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The experimental study of the CO₂ hydrates formation

By

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Statement

I declare that I have worked out this thesis independently assuming that the results of the thesis can also be used at the discretion of the supervisor of the thesis as its co-author. I also agree with the potential publication of the results of the thesis or of its substantial part, provided I will be listed as the co-author.

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Signature

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Abstract

Clathrate hydrates, complex molecular formations with significant potential in the energy sector, are the focal point of this thesis. These compounds are increasingly recognized for their versatile applications, including carbon capture and storage, renewable energy sources, water desalination, and gas mixture separation. In the context of contemporary environmental challenges, particularly global warming, clathrate hydrates, especially those in the seabed, have garnered attention due to the risk of methane release—an extremely potent greenhouse gas—into the atmosphere.

This thesis aims to comprehensively review the existing body of knowledge surrounding clathrate hydrates, exploring their potential applications and the advancements in reactor technology that facilitate their study and utilization. A significant portion of this research is devoted to the construction and implementation of an experimental setup designed to observe and analyse the crystallization process of CO_2 hydrates. Through detailed observation and documentation of this process, the study seeks to deepen the understanding of hydrate formation dynamics. This insight is crucial for harnessing the potential of clathrate hydrates in various industrial applications and for mitigating their environmental impact, particularly in relation to climate change and greenhouse gas emissions.

By bridging gaps in current knowledge and exploring innovative experimental methodologies, this thesis contributes to the broader scientific understanding of clathrate hydrates, underscoring their significance in both environmental and energy contexts.

Contents

1.Introduction

1.1   Motivation

Clathrate hydrates, often referred to as gas hydrates, are fascinating crystalline structures formed when water molecules trap guest molecules within their cages. These guest molecules can be most gases, for example methane, ethane, carbon dioxide, hydrogen sulphide or nitrogen. This results in formation of solid compounds with distinct properties [1]. The study of clathrate hydrates has garnered significant attention due to their abundance in nature and their potential as an energy resource, as well as their implications in environmental and industrial processes.

One fundamental aspect that plays a crucial role in understanding clathrate hydrates is the process of crystallization. The crystallization rate, in particular, provides insights into the kinetics and dynamics of clathrate hydrate formation. By examining the factors influencing crystal nucleation, growth, and stability, researchers can gain a deeper understanding of the mechanisms governing the formation and behaviour of these complex structures.

The crystallization rates of clathrate hydrates are influenced by various parameters, such as temperature, pressure, guest molecule composition, and water structure [1]. Understanding the interplay between these factors is essential for predicting the occurrence and stability of clathrate hydrates in different environments, including natural gas reservoirs, permafrost regions, and marine sediments. Moreover, the crystallization rates have practical implications in numerous industries, including energy production, carbon capture and storage, and flow assurance in oil and gas pipelines.

Despite the significance of crystallization rates in the study of clathrate hydrates, there remain several challenges and knowledge gaps that warrant further investigation. The dynamics of crystal nucleation and growth, the role of impurities and additives, and the influence of confinement on crystal formation are among the areas that require a deeper understanding to develop more accurate models and predictive tools.

This bachelor thesis aims to contribute to the existing body of knowledge by investigating the crystallization rates of clathrate hydrates with various impurities and additives. By conducting experimental studies, we seek to explore the effects of various parameters on the nucleation and growth rates of clathrate hydrates. The results obtained from this research hopefully enhance our fundamental understanding of clathrate hydrates but also have practical implications in the design and optimization of clathrate-related technologies.

Overall, this thesis endeavours to shed light on the intricate processes involved in the crystallization rates of clathrate hydrates. By investigating the underlying mechanisms and factors governing their formation, this research aims to contribute to the broader scientific understanding of clathrate hydrates and their potential applications in energy and environmental fields.

2.Theoretical Background

2.1 Clathrate Hydrates

Pure water exhibits solidification at a temperature of 0°C and a pressure of 1 bar, while pure chlorine gas solidifies at -101°C under the same pressure conditions [2]. Notably, in 1811, it was observed that a solution of oxymuriatic gas (chlorine) in water freezes more readily than pure water. This intriguing phenomenon extends beyond chlorine-water solutions, as various aqueous solutions containing small nonpolar or moderately polar atoms or molecules, such as xenon, bromine, iodine, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, and ethane, also display an increased solidification temperature. The application of higher pressures to these gas-water solutions raises the temperature at which solidification occurs. For instance, at 50 bar, a methane-water solution solidifies at approximately 8°C [1]. This solidification process arises from the entrapment of gas molecules or atoms within a three-dimensional lattice network of water molecules known as a clathrate hydrate. Clathrate hydrates encompass various cage structures with different types, sizes, and geometries, and they are named based on the trapped molecule, such as methane clathrate hydrate when methane is trapped. The interaction between the hydrate and the enclosed molecule occurs through non-covalent van der Waals forces.[1]
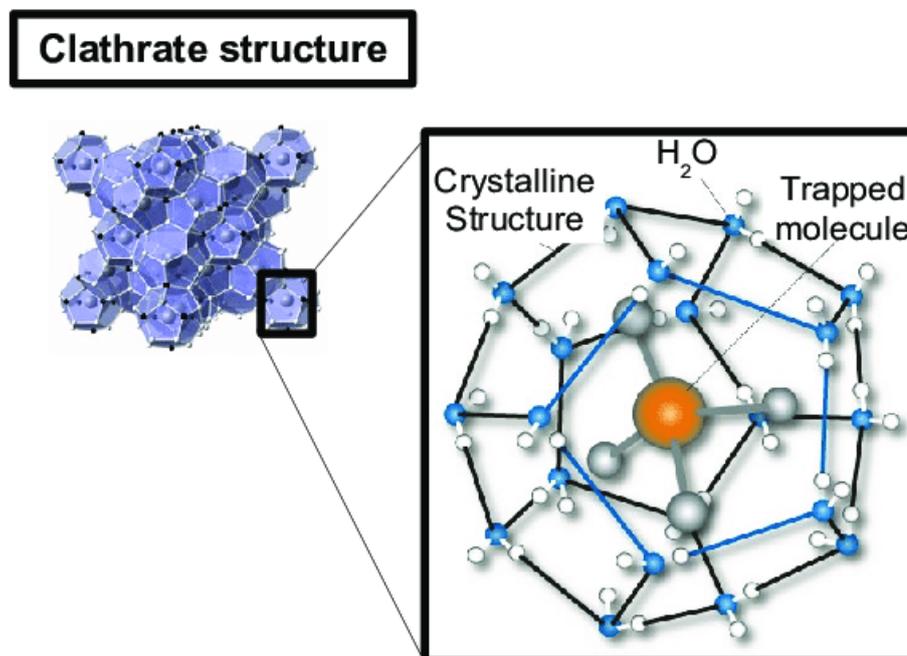

Figure 1 - Structure of Clathrate Hydrate [3]

The scientific exploration of clathrate hydrates traces its origins back to 1811, when Sir Humphrey Davy initially investigated and identified clathrates comprising solidified gas mixtures. In 1823, Michael Faraday conducted a study on fluid chlorine, providing the earliest description of a substance that would later be referred to as a hydrate [2]. These pioneering studies laid the groundwork for the subsequent discovery of hydrates responsible for obstructing natural gas transmission pipelines. Since then, the petroleum industry has invested significant resources into developing technologies for detecting and removing solid-state gas hydrates from pipelines, either by dislodging them or preventing their formation. Recent years have revealed vast quantities of methane stored within these hydrates in seabed and permafrost regions, presenting both an opportunity for novel electricity production and a looming climate catastrophe. Global warming has led to permafrost melting and increased ocean temperatures, which could result in the massive release of methane—an extremely potent greenhouse gas—into the atmosphere. Furthermore, studies have indicated that clathrate hydrates are widely distributed throughout the known universe. [1]

According to the International Union of Pure and Applied Chemistry (IUPAC), clathrates are inclusion compounds where guest atoms or molecules are confined within cages formed by host molecules or a lattice of host molecules. The interaction between the host and guest occurs via van der Waals or hydrogen forces. The term "clathrate" originates from the Latin word "clatratus," meaning grid or bar. Traditionally, in the realm of science and engineering, clathrates refer to materials composed of hosts (polymers) that trap guests (atoms or molecules). However, the meaning has expanded to encompass other molecular host systems, including calixarenes, cyclodextrins, and even inorganic polymeric systems like zeolites and chibaites [4]. Hofmann compounds and metal-organic frameworks (MOFs) can also serve as clathrates by hosting small aromatic guest molecules such as carbon tetrachloride, benzene, toluene, and xylene. Clathrates can be classified into two general types based on how the guest atoms or molecules are encapsulated by the host molecules. [4][5].

Molecular clathrate hydrates are a specific type of clathrate hydrates where each guest molecule is trapped within an individual cage formed by host water molecules. In these structures, the guest molecules are located at specific sites within the lattice of water molecules. The formation of these clathrate hydrates occurs when the guest molecules are small enough to fit into the available cage spaces. The host water molecules arrange themselves around the guest molecule, creating a stable and well-defined structure. The stability of molecular clathrate hydrates is maintained by the hydrogen bonding interactions between the water molecules and the guest molecules. [1]

Molecular clathrate hydrates can exist in both the liquid and solid states. In the liquid phase, the host and guest molecules remain mobile, and the cages are constantly forming and breaking. In the solid state, the structure becomes more rigid, and the cages retain their shape. This type of clathrate hydrates have been extensively studied due to their importance in various fields. They have applications in gas separation and gas storage, as they can effectively trap gases within their cages as well as they show

potential for being a material for gas transportation, especially for energy-related applications. [6] Furthermore, molecular clathrate hydrates have found applications in the fields of drug delivery and encapsulation. The ability to trap guest molecules within the cages of clathrate hydrates offers a unique way to protect and transport sensitive or reactive molecules. [5]

Lattice clathrate hydrates are another type of clathrate hydrates where the trapping sites for guest molecules are formed by multiple host molecules arranged in a lattice or array. In contrast to molecular clathrate hydrates, where each guest molecule is confined within an individual cage, lattice clathrate hydrates have a more extended network structure with interconnected cages. [5][7]. The lattice structure of these clathrate hydrates consists of water molecules forming a three-dimensional framework held together by hydrogen bonding. Within this lattice, cavities or cages are formed, which can accommodate guest molecules. The size and shape of these cages depend on the arrangement of the host water molecules, and different lattice clathrate hydrate structures can exist, each with its own unique cage size and geometry. [6]

The guest molecules in lattice clathrate hydrates are typically nonpolar or weakly polar gases, similar to those found in molecular clathrate hydrates. These guest molecules become trapped within the cages, stabilized by the van der Waals or hydrogen bonding interactions with the surrounding water molecules. [1]

These types of clathrate hydrates have significant implications in various fields. In the energy industry, lattice clathrate hydrates have been of particular interest due to their occurrence in natural gas reservoirs and their potential as a future energy source. They pose challenges in gas extraction and transportation, as the presence of these hydrates in pipelines can lead to flow blockages and operational issues. Furthermore, lattice clathrate hydrates have been investigated for their applications in gas storage and separation, as well as in catalysis and materials science. The unique properties of these structures, including their guest selectivity and tuneable pore sizes, make them promising candidates for various technological advancements.

2.2 Types of Clathrate Hydrates

Clathrate hydrates encompass a diverse range of structures, each associated with different guest molecules and host lattice arrangements. In order to properly understand the processes of crystallization it is crucial to understand types of structures that Clathrate Hydrates can form:

2.2.1 Structure I

Structure I clathrate hydrates, also known as sI clathrate hydrates is a specific type of clathrate hydrate structure that is characterized by a cubic lattice arrangement. They are the most extensively studied and commonly encountered clathrate hydrates. In Structure I clathrate hydrates, the host water molecules form a face-centred cubic lattice, creating a network of interconnected cages. These cages consist of two distinct sizes: small cages and large cages. The small cages are formed by 20 water molecules,

while the large cages are composed of 24 water molecules. The sizes of these cages are conducive to trapping guest molecules within their confines. [1]

The cubic lattice structure of Structure I clathrate hydrates enables the formation of an organized and stable framework, in which guest molecules, such as gases, occupy the cavities or cages. The guest molecules are held in place by van der Waals forces or hydrogen bonding interactions with the surrounding water molecules. [1]. Methane hydrate is a prominent example of Structure I clathrate hydrates, where methane gas molecules are trapped within the cages of the lattice. However, other guest molecules, such as ethane, propane, and carbon dioxide, can also form Structure I clathrate hydrates depending on the specific conditions of temperature and pressure. [4]

Structure I clathrate hydrates exhibit intriguing properties and behaviours due to their well-defined lattice structure. Their stability and physical properties are influenced by factors such as temperature, pressure, guest molecule composition, and the presence of impurities. Understanding the characteristics and behaviour of Structure I clathrate hydrates is essential for various applications, including energy exploration, gas storage, and environmental studies related to climate change and natural resource management. [1]

2.2.2 Structure II

Structure II clathrate hydrates, also known as sII clathrate hydrates, refer to a specific type of clathrate hydrate structure characterized by a cubic lattice arrangement distinct from Structure I clathrate hydrates. These hydrates exhibit unique properties and cage configurations, offering diverse hosting environments for guest molecules. [1]

In Structure II clathrate hydrates, the host water molecules form a cubic lattice structure with a different arrangement compared to Structure I. The cages in Structure II hydrates have a specific distribution of sizes, resulting in a distinct ratio of small cages to large cages within the lattice framework.

Guest molecules, typically nonpolar or weakly polar gases, are trapped within the cages of Structure II clathrate hydrates. The inclusion of guest molecules occurs through intermolecular forces, such as van der Waals interactions or hydrogen bonding, established between the guest molecules and the surrounding water molecules. [1]

Carbon dioxide hydrate is a notable example of Structure II clathrate hydrates, where carbon dioxide gas molecules are confined within the lattice cages. Other guest molecules, including nitrogen and certain hydrocarbons, can also form Structure II clathrate hydrates under specific temperature and pressure conditions.

The unique configuration and properties of Structure II clathrate hydrates contribute to their relevance in various fields. Understanding their formation, stability,

and behaviour is essential for applications such as gas storage, separation processes, and studies related to energy exploration and environmental sciences.

Research on Structure II clathrate hydrates involves investigating their lattice structure, thermodynamic properties, and kinetic behaviour. These studies aim to enhance our understanding of Structure II clathrate hydrates and their potential applications in fields such as gas transportation, gas recovery, and environmental management.

2.2.3 Structure H

Structure H clathrate hydrates, also known as sH clathrate hydrates, refer to a specific type of clathrate hydrate structure characterized by a hexagonal lattice arrangement. They possess distinct properties and host-guest configurations compared to other clathrate hydrate structures.

In Structure H clathrate hydrates, the host water molecules form a hexagonal lattice structure. This lattice arrangement gives rise to alternating layers of small cages and large cages within the hydrate framework. The small cages consist of 16 water molecules, while the large cages are composed of 34 water molecules. [1][6]

Guest molecules, typically including hydrogen sulphide (H2S) and other related compounds, are encapsulated within the cages formed by the host water molecules. The inclusion of guest molecules occurs through intermolecular interactions such as van der Waals forces or hydrogen bonding between the guest molecules and the surrounding water molecules [6]. The unique hexagonal lattice structure of Structure H clathrate hydrates leads to specific properties and behaviours. Understanding these characteristics is crucial for applications in fields such as energy exploration, gas storage, and environmental studies. [7]

Studies related to Structure H clathrate hydrates involve investigating their formation conditions, thermodynamic properties, and the effects of temperature and pressure on their stability. Additionally, research focuses on understanding the interactions between the host and guest molecules within the hexagonal lattice structure.

2.2.4 Mixed Clathrates

Mixed clathrate hydrates refer to a type of clathrate hydrate structure that arises from the combination or coexistence of different clathrate structures within a single hydrate sample. These structures can include variations of Structure I, Structure II, or other known clathrate structures. [1]

In mixed clathrate hydrates, the host water molecules form a lattice structure that incorporates multiple types of cages or cavities. These cages can have different

sizes, shapes, and arrangements, accommodating a diverse range of guest molecules within the hydrate lattice.

The formation of mixed clathrate hydrates typically occurs when the hydrate-forming system contains a mixture of guest molecules with varying properties. This can result in the simultaneous occupation of different types of cages within the lattice, leading to the coexistence of multiple clathrate structures. [7]

The presence of mixed clathrate structures introduces complexity to the hydrate system, impacting its thermodynamic properties, stability, and guest molecule encapsulation behaviour. The behaviour of mixed clathrate hydrates may differ from that of pure clathrate structures, necessitating further investigation and understanding. [8]

The study of mixed clathrate hydrates involves characterizing their composition, crystal structure, and the interactions between the host and guest molecules. Experimental and computational techniques are employed to analyse the properties and behaviour of mixed clathrate hydrates, aiding in their comprehension and potential applications.

Understanding mixed clathrate hydrates is crucial for various fields, including energy storage, gas separation, and environmental sciences. By elucidating their formation mechanisms and properties, researchers can explore ways to optimize their use in practical applications and enhance our knowledge of clathrate hydrates' complex behaviour.

a

| Cavity types | Hydrate structure | 'Guest molecules' |

$5^{12}6^2$ → **6** → Structure I — 46 H_2O — Methane, ethane, carbon dioxide and so on

5^{12} → **16** → $5^{12}6^4$ → **8** → Structure II — 136 H_2O — Propane, iso-butane and so on

$4^35^66^3$ → **2** → $5^{12}6^8$ → **1** → Structure H — 34 H_2O — Methane + neohexane, methane + cycloheptane, and so on

b

Hydrate crystal structure	I		II		H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91[†]	4.06[†]	5.71[†]
Coordination number*	20	24	20	28	20	20	36
Number of waters per unit cell	46		136		34		

*Number of oxygens at the periphery of each cavity.
†Estimates of structure H cavities from geometric models.

Figure 2 - Types of Clathrate Hydrate Structure [1]

2.3 Crystallization of Clathrate Hydrates

The crystallization of clathrate hydrates refers to the process by which these structures form from a mixture of host water molecules and guest molecules. This process occurs under specific conditions of temperature and pressure, where the intermolecular interactions between the host and guest molecules facilitate the formation of the clathrate hydrate lattice. [1]

The crystallization of clathrate hydrates typically begins with the nucleation stage, where small clusters or nuclei of hydrate cages start to form within the liquid phase. This nucleation process requires an initial formation of a critical-sized cluster that can grow further into larger hydrate crystals. [7]

Once nucleation occurs, the growth of the hydrate crystals proceeds through the continued incorporation of host and guest molecules into the lattice structure. The growth process involves the attachment of additional water molecules and guest molecules onto the existing crystal surface, leading to the expansion of the hydrate crystal structure. [7]

The rate of clathrate hydrate crystallization is influenced by various factors, including temperature, pressure, guest molecule concentration, and the presence of hydrate inhibitors or promoters. Higher pressures and lower temperatures generally favor the formation of clathrate hydrates, as they provide conditions where the host-guest interactions are more favorable.[1]

The nucleation of clathrate hydrates, which refers to the initial formation of small clusters or nuclei of hydrate crystals, is highly dependent on temperature and pressure conditions.

