall transfer coefficients associated with the equipment are typically assumed to be constant since they are manufactured to standardized specifications.

Table 4 shows the equipment purchased cost [85,91,92]

Component	Purchase cost equations	Year	CEPCI
Compressor	$Z_{Comp} = 7.9 \times (1.34 \cdot W_C)^{0.62}$, kUSD W_C : required power, kW	2012	584.6
Pump	$Z_P = 1120 \cdot W_P^{0.8}$, USD W_P : required power, kW	2005	468.2
Plate Exchanger	$C_B = \exp(8.202 + 0.01506(A) + 0.06811 \ln(A_{hex}^2))$ $Z_{Hex} = C_B \cdot F_D \cdot F_M$	1982	314
Separator	$Z_{SEP} = 8093 \cdot V_{SEP}$, USD V_{SEP} : capacity, m ³	2018	603.1
Hydrate reactor and dissociator	$Z_{reactor} = 48000 \cdot \left(\frac{Q}{910}\right)^{0.6}$, kUSD Q : duty, MW	2020	596.2

Table 4 shows equipment cost of dual effect absorption refrigeration [93,94]

Equipment	Purchased equipment cost function	Year	CEPCI
Desorbers	$Z_{VG} = 17500 \left(\frac{A_{Desorber1\&2}}{100} \right)^{0.6}$	1995	427.3
Condenser	$Z_{con} = 8000 \left(\frac{A_{condenser}}{100} \right)^{0.6}$	1995	427.3
SHX	$Z_{IHE} = 12000 \left(\frac{A_{IHE}}{100} \right)^{0.6}$	1995	427.3
Absorber	$9.976 \times A^{1.80}$	2001	397
Evaporator	$Z_{EVA} = 16000 \left(\frac{A_{EVA}}{100} \right)^{0.6}$	1995	427.3
Pump	$Z_{Pump} = 2100 \left(\frac{W_{pump}}{10} \right)^{0.26} \left(\frac{1 - \eta_{is, pump}}{\eta_{is, pump}} \right)^{0.5}$	1995	427.3
THV	$Z_{THV} = 114.5 \dot{m}_{thv}$	1995	427.3

The overall coefficients associated with the absorption refrigeration heat transfer equipments are summarized below[95–97]:

- $U_{EVAP} = 1.5 \text{ kW/K.m}^2$
- $U_{ABSORBER} = 0.7 \text{ kW/K.m}^2$
- $U_{DESORBER1,2} = 1.5 \text{ kW/K.m}^2$
- $U_{CONDENSER} = 2.5 \text{ kW/K.m}^2$
- $U_{SHX1,2} = 1 \text{ kW/K.m}^2$

3.4 Environmental analysis

In an era where greenhouse gas emissions are restricted, it is vital to take the environmental analysis into account when process designing. CO₂ a major greenhouse gas is produced throughout the process either by the process of heating and cooling, or it gets emitted in the process of electricity consumption.

CO₂ emissions are calculated using the following equation: [98,99]

$$CO_2 emissions = \frac{Q_{fuel}}{NHV} \times \frac{C\%}{100} \times \alpha$$

Where α is the molar ratio of CO₂ and C which is equivalent to 3.67 and the NHV implies the net heating value of the fuel burnt here both natural gas and heavy fuel oil are used.

CHAPTER 4

Process Design

As mentioned previously, the main aim of this work is to study two things; the first is to explore the effect of using refrigerants as hydrate formers in the desalination process; and the second is to propose a new cooling system to cool the feed.

4.1 Hydrate formation conditions

Before describing the proposed processes, it is crucial to know the hydrate formation conditions using the hydrate former used in this study which is R-152a. As previously mentioned, R-152a refrigerant is selected as the hydrate former due to its superior hydrate forming capabilities compared to other refrigerants and conventional hydrate promoters. The hydrate formation reaction involves a phase change, transforming liquid water into a hydrate crystal that encases the hydrate former, leaving behind a concentrated brine solution. Understanding the hydrate forming conditions is crucial because the reaction is exothermic, which could lead to significant temperature changes and potential hydrate dissociation.

To determine the hydrate forming conditions and prevent dissociation, plotting a phase equilibria diagram is essential. Figure 11 illustrates the phase diagram of R-152a hydrates[100,101], indicating that at a specific pressure, the feed must be cooled below the equilibrium temperature for hydrate formation. At our operating pressure of 300 kPa, the equilibrium temperature is approximately 284 K. To ensure successful hydrate formation, the reaction is maintained at 283 K.

4.2 Refrigerant hydrate-based desalination (RHBD)

The main aim simulating the same process available in the literature is to compare the performance of R-152a in forming hydrates with other conventional formers. Figure 14 illustrates the process flow diagram of hydrate-based desalination coupled with the external vapor compression cycle with propane as the working fluid. To maintain hydrate crystals stability, the temperature of the reactor must be regulated at 283 K, considering the exothermic nature of the hydrate formation reaction which dissipate 82.2 kJ/(mol-R-152a) of heat [50] , An ethylene-glycol cycle (EG1) continuously cooled in HEX-5, is employed to regulate the temperature, and consequently inhibit hydrate crystal dissociation, the number of moles of EG1 required is calculated by a simple energy balance. To ensure a fair comparison with previous studies, the same working fluid and heat exchanger network in the refrigeration cycle are simulated in this research. [33] R-152a is usually stored in containers up to 500 kPa at temperature ranges of 293-298 K to remain in gaseous state, R-152a is cooled by propane HEX-4 to reach the hydrate formation conditions at HF2. 10% excess of the hydrate former is added to ensure effective water to hydrate transfer ratio. The feed sea water at ambient conditions is pumped to 315 kPa to account for any pressure losses in the pipes and heat exchangers. SW1 is then pre-cooled by pure water and brine in HEX-1 and HEX-2 respectively. Then, it undergoes further cooling in the refrigeration cycle by propane in HEX-3. Now that the two feed streams (HF2 and SW4) are cooled to the required conditions, they both enter the hydrate formation reactor forming hydrate crystals. The reactor effluent containing a mixture of crystals, brine, and excess hydrate former, undergoes separation in a three-phase separator where hydrate crystals are separated from the mixture entering a dissociation vessel. Dissociation happens either by

depressurization or by heating. In this process depressurization is used disturbing equilibrium conditions, producing pure water and excess R-152a.

