

AN EXPERIMENTAL INVESTIGATION OF R134a CLATHRATES

WITH LIQUID ADDITIVES

by

Hafiz M. Ahmad Gulzar

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Approval Signatures

We, the undersigned, approve the Master's Thesis of Hafiz M. Ahmad Gulzar.

Thesis Title: An Experimental Investigation of R134a Clathrates with Liquid Additives.

Signature

Date of Signature
(dd/mm/yyyy)

Dr. Saad Ahmed
Professor, Department of Mechanical Engineering
Thesis Advisor

Dr. Mohamed Gadalla
Professor, Department of Mechanical Engineering
Thesis Co-Advisor

Dr. Basil Darras
Associate Professor, Department of Mechanical Engineering
Thesis Committee Member

Dr. Zarook Shareefdeen
Professor, Department of Chemical Engineering
Thesis Committee Member

Dr. Mamoun Abdel Hafez
Department Head, Department of Mechanical Engineering

Dr. Mohamed El Tarhuni
Associate Dean, College of Engineering

Dr. Richard T. Schoephoerster
Dean, College of Engineering

Dr. Khaled Assaleh
Interim Vice Provost for Research and Graduate Studies

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Dedication

In the name of Almighty Allah, the source and origin of all the knowledge of present and otherwise, I dedicate this effort of mine to:

My Parents, who, in their life and death are a constant source of inspiration and strength to me.

My Sister, whose countless sacrifices enabled me to achieve this goal.

Abstract

Thermal energy storage (TES) using phase change materials is one of the most effective solutions for energy conservation. The selection of a phase changing material (PCM) with different liquid additives could improve the crystal growth rate and heat transfer characteristics. Direct contact heat transfer of PCM is one of the most influencing factors in improving the TES system performance. Numerous experimental runs were conducted to investigate the crystal growth formation time and its structural characteristics using different liquid additives under different operating conditions. The investigation was mainly based on the crystal growth formation time of the inclusion compound of R134a and the distilled water in the cold storage applications. Four different additives with different percentages were used to investigate their effectiveness on the clathrates characteristics. The additives used for this investigative work were ethanol, butanol, ethylene glycol, and glycerin. The onset time of crystal growth formation and the final endset time were recorded at different operating temperatures. Percentage of additives (for ethylene glycol, butanol and glycerin) used in this investigation varies between 1-4% while for the ethanol as additive, the percentage varies between 1.5%-4.5%. For the case of butanol, the refrigerant percentage was also varied in addition to the liquid additive percentage. The experimental results showed that additives impact on the clathrates formation time as well as clathrates characteristics. Minimum clathrates formation time was found to be 17 minutes for the ethylene glycol (as an additive) with the highest percentage of 4%. At the same time, the crystal structure remains fluffy. Although, the clathrates formation time was higher for the butanol initially but there was a sharp decrease in the clathrate crystal growth formation time throughout. Minimum clathrates formation time for the butanol (as an additive) was found to be 17.67 minutes for highest percentage of 4%. The clathrates formation for the butanol results into rock solid crystals. Same nature of crystals formation was demonstrated by the ethanol. The experimental results also concluded that there has to be a specific ratio between water and refrigerant on a mass basis in order for the clathrates to form with optimum operating conditions, which is close to 35%.

Search Terms: Thermal energy storage TES, Phase change materials PCM, Gas hydrates, Crystal growth, Refrigerant 134a, Liquid additives, Energy conservation.