1. Temperature Dependence:
    o   Temperature plays a crucial role in the nucleation process of clathrate hydrates. Lower temperatures typically promote nucleation by providing a thermodynamically favourable environment for the formation of hydrate crystals. [6]
    o   As the temperature decreases, the driving force for hydrate formation increases due to the release of heat during the hydrate crystallization process. [6]
    o   At temperatures above the equilibrium hydrate formation temperature, nucleation may be hindered or suppressed, and the system remains in a metastable state. [6]
2. Pressure Dependence:
    o   Pressure is another critical factor influencing the nucleation of clathrate hydrates. Increasing pressure generally enhances the stability and formation of hydrate nuclei. [6]
    o   Higher pressures favour nucleation by increasing the density and proximity of gas molecules, which promotes their adsorption and encapsulation within the water lattice. [1]
    o   The relationship between pressure and nucleation can be explained by the phase behaviour of the gas-water system, as represented by the phase diagram. At higher pressures, the hydrate stability zone expands, providing a larger region for nucleation to occur. [6]
3. Combined Temperature and Pressure Effects:
    o   The temperature and pressure conditions must be carefully controlled to optimize clathrate hydrate nucleation.
    o   The nucleation temperature and pressure can be determined from experimental measurements or estimated using phase equilibrium models, such as the van der Waals and Platteeuw theory or the statistical mechanical theories. [1]
    o   The phase diagram for the specific gas-water system of interest provides insights into the conditions where nucleation is favoured, such as within the stable hydrate region or near the hydrate equilibrium curve. [6]

Understanding the temperature and pressure dependence on nucleation is essential for designing and operating clathrate hydrate systems effectively. By manipulating these parameters, researchers and engineers can control the nucleation

process, optimize hydrate formation conditions, and develop strategies for applications such as gas storage, separation, or flow assurance.
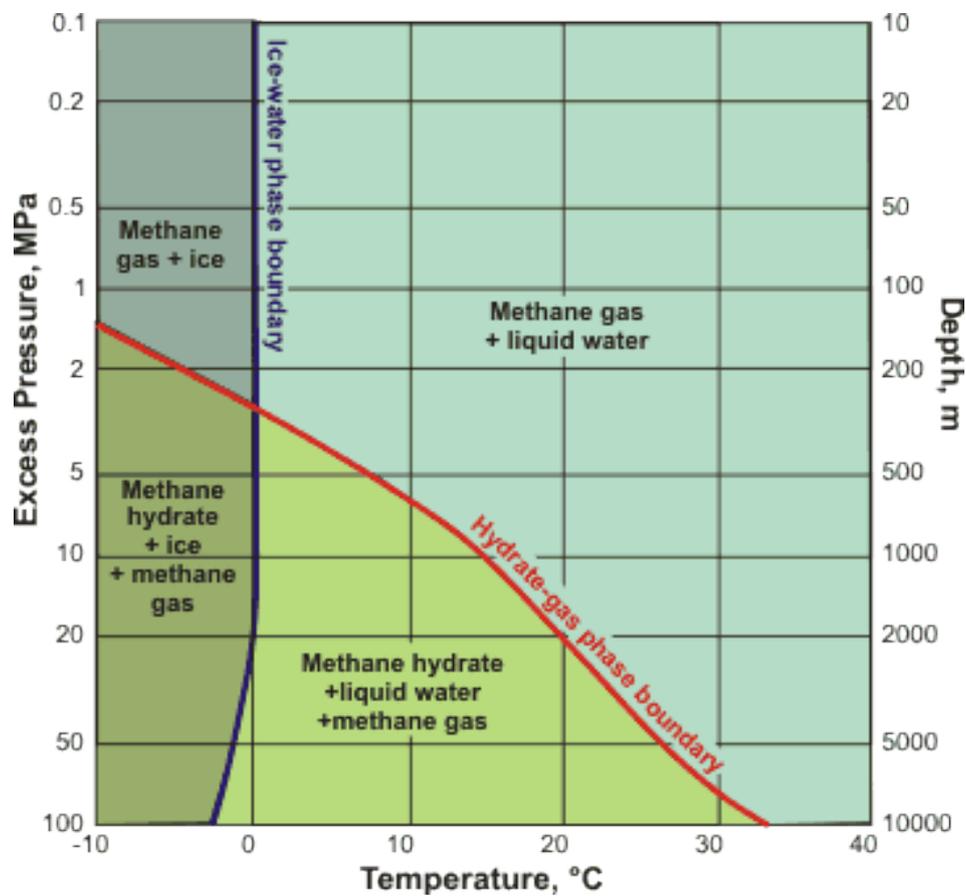

Figure 3 - Methane Hydrate phase diagram [8]

2.4 Applications of Clathrate Hydrates in different industries

2.4.1 Petroleum industry

Clathrate hydrates are one of the key research areas in petroleum industry, due to its role in natural gas production, transportation and flow assurance. We can name couple of key areas of application:

1. Natural Gas Storage and Transportation:
   - Clathrate hydrates can be utilized for the storage and transportation of natural gas. Methane clathrate hydrates, in particular, can store large volumes of natural gas within their crystalline structures. [9]
   - By forming hydrates under suitable pressure and temperature conditions, natural gas can be stored in a solid form, which reduces the volume and facilitates transportation. [9]
   - Hydrate-based storage and transportation systems offer potential benefits in terms of safety, energy efficiency, and reduced environmental impact compared to conventional methods. [9]

2. Flow Assurance in Pipelines:
   o Clathrate hydrates pose a significant challenge in offshore oil and gas production due to their potential formation and subsequent blockage in pipelines and flowlines. [10]
   o Understanding the formation and behaviour of hydrates is crucial for designing effective flow assurance strategies. [10]
   o Hydrate inhibitors, such as thermodynamic inhibitors (e.g., methanol, glycols) or kinetic inhibitors (e.g., polymers, surfactants), can be employed to prevent or mitigate hydrate formation and blockage issues in pipelines. [10]
3. Subsea Hydrate Recovery:
   o In some cases, clathrate hydrates that have formed in subsea environments can cause operational difficulties or impact the integrity of subsea structures.
   o Various methods have been developed to remove or dissociate hydrates, including thermal methods (e.g., hot water or steam injection), chemical methods (e.g., methanol injection), and depressurization techniques.
   o Proper management of hydrate-related risks is crucial to ensure the efficient and safe operation of subsea oil and gas facilities. [11]


Figure 4 - Hydrate Clog [10]

2.4.2. Energy source

Clathrate hydrates have gained attention as a potential energy source due to their vast reserves of trapped methane, which is a potent greenhouse gas and a valuable fuel. Recent United States Geological Survey report show that methane hydrate has more stored potential energy than all other fossil fuel sources combined. It is estimated that there are up to 12 400 gigatons of carbon which corresponds to $24,8 \times 10^{15}$ cubic meters of methane in those hydrates that can be utilized as a potential energy source. [11]

Exploiting clathrate hydrates as an energy source involves extracting and utilizing the trapped methane. The key considerations regarding the potential of clathrate hydrates as an energy source:

1. Vast Methane Reserves:
   o Clathrate hydrates are estimated to contain enormous amounts of methane globally, potentially surpassing all conventional natural gas reserves.
   o These hydrates are found in abundance in marine sediments, especially in deep-water continental margins, as well as in Arctic permafrost regions. [12][13]
2. Extraction Challenges:
   o Extracting methane from clathrate hydrates poses significant technical challenges. The extraction methods must overcome the stability of the hydrate structure and the low permeability of the sediments.
   o Current extraction techniques include depressurization, thermal stimulation, and chemical methods, but these approaches are still in the experimental or pilot phase. [12][13]
3. Environmental Considerations:
   o Clathrate hydrate extraction and utilization raise environmental concerns due to the release of methane, a potent greenhouse gas, during the extraction process and potential risks associated with destabilizing hydrate formations.
   o Proper management and mitigation strategies are necessary to minimize methane emissions and potential ecological impacts during extraction operations. [12]
4. Research and Development:
   o Extensive research and development efforts are underway to advance the understanding of clathrate hydrate behaviour, develop safe and efficient extraction technologies, and assess the environmental and economic viability of hydrate-based energy production.
   o Experimental field programs and pilot projects are being conducted to test extraction techniques and evaluate the commercial potential of clathrate hydrates as an energy source. [12]

2.4.3 Water Desalination

Water desalination is another promising use of Clathrate hydrates. With increasing world population more and more fresh water is needed and currently used desalination process - reverse osmosis is very energy consuming. Clathrate hydrates can be a great alternative. Not only it is much more energy efficient but there is also a possibility of utilizing cold LNG energy to further improve efficiency. [14] The main drawback, for now, is the speed of the process as clathrate hydrates require a lot of time to crystallize. However, with improvements in hydrate reactors and with possible

additives such as forming agents or catalysts we should be able reach nucleation speed that will be satisfactory for industrial use. [14]

Key aspects of water desalination using Clathrate Hydrates

1. Principle of Operation:
    o Water desalination using clathrate hydrates involves the formation and dissociation of hydrates to selectively separate freshwater from saline water.
    o Clathrate hydrates can selectively trap water molecules while excluding dissolved salts, thus enabling the separation of freshwater from the saline solution.
2. Hydrate Formation and Dissociation:
    o The process typically involves lowering the temperature and/or increasing the pressure of the saline water to induce hydrate formation.
    o As hydrates form, they encapsulate the water molecules, leaving the salts and impurities behind in the liquid phase.
    o Subsequently, the hydrates can be dissociated by raising the temperature or reducing the pressure, releasing the freshwater while the salts remain in the brine solution.
3. Challenges and Research:
    o Water desalination using clathrate hydrates is a relatively novel concept, and significant research and development efforts are underway to explore its feasibility and practicality. [14]
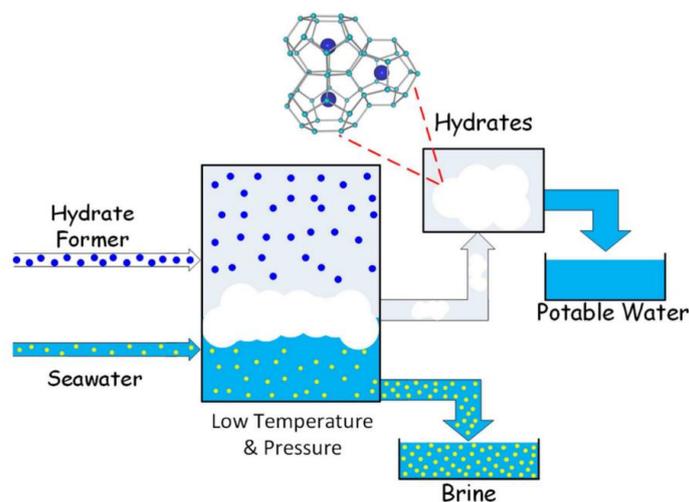

Figure 5 - Water desalination process [14]

2.4.4 Gas sequestration

Clathrate hydrates are also researched as a potential way of long-term gas storage. It is believed that CO_2 sequestration in hydrates can be a viable option for reducing CO_2 levels in the earth's atmosphere. [15] The resulting Clathrate hydrate can potentially be stored in permafrost regions or in the ocean seabed as it requires low temperature and relatively high pressure to not decompose. Further research in this

field is needed to accurately describe needed conditions and potential risks as any decomposition of said hydrates might lead to environmental catastrophe. [14]
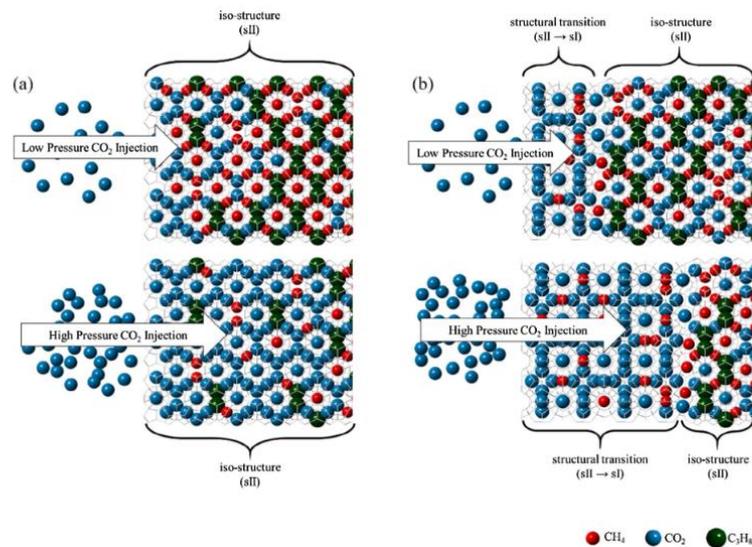

Figure 6 - Gas sequestration scheme[15]

The process of gas sequestration using clathrate hydrates typically involves the following steps:

1. Formation: CO_2 or other gases are brought into contact with water under conditions of temperature and pressure that promote the formation of clathrate hydrates. The gas molecules become trapped within the cages formed by the water molecules, resulting in the formation of gas hydrates. [1]
2. Storage: The gas hydrates, containing the trapped gases, are stored either in underground geological formations or in specialized containment systems designed to maintain the necessary temperature and pressure conditions for stability. Geological storage may involve injecting the gas hydrates into suitable reservoirs, such as deep saline aquifers or depleted oil and gas fields. [15]
3. Stability: To ensure the long-term stability of the gas hydrates, it is important to maintain the appropriate temperature and pressure conditions. This may involve insulation or heating/cooling systems, depending on the storage environment. [15]
4. Monitoring: Monitoring techniques are employed to assess the integrity and behaviour of the gas hydrate storage system. This includes monitoring the pressure, temperature, and gas composition within the storage reservoir to ensure the integrity of the containment and to detect any potential leaks. [15]

2.4.5 Wastewater Reclamation

Similarly, to water desalination, it is possible to use clathrate hydrates in wastewater reclamation in a process in which the hydrate is trapping water molecules and later dissolved to obtain pure water. The process is potentially more cost efficient

than currently used techniques, but further research is cost efficiency and reactor technology needed to support those claims. [16]
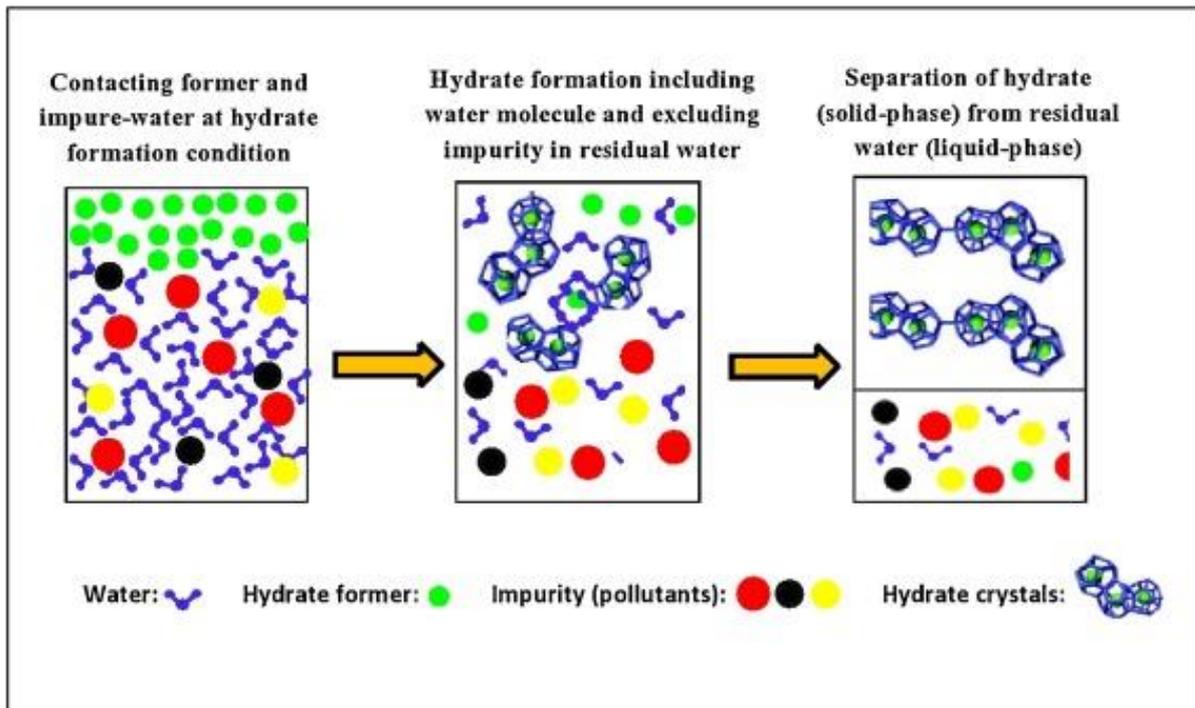

Figure 7 - Process of Wastewater reclamation [16]

The process of wastewater reclamation using clathrate hydrates typically involves the following steps:

1. Contaminant Removal: The wastewater is treated using conventional methods to remove solid particles, organic matter, and larger contaminants. This step may include processes such as screening, sedimentation, and filtration. [16]
2. Clathrate Hydrate Formation: In this step, clathrate hydrates are induced to form in the treated wastewater. This can be achieved by adjusting the temperature and pressure conditions to create an environment favourable for clathrate hydrate formation. [16]
3. Hydrate Former Capture: The clathrate hydrates selectively trap introduced hydrate former present in the wastewater. The hydrate former can be neutral molecule that promotes hydrate formation ex. CO_2. [16]
4. Separation: The clathrate hydrates, along with the trapped hydrate former, are separated from the leftover wastewater. This can be done through processes such as filtration, sedimentation, or centrifugation. [16]
5. The formed hydrates are then turned into water, releasing Hydrate Former that can be later captured and reused. [16]

2.4.6 Gas Mixture Separation

Clathrate hydrates may also be used as an alternative technique of gas mixture separation, utilizing the ability of hydrates to capture selective components of a system. While more research is required current research is pointing out that for some gas mixtures clathrate hydrate is advantageous to other methods while being more energy efficient. [17]

The process of gas mixture separation using clathrate hydrates typically involves the following steps:

1. Clathrate Formation: The gas mixture is brought into contact with water under controlled temperature and pressure conditions that favour the formation of clathrate hydrates. These conditions are selected based on the specific properties of the gas mixture and the desired separation objectives. [17]
2. Selective Capture: The clathrate hydrates selectively trap certain gas components from the mixture based on their affinity for clathrate formation. Different gases have varying degrees of affinity for clathrate hydrate formation, allowing for the preferential capture of specific gases while leaving others untrapped. [17]
3. Separation: Once the clathrate formation has occurred, the gas mixture is separated from the clathrate hydrates. This can be achieved through various methods, such as reducing the temperature or pressure to break down the clathrate structure and release the trapped gases. Alternatively, other separation techniques like filtration or centrifugation may be employed to separate the solid clathrate hydrates from the gas mixture. [17]
4. Purification and Recovery: After separation, the captured gases can undergo further purification processes to meet desired purity requirements. The purified gases can then be collected and utilized for various applications, while the clathrate hydrates can be regenerated for subsequent separation cycles. [17]
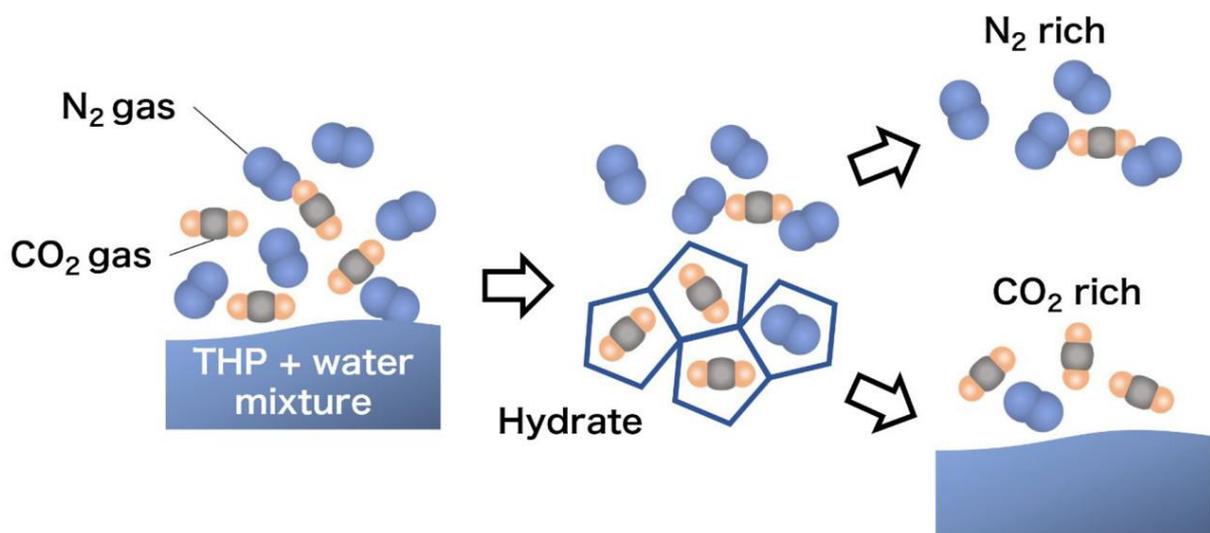

Figure 8 - Gas Separation Process [18]

2.5 Environmental Issues

Clathrate hydrates are a long-term danger to the environment as they slowly release methane into the atmosphere. Global warming also causes the permafrost to melt which may lead to release of the methane stored there into the atmosphere [19]. This process is also known as clathrate gun hypothesis [20] and poses great threat to our climate. Another concern is that when oil companies drill for oil through hydrate bearing sediments, the temperature melts the hydrates and releases large amounts of methane. In recent years many craters and blowouts were discovered at the bottom of Barents Sea that are created by decomposing methane hydrate. [21]
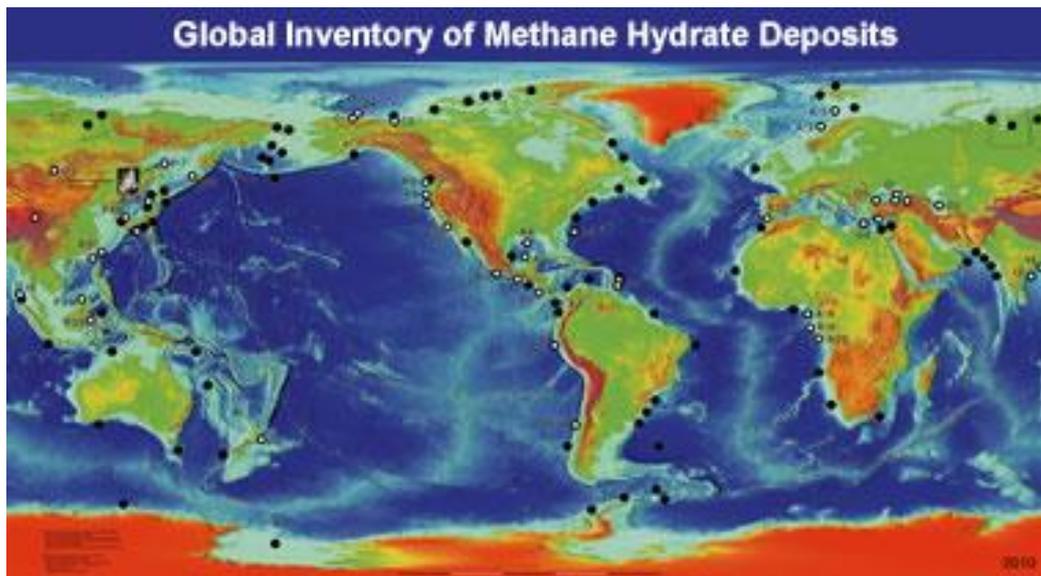
Figure 9 - Global depostits of Methane Hydrate [21]
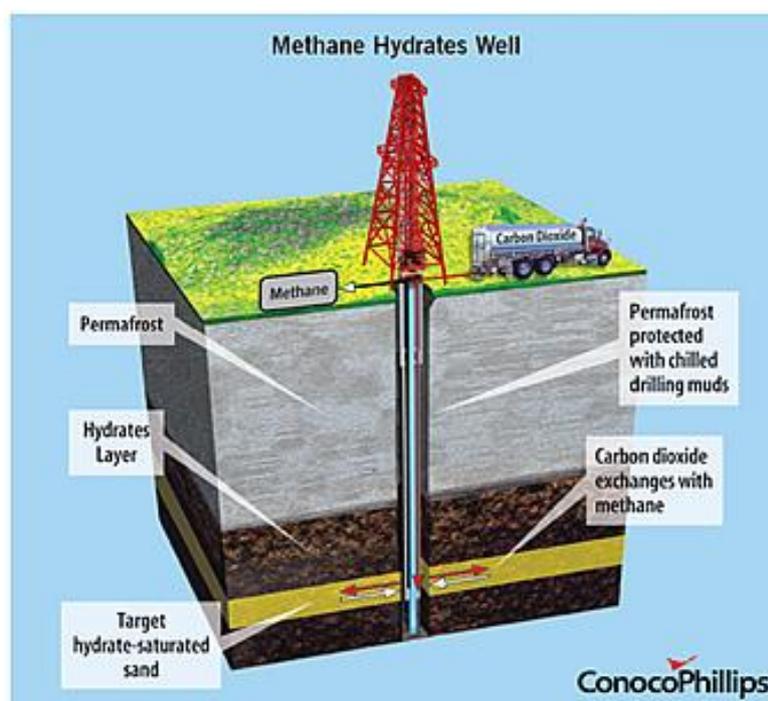

Figure 10 - Example of Methane Hydrate Well [22]

2.6 Clathrate Hydrate Formation Technologies and Types of Reactors

1. Pressure Swing Technology:
   - In this method, clathrate hydrates are formed by increasing the pressure of the gas and water mixture while maintaining a constant temperature. The increased pressure promotes the formation of clathrate hydrates, which can then be separated by reducing the pressure or by other methods such as thermal stimulation or chemical inhibition. [23]
2. Temperature Swing Technology:
   - Clathrate hydrates can be formed by lowering the temperature of the gas and water mixture while maintaining a constant pressure. As the temperature decreases, the gas molecules become trapped within the water lattice, forming clathrate hydrates. The hydrates can then be dissociated by raising the temperature or by other methods such as depressurization. [23]
3. Promoters and Additives:
   - Certain substances, known as promoters or additives, can enhance the formation of clathrate hydrates. These substances alter the interfacial properties between gas and water, facilitating nucleation and growth of hydrates. Promoters can be surfactants, hydrate crystal growth enhancers, or compounds that modify the surface tension and interfacial energies. [23]
4. Sonication and Ultrasonic Technology:
   - Ultrasonic waves can be applied to the gas and water mixture to promote clathrate hydrate formation. The high-frequency waves induce cavitation and microscale mixing, leading to enhanced mass transfer and nucleation of hydrates. Ultrasonic technology can improve the kinetics and efficiency of clathrate hydrate formation. [23]
5. Membrane Technology:
   - Membrane-based systems can be used to separate and control the flow of gas and water, creating conditions favourable for clathrate hydrate formation. Membranes with specific pore sizes or surface properties can selectively allow water molecules to pass through, enabling the formation of hydrates. [23]

These clathrate hydrate formation technologies offer different advantages and are applied based on the specific requirements of the application or research. The choice of technology depends on factors such as the gas composition, desired production scale, temperature and pressure conditions, and the presence of inhibitors or promoters.

2.6.1 Gas Dispersion Reactors

Gas dispersion reactors for clathrate hydrate formation are specialized systems designed to facilitate the production of clathrate hydrates by promoting the efficient mixing and interaction of gas and water. [1] These reactors play a crucial role in studying clathrate hydrates and their potential applications. Here are some key aspects of gas dispersion reactors for clathrate hydrate formation:

1. Design and Configuration:
   - Gas dispersion reactors are typically constructed as vessels or chambers with provisions for the controlled introduction of gas and water streams.
   - The reactor design may vary depending on the scale of operation, ranging from laboratory-scale setups to industrial-scale systems.
   - The configuration of the reactor includes features such as inlet ports, distribution systems, mixing elements, and outlets for the produced hydrate mixture. [24].
2. Gas and Water Mixing:
   - Gas dispersion reactors ensure effective mixing of the gas and water streams to promote the formation of clathrate hydrates.
   - Various techniques can be employed for mixing, such as sparging, stirring, agitators, or ultrasonic agitation, depending on the specific requirements and characteristics of the gas and water system.
   - The mixing process aims to achieve a homogeneous gas-water mixture, facilitating the interaction between the gas molecules and the water lattice. [24]
3. Temperature and Pressure Control:
   - Gas dispersion reactors maintain precise control over temperature and pressure conditions to promote clathrate hydrate formation.
   - Temperature control can be achieved through external temperature baths, temperature jackets, or other heating/cooling methods, ensuring the desired temperature range for hydrate formation.
   - Pressure control systems, such as gas supply systems or pressure regulators, enable the adjustment and maintenance of the desired pressure conditions within the reactor. [24]
4. Reactor Operation and Monitoring:
   - Gas dispersion reactors are operated under specific conditions to allow for clathrate hydrate formation. The gas and water streams are introduced into the reactor, and the system is allowed to reach equilibrium.
   - Monitoring and measurement techniques, such as temperature and pressure sensors, optical sensors, or analytical methods, are employed to track the progress of clathrate hydrate formation within the reactor.
   - Reactor operation parameters, including flow rates, gas-water ratios, and residence times, can be adjusted to optimize the formation of clathrate hydrates. [24]

2.6.1.1 Stirred Tank Reactor

Stirred tank reactor utilizes stirring as a way to improve both heat and mass transfer. As result we can expect improvement is speed of crystallization and increased storage capacity. In this kind of reactor is introduced in the top part of a stirring vessel and later mixed with water. Number of devices can be used to control the process: we can put a camera inside to observe the nucleation process, we can also observe and control the pressure and temperature in the reactor. [24]

The main components of this setup are:

- Gas supply
- High pressure reactor
- Cooling system
- Data logging system

This relatively simple design allows the fundamental studies of hydrates and is widely implemented. The main disadvantages of this type of reactor are:

- Energy cost of stirring increases with nucleation
- Some amount of water will remain between hydrate grains [48]
- The problems in scaling-up the reactor – Agitation power increases with 5th power of the impeller size [46]
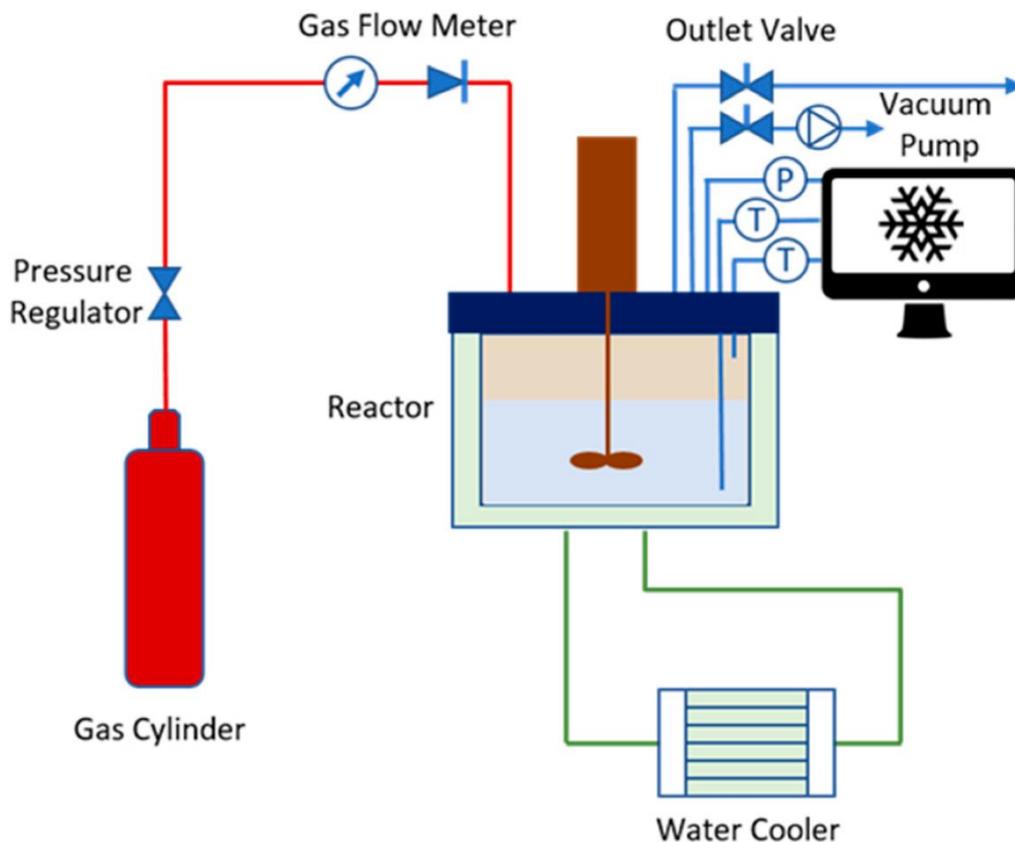
Figure 11 - Stirred tank reactor [24]

2.6.1.2 Bubble Forming Reactor

Bubble forming reactor, also known as Bubble-tower reactor is a reactor developed for gas/liquid reaction for industrial applications. For hydrate formation it utilises patented microbubble technology and is based in ejector type loop reactor (ELR). In this type of reactor, the kinetic energy of high velocity liquid is used to form microbubbles in fluid which leads to full mixture of gas and liquid. [24]

Main advantages of Bubble forming rector

- Improved mixing characteristics and mass transfer
- Possibility of utilizing external heat exchangers
- Optimum gas usage which removes a need for additional gas compression
- Easier operation and less sealing problems [24]
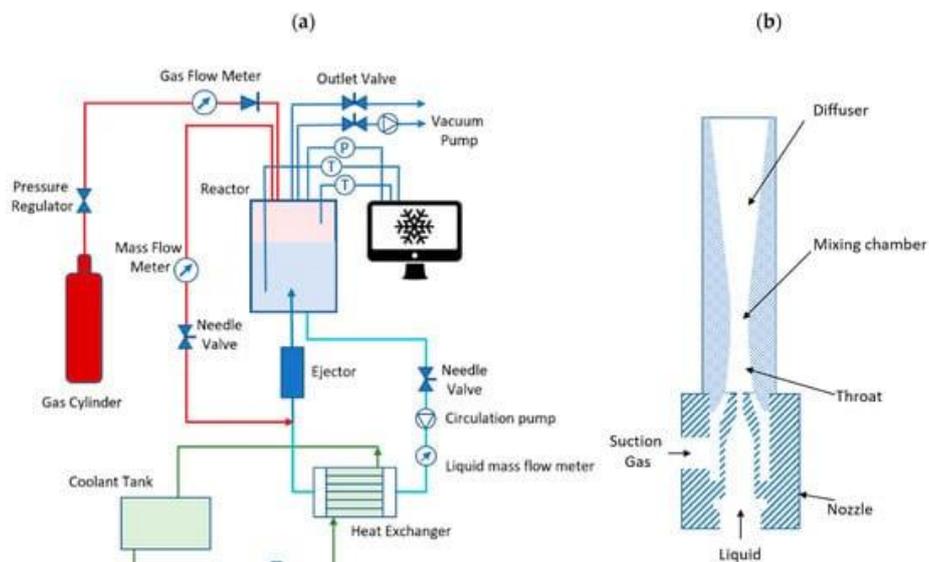
Figure 12 - (a) Schematic plot of the hydrate formation system with ELR. (b) Scheme of the ejector. [24]

Main problems of this type of reactor are limited heat transfer during hydrate formation and difficulty in separation of crystalized hydrate. Those problems are lowering the efficiency of such a reactor, that's why there are number of propositions how to overcome those problems. One of them is a system with a tube with internal spiral grove, this results in secondary flow and centrifugal force, which causes the removal of formed hydrate from the walls. [50][52]
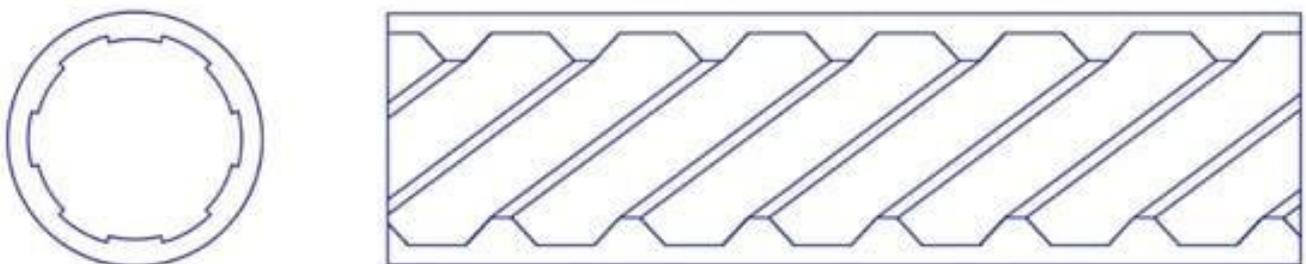

Figure 13 - Schematic diagram of the internal spiral-grooved tube [24]