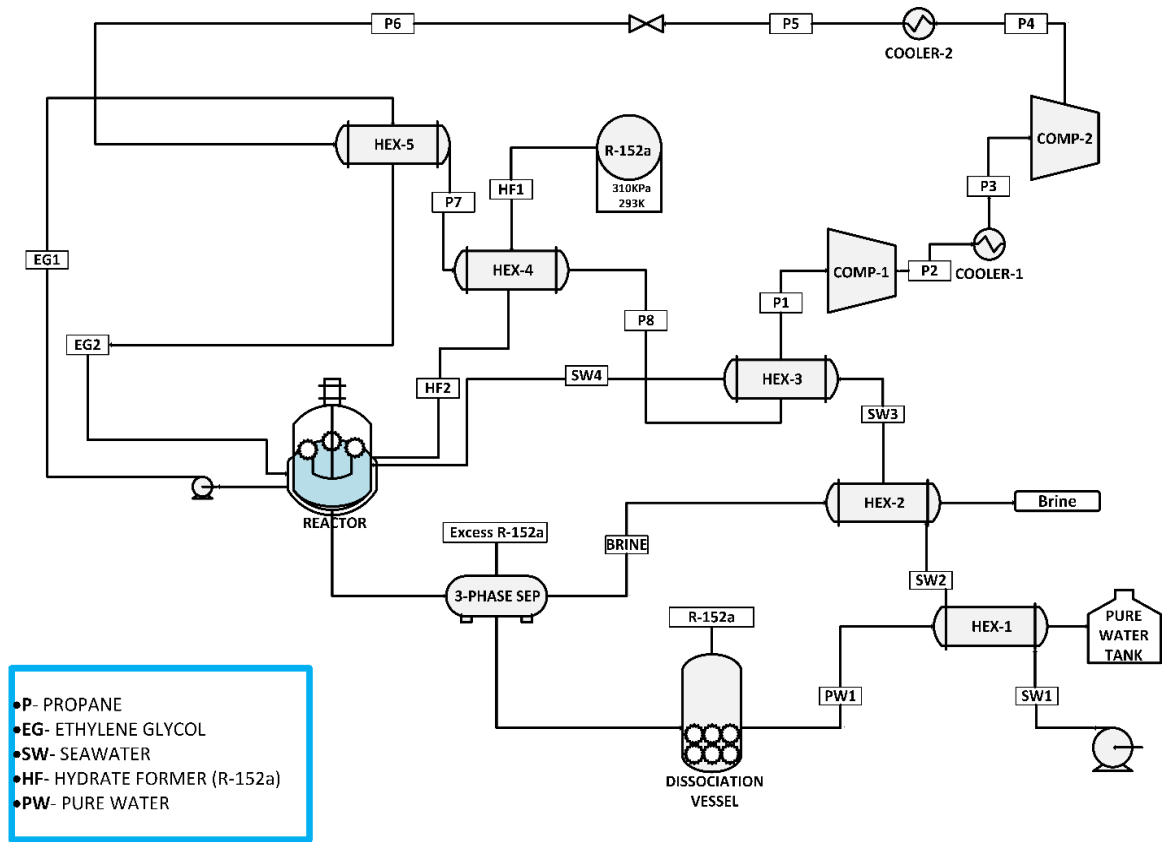


Figure 14 Refrigerant hydrate based desalination

4.3 Proposed Integrated RHBD-DEAB system

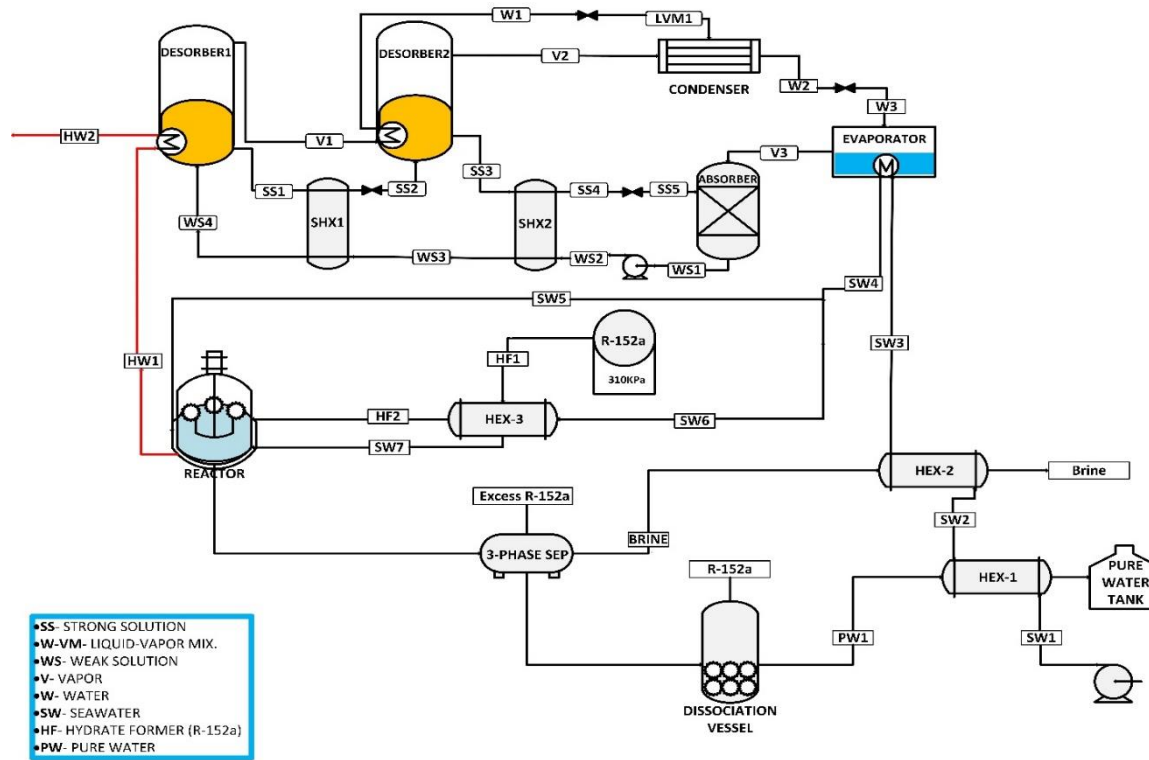


Figure 15 Integrated DEAB-R-HBD process

The integrated system consists of a dual-effect absorption refrigeration system (DEAB) coupled with a Refrigerant Hydrate-Based Desalination system (RHBD). The primary objective of this combined system is to significantly reduce energy consumption across the entire plant, thereby creating a more sustainable approach to its design and operation. Utilizing the exothermic heat released during hydrate formation (82.2 kJ per mole of R-152a), the DEAB system efficiently utilizes this heat to power the absorption refrigeration cycle. In the DEAB system, there are two desorbers (Generators) operating under different conditions, along with a condenser, evaporator, absorber, two solution heat exchangers, four throttling valves, and a pump.

The working fluid for the cycle is chosen to be 54% Water/LiBr solution [21], it is thermodynamically stable, operates at low pressure and there is no risk for leakage because the refrigerant is water vapor, unlike the ammonia water systems which possess the risk of ammonia leakage during operation. Desorber1 containing a Water/LiBr concentrated solution runs by the thermal energy supplied by the Hot water stream at 134°C (HW1), this vaporizes the solution producing two streams V1 and SS1. The concentrated strong solution (SS1) is preheated in a solution heat exchanger (SHX1) and passes through a throttling valve to match the pressure of the second desorber. In Desorber2, the depressurized strong solution (SS2) is heated again by the vapor stream(V1) produced from Desorber1, implying the cooling and condensation of V1 steam to produce water (W1). (W1) is depressurized to meet the condenser pressure, this depressurization increases the vapor fraction content forming Vapor liquid water state. (VLM1). The process occurring in Desorber2 leads to a more concentrated solution SS3 by producing further vapor (V2), both the (VLM1) and (V2) streams enters the condenser where heat is dissipated to the surrounding producing water (W2). The condenser effluent W2 passes through a throttling valve to reach the evaporator pressure. The evaporator serves as the cooling space within the absorption refrigeration cycle primarily because the process of evaporation necessitates energy. This energy is acquired by the evaporator through a heat exchange mechanism, where a stream releases heat to facilitate the conversion of liquid water (W3) into water vapor (V3). As the water vaporizes, it absorbs thermal energy from its surroundings, leading to a cooling effect within the evaporator space. This vapor is then absorbed to weaken the strong solution (SS5). After absorption occurs, the produced weak solution (WS1) is pressurized to meet the pressure of Desorber1, it is also pre-heated by the

incoming strong solution SS1 and SS3 (the outlets of Desorber1 &2 respectively) in two consecutive unmixed heat exchangers reaching the state of WS4 where it is regenerated again and the cycle continues.

According to the Air-Conditioning, Heating, and Refrigeration Institute (AHRI) standards the evaporator chilled water enters the evaporator at 285 K (12 °C) and leaves at 280 K (7 °C) [102]. The evaporator inlet stream (SW3) achieve the inlet temperature constraints by being pre-cooled in HEX-1 and HEX-2 by both pure water and brine respectively, and further cooled by a cooling utility as mentioned in section 2.2 . The cooled stream (SW4) splits into two streams (SW5) and (SW6). (SW6) , the reaction feed is at 280 K and the hydrate formation reaction runs at 283K, to make use of this change in temperature it is used to cool R-152a feed in HEX-3, where the both enters the hydrate formation vessel at the required condition. (SW5) is directed to control the temperature of the reactor by absorbing the heat emitted during the reaction; hence preventing hydrate crystal dissociation, this heat exchange produces very hot pressurized water (135 °C, 300 kPa) which runs Desorber1, vaporizing the 54% LiBr solution. In this integrated process, there are three sources of waste heat: condenser, absorber and the hydrate formation reactor.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Effect of using R-152a as a hydrate former

In this section, we solely examine the effect of altering the hydrate former while maintaining consistent vapor compression cycles and mole basis for a fair assessment with existing literature. We focus on comparing the efficiency of R-152a with methane. This comparison is limited to methane only because of the mole basis being the same as R-152a due to its widespread usage in existing literature, especially in cases where LNG cold energy was not utilized. [33] [103]

5.1.1 Energy Consumption

It is crucial to assess the performance of R-152a in comparison to other hydrate formers to determine its effectiveness. From the provided data, it is evident that R-152a significantly reduces energy consumption when compared to propane and methane. Specifically, R-152a leads to approximately a 76% reduction in energy consumption compared to propane (on the same basis of 10kmol of hydrate former)[33] , and a substantial 90% reduction compared to methane. The energy savings with methane are attributed to R-152a's ability to form hydrate crystals at a lower pressure (293K and 300 kPa) compared to methane's formation conditions (4000 kPa and 273K), which require more energy. Additionally, propane hydrates require more energy due to their lower formation temperature (274K) and the exothermic nature of their reaction compared to R-152a. This requires greater coolant usage to control reactor temperature, thereby increasing the cooling requirement to be

provided by the vapor compression cycle. Our energy analysis, which aligns with the previous studies on methane and propane, identifies compressors as the primary contributors to energy consumption in the vapor compression cycle. This prompts further evaluation of the process when integrated with dual-effect absorption refrigeration cycle.