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Nomenclature

Symbols

h	Specific enthalpy (kJ/kg)
c_p	Specific heat capacity [kJ/kg K]
m	Mass (kg)
T	Temperature [°C]
t	time[minutes]
w	Percentage of Additive
ρ	Density [kg/m^3]
Q	Energy (kJ)
μ	Supersaturation factor
K	Boltzman constant
S	Supersaturation ratio
N_i	Number of i th ions in the molecule of the crystal
a_i	Actual activity of the i th molecule in the crystal
$a_{i,e}$	Equilibrium activity of the i th molecule in the crystal
r	Spherical radius of nuclei
σ	Free energy of the nuclei
t_r	Time required by the solution to reach a quasi-state equilibrium.
t_n	Time required for nucleus formation
t_g	Growing time of crystal
n	Nucleation exponent

Subscripts

f	final
i	initial

m medium

s stored

Abbreviations

CWS Chilled Water Storage

LED Light Emitting Diode

LHS Latent Heat Storage

PCM Phase Change Material

RCB Refrigerated Cooling Bath

SHS Sensible Heat Storage

TES Thermal Energy Storage

Chapter 1: Introduction

1.1. Motivation

There has always been an increasing demand of electricity. With the increasing population and their requirements, the resources must be available to support the necessities. There is no substitute of electricity. Power loss for few minutes may actually result into huge resources loss and financial crises. A lot of developing countries in the world are still facing the problem of electricity shortage. Statistics shows that a big share of power generation comes from utilizing the natural resources/fossil fuels. Besides the negative environmental impact due to the combustion of these fossil fuels in power plants, increasing cost of these fossil fuels also creates financial burden.

Because of the previously mentioned problems; a need of the suitable, applicable and reliable solutions has emerged. Many efforts have been made to decrease the load on the natural resources. The solution for this issue can actually be a two way strategy i.e. to decrease the power consumption somehow, or to find some other resources for power generation. While most of the research has been done on finding the other resources, researchers have made efforts to find some practical solutions in order to manage the dramatically increasing phenomenon of electricity utilization. Thermal energy storage (TES) is one of the techniques that can bridge the gap between electricity production and consumption. This technique can be used for both cooling and heating redistribution. The basic idea is to shift the load from on-peak hours to the off-peak hours [1]. In this way, energy can be stored during the off-peak hours when there is less demand while this stored energy can be utilized during the peak load hours. Cool thermal energy storage is basically the use of the stored cold energy for the purpose of cooling applications during the on-peak hours by circulating the cooling medium instead of using the conventional refrigeration cycles [2].

Thermal energy storage can be either sensible thermal energy storage or latent thermal energy storage. In sensible thermal energy storage, thermal energy is stored by raising the temperature of any solid or liquid medium. In this case, no phase change occurs. System absorbs energy by the simple heat transfer mechanisms of conduction, convection and radiation. Using the latent thermal energy storage is the most common and efficient practice to decrease the volume to energy ratio. In this way, thermal energy

is stored while material goes through a phase changing process. This system is also much more efficient as compared to sensible thermal energy storage because of its higher storage density with a smaller range of swing temperature between storing and releasing heat [3].

Looking at the broader perspectives of its applications, thermal energy storage can be really handy for the countries like UAE where the weather conditions particularly require more cooling loads most of the year. On-peak hours in UAE is considered to be to be the biggest share of energy consumption. At night, the energy consumption falls as most of the industrial units and offices close their operations and there is less usage of air conditioning systems. So, the best solution is to use thermal energy storage and utilizing phase change materials (PCM) for practical cold storage applications. Research on phase changing materials shows that characteristics of phase changing material can be optimized using different additives. In order to use different thermal energy storage systems on industrial scale, great need is available for further research.

1.2. Problem Statement

The optimum design of cold thermal energy storage has always been an interesting area of research as limitations can restrain the desired results. Thermal energy storage can be really effective when it comes to the energy conservation technology. However, for having sustainable industrial scale applications, further research efforts can be done for improving the cold storage media. Clathrates formation time is one of the key factors in this technology that determines the time needed for the phase changing material to reach a specified rise in temperature by absorbing energy during the cooling applications. At the same time, additive materials can be used to improve clathrates' characteristics and its formation time.