2.6.1.3 Water in Oil Emulsion Reactor

Another technology of reactors that is being explored is water in oil emulsion. This technology utilizes oil emulsion alongside water for hydrate formation, this causes a great increase of gas-water contact area due to presence of nanodroplets of water in oil phase. This allows much higher hydrate yield and consequently higher hydrate production. This process can be further improved by addition of anti-agglomerant agent that further improves the yields. Finding proper balance as well as adequate anti-agglomerate agent can be challenging, and the research and many researchers are focusing on this problem. [24]

One of them is a reverse-micelle process in which a water-insoluble co-guest is added. This increases the hydrate formation rate due to increase of surface to volume ratio of the water pseudo-phase. This marks interesting field of further improvement as it allows us manipulate surface to volume ratio. [24]

Another design proposes two liquid jets impinging each other in high pressure reactor. One jest is ejecting liquid water and the other one is releasing a hydrophobic liquid with considerably lower freezing point. When we use large-molecule guest substance (LMGS) as hydrophobic component, in addition to main guest gas, the liquid will serve as companion hydrate guest and greatly increase the speed of crystallization. [24]
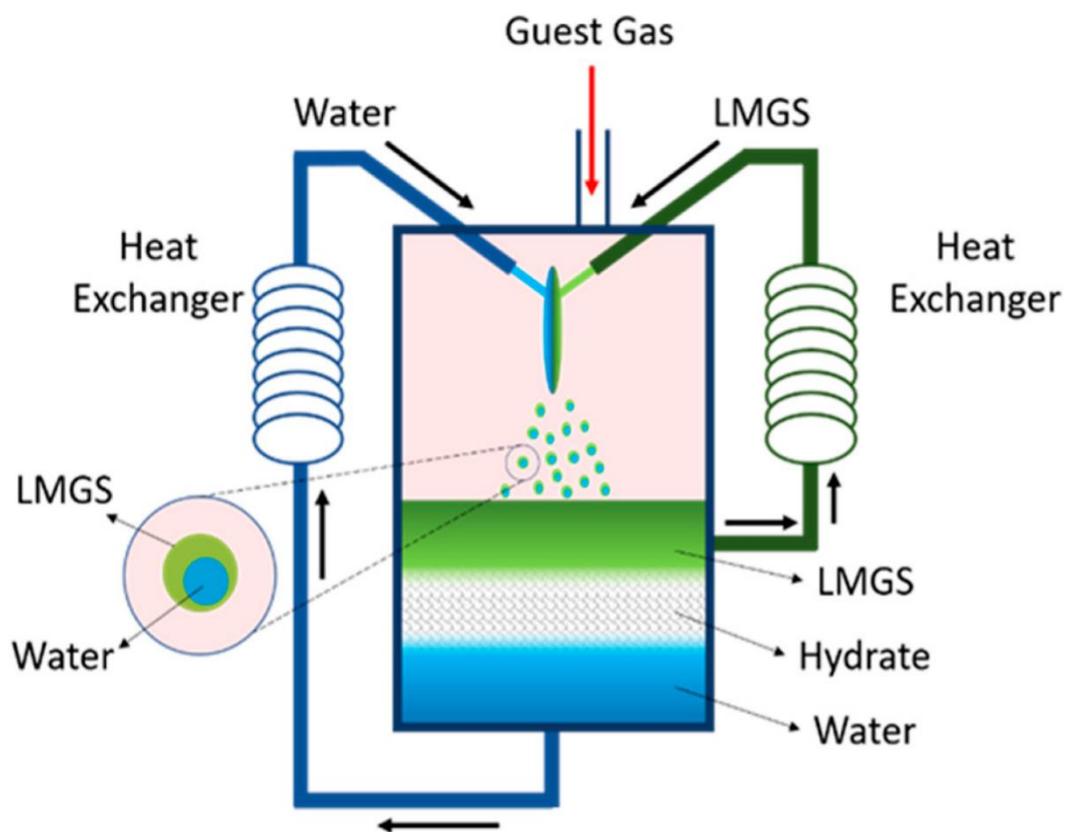

Figure 14 - Conceptual illustration of a twin-jet hydrate-forming system [24]

2.6.1.4 Fixed Bed Reactor

Fixed bed reactor is a reactor already widely used in chemical industry for heterogeneously catalysed gas-phase reactions. When applied to hydrate crystallization it greatly enhances the kinetics of a hydrate formation.[56] The experimental apparatus of Fixed-Bed reactor is the same as for the stirred tank reactor with an exception that in FBR a porous medium is set up at the bottom of the tank. The reason for that is to increase gas/liquid contact as it provides more surface for nucleation. Another advantage of this technology is that it eliminates the agitation, what is an energy consuming step of hydrate formation. Main types of media that are used in these reactors are: silica gel, silica sand or lightweight and highly porous foam. The technology however is not without its problems as the presence of added material can cause certain challenges in final applications. [24]
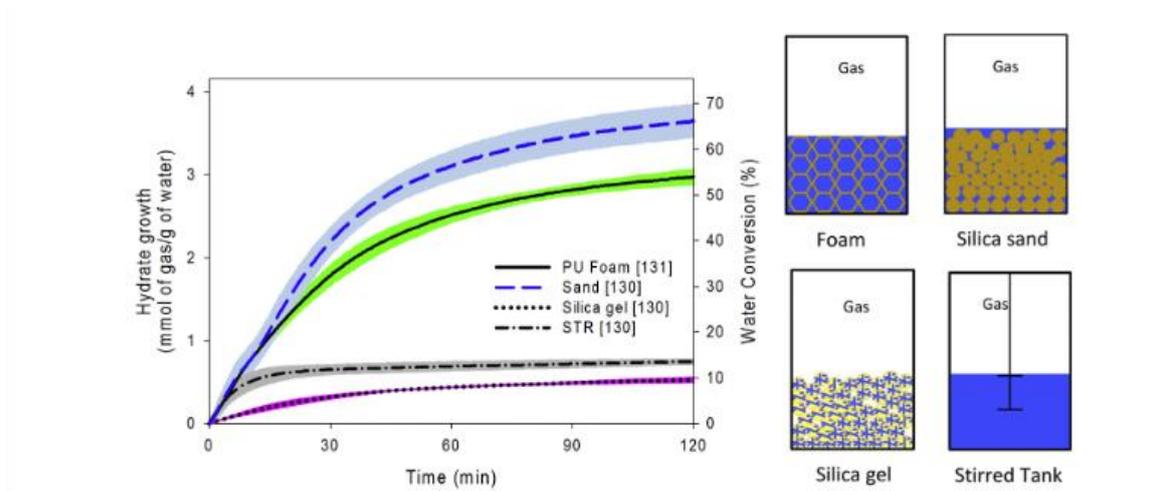
Figure 15 - Normalized gas uptake curve for 120 min from Induction Point (IP) in different reactor configurations from CO2 (38.1%)/H 2 (59.4%)/C 3H8 (2.5%) [24]

2.6.2 Water Dispersion Reactor

Water dispersion reactors for clathrate hydrate formation are specialized systems designed to facilitate the production and study of clathrate hydrates by promoting the efficient mixing and interaction of water and gas. These reactors play a crucial role in understanding the formation kinetics, growth mechanisms, and properties of clathrate hydrates. Here are some key aspects of water dispersion reactors for clathrate hydrate formation: [1]

1. Reactor Design:
   o Water dispersion reactors are typically designed as vessels or chambers with provisions for controlled water and gas inlet ports.
   o The reactor configuration may vary depending on the specific requirements and scale of operation, ranging from laboratory-scale setups to industrial-scale systems.
   o The reactor design includes features such as baffles, stirrers, or agitators to promote uniform mixing of water and gas and enhance mass transfer. [24]
2. Water and Gas Mixing:
   o Efficient mixing of water and gas is critical for the formation of clathrate hydrates. Water dispersion reactors employ techniques to ensure thorough mixing.
   o Common methods include stirring, agitation, or the use of mixing elements to create turbulence and enhance contact between water and gas.
   o The aim is to achieve a homogeneous mixture of water and gas, allowing for the interaction and encapsulation of gas molecules within the water lattice structure. [1][24]
3. Temperature and Pressure Control:
   o Water dispersion reactors maintain precise control over temperature and pressure conditions to facilitate clathrate hydrate formation.
   o Temperature control is achieved through external temperature control systems, such as temperature baths, jackets, or heaters, ensuring the desired temperature range for hydrate formation.
   o Pressure control systems, including gas supply systems or pressure regulators, enable the adjustment and maintenance of the desired pressure conditions within the reactor. [24]
4. Monitoring and Analysis:
   o Water dispersion reactors are equipped with sensors and monitoring devices to track the progress of clathrate hydrate formation.
   o Parameters such as temperature, pressure, gas and water flow rates, and concentrations can be monitored to optimize the formation process and study the kinetics of hydrate growth.
   o Analytical techniques such as spectroscopy, microscopy, or calorimetry may be employed to analyse the properties and structure of formed clathrate hydrates. [24]

2.6.2.1 Water spraying reactor

Other method of obtaining a clathrate hydrate is spraying reactor. This reactor is different to the other ones as it doesn't utilize water as the main medium to which gas is introduced, rather water is sprayed into a chamber filled with gas. [25]

There are 5 main parts of this design.

- Gas-supply
- Refrigeration system
- Reactor chamber
- Spraying system
- Data-logging system
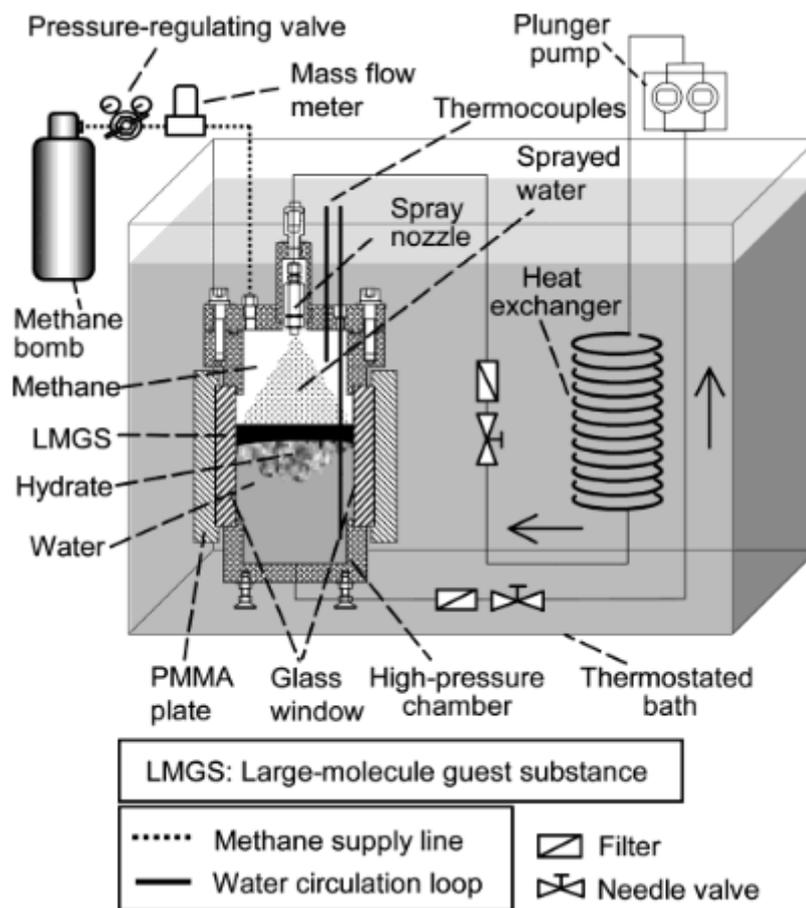
Figure 16 - Schematic of a Spraying Reactor [25]

Main advantages of this design are increased gas/water interfacial area and no need for mechanical stirrer. While to its downsides we can count difficulty of dispensing the latent heat and limited hydrate to water volume ratios. [25]

2.7 Summary of Literature Review

Section 2.1 and 2.2 provides a detailed examination of the various types of clathrate hydrates. It delineates the distinct structural categories of clathrate hydrates, namely, structures I, II, H, and mixed clathrate hydrates. Each type is characterized by its unique lattice structure, guest molecule accommodation, and stability conditions. The section delves into the molecular geometry and bonding characteristics of these structures, offering insights into their formation and stability mechanisms. Moreover, it discusses the typical guest molecules associated with each type, such as methane, carbon dioxide, and various hydrocarbons, elucidating their role in the stabilization of the hydrate structure. This comprehensive analysis of the different types of clathrate hydrates lays the groundwork for understanding their diverse applications and behaviour under various environmental conditions.

Section 2.3 shifts the focus to the crystallization process of clathrate hydrates. This section explores the physicochemical conditions necessary for the formation of clathrate hydrates, including pressure, temperature, and composition of the guest-host system. It examines the kinetics of hydrate formation, discussing the nucleation and growth phases, and how factors such as supercooling and supersaturation influence these processes. The section also addresses the role of inhibitors and promoters in the crystallization process, highlighting how these substances can be utilized to control or facilitate hydrate formation. Additionally, the dynamics of hydrate dissociation are explored, emphasizing the importance of understanding both formation and decomposition processes for practical applications. Through this detailed exploration, the section aims to provide a thorough understanding of the crystallization phenomena of clathrate hydrates, which is essential for their effective application in various industrial and environmental contexts.

These three sections, 2.1, 2.2 and 2.3, are crucial for establishing a comprehensive understanding of clathrate hydrates, from their structural diversity to the intricate processes governing their formation and stability. This foundational knowledge is pivotal for the subsequent exploration of their applications and implications in various fields, as discussed in the following sections of the literature review.

Section 2.4 of the literature review casts light on the multifaceted applications of clathrate hydrates across various industries. In the realm of the petroleum industry, these hydrates are gaining prominence as an innovative means for the transportation and storage of natural gas. They are also being employed to ensure uninterrupted flow within pipelines. Beyond the petroleum sector, clathrate hydrates are emerging as a potential energy source, particularly due to the vast reserves trapped in permafrost regions. Their ability to selectively capture specific particles positions them as a promising solution for water desalination, gas sequestration, wastewater reclamation, and gas mixture separation. This section comprehensively discusses these applications, highlighting the technological advancements and potential challenges associated with the utilization of clathrate hydrates.

Section 2.5 addresses the environmental implications of clathrate hydrates, with a specific focus on the potential risks associated with methane release from these compounds in permafrost regions. This section delves into the environmental impact assessments, examining the delicate balance between the exploitation of clathrate hydrates for energy and the consequent ecological footprints. The discussion extends to the broader implications of methane release on global warming and climate change, underscoring the need for responsible and sustainable management of clathrate hydrate reserves.

Finally, section 2.6 provides an in-depth analysis of various reactor designs utilized in the study and manipulation of clathrate hydrates. This section evaluates diverse reactor configurations, each with its distinctive advantages and limitations. It covers the operational principles, design intricacies, and application scopes of these reactors, thereby offering insights into the technological innovations driving advancements in clathrate hydrate research. The comparative analysis of these reactor designs underlines the importance of selecting the appropriate reactor type based on the specific requirements of each application, whether it be for energy production, environmental management, or industrial processes.

3.Hardware Selection

In this chapter, the focus is on selection of the appropriate hardware for observing and documenting the formation of hydrate crystals within the reactor environment. The successful capture and analysis of this process hinge on two critical components: a high-fidelity camera for image acquisition and a robust computing device for image processing and data management.

3.1 Camera Selection

The choice of camera is pivotal, as it must possess the capability to capture high-resolution images under the specific conditions within the reactor. Factors such as sensitivity to light, resolution, and the ability to operate under varying temperature and pressure conditions are considered. Additionally, the camera's compatibility with the chosen computing device and its adaptability to the reactor's physical constraints are evaluated. This section will detail the criteria used for camera selection and will discuss the rationale behind choosing a specific model that meets the experimental requirements.

3.2 Computing Device for Image Processing

Parallel to the camera, the selection of a computing device capable of handling and processing the captured images is crucial. This device must offer not only the necessary computational power to process high-resolution images efficiently but also the stability and reliability required for prolonged experiments. Factors such as processing speed, storage capacity, software compatibility, and physical robustness are considered in the selection process. The section will elaborate on the chosen computing device and its configuration, explaining how it aligns with the needs of the experimental setup.

3.3 Observing setup

The observational setup represents a crucial component of our experimental apparatus, essential for accurately assessing the outcomes and monitoring the dynamic changes occurring within the reactor. A critical requirement for this setup is a compact, yet powerful computing device capable of supporting an external camera. This device must be encased appropriately to withstand the challenging conditions inside the reactor.

For this purpose, I have selected the Raspberry Pi 3 Model B+ as the computing platform, coupled with the Raspberry Pi Camera V2. This combination is expected to deliver high-quality photographic documentation, while ensuring sufficient computational power and data storage capacity to facilitate our experiments efficiently.

The Raspberry Pi 3 Model B+, known for its robust performance and compact size, is an ideal choice for this application.

The Raspberry Pi Camera V2, on the other hand, is chosen for its high-resolution imaging capabilities and compatibility with the Raspberry Pi 3 Model B+. This camera is capable of capturing detailed images, which is crucial for closely examining the processes and transformations occurring within the reactor. Its compact design and ability to integrate seamlessly with the Raspberry Pi further enhance the overall effectiveness of the observational setup.

Together, the Raspberry Pi 3 Model B+ and the Raspberry Pi Camera V2 form a powerful and efficient system for monitoring and data collection within the reactor. The small form factor of this setup is a significant advantage, allowing for easy installation inside the reactor without compromising the integrity or functionality of the experimental setup. This observational system is expected to provide valuable insights and detailed visual records of the experiments, thereby playing a crucial role in the success of our research endeavours.
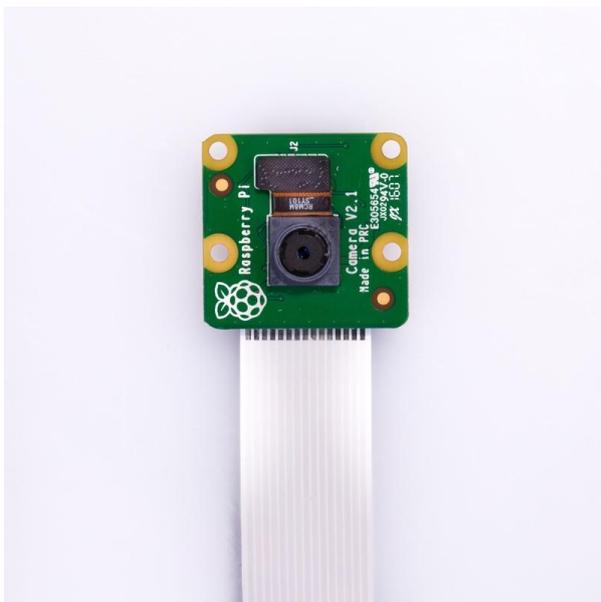
Figure 17 - Raspberry Pi camera version 2 [26]   *Figure 18 - Raspberry Pi 3 version B+ [27]*

Specification of Raspberry Pi 3 Model B+

- Broadcom BCM2837B0, Cortex-A53 (ARMv8) 64-bit SoC @ 1.4GHz
- 1GB LPDDR2 SDRAM
- 2.4GHz and 5GHz IEEE 802.11.b/g/n/ac wireless LAN, Bluetooth 4.2, BLE
- Gigabit Ethernet over USB 2.0 (maximum throughput 300 Mbps)
- Extended 40-pin GPIO header
- Full-size HDMI
- 4 USB 2.0 ports
- CSI camera port for connecting a Raspberry Pi camera
- DSI display port for connecting a Raspberry Pi touchscreen display
- 4-pole stereo output and composite video port
- Micro SD port for loading your operating system and storing data
- 5V/2.5A DC power input
- Power-over-Ethernet (PoE) support (requires separate PoE HAT) [63]

Specification of Raspberry Pi camera V2

- VideoFPS: 1080p/30, 720p/60
- Photos : 3280x2464 px
- Chip: 8Mpx Sony IMX219 CCD
- Connection: CSI
- Dimensions: 25 × 20 × 9 mm [64]

3.4 Preparation of the observing setup

The initial stage of preparing the experimental setup involved the assembly of the Raspberry Pi 3 Model B+ with its peripherals. This process was relatively straightforward, thanks to the near-complete assembly state of the Raspberry Pi computer upon purchase. The primary tasks that I undertook during this phase were focused on enhancing the thermal management and ensuring the protection of the device.