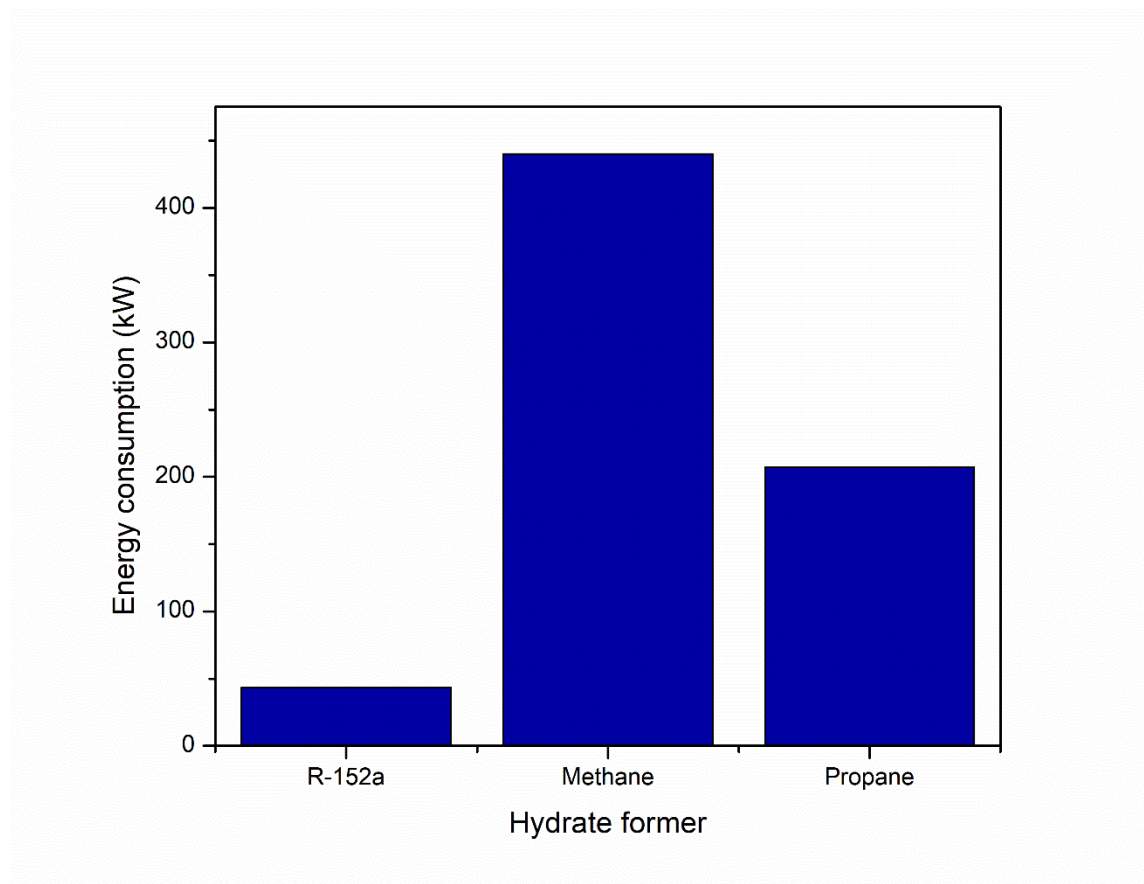


Figure 16 comparison of energy consumption with conventional hydrate formers

5.1.2 Specific energy consumption

$$SEC = \frac{\text{Total Work}}{\text{Volume of Pure water produced per hour}} \quad (10)$$

The specific energy consumption (SEC) serves as a crucial parameter for evaluating desalination unit performance, quantifying the energy required to desalinate 1 m³ of water. Previous studies, reported SEC values of 99.6 kWh/m³ when using methane [103] and 65.14 kWh/m³ when using propane as hydrate formers [33]. The study associated with methane assumes that it enters the process at 4000 kPa. As previously mentioned, the water transfer rate is 60% which means that 8.32 m³ of pure water are produced per hour from this process. With a significantly lower SEC of around 4 kWh/m³, R-152a demonstrates significant potential for commercialization.

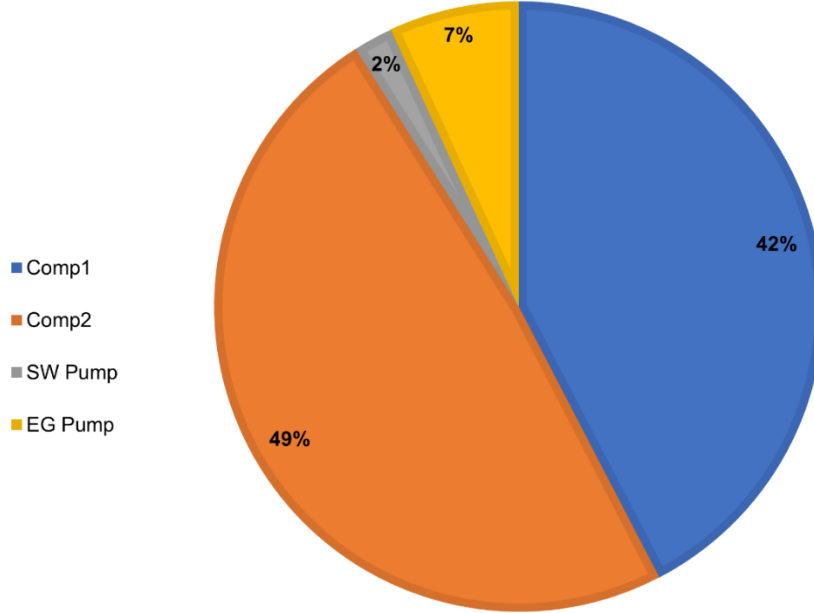


Figure 17 Energy consumption per equipment

5.2 Absorption refrigeration performance

5.2.1 Energy quantities of integrated systems

Table 5 below shows the thermodynamic results of the absorption refrigeration cycle used. The results shows that the pumping power is significantly low, which means that the total energy consumption of the integrated system is way lower than the case where vapor compression cycle is used for cooling; hence more sustainable process with lower CO₂ emissions. In addition as it can be seen, that both the absorber and condenser gives off heat which must be cooled to ensure smooth operation.