The absorbed energy of phase change material can be used to distribute partial/full load during the top on-peak hours. So, finding a set of additives with the optimum required properties to help in the clathrates formation process for its usage in cold thermal energy storage is the key area of interest in this research. By taking this goal into consideration, the main objectives of the current work are:

- Reviewing open literature, select and study the easily accessible, sustainable and easy to use additives in order to improve the clathrates formation process.

- Working on the different scenarios of clathrates formation using comparative analysis of these selected additives.

1.3. Significance of the Research

Considering the scenario of future energy requirements, the research focuses on the key strategy to the problem i.e. improvement in the energy conservation technologies so as to apply the technology on industrial and domestic scale. By looking at the electricity distribution and usage, it is evident that air conditioning systems use the largest share of electricity. Conserving energy through different technologies means decreasing the maximum load factor of electricity grid. This idea gave researchers a view to focus on different technologies for energy conservation. If we look at the energy consumption requirements for the heating ventilation and air conditioning (HVAC) systems in different parts of the world, statistics show that in US, HVAC systems consume around 50% of the electricity, whereas the requirement for the residential and commercial areas in Europe for HVAC systems is around 40%. In the Middle East, the figures of building electricity consumption go up to 70% for usage of cooling systems which is increasing with the number of buildings construction [36]. Therefore, it is highly desired to invent and improve the methods for energy conservation in order to stop this rapid increase in electricity requirements, if not possible to decrease.

Thermal Energy Storage (TES) is one of the methods that can shift the load from top peak hours, if improved and applied properly. Shifting the electricity load for air conditioning requirement from peak hours to off-peak hours is the main strategy. Gas hydrates of the refrigerants are among the phase change materials that can be used to store thermal energy. The research in this thesis focuses on storing the cold thermal energy using gas hydrates of the refrigerant. When integrated with the conventional air conditioning systems for load management, a thermal energy storage system improves the system performance for energy conservation purpose. The performance of the system also depends on the operational modes of the system i.e. using a full load thermal storage or the partial load thermal storage. In full load thermal storage, the air conditioning load is fully supplied by the thermal energy storage system, while in the partial load thermal storage, only part of the cooling load is supplied by the thermal energy storage system. Finally, any improvements in the thermal energy storage system's capability results into an effective energy conservation which gives a clear edge to the integrated HVAC systems as compared to the conventional HVAC systems.

1.4. Thesis Organization

Experimental work has been done in this thesis in order to have a practical view of the clathrates formation using different conditions. In order to have a better understanding of the clathrates formation process, pretext, problem statement and the significance of the research is given in the first chapter. In the second chapter of the thesis, background of the thermal energy storage system and the basic concepts of the clathrates formation are given in details. The third chapter of the thesis extensively covers literature review. This chapter covers all the aspects of the research work already available. In the fourth chapter of the thesis, experimental work of clathrates formation is added in details along with the apparatus used for the experimental purpose. This chapter completely covers all the experimental results obtained and their respective analysis for clathrates formation time at different operating temperatures. The error analysis has also been done in this chapter for the experimental results. The last chapter consists of the conclusions and the recommendations for the future work. All the experimental values are given in the appendix of the current thesis.

Chapter 2: Background of the System and Basic Concepts

In general, the scope of thermal energy storage is broad. The objective of this thesis is to support research in the field of energy conservation and management. Thus, it requires the detailed survey of the work that has been previously done in this specific field. In this chapter, basic concepts are presented in details.

2.1. Thermal Energy Storage

In this section, the basic concepts of thermal energy storage systems are described in details. Moreover, different other helpful terminologies and definitions are explained technically in order to guide readers for better understanding about types thermal energy storage and their working characteristics and applications.