The first step in the assembly process was the installation of heat sinks on the central processing unit (CPU) and memory modules of the Raspberry Pi. These heat sinks are crucial for dissipating heat generated during operation, thereby maintaining optimal operating temperatures and preventing thermal throttling or damage due to overheating. The heat sinks, typically made of materials with high thermal conductivity like copper, were carefully attached to the respective components using thermal adhesive pads. This attachment ensures efficient heat transfer from the components to the heat sinks.

Following the installation of the heat sinks, the next step involved enclosing the Raspberry Pi's printed circuit board (PCB) within a protective casing. This casing is essential for safeguarding the delicate electronic components from environmental hazards.

This preparatory phase laid the foundation for the subsequent installation of the Raspberry Pi Camera V2 and the integration of the entire system into the reactor environment for our experimental observations.
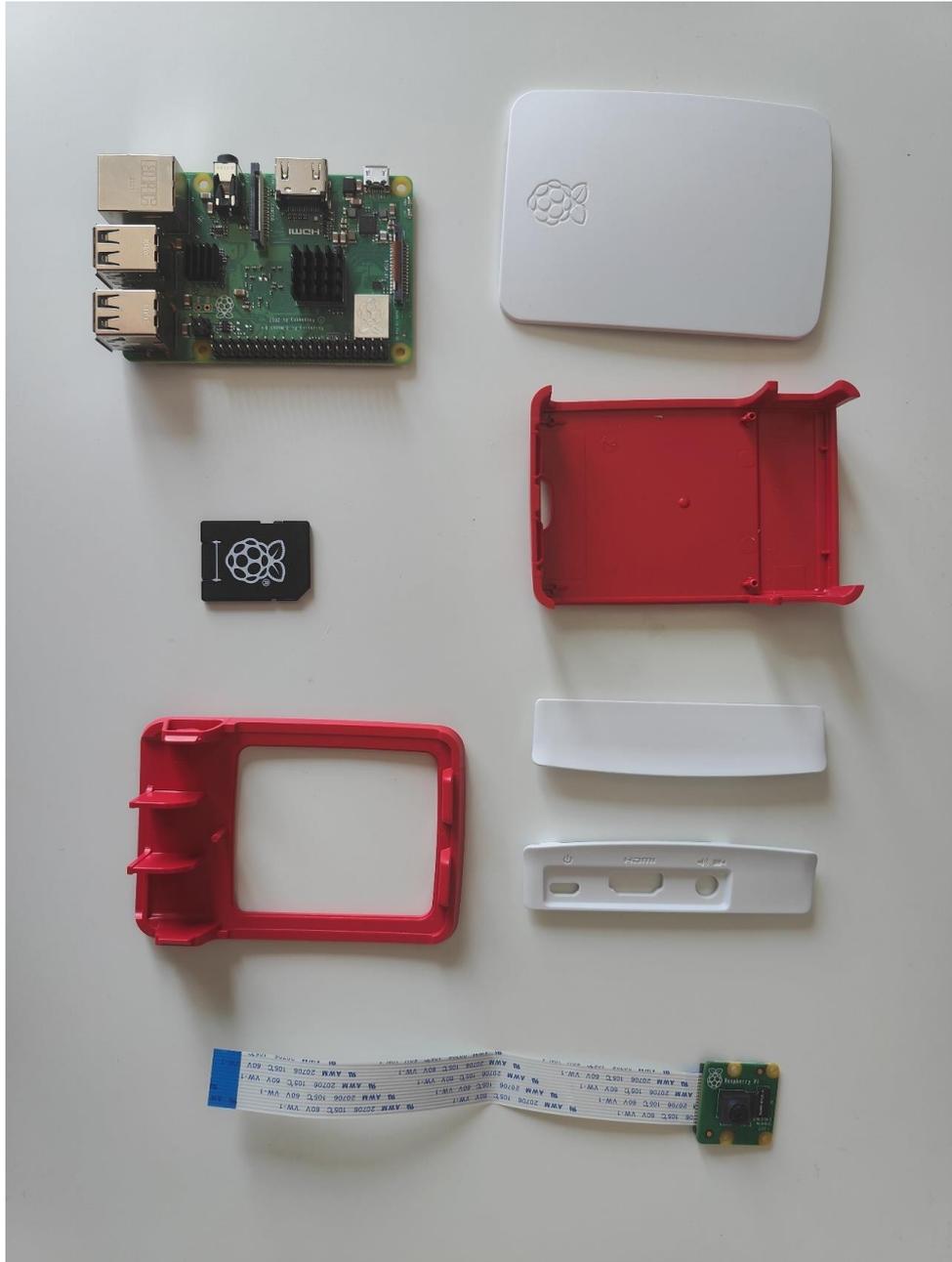

Figure 19 - Parts for computer assembly

Figure 20 - Assembled Raspberry Pi computer

The camera is installed by sliding the cable into appropriate socket.

Figure 21 - Assembled Raspberry Pi with attached camera

The initial setup of the Raspberry Pi 3 Model B+, while straightforward in terms of physical assembly, presented challenges during the software installation and boot-up phase. The initial boot-up of the system was successful, and I was able to install the operating system as planned. However, an issue arose during the post-installation reboot process.

The Raspberry Pi, upon attempted reboots, behaved as if the operating system had not been installed, failing to boot up properly from the microSD card. This issue persisted despite several attempts, suggesting a problem that was not immediately resolvable through standard troubleshooting procedures. Considering the symptoms, the most plausible cause appeared to be a malfunction or damage to the microSD card. MicroSD cards, while convenient and widely used in Raspberry Pi setups, can sometimes be prone to corruption or physical damage, which can lead to such boot issues.

To circumvent this problem, I decided to switch the boot medium from the microSD card to a USB stick. This decision was based on the Raspberry Pi's ability to boot from alternate media, a flexibility that can be advantageous in situations where the primary boot device is compromised. Upon installing the operating system on a USB stick and initiating the boot process, the system started up without any further complications, indicating that the issue was indeed related to the microSD card.

3.5 Process of writing the script

Next step was to write the script that will be able to take a photo using installed camera every couple of seconds as none of available programs is able to perform the tasks. I've decided to use python for that task as I have some previous experience with programming in this language.

First working draft of a script:

```
from time import sleep
from picamera2 import Picamera2, Preview
from datetime import datetime

TICKS = 5 # set time between photos (seconds)
FILE = "photo" # file name of photo
EXTENSION = ".jpg"

camera = Picamera2()
config = camera.create_still_configuration(main={"size": (1920,
1080)}, lores={"size": (640, 480)}, display="lores")
camera.configure(config)

while True:
    camera.start_preview(Preview.QTGL)
    camera.start()
    sleep(TICKS)
    camera.capture_file(str(datetime.now()) + EXTENSION)
    camera.stop_preview()
    camera.stop()
```

First working draft can take photos every couple of seconds – adjustable by number of ticks, we can also change of name of our photos. As a result, we obtain a folder of files with photos named: photo + time of day.

Final version of a script

```python
from time import sleep
from picamera2 import Picamera2, Preview
from datetime import datetime

TICKS = 5 # set time between photos (seconds)
EXTENSION = ".jpg"
CURRENT = 0
DEFAULT = TICKS #

camera = Picamera2()
config = camera.create_still_configuration(main={"size": (1920,
1080)}, lores={"size": (640, 480)}, display="lores")
camera.configure(config)

def calculate_time(time):
    hours = time // 3600
    time %= 3600
    minutes = time // 60
    time %= 60
    seconds = time
    if (hours < 10):
        hours = ("0" + str(hours))
    if (minutes < 10):
        minutes = ("0" + str(minutes))
    if (seconds < 10):
        seconds = ("0" + str(seconds))
    return (str(hours) + ":" + str(minutes) + ":" + str(seconds))

while True:
    camera.start_preview(Preview.QTGL)
    camera.start()
    sleep(TICKS)
    #camera.capture_file(str(datetime.now()) + EXTENSION)
    camera.capture_file(calculate_time(DEFAULT) + EXTENSION)
    #CURRENT = CURRENT + TICKS
    camera.stop_preview()
    camera.stop()
    DEFAULT = DEFAULT + TICKS
```

In final version of a script, I added an improvement in which the file is named based on time into measurement which makes it easier to read and obtain data from it.

3.6 Testing the observing setup

After the code is finished it is important to check if the setup is working as intended, for this I decided to observe the process of melting ice cube. This will allow to check picture quality, check if the script is working as intended and anticipate eventual problems that may occur in the reactor environment.
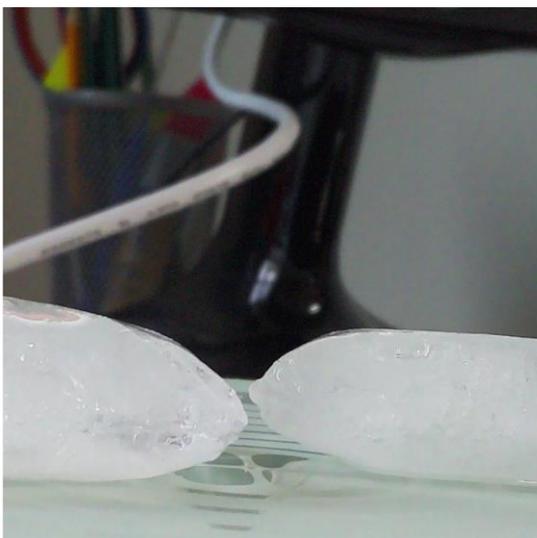
Figure 23 - Melting Ice Cube 0:00

Figure 22 - Melting Ice Cube 0:30
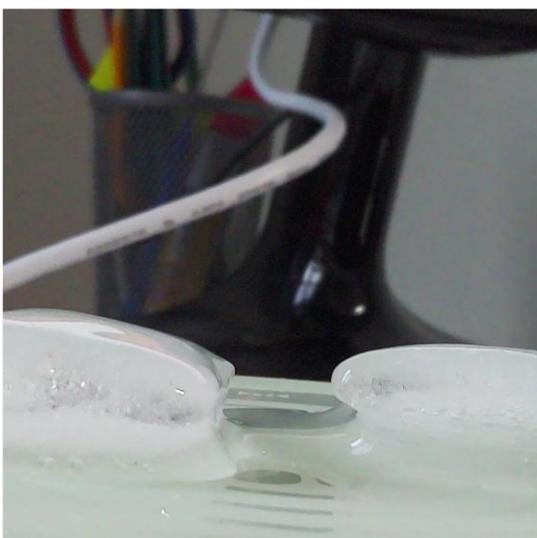
Figure 25 - Melting Ice Cube 1:00
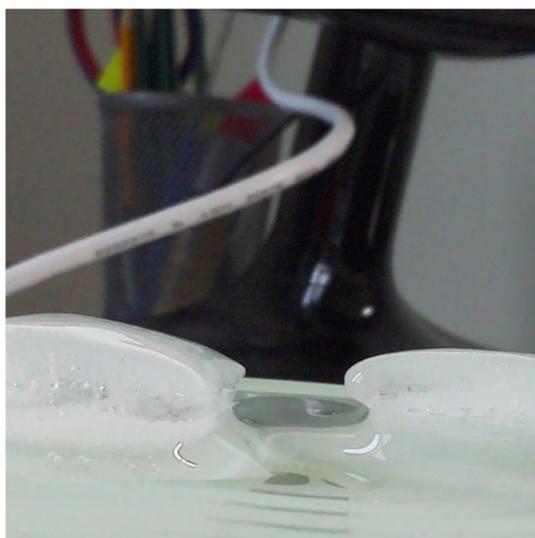
Figure 24 - Melting Ice Cube 1:30

Following the test phase, we confirmed that both the camera and the script function as designed. The image quality from the camera is good, and the script runs without issues. However, two key considerations for reactor installation emerged:

1. **Vibration Sensitivity**: The camera's image quality is significantly affected by vibrations, leading to distorted images. This factor is crucial in the reactor environment, where vibrations are likely.
2. **Manual Focus Requirement**: The camera lacks autofocus, necessitating manual focal distance adjustment for clear imaging. This manual setting, while requiring extra setup, ensures consistent focus during observations and allows for targeted focusing on specific reactor areas.

Addressing these issues is essential for the effective use of the camera system in the reactor environment.

4.Process of designing the enclosure

4.1 Assessing the Reactor Environment for Camera Integration

The foremost consideration in deploying a camera within a reactor is understanding the reactor's internal environment and its potential impacts on the camera's functionality. Throughout the experimentation phase, we anticipate encountering specific conditions:

- Elevated Pressure: Essential for the formation of clathrate hydrates.
- Reduced Temperature: Necessary for clathrate hydrate formation, typically around 2 degrees Celsius.
- Potential Corrosive Elements: Predominantly due to the substantial presence of water within the reactor.

While temperature fluctuations pose minimal threat to camera operations (given their resilience at temperatures near freezing), it is the high pressure and humid conditions that present significant challenges. These factors could compromise the camera's integrity, leading to failure or complete malfunction. To mitigate these risks, it is imperative to develop a protective enclosure for the camera that can withstand these harsh conditions without compromising the quality of the captured images.

4.2 Design Methodology for the Raspberry Pi Camera Enclosure

Criteria for an Effective Enclosure:

The proposed enclosure design for the Raspberry Pi Camera must meet the following criteria:

- High-Pressure Resistance: The enclosure must withstand substantial pressure without hindering the camera's observational capabilities.
- Non-Interference with the Reactor's Internal Environment: The design should not alter or affect the reactor's conditions.
- Watertight Seal: To safeguard the camera from moisture-related damage, the enclosure must be impermeable.

4.2.1 Selection of Materials for the Enclosure

The process of selecting materials for the camera's enclosure involved a comprehensive analysis of how to effectively isolate the camera from external elements while maintaining structural integrity. An analogous project in marine exploration provided valuable insights [28]. In this precedent, the camera was encased in epoxy resin to shield it from seawater, allowing for underwater photography. Epoxy resin emerged as an ideal material for its sealing properties and resistance to leakage, combined with high tensile and compressive strength.

To enhance protection, a layer of metal shielding over the epoxy resin is proposed. Steel, known for its robustness and resistance to various environmental conditions, is the preferred choice for this application. Lastly, for the camera's lens cover, glass is selected for its strength, transparency, and ability to maintain the camera's focus quality without distortion.

This multi-layered approach, integrating epoxy resin, steel, and glass, ensures a durable, reliable, and effective enclosure for the Raspberry Pi Camera, capable of operating in the challenging conditions of the reactor.

4.3 Development of the Enclosure Design for the Raspberry Pi Camera

Upon finalizing the material selection, the next phase in the enclosure design process involves determining its shape and size, taking into account the specific requirements and constraints of the reactor environment.

4.3.1 Considerations for Enclosure Shape

The primary consideration for the enclosure's shape revolves around compatibility with the camera's form factor and ease of manufacturing. Given the rectangular

configuration of the Raspberry Pi Camera's printed circuit board (PCB), a corresponding rectangular enclosure is the most logical choice. This shape not only ensures a snug fit for the camera but also simplifies the manufacturing process, particularly in terms of fabricating steel plating. Therefore, a rectangular design is selected as the most practical and efficient for this application. This shape is conducive to streamlined production processes and ensures a coherent and functional integration of the camera within the enclosure.

4.3.2 Considerations for Enclosure Size

The size of the enclosure is a critical aspect, particularly in deciding whether to include the camera's cable within its confines. The reactor's internal environment is characterized by consistent conditions, including high pressure, moderate low temperatures, elevated humidity levels, and a significant concentration of carbon dioxide (CO_2). The camera's cable, being coated with a durable plastic insulation, is inherently resistant to these environmental factors. Consequently, it is determined that incorporating the entire length of the cable within the enclosure is unnecessary. By excluding the cable from the enclosure, the design can be considerably more compact and simpler to fabricate.

This decision significantly impacts the enclosure's overall dimensions, leading to a more streamlined and lightweight design. The resulting enclosure size is optimized to encase the camera unit effectively while minimizing excess volume and material usage. This approach not only enhances the practicality of the enclosure but also contributes to cost-efficiency and ease of installation within the reactor's confines. The final design ensures that the camera is adequately protected from the reactor's harsh conditions, while also maintaining functionality and ease of use.

4.4 Final Design

Having thoroughly assessed the required specifications for the camera enclosure, I initiated the 3D modeling phase. For this task, Autodesk Fusion 360 was the chosen software, primarily due to its robust design capabilities and my personal familiarity with its features and interface. This software facilitates intricate design processes and allows for precise modeling, which is crucial for the creation of a specialized enclosure tailored to the unique environment of the reactor.

To accurately represent the camera within the enclosure design, I utilized a pre-existing model of the Raspberry Pi Camera available on the GrabCAD online library [29]. This approach ensured a high degree of accuracy in the model, as the dimensions and physical characteristics of the camera were represented based on an existing, verified design. Incorporating this detailed model into the Fusion 360 workspace allowed for precise adjustments and customization of the enclosure to fit the camera's specific dimensions and mounting requirements.