Table 5 Summary of energy quantities of DEAB process

Equipment	Heat transfer rate(kW)
Desorber 1	170.0
Desorber 2	93.66
Condenser	130.10
Evaporator	208.65
Absorber	271.0
SHX1	22.0
SHX2	99.03
Pump	0.177

Referring to the previous overview of the two integrated processes, It is evident that the cooling utility needed for the propane compression cycle (VCR-RHBD), particularly in the condenser and intercooling stages of the compressors, far exceeds the cooling utility required in the both the condenser and the absorber of DEAB (Fig. 18). Regarding electricity consumption, the integrated DEAB-RHBD system operates using waste heat from the hydrate formation reaction, with only the pumps requiring electricity (0.177 kW),

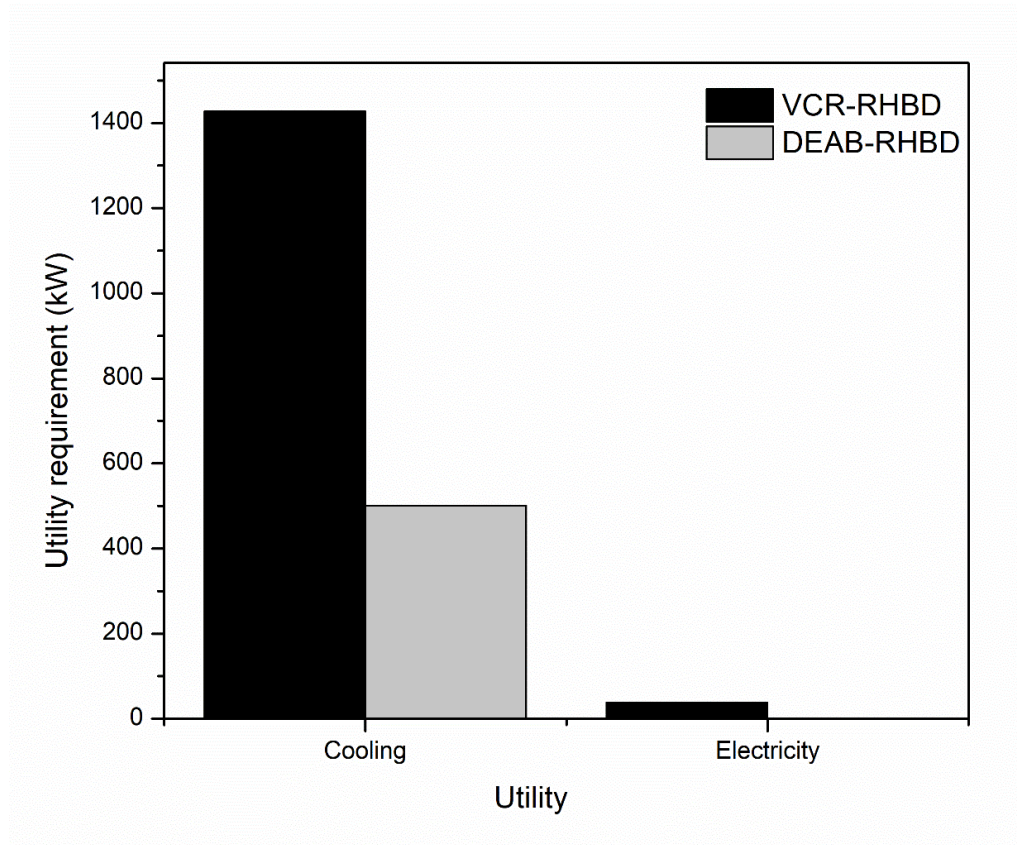


Figure 18 Utilities required by the RHBD-VCR and RHBD-DEAB processes.]

5.3 Economic Analysis

Considering the assumptions mentioned previously, the total annualized cost is to be calculated for the novel proposed dual-effect integrated process and the base case of Propane refrigeration VCR cycle. Fig. 19 shows the breakdown of the total capital

investment showing that VCR-RHBD process has higher capital cost than DEAB-RHBD. The Purchasing capital cost is calculated as 4.54 M\$/y and 4.71 M\$/y for the VCR-RHBD and DEAB-RHBD, respectively. The working fluids, coolants and hydrate formers used as raw materials are considered in the capital cost as no leakage is assumed. Also, because the hydrate former is insoluble in water so it is recycled and used again in the process. The cost of raw materials of VCR-RHBD nearly doubles that of DEAB-RHBD. This difference arises primarily from the additional materials required in the VCR-RHBD process, such as propane and ethylene glycol, alongside the hydrate former. Conversely, the DEAB integrated system necessitates only the hydrate former and a small quantity of working fluid (Water–LiBr). Total annual cost (TAC) has been calculated based on the assumptions shown earlier and the estimation of CAPEX and OPEX. The results show that VCR-RHBD has a higher TAC of 0.46 M\$/y compared to DEAB-RHBD, which has TAC of 0.31 M\$/y. This results in a total product cost of \$4.31/ m³ and \$6.39/m³ for DEAB-RHBD and VCR-RHBD respectively. Utilizing R-152a as a hydrate former lead to a reduction in the product cost when compared to conventional hydrate formers[32,104]. In addition, integrating our RHBD system with DEAB often lead to an additional 44% reduction in the product cost. Limitations like small scalability and low production capacity accompanied with RHBD technology remain a barrier. This is why research in areas of kinetics are emerging to increase the hydrate former conversion rate and hence increasing the water production.

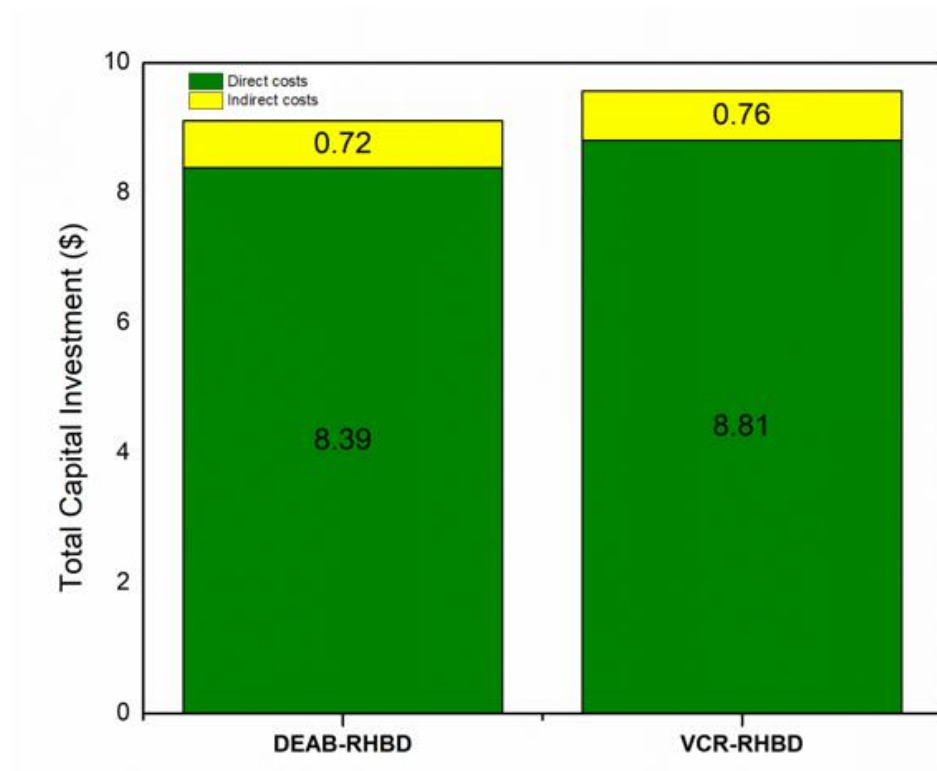


Figure 19 Total Capital investment breakdown

The operating costs of the previously mentioned integrated processes are compared (Fig. 19.), revealing that the total operating cost of VCR-RHBD exceeds that of DEAB-RHBD by 30%. This difference arises primarily from the utility cost of the base case amounts to 0.232 M\$/y, which is five times higher than the 0.063 M\$/y utility cost of DEAB. This is primarily due to the energy-intensive nature of propane condensation in the base case, which demands cooling utilities at lower temperatures compared to the cooling utilities

required by DEAB. Additionally, the base case incurs electricity expenses, which are eliminated in the DEAB-RHBD case as thermal energy serves as the primary driving force.