4.4.1 Step 1

To the imported model of the camera I've added the cable to make the camera model complete. Then, I added the resin filling that covers the camera while removing the part where it intersects with the body of camera. I have also left the camera lens without resin cover to avoid distortions and for better visibility.
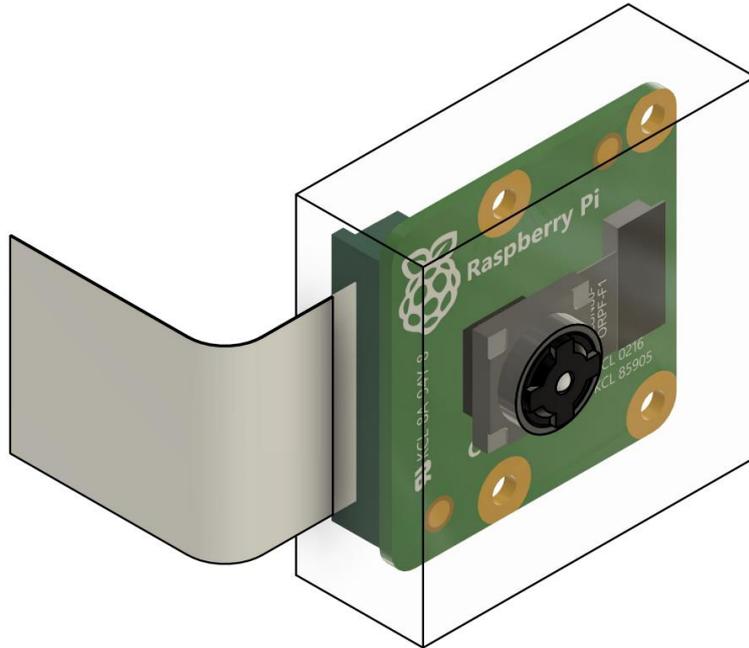

*Figure 27 - Raspberry Pi camera covered in epoxy resin*
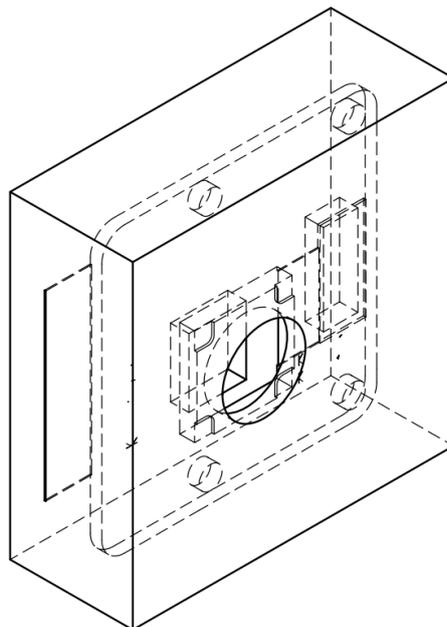
Figure 26 - Epoxy resin

4.4.2 Step 2

Next step was to create the steel plating around the resin. I decided to split the steel plating into two separate pieces for easier access to the camera in case of a need for any maintenance. To connect them I used screws as I wanted to keep the possibility of opening the case which other techniques like welding or soldering do not offer. I've also decided to add a rubber seal between the plates for better sealing off the environment.
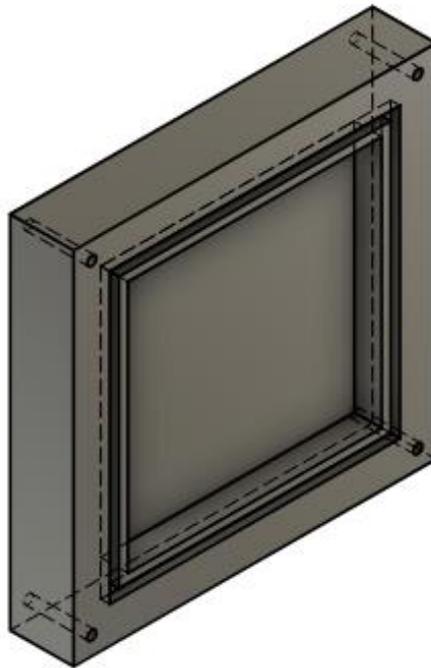
Figure 28 - Back part of enclosure
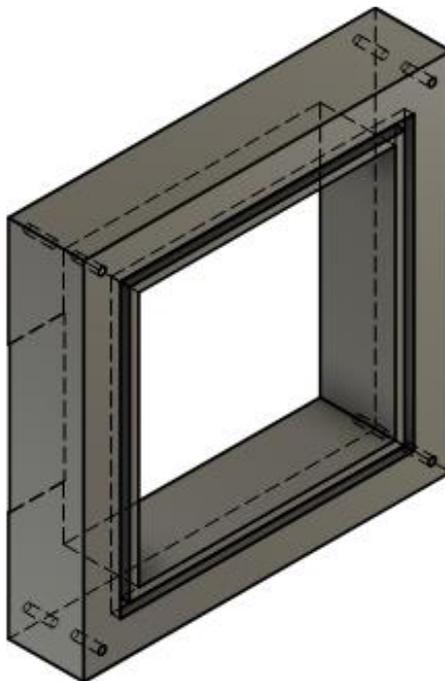
Figure 29 - Middle part of enclosure
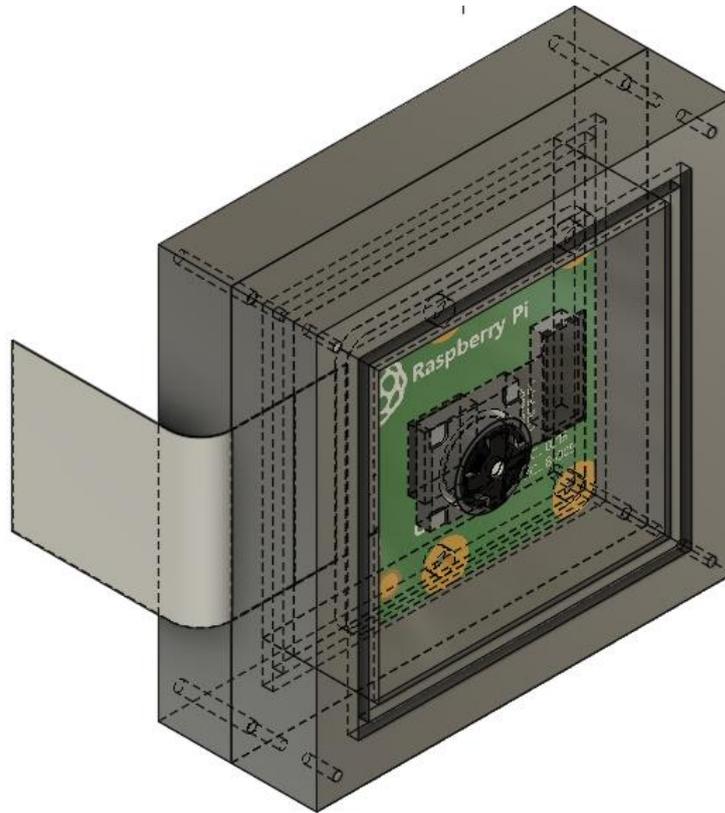
Figure 30 - Camera cover with epoxy resin and metal cover

4.4.3 Step 3

The final step is adding the glass front cover. I've also decided to use screws to secure it in place for easier removal of glass panel.
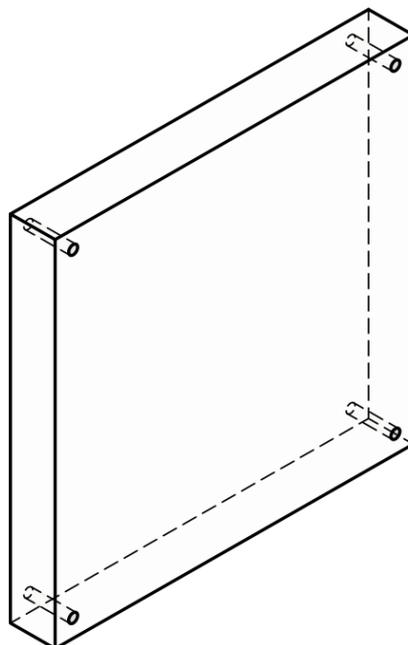
Figure 31 - Plexi glass front cover

4.4.5 The result of my design looks as follows:

Parts List

Item	Qty	Part Number	Description	Material
1	1	Cam V2.1 v1		Steel
2	1	Cable		ABS Plastic
3	1	Resin Filling		Epoxy Resin
4	1	Steel Back Cover		Steel
5	1	Glass Panel Front		Glass
6	1	Cable Socket		FR4
8	4	91800A062_18-8 Stainless Steel Narrow Cheese Head Slotted Screws		Steel
9	4	91800A060_18-8 Stainless Steel Narrow Cheese Head Slotted Screws		Steel
10	1	Rubber Seal		Rubber, Black
11	1	Rubber Front Seal		Rubber, Black
12	1	Steel Side Cover		Steel

Created by Michał Mikołajczyk 08.09.2023

Title **Pi Camera Case**

Sheet 1/1

Figure 32 - Exploded scheme of the camera with enclosure

5.Challenges for Enclosure Connectivity

The design of the enclosure, while comprehensive in its initial form, raised significant challenges regarding the connectivity between the enclosed camera and the external Raspberry Pi computer. The core issue is centred around routing the connecting cable through the reactor wall while maintaining a hermetic seal and accommodating the physical constraints of the reactor's design.

5.1 Assessing Cable Routing Options and Challenges

Three potential methods for cable extension and routing were evaluated:

5.1.1 Dual-Interface Cable Transition:

This approach involves transitioning from a 15-pin cable to an HDMI cable and then back to a 15-pin cable. The primary challenge here is the bulky HDMI connector, which exceeds the 10 mm valve diameter. A proposed solution is to strip the HDMI cable into individual wires, thread them through the valve, and then re-solder them. This method provides a direct connection from the camera to the Raspberry Pi but presents significant complexity in terms of cable modification and reassembly.

5.1.2 Flexible 15-Pin Extension:

Another option considered is using a flexible, rollable 15-pin extension cable. The feasibility of this method depends on the cable's ability to withstand the rolling process without damage. While the rolled cable could potentially fit through the narrow valve, the risk of cable integrity compromise remains a concern.

5.1.3 Node-Based 15-Pin Extension:

The third option is to disassemble the 15-pin cable into individual nodes, similar to the HDMI approach, and thread these through the valve. This method eliminates the need to re-solder the cable, as seen in the HDMI solution, potentially simplifying the process. However, it shares similar complexity and labor-intensiveness.

5.2 Re-evaluating the Design Strategy

After thorough analysis, it became evident that each proposed solution, while theoretically feasible, posed significant practical challenges. These included the complexity of cable modification, the risk of damaging the cable during the modification process, and the difficulty in ensuring a reliable seal in the reactor valve.

Consequently, a decision was made to revisit and modify the overall design approach. This involved exploring alternative strategies that could circumvent the need

for complex cable routing and modifications. The revised design strategy aimed to simplify the installation process, reduce the risk of operational failure, and ensure the integrity of the seal, thereby aligning with the overarching objective of maintaining the camera's functionality and reliability within the reactor environment.

5.3 Updating the design

While the design of the case is plausible, the cable is the main problem. The solution might be to install the enclosure as part of the wall of the reactor. This way cable doesn't require any sealing as it is not in the reactor environment. After checking the cable and the valve we established that it is possible to roll the 15 pin cable and lead it through the valve without destroying it. This makes it possible to have 10mm tube that will be connected to the case, led through the valve and held by a nut.
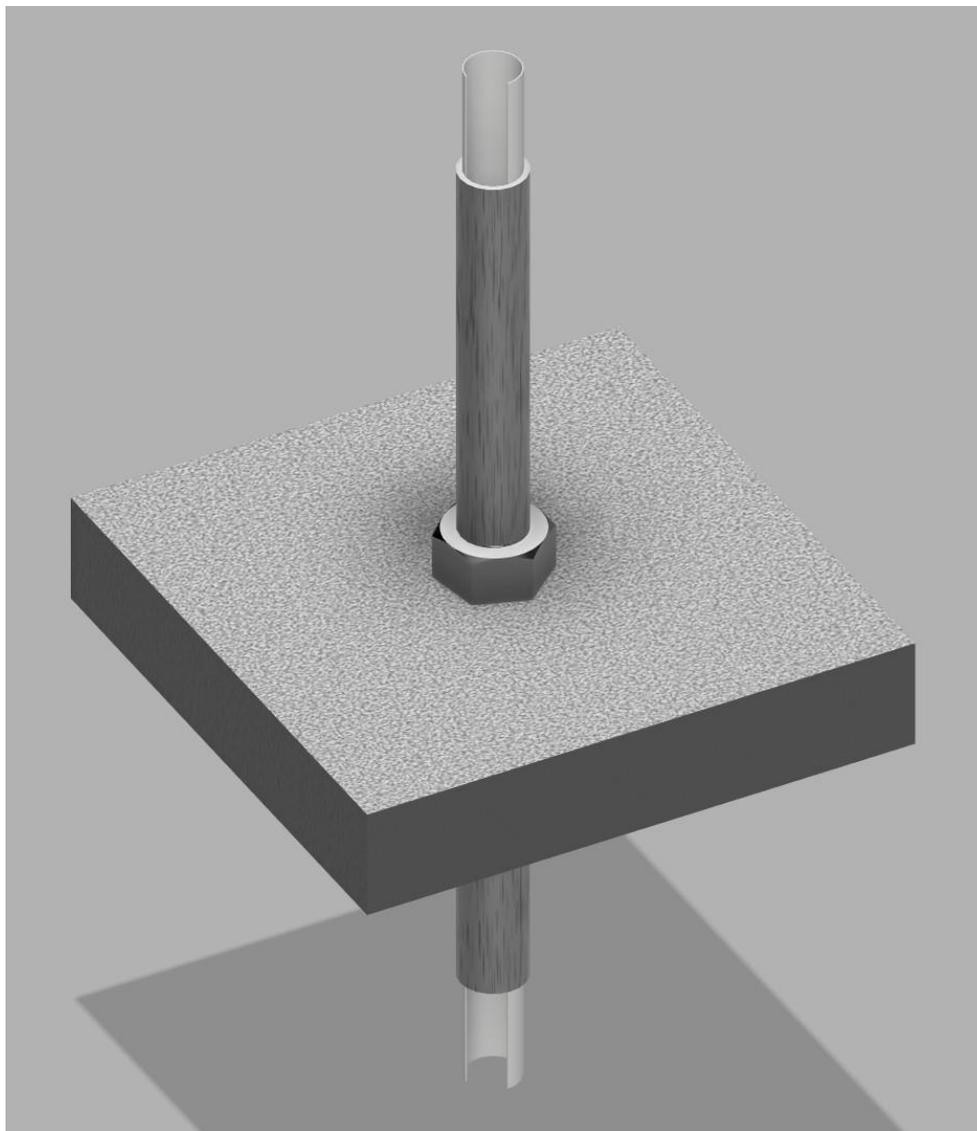
Figure 33 - Way of leading the cable through the reactor wall

5.4 Change of shape of the enclosure

Next improvement over previous design is to change the shape of the enclosure. Making the enclosure round will make it easier to produce as we can use turning lathe. This will also allow to easily include it into the reactor wall.
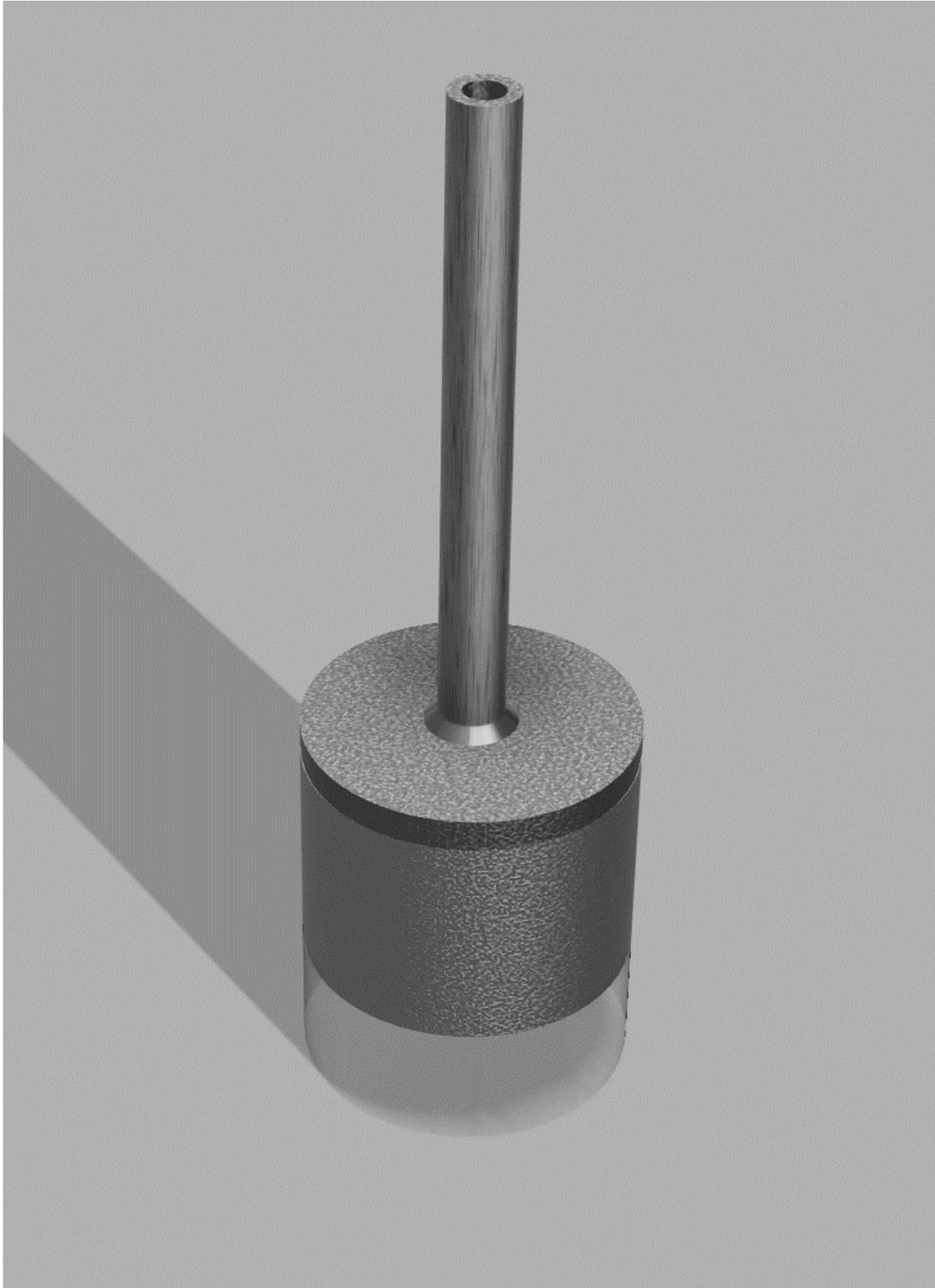
Figure 34 - Redesigned Circular enclosure

5.5 Final Design

The final result that will be produced and will looks as follows:

Figure 35 - Exploded view of the circular enclosure

5.6 Incorporating the enclosure into the wall

Figure 36 - Enclosure in the wall of the reactor

5.6 Incorporating the enclosure into the wall

6.Inside of the reactor

6.1 Design of the reactor

Figure 37 - Reactor Design

6.2 Experimental Environment Configuration

The experimental setup was meticulously designed to monitor various critical parameters within the reactor. This involved the integration of probes and sensors, each serving a specific function in the data collection process.