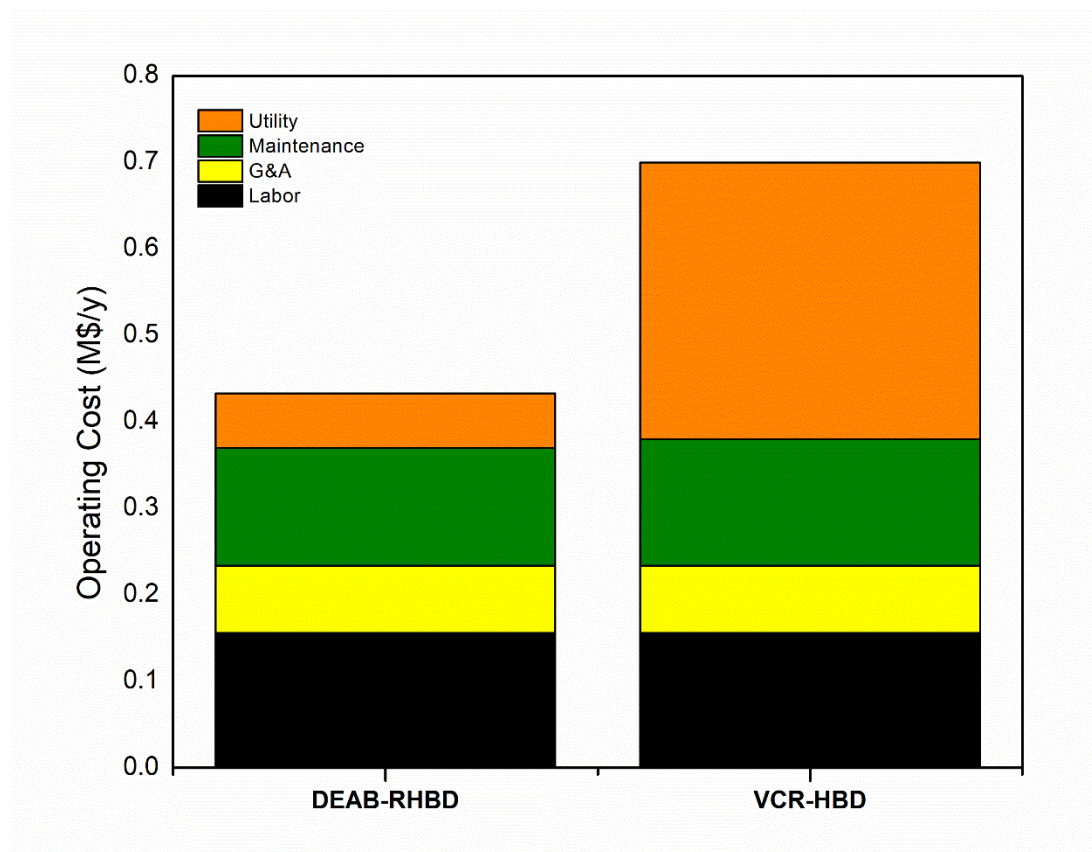


Figure 20 Operating expenses

Figs. 20a and b show the cost analysis of both the VCR cycle and DEAB, underlining which equipment is the highest contributor for their respective costs. For DEAB, the costliest equipment tends to be HEX-1. This is reasonable, since 1400 kmol/h of seawater is pre-heated by 504 kmol/h of pure water at a minimum approach temperature of around 2 K. Such huge flowrates and low minimum temperature approach lead to a high surface area affecting the cost drastically. On the other hand, for the vapor compression cycle it is clear why HEX-5 dominates the share of total capital investment, this is because of the coolant Ethylene glycol which is continuously cooled to at a flowrate of around 3388 kmol/h, such flowrate requires huge heat transfer area which in turn affects the capital cost.

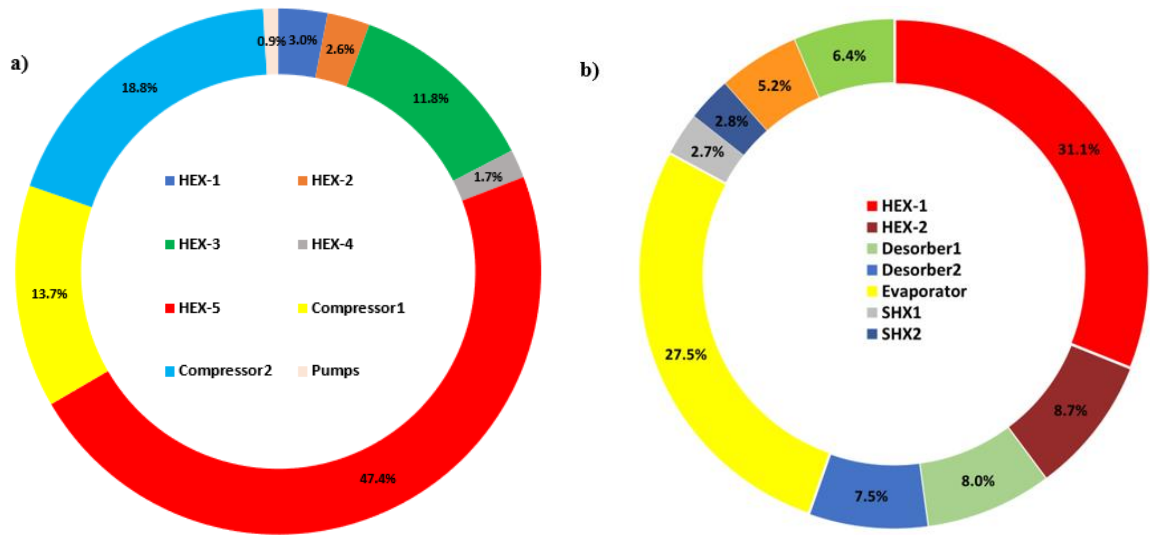


Figure 21 (a) VCR equipment shares in TCI; (b) DEAB's equipment share in TCI.

5.3 Environmental analysis

Given that the absorption refrigeration cycle runs on electricity to supply energy for both the generator and pumps, this integrated system utilizes the waste heat from the hydrate formation reaction to run the absorption refrigeration cycle, creating a fully integrated system. However, both the process of absorption and condensation in DEAB requires continuous cooling which is provided by a cooling utility. On the other hand, the R-HBD process where vapor compression refrigeration cycle (VCR) is the refrigeration system, it requires cooling between the compressor stages to ensure a sufficient cooling operation for the feed of the hydrate formation reaction. Figure 6 below shows the environmental analysis in terms of CO₂ emissions in ton/day. It clearly shows that using DEAB as the refrigeration cycle for hydrate based desalination reduces the CO₂ emissions by 72%. The percentage reduction can even be higher if the waste heat from both the absorber and condenser to run a direct contact membrane [73], or the hot water outlet from the generator which can be further utilized in steam generation and/or electricity production. Integrating

DEAB with Refrigerant hydrate based desalination process offers a more sustainable solution, addressing both energy efficiency and environmental considerations.