6.2.1 Integration of Probes and Sensors

The configuration included four PT100 temperature probes, a pressure sensor, and a CO_2 flow meter.

6.2.1.1 Temperature Probes

The specifications of the temperature probe OMEGA 2PT100KN3026CLA [30] are as follows:

- Resistance: 2 x 100 Ω
- Well diameter: 2.6 mm
- Well length: 30 mm
- Well material: Ceramic
- Number of wires: 4
- Temperature range: -200 to 600 °C
- Accuracy: Class A (± 0.15 + (0.002 * t) °C)
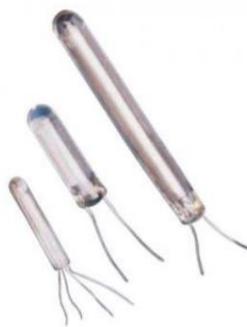
Figure 38 - Temperature probe OMEGA 2PT100KN3026CLA [30]

- **Placement**: The temperature probes were placed at different locations: one at the bottom, another in the middle of the reactor, a third just above the water level inside the reactor, and the fourth outside the reactor submerged in the cooling water.
- **Expected Behaviour**: These probes were expected to show a decrease or stabilization in temperature during the pressurization of the reactor. Upon reaching the target pressure of 2MPa, where hydrate formation was anticipated, an increase in temperature was expected due to the exothermic nature of the hydrate formation process.

6.2.1.2 Pressure Sensor

The specifications of used pressure sensor the OMEGA PXM309-070G10V [31] are as follows:

- Output: 0-10 V
- Pressure range: 70 mbar to 70 bar (g)
- Sensor material: Silicon sensor with stainless steel diaphragm
- Case material: Stainless steel
- Total error: 70 mbar, ±4.5%; 70 bar, ±1%
- Protection rating: IP67

Figure 39 - Pressure sensor OMEGA PXM309-070G10V [31]

- **Function**: The main pressure sensor was tasked with monitoring the internal pressure of the reactor, providing crucial data for analysing the conditions under which hydrate formation occurs.

6.2.1.3 Flow Meter

The specifications of used flowmeter the OMEGA FMA5516A-ST [32] as follows:

- Range: 0-2 l/min (N2)
- Accuracy: ± 1% of range
- Repeatability: ± 0.5% of range
- Temperature coefficient: 0.15% of range/°C
- Pressure coefficient: 0.01% of range/0.07 bar
- Maximum pressure drop: 3.5 bar
- Response time: 5 seconds
- Maximum media pressure: 35 bar (g)
- Maximum media temperature: 50 °C
- Output signal: 0-5 VDC
- Power supply: 12-15 VDC @ max. 800 mA

Figure 40 - Flow meter OMEGA FMA5516A-ST [32]

- **Purpose**: The flow meter was employed to measure the CO_2 flow into the reactor. This measurement is vital for controlling and understanding the kinetics of the hydrate formation process.

6.2.2 Preliminary Test Run

A test run was conducted to evaluate the resilience of the camera in the reactor environment and to assess the quality of images it could capture. Additionally, this test aimed to verify the functionality of all probes and sensors and to check for any potential leaks in the reactor. For this test, the camera, housed in its protective enclosure, was placed inside the pressurized reactor, set at 2MPa. No hydrate formation was observed during this test, as the temperature remained in the 5-6°C range, which is higher than the optimal range for hydrate formation under these pressure conditions.

6.2.3 Test Conclusions

The test proceeded as planned, successfully recording temperature variations during the reactor's cooling phase and capturing images of the reactor's interior during pressurization. The camera enclosure proved effective, showing no signs of failure under the tested conditions. However, it was observed that the camera's positioning directly above the CO_2 inlet led to water splashes from the CO_2 emissions, resulting in droplets forming on the epoxy cover and obscuring the camera's view. This outcome has led to the decision to reposition the camera to avoid such obstructions and ensure clearer visibility for future observations.

Figure 41 - Inside of the reactor without droplets
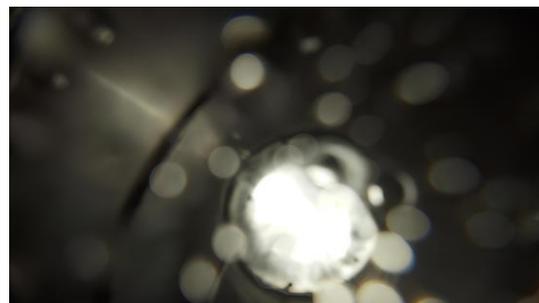
Figure 42 - Inside of the reactor with droplets

The temperature probes worked as expected providing us with following results:
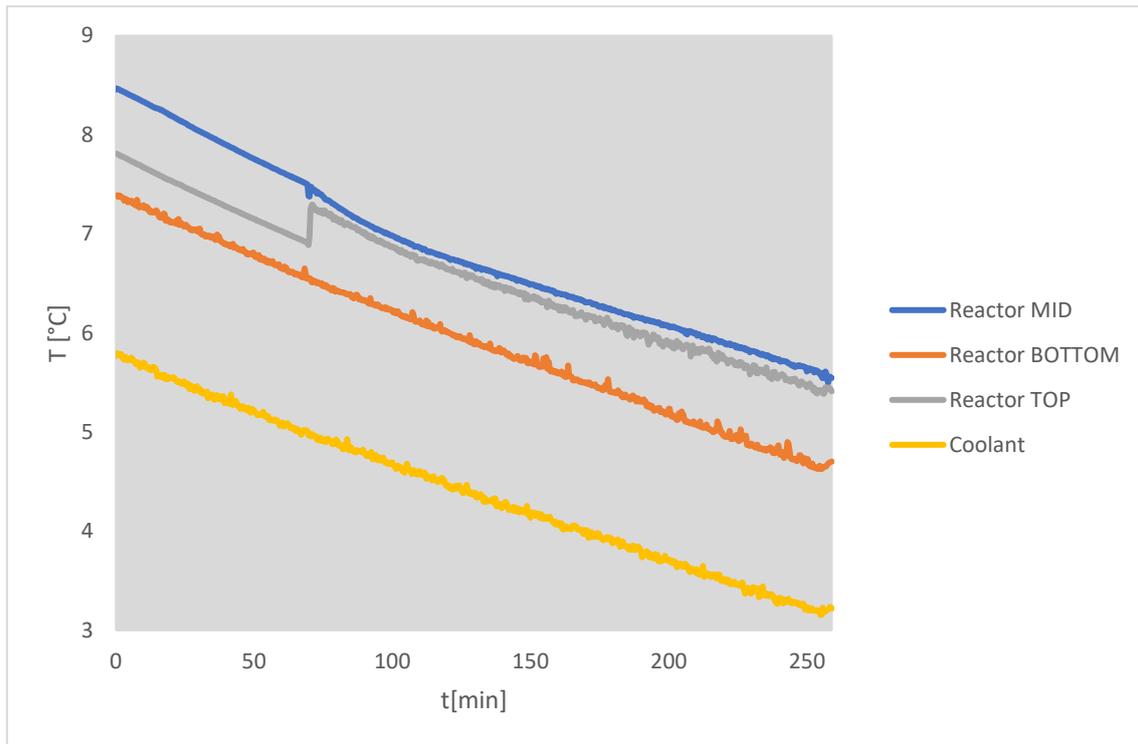
Figure 43 - Temperatures during reactor testing

We can see the temperature decrease with time. Around the 60min mark we observe a temperature increase in the top of the reactor which is caused by a start of pressurising the reactor with CO_2.

7 Experiment

7.1 Goals of the experiment

The primary objective of this experiment is to facilitate the formation of carbon dioxide (CO_2) hydrates within a controlled reactor environment. A significant aspect of this experiment involves the utilization of photographic equipment to capture images of the hydrates as they form. These images are expected to provide valuable insights into the formation process of CO_2 hydrates. Understanding this process is crucial for improving the understanding of the formation process which may lead to advancements in various scientific and industrial applications where CO_2 hydrates are relevant.

7.2 Setting up the Experimental Environment

Preparation for the experiment commenced a day prior, with the activation of the cooling system. This step was critical to lower the temperature sufficiently, creating an environment conducive to the formation of hydrates. On the day of the experiment, a thorough inspection was conducted to ensure the functionality of all probes and the camera system. Following this, the reactor was pressurized, checked for eventual leaks and prepared for formation of CO_2 hydrates

7.3 Calibration of the sensors

7.3.1 Temperature sensor calibration

The calibration of the temperature sensors was performed referencing the methodology and data from Ing. Matej Hrncir's work [33], as the same sensors and environmental conditions were employed. The process involved a comparative method using a standard calibration furnace. The calibrated sensor was placed in one well of the furnace, while a standard temperature probe connected to a digital thermometer was placed in another. The selection of wells was based on the diameter of the sensors to ensure full immersion and optimal calibration conditions. An insulating layer was used to cover the furnace, enhancing the accuracy of the calibration process.

Calibration was executed at three distinct temperature points: -5°C, 0°C, and 5°C, to encompass the operational range of the sensors. Both the standard and calibrated sensors were allowed to stabilize at each temperature point. Subsequently, five consecutive readings were recorded every 2 to 3 seconds. These readings, obtained from both the standard and the calibrated sensors, were then used to plot the calibration curves for the temperature sensors.

Table of calibration curves

CH107	$y = 1{,}023 * x - 0{,}027$
CH108	$y = 1{,}003 * x - 0.045$
CH109	$y = 1{,}025 * x - 0{,}025$

Table 1 - Table of calibration curves

7.3.2 Pressure sensor calibration

The calibration of the pressure sensors followed a methodology similar to that of the temperature sensors, using data from Ing. Matej Hrncir [33]. The process involved a CO_2 pressure bottle, a thermometer for ambient air temperature measurement, and a pressure calibrator. Initially, the pressure sensor was connected to the CO_2 pressure bottle. The ambient air temperature was measured at 19.5°C, correlating to the saturation point of CO_2 at the specific pressure, allowing for the use of the CO_2 saturation curve to deduce a pressure of 5.6621 MPa. This step was critical in ensuring that the pressure inside the bottle matched the calculated value.

Further calibration at lower pressures was achieved using the pressure calibrator, with a maximum capacity of 0.4 MPa. The calibration results were tabulated (Figure 44), with the pressure values serving as the standard against which the voltage

readings from the sensor were compared. This calibration ensured the accuracy and reliability of the pressure sensor for subsequent experiments.

	P [MPa]	U [V]
1	5,6621	5,541
2	0,3416	0,325

Table 2 - Table for pressure calibration
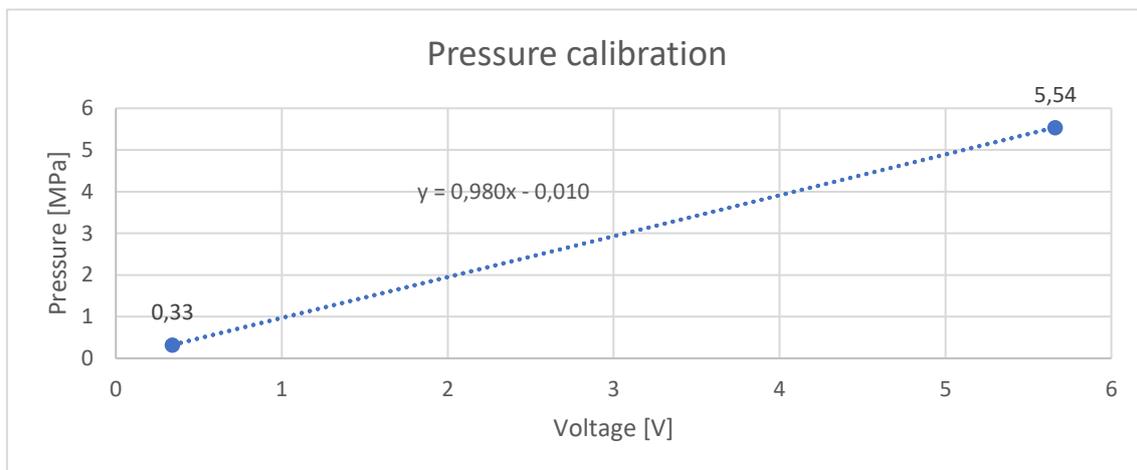
Figure 44 - Pressure calibration graph

From the calibration curve of the pressure sensor, its calibration equation is derived in the form:

$$y = 0.980 \times x - 0.010$$

This equation translates the voltage readings from the sensor into pressure values (in MPa), indicating that for each unit of voltage measured, the corresponding pressure can be calculated by multiplying the voltage by 0.980 and subtracting 0.010. This calibration equation is pivotal in converting raw sensor data into precise and reliable pressure readings, vital for the accuracy of experiments involving the sensor.

7.4 Experiment procedure

The experiment began with the temperature of water in the reactor around 1°C, then we proceeded to slowly pressurizing the reactor with the CO_2 flow at approximately 1,75L/min. The pressurization process was executed smoothly, and the reactor was successfully pressurized to over 2.5 MPa. This pressure level was chosen based on prior research and experimental data indicating its suitability for the formation of CO_2 hydrates under the given temperature conditions.
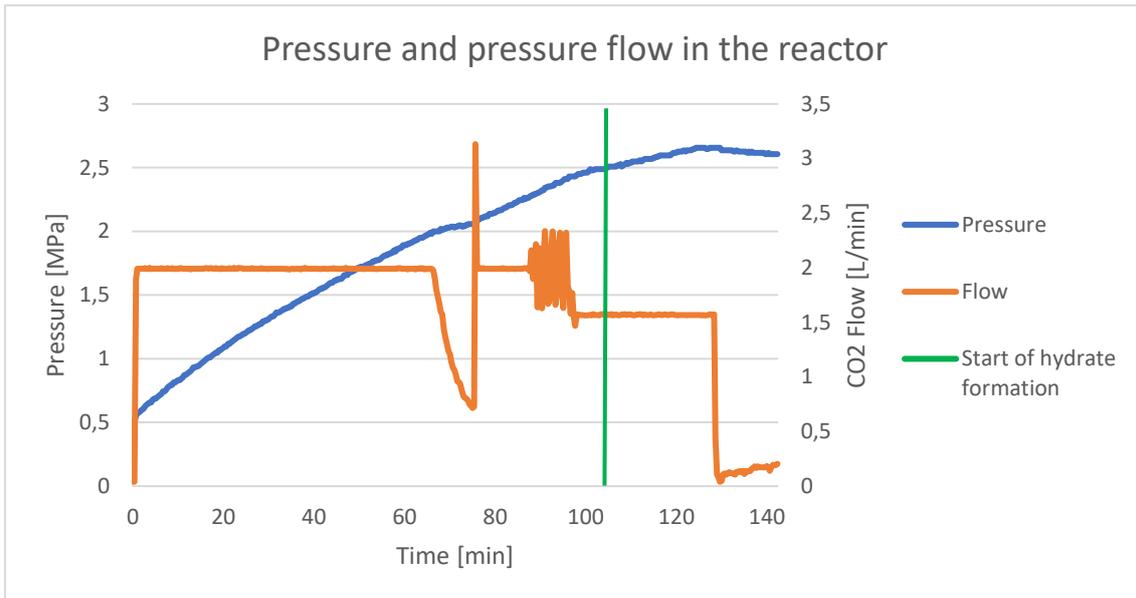
Figure 45 - Graph of pressure and CO2 flow
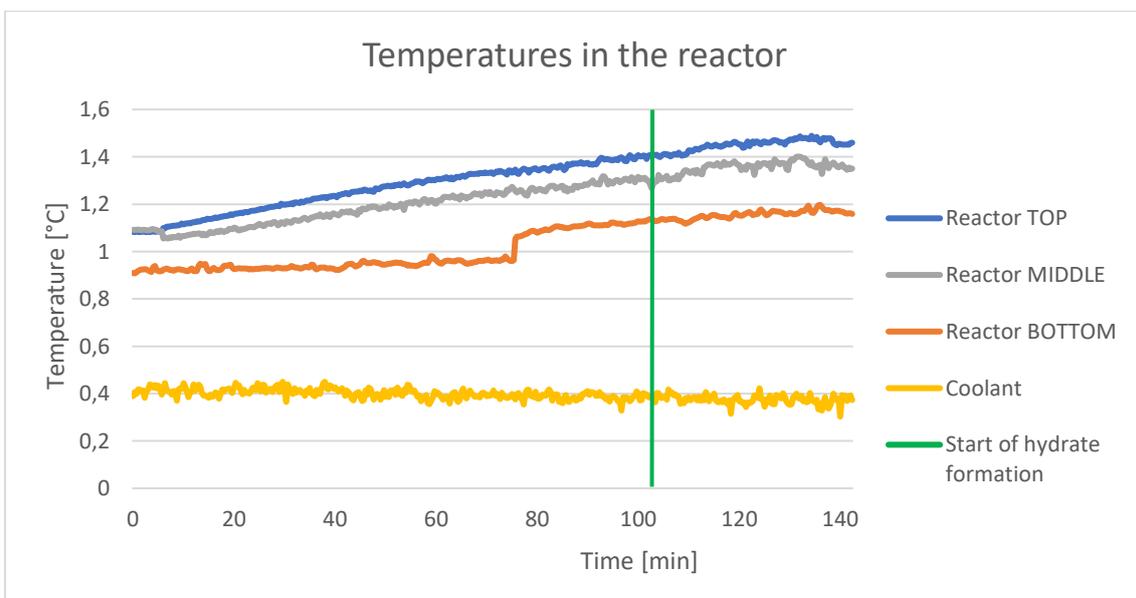
Figure 46 - Temperatures inside of the reactor

During the experimental phase, continuous monitoring of the reactor's internal temperature, coolant temperature, pressure and CO_2 flow was performed. The recorded data provided insightful observations on the behaviour of carbon dioxide (CO_2) flow within the reactor, as depicted in Figure 46. Notably, a fluctuation in the CO_2 flow was observed, initially decreasing to 0.6 L/min, followed by a surge exceeding 2.5 L/min, before finally stabilizing at the predetermined rate of 1.75 L/min. This variability in flow rate was attributed to the partial opening of the CO2 bottle valves, a deliberate action taken to prevent potential damage to the flow meter. Upon opening the valves, a marked increase in CO_2 flow was noted, preceding the stabilization phase executed by the flow meter. Additionally, a resonance issue with the flow meter was encountered

around the 90th minute of the experiment, necessitating a reduction in flow rate to achieve stabilization.

A critical observation was made around the 130-minute mark, where the CO_2 flow reduced to zero and then exhibited a minor increase without concurrently raising the reactor's internal pressure. This indicates that post this juncture, all incoming CO_2 was directly converted into hydrates. This observation is pivotal as it potentially enables the calculation of the hydrate formation rate based on the CO_2 flow metrics.