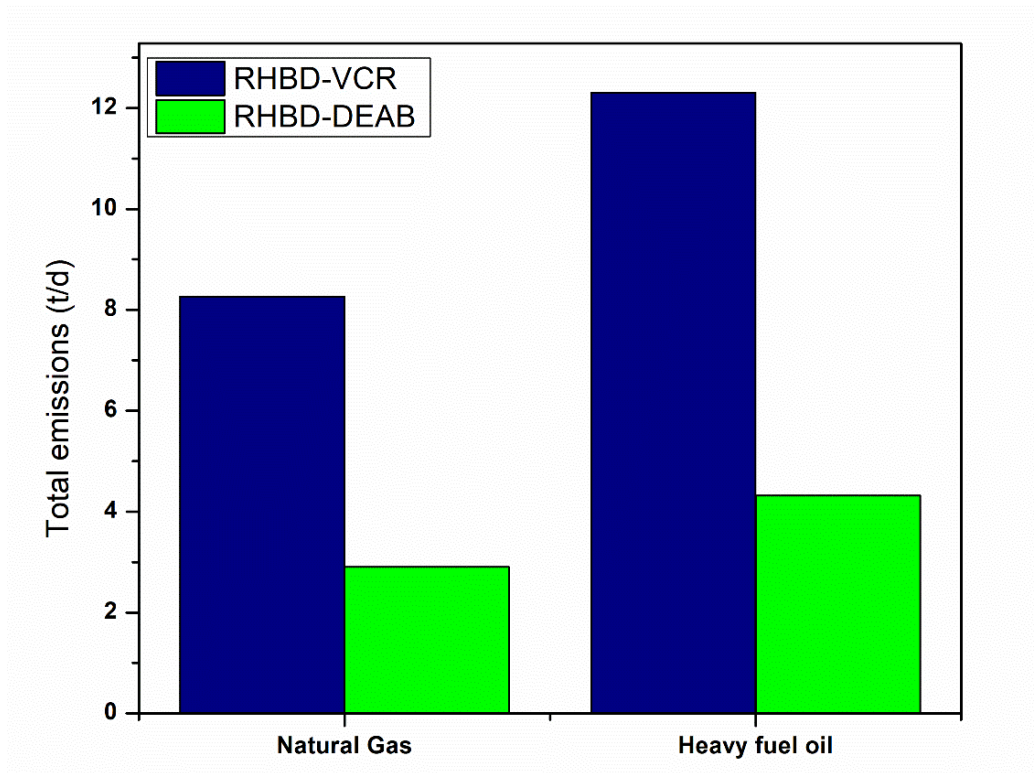


Figure 22 Environmental analysis of integrated processes

5.4 SENSITIVITY ANALYSIS

5.4.1 Absorption refrigeration system

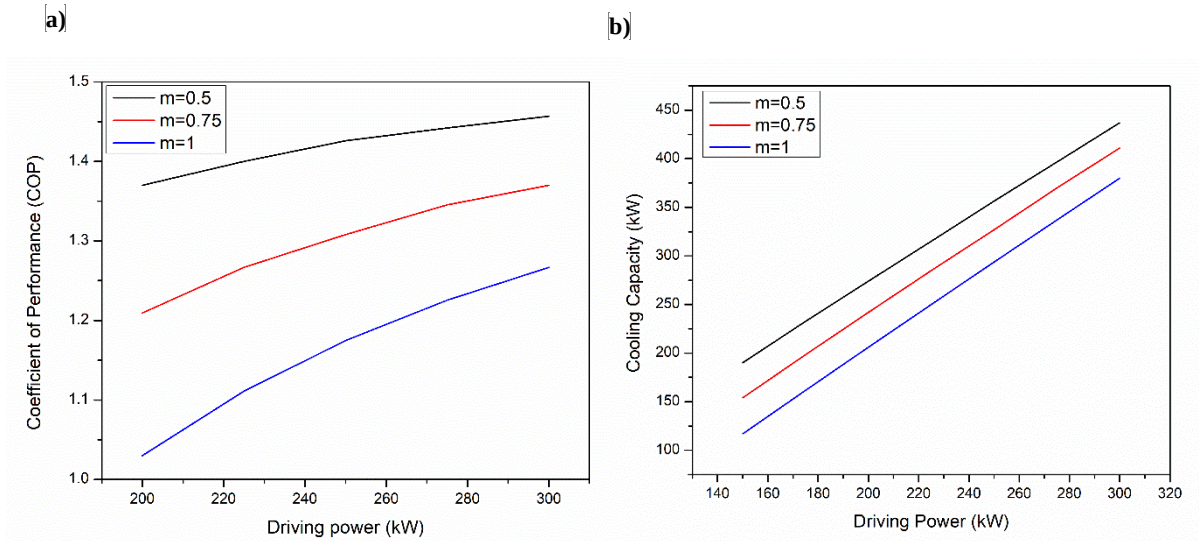


Figure 23 shows the effect of driving power on (a) performance; (b) cooling capacity

Referring to the figures above it can be clearly shown that the driving power which is supplied by the heat source plays a crucial role in determining the performance of the absorption refrigeration cycle. Figure 9 (b) shows that as the driving power in the generator (desorber) increases, the cooling capacity gets higher, and this is reasonable due to the fact that more water vapor is generated from the Water/LiBr solution at higher driving power; this vapor is then condensed and evaporated in the evaporator (higher evaporator duty means higher cooling capacity). Figure 9(a) is related to figure 9(b); as the cooling capacity increases the coefficient of performance COP increases. It can be clearly shown from the figures that lower cooling capacities and COP are associated with the flowrates.

5.4.2 Hydrate formation process

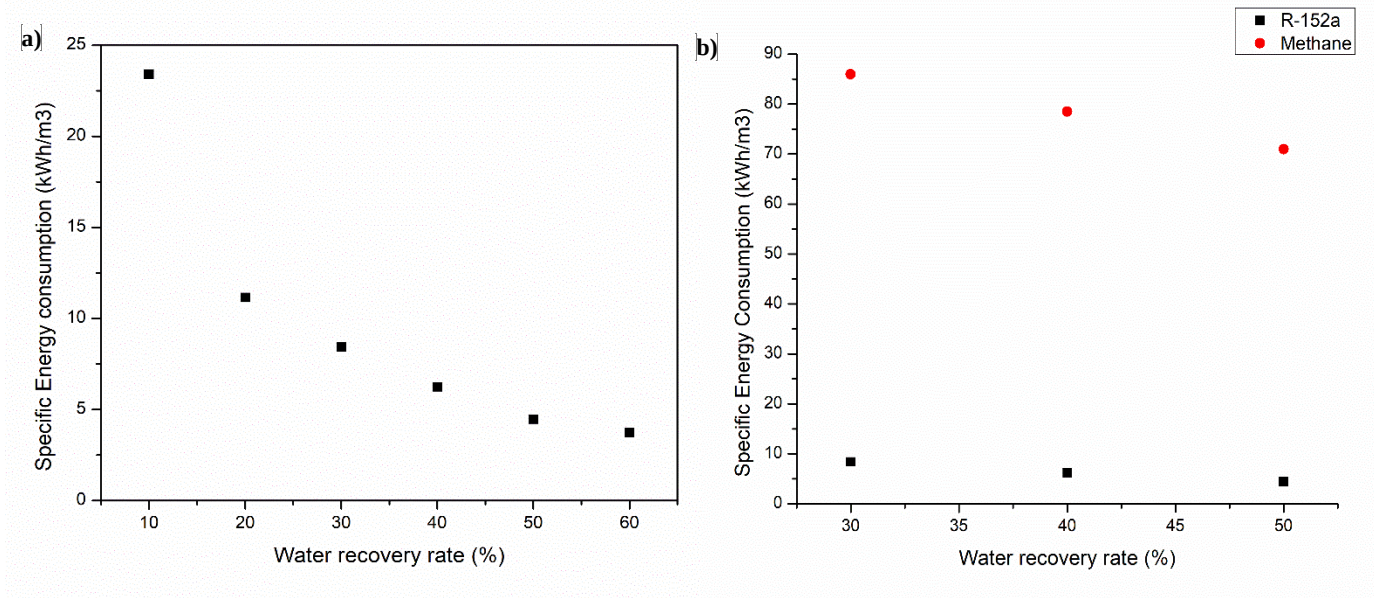


Figure 24 Water recovery rate vs SEC for a) R-152a ; b) R-152a VS Methane

Referring to the figures above, it can be clearly shown that the specific energy consumption decreases as the water recovery rate increases. Water recovery rate explains the conversion of water to hydrate. In this study it was taken at 60%. Given that Specific energy consumption is inversely proportional to fresh water produced, this relationship is reasoned by the fact that as water recovery rate increases, more water is produced which in turn decreases specific energy consumption. By taking a look at figure 10 b, both hydrate formers show the same trend however, the specific energy consumption values when methane is used is way higher than R-152a; this proves R-152a as a strong contender when it comes to hydrate formation.

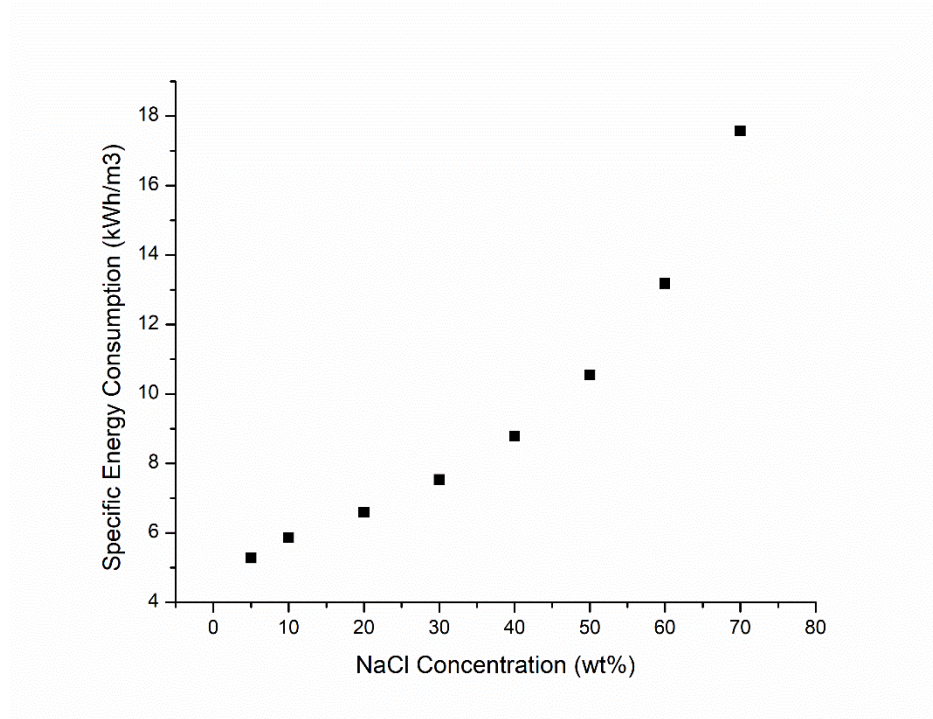


Figure 25 SEC VS water salinity

Analyzing the impact of sea water salinity, particularly the concentration of NaCl, on specific energy consumption (SEC) is crucial. In the study, a range of NaCl concentrations from 10% to 70% were examined. According to Figure 11, there is a clear trend: as the concentration of NaCl rises, SEC also increases. This can be attributed to the fact that as the concentration of salts increases, the production of water per hour decreases. Consequently, more energy is required per cubic meter of water produced.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The utilization of R-152a as a hydrate former in the desalination process represents a significant leap forward in efficiency and sustainability. The formation of hydrate crystals at higher temperatures and lower pressures results in remarkable water transfer rates, achieving a significant reduction in SEC to 4 kWh/m³. These advancements position R-152a as a highly promising candidate for commercialization, surpassing methane, and propane by 90% and 70%, respectively, in terms of energy efficiency within the VCR cycle.

Energy analysis identifies compressors within the refrigeration cycle as the primary contributors to overall energy consumption. To pursue lower energy consumption and a more sustainable approach, the integration of an absorption refrigeration cycle presents a compelling solution. By incorporating the dual-effect absorption refrigeration cycle, CO₂ emissions are reduced by 65%. Moreover, the dual-effect absorption refrigeration cycle proves advantageous in terms of reducing both operating and capital costs. The precooling of the feed enables a reduction in equipment size requirements, resulting in a more cost-effective system.

Furthermore, the proposed integrated process offers the potential for utilizing waste heat from the absorber and condenser, as well as providing hot water (outlet of desorber). These heat sources can be effectively employed to run a direct contact membrane distillation

system and a humidification-dehumidification desalination system. Additionally, the hot water can be utilized for steam generation, which can then be used to generate electricity.

Overall, the combination of R-152a as a hydrate former and the integration of a dual-effect absorption refrigeration cycle displays significant advancements in desalination efficiency, sustainability, and cost-effectiveness. This research opens possibilities for further exploration in utilizing waste heat and expanding the application of the integrated process in various desalination technologies, ultimately contributing to the development of more efficient and environmentally friendly solutions to address freshwater scarcity.

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APPENDIXA: CALCULATING REQUIRED COOLING AND THE HEAT OF REACTION

This Appendix is considered as a summary for the overall process. According to the process description, the hydrate-based desalination process requires cooling which have high operational cost. In this process cooling is required in 3 parts:

1. Heat dissipated from exothermic reaction to prevent hydrate crystal dissociation
2. Pre-cooling of seawater
3. Pre-cooling of propane

The basis of calculation is based on unit of seawater feed. The heat capacities of various streams are retrieved from HYSYS simulator as the average value between the inlet and outlet streams. For 770 kmol/hr of seawater as basis:

$$m_{R-152a} = 770 \frac{\text{kmol}}{\text{hr}} \cdot H_2O \times \frac{66.05 \text{ kg} \cdot R-152a}{7.7 \text{ kmol} \cdot R-152a} = \frac{100 \text{ kmol}}{\text{hr}} = 6605 \text{ kg of R-152a}$$

The heat of formation of R-152 hydrates is -82.2 kJ/mol of R-152a. Converting the heat of formation into the mass of water:

$$\Delta H_f = -82.2 \frac{\text{kJ}}{\text{mol} \cdot R-152a} \times \frac{1 \text{ mol} \cdot R-152a}{7.7 \text{ mol} \cdot H_2O} \times \frac{1 \text{ mol} \cdot H_2O}{18 \text{ g} \cdot H_2O} \times \frac{1000 \text{ g} \cdot H_2O}{1 \text{ kg} \cdot H_2O} = -539.1 \frac{\text{kJ}}{\text{kg} \cdot H_2O} \times 3.85 \frac{\text{kg} \cdot H_2O}{\text{s}} = 2080 \text{ kJ/s}$$

With 60% water recovery, the amount of heat removed in per kg of seawater is

$$\Delta H_1 = 2080 \frac{\text{kJ}}{\text{s}} \times 0.6 \text{ kg} = \frac{1284 \text{ kJ}}{\text{s}}$$

To remove this, two coolants are proposed, in the **propane refrigeration cycle**, Ethylene glycol was used to remove the heat, the number of moles required per kg of sea water is given that delta T is 10:

$$\frac{1284 \text{ kJ/s}}{10 * 2.2} = 58,36 \frac{\text{kg}}{\text{s}} * \frac{\text{kmol}}{62 \text{ kg}} * 3600 = 3388 \text{ kmol/hr}$$

For the Dual effect absorption refrigeration cycle:

1kg/s of the Water leaving the evaporator is used to cool the reactor As mentioned previously, water leaves the cooling space (evaporator) at 7°C and 3 bar. After absorbing the heat dissipated from the exothermic reaction, the temperature is increased to 134°C:

The energy required for cooling of 1 kg seawater feed from 293 K to 282 K is:

$$\Delta H_2 = 1 \text{ kg} \times 4.47 \frac{\text{kJ}}{\text{kg.K}} \times (293 - 282) \text{ K} = 49.17 \text{ kJ}$$

The energy required for cooling stoichiometric amount of refrigerant R-152a from 293 K to 282 K is:

$$\Delta H_3 = 0.477 \text{ kg} \times 1.25 \frac{\text{kJ}}{\text{kg.K}} \times (293.1 - 282.1) \text{ K} = 5.96 \text{ kJ}$$

Therefore, the summation of energy for the overall process is:

$$\Delta H_{req} = \Delta H_1 + \Delta H_2 + \Delta H_3 = \mathbf{410.6 \text{ kJ}}$$

Some energy can be **recovered** from brine and pure water after hydrate crystal dissociation.

Given that 60% of water is converted to hydrate, 40% of brine (i.e. ~0.4 kg of brine)

remains in the solution and the energy recoverable from brine after hydrate formation reaction is:

$$\Delta H_4 = 0.4kg \times 4.579 \frac{kJ}{kg.K} \times (290.1 - 282.1)K = 17 kJ$$

After hydrate dissociation, the cold energy from pure water stream can also be recovered to decrease the cooling load.

$$\Delta H_5 = 0.6kg \times 4.32 \frac{kJ}{kg.K} \times (290.1 - 282.1)K = 23.3kJ$$

Therefore, the cold energy recoverable from brine and pure water streams are:

$$\Delta H = \Delta H_4 + \Delta H_5 = \mathbf{40.3 kJ}$$

APPENDIX-B: STREAM DATA

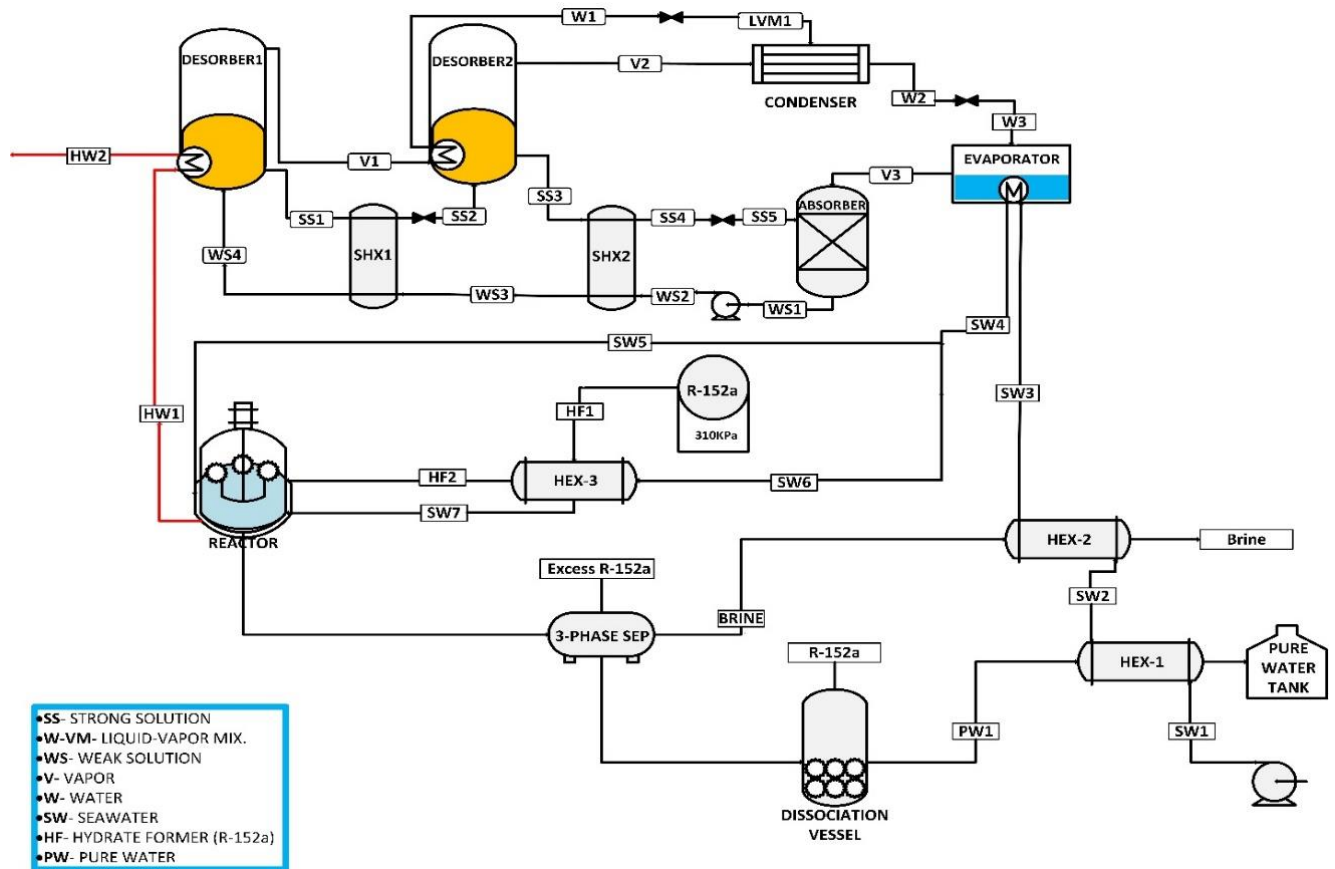


Table 6 shows the streams data of the proposed integrated DEAB-RHBD process

STREAM	T(K)	P(KPa)	Flowrate(kg/s)	Concentration	Vapor quality
SW1	293	315	8	5wt% NaCl	0
SW2	288	310	8	5wt% NaCl	0
SW3	286	305	8	5wt% NaCl	0
SW4	280.5	305	8	5wt% NaCl	0
SW5	280.5	300	1	5wt% NaCl	0
SW6	280.5	300	3.8	5wt% NaCl	0
SW7	280.5	8.75	3.8	5wt% NaCl	0
HW1	280	300	4	5wt% NaCl	0
HW2	406	300	4	5wt% NaCl	0.19
HF1	293	310	1.833	99.9% R-152a	-
HF2	283	300	1.833	99.9% R-152a	-
SS1	413.15	77.046	0.988	0.57 (LiBr)	-
SS2	343.463	4.3550	0.988	0.57 (LiBr)	-
SS3	343.71	4.355	0.962	0.624(LiBr)	-
SS4	329.02	4.355	0.962	0.624(LiBr)	-
SS5	323	0.874	0.962	0.624(LiBr)	-
WS1	301.4	0.874	1	0.54(LiBr)	-
WS2	301.46	4.4	1	0.54(LiBr)	-
WS3	326.23	4.4	1	0.54(LiBr)	-
WS4	371.21	77.046	1	0.54(LiBr)	-
V1	406	77.046	0.012	-	1
V2	343.56	4.355	0.025	-	1

V3	278.89	0.874	0.037	-	1
W1	365.65	77.076	0.012	-	0
W2	303.52	4.355	0.037		0
W3	278	0.874	0.037	-	0.043
LVM1	303.52	4.355	0.012		0.107
BRINE	291	300	1.2	-	-
PW1	282	300	2.5	-	-
Pure water tank	293	300	-	-	-

The rest of the chilled sea water can be stored in tanks to be used further as a cooling utility.

APPENDIX C: ECONOMIC AND ENVIRONMENTAL ANALYSIS

ECONOMIC RESULTS

Table 7 shows the cost of heat exchanges for the VCR-RHBD integrated system

	CB	FD	FM	TOTAL (1982)	CEPCI(2024)/CEPCI(1982)	CAPITAL COST
HEX-1	\$5,923.93	0.51	2.01	6104.74	2.54	\$15,476
HEX-2	\$5,403.61	0.50	1.95	5268.40	2.54	\$13,356
HEX-3	\$15,720.39	0.61	2.47	23751.80	2.54	\$60,212
HEX-4	\$4,323.63	0.46	1.76	3529.13	2.54	\$8,947
HEX-5	\$48,238.10	0.70	2.82	95737.56	2.54	\$242,698
Total Heat exchangers capital cost associated with VCR						\$340,694

Table 8 shows the cost of heat exchangers associated with DEAB integrated system

	CB	FD	FM	TOTAL (1982)	CEPCI(2024)/CEPCI(1982)	CAPITAL COST
HEX-1	\$11,451.09	0.58	2.34	15656.82	2.54	\$39,691
HEX-2	\$4,862.02	0.48	1.87	4402.49	2.54	\$11,161
Solution Heat exchanger-1 (SHX1)						\$2,640
Solution Heat exchanger-2 (SHX2)						\$3,405
Total Heat exchangers capital cost associated with DEAB						\$56,896

Table 9 shows the cost of main components of the hydrate-based desalination

Equipment	CAPITAL COST
HYDRATE REACTOR	\$1,960,313
DISSOCIATION VESSEL	\$1,960,313
THREE PHASE SEPARATOR	\$350,000
TOTAL CAPITAL COST	\$4,270,627

ENVIRONMENTAL ANALYSIS DATA

Equipment	Q _{proc} (kW)	Q _{fuel} (kW)	NHV (kJ/kg)	C %	CO ₂ Emiss (kg/s)	CO ₂ Emiss (t/d)
<i>VCR-RHBD(NG)</i>						
Whole scheme <i>DEAB-RHBD (NG)</i>	1427	1783.75	51600	75.4	0.095658088	8.26
Whole scheme	501	626.25	51600	75.4	0.033584234	2.90

Equipment	Q _{proc} (kW)	Q _{fuel} (kW)	NHV (kJ/kg)	C %	CO ₂ Emiss (kg/s)	CO ₂ Emiss (t/d)
<i>VCR-RHBD (HFO)</i>						
Whole scheme <i>DEAB- RHBD (HFO)</i>	1427	1783.75	39771	86.5	0.142380216	12.30
Whole scheme	501	626.25	39771	86.5	0.049987728	4.32

APPENDIX D: SUMMARY OF SIMULATION DETAILS

Operating Conditions and Input parameters
Vapor compression refrigeration cycle
• HEX $\Delta T_{min} = 2$ • Isentropic Compressors efficiency: 75% • Propane conditions: 250 kmol/hr at 293K and 300 KPa • Intercoolers between compressors: 293K
Hydrate formation reactor
• Temperature = 283 K • Pressure = 300 KPa • H₂O/ R-152a (mol./mol.) = 7.7 [50] • Water transfer rate = 60% [53]
Absorption Refrigeration Cycle[95–97]
• Heat source: Hot water at 134 °C at a rate of 1 kg/s • $U_{EVAP} = 1.5 \text{ kW/K.m}^2$ • $U_{Absorber} = 0.7 \text{ kW/K.m}^2$ • $U_{Desorber1,2} = 1.5 \text{ kW/K.m}^2$ • $U_{Condenser} = 2.5 \text{ kW/K.m}^2$ • $U_{SHX1,2} = 1 \text{ kW/K.m}^2$ • Other heat exchangers are taken at a minimum temperature of approach of 2 • Evaporator exit and inlet temperatures are 12 and 7 °c respectively. [72,102]
Feed Conditions
Sea water: 770 kmol/hr at ambient conditions (293 K and 101.3KPa) Hydrate former (R-152a) : 110 kmol/hr at (293 K and 310 kPa) Ethylene Glycol: 3388 kmol/hr for a temperature change of 10 °C LiBr solution of DEAB: 1kg/s

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