Turning to the temperature dynamics within the reactor, as illustrated in Figure 47. From the time the crystallization started (represented by the green line) we can observe a slight temperature rise. While an increase in temperature at the reactor's upper section was anticipated, the actual rise observed was relatively modest. This discrepancy is likely due to the positioning of the temperature probe, which was not submerged in water. To gain a clearer understanding of the temperature variations, I created trendline for the temperature rise before the crystallization and compared it with real temperature in order to obtain change in temperature (ΔT)

$$\Delta T = -0{,}000007x^2 + 0{,}0011x - 0{,}0073$$

This temperature change indicates that the temperature did increase with the crystallization and the temperature increase in the water was more substantial.
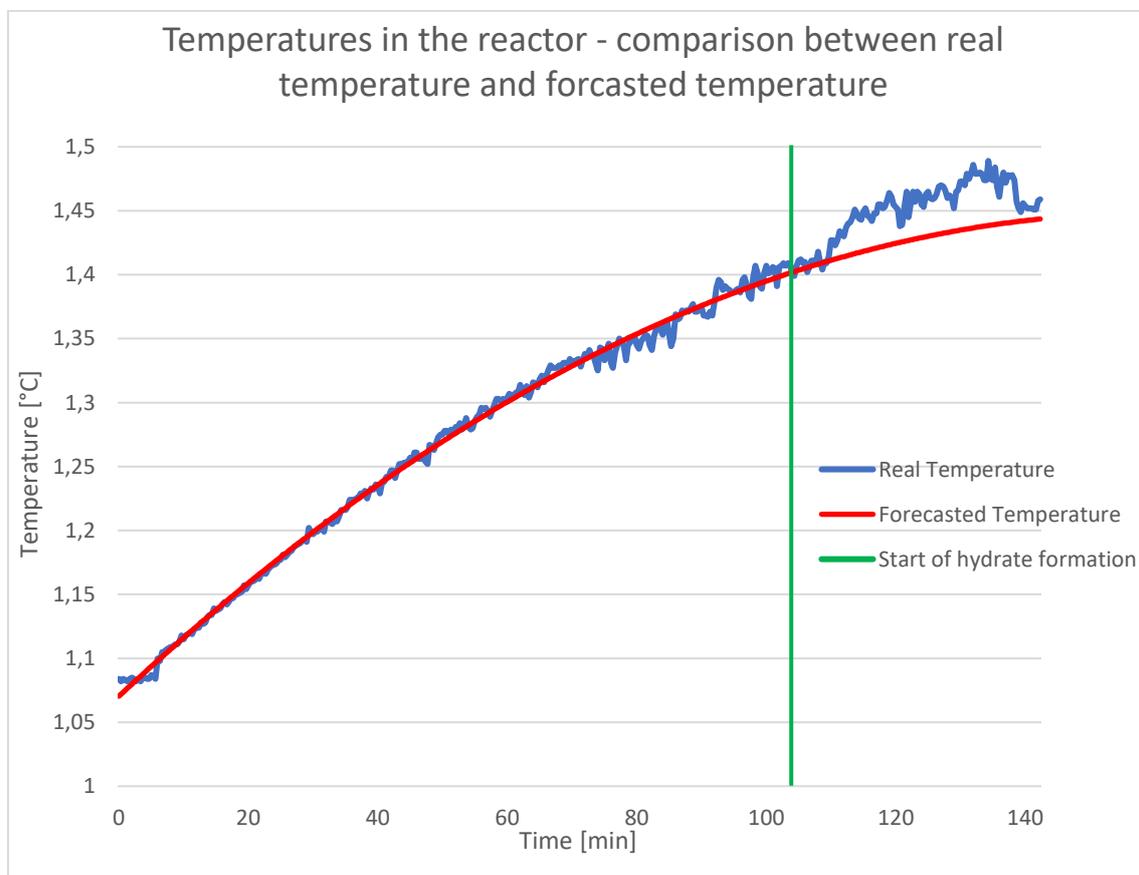
Figure 47 - Comparison between real temperature and forecasted temperature

8.Hydrate formation

The hydrate formation started to occur around 100min after starting the experiment, with our first image of hydrates in 101 minutes and 30 seconds into the experiment.
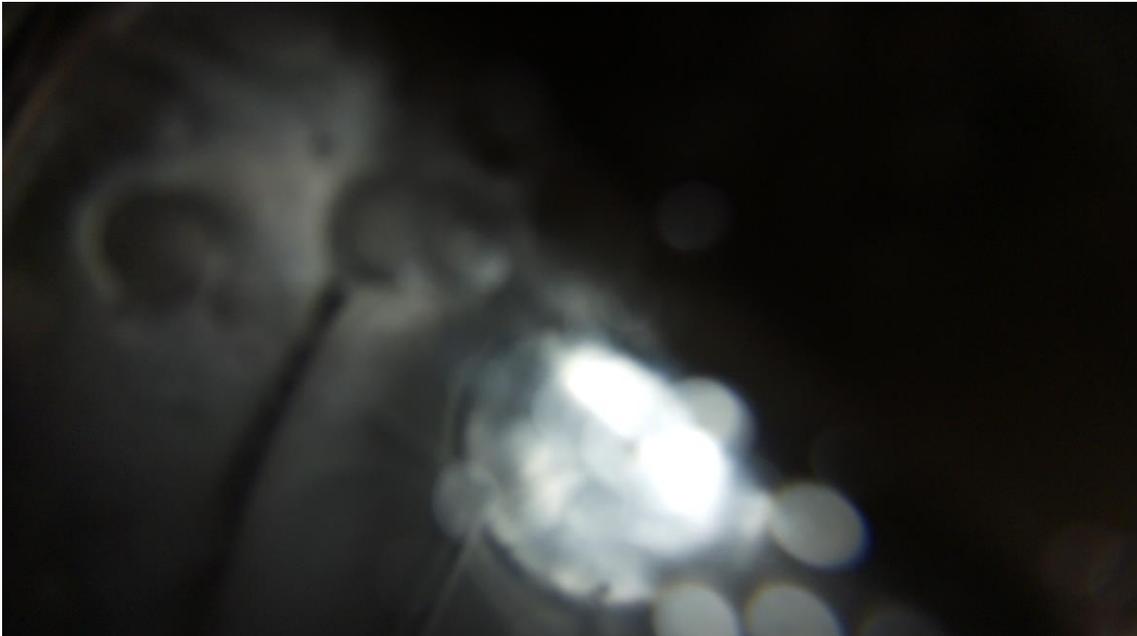
Figure 48 - First Crystalized Hydrates

Here we can see first image of the crystalized hydrates on the paddle of the mixer.

Figure 49 - Crystalized hydrates after 30 sec

We can easily see the increase of number of hydrate in that 30 second period

8.1 Hydrate layer

After around 5 minutes of hydrate crystallization thin layer was created on the surface of the water. This layer seems to capture the CO_2 before it can escape the water, creating bubbles of CO_2 that are quickly turned into new Hydrates
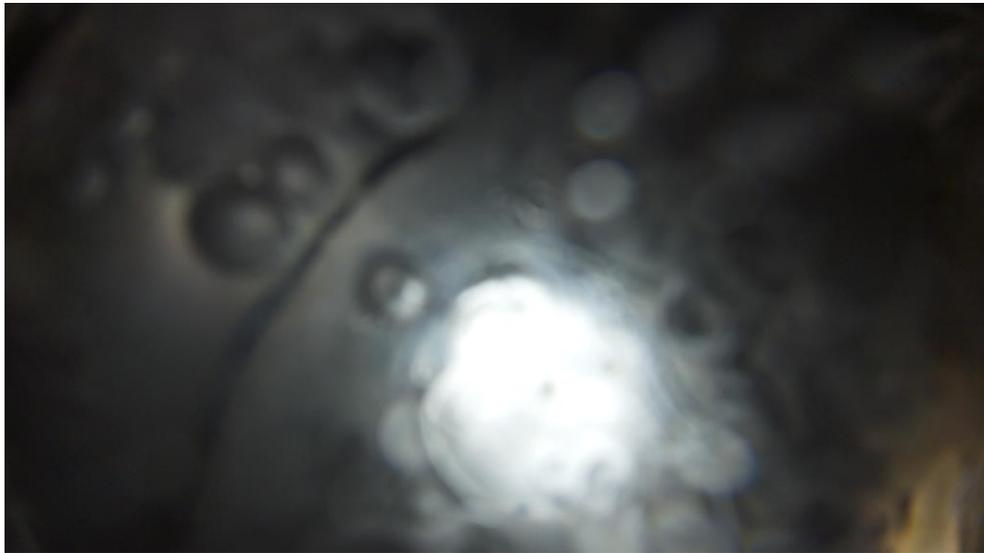
Figure 50 - Hydrate Layer

8.2 Hydrates on the mixer

Figure 51 - Hydrate bubbles on the mixer

On this image we can see hydrates that formed on top of the mixer which was not in the water. This is interesting as Hydrates formed without direct source of water. Which may suggest that under certain conditions the hydrates may be crystallized

from water vapour which is in agreement with the water spraying reactor discussed earlier.

8.3 Growth process of a hydrate

For the conclusion of the experiment, I have decided to capture process of Hydrate growth in 30 second intervals. This will hopefully give us more insight into this process.

Figure 52 - Start of observing growth

Figure 53 - Growth 30 seconds
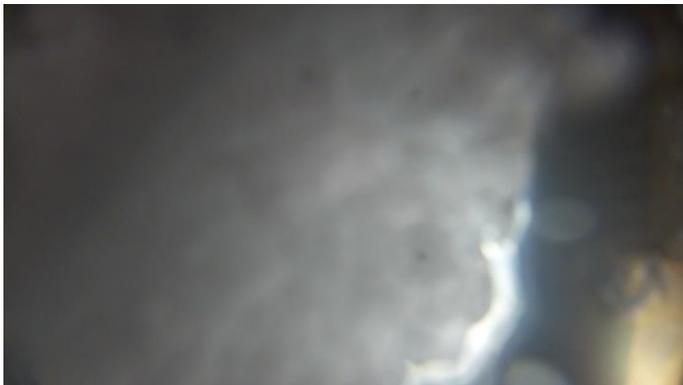
Figure 54 - Growth 1 minute

Figure 55 - Growth 1 minute 30 seconds
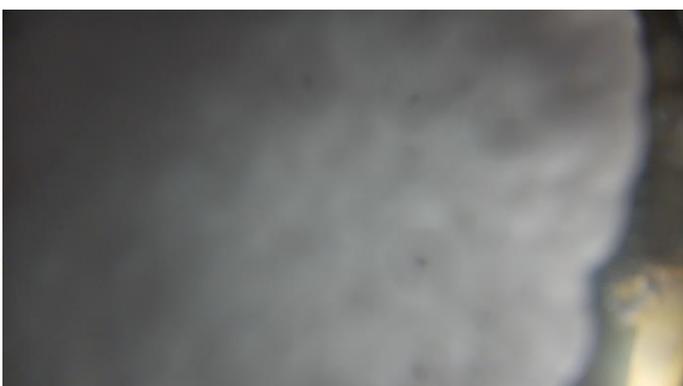
Figure 56 - Growth 2 minutes
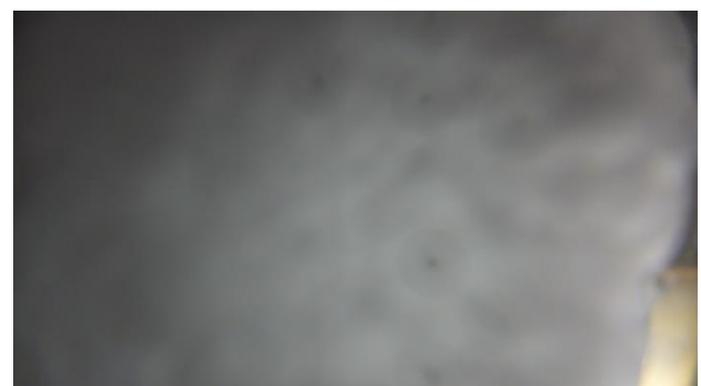
Figure 57 - Growth 2 minutes 30 seconds

Figure 58 - Growth 3 minutes

Figure 59 - Growth 3 minutes 30 seconds

Figure 60 - Growth 4 minutes
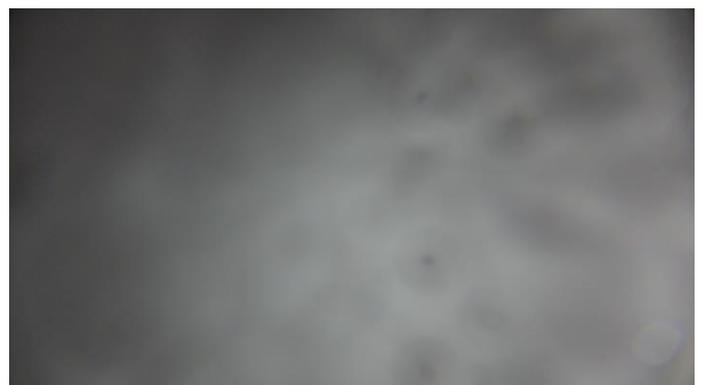
Figure 61 - Growth 4 minutes 30 seconds

On these images we can observe the formation process of Hydrates in regular intervals. We can see that existing hydrates are catching the CO_2 bubbles and slowly incorporate it into the structure of the hydrate. We can also observe the thickening of the hydrate which might suggest that they are getting denser as the crystallization progresses.

9.Conclusion

In this Bachelor Thesis has provided a comprehensive overview of the theoretical background and practical applications of clathrate hydrates. The exploration began with an in-depth analysis of the types of hydrates and the intricate process of their crystallization, emphasizing the crucial role of pressure and temperature in their formation. This set the foundation for understanding the versatile applications of clathrate hydrates across various industries.

In the petroleum and energy sectors, clathrate hydrates have shown promising potential in enhancing efficiency and sustainability. Their role in water desalination, gas sequestration, wastewater reclamation, and gas mixture separation underscores their versatility and relevance in addressing current environmental challenges. Furthermore, the exploration of their use in environmental preservation highlights the growing importance of sustainable practices in industrial processes.

The thesis then delved into the hydrate formation technologies, such as pressure swing, temperature swing, the use of promoters and additives, ultrasonic, and membrane technologies. Each of these technologies offers unique advantages and showcases the innovative approaches being developed to optimize the formation and utilization of clathrate hydrates.

Subsequently, the discussion of various types of reactors, including gas dispersion, stirred tank, bubble forming, water in oil emulsion, fixed bed, water dispersion, and water spraying reactors, provided insight into the practical aspects of hydrate formation and handling. These reactors are critical in scaling the laboratory findings to industrial applications, demonstrating the feasibility and adaptability of clathrate hydrate technologies in real-world scenarios.

Then I proceeded to develop the observing setup for hydrate formation. This was done to ensure better understanding of the intricate formation processes and give us potential insight into the potential of improving rate of formation or its dependence on pressure and temperature.

I began with selection of hardware for the observation setup which ended up being Raspberry Pi 3B+ and Raspberry Pi camera V2. My choice was influenced by the seamless integration between those two components, their ease of configuring, stellar performance, quality and strong online support community.

To prepare those two components to work I assembled the computer, attached the camera to it and proceeded to configure the system of the computer. This is where I have encountered first issue as the microSD card that held the system was corrupted so I had to find a workaround in form of USB stick on which I have installed the system instead.

After the preparation I wrote the script in Python that is responsible for controlling the camera and taking series of photos in predefined intervals. Later I decided to improve the script so the name of the picture is the time from start of the experiment. Then I proceeded with testing the setup which went as expected, although I have noticed that the camera is very susceptible to vibrations that can affect the quality of the images.

Next step of my bachelor thesis was the designing process of the enclosure for the components. After careful evaluation of the environment inside of the reactor I chose the suitable materials for enclosure and proceeded to model it in 3D modelling software – Fusion 360. After the discussions about production, I was prompted to change the design to round shape to simplify the production process and to include the cable inside of the enclosure to avoid sealing problems of the reactor as there was no valve big enough to facilitate the cable.

Configuration of the environment was another crucial step to check if my setup is working in reactor environment. I provided models of the reactor and the enclosure embedded into top cover. I also described the sensors that are utilized to capture temperature and pressure data. The finalization of the configuration process was the preliminary run in which I checked the camera in reactor environment as well as check the reactor itself for any potential leakages or other issues.

Finally, after configuration and test run, I was ready to proceed with real experiment. I calibrated the sensors and begun the experimental procedure. We stated with lowering the temperature of the reactor overnight to ensure the temperature required for formation of the hydrates. On the day of the experiment, we started to pump in the CO_2 to pressurize the reactor and provide gas required for hydrate formation. I closely followed the pressure and temperature readings as I expected the temperature increase when the hydrate formation begins. This, however, did not happen, probably due to lack of temperature sensor in top water layer of the reactor. It is something that should be improved in future experiments.

Another aspects that could be improved in future experiments is the illumination and glass panel of the enclosure. The illumination which was utilized caused internal reflection in the plexiglass which deteriorated the image quality and forced us to lower the brightness. The plexiglass itself was not without its problems too. While strong enough, it caused the image quality to deteriorate, main issue was focusing the camera as the glass covered was strongly affecting it. Despite manually focusing the camera I was not able to obtain images of similar sharpness to ones without the cover, this might be due to internal reflections, poor light transmission percentage or other properties of the plexiglass. Potential change of the plexiglass to hardened glass, laminated glass or polycarbonate glass might solve this issue and its worth checking in future experiments.

Despite those issues I was able to successfully capture the crystallization process of CO_2 hydrates. I observed that the formation started first on the mixer which might suggest that porous media on water-gas barrier may speed up the formation process. Next interesting process I was able to observe is the formation of thin hydrate layer on the

water that was catching the CO_2 bubbles that were coming from the bottom of the reactor. This might be important due to the fact that the formation on top of the layer seemingly stopped after the layer was created what underlines the importance of mixing to constantly create interstitial area on the water-gas border. Lastly, I noticed that the hydrates formed on top of the mixer, which was not in direct contact with water, this seems to confirm the design of water spraying reactor I discussed in this thesis earlier.

Concluding, the experiment went well, but not without its issues. The images I have gathered gave me better understanding of the formation processes of hydrates. Further work on hydrates can be done in various fields. The speeding up the formation process is one of them, I can implement the knowledge I have gather during this experiment about porous media as a potential speeding agent for the formation.

Improvements to the reactor design can also be implemented. Reducing the volume of water by decreasing height of the reactor is one of them. This should speed up the cooling process without hampering the crystallization of hydrates as the crystallization happens of water surface. More advanced mixing processes may also speed up the crystallization as it will introduce more gas into the water, thus increasing contact area required for formation. Various catalysts can also be explored for potential of speeding up the reaction or decreasing pressure requirements for hydrate formation.

Those rector improvements and potential inclusion of catalysts or speeding agents can further improve the crystallization process making clathrate hydrates a sustainable and exciting technology for the future.

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11.Table of Figures

12.Table of Tables