2.1.1. Concept of thermal energy storage system. Thermal energy storage is a technology used for energy conservation. Nowadays, it is being used in cooling applications in order to decrease the electrical load on the power generation systems. The main concept of thermal energy storage system concept lies in storing thermal energy through an appropriate medium when there is no much load on the electrical network and then using the stored thermal energy at a time when there is a peak load on the energy generation system. This concept helps out in two ways. First, the load on the power generation system does not increase dramatically. Hence, fewer burdens on the power generation system results in low/no power outage. Secondly, energy can be stored at off-peak hours when there are low per unit electricity generation charges. This stored energy can then be used to bear the partial or complete load during the on-peak load hours when there are high per unit electricity charges. In this way, thermal energy storage results in a positive impact on power production investments. A desired thermal energy storage system must decrease the energy consumption load. This has immense potential around the world especially for the current scenario when the fossil fuel prices are not constant which result in change of preferences for the power generation.

Thermal energy storage can be used for both cooling and heating applications. The cooling energy can be stored in the form of ice, chilled water, phase change material or eutectic eutectic solution [5]. While heating energy system can store the heat from the solar collectors, steam storage tanks or solar ponds for the further usage [6]. Thermal energy can be stored in any appropriate storage material in the form of sensible heat storage, latent heat storage or a combination .An overview of basic types

of thermal energy storage can be seen in the Figure 1 [7].

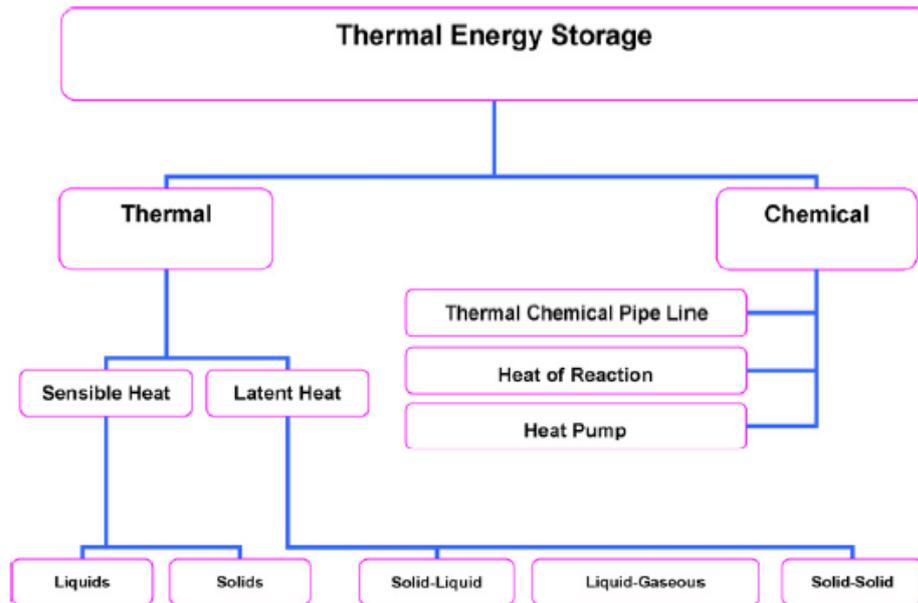


Figure 1: Types of TES by solar energy [7]

2.1.2. Sensible heat storage. In sensible heat storage system, the energy is stored by raising the temperature of medium. The amount of heat stored depends upon the heat storage capacity, total temperature change and the amount of thermal energy storage medium as can be seen from the following relation.

$$Q_s = m * C_p * [T_f - T_i]$$

Where, m is the mass of storing medium, T_f is the final specified temperature in Kelvin, T_i is the initial specified temperature in Kelvin, and c_p is the specific heat capacity at constant pressure.

Usually, appropriate sensible heat storage (SHS) medium must have a high specific heat capacity and it must be inexpensive in order to be used on an industrial scale. Water and some other oils are mostly used for SHS system applications [8].

2.1.3. Latent heat storage. In latent heat storage system (LHS), the thermal energy is stored or released with the help of a medium that has the capability of changing its phase. When a medium absorbs or releases thermal energy, its phase gets changed from one state to another. By this, the medium gets capable of storing energy with less temperature difference. The storage capacity of the LHS system using phase

change can be calculated using the following relation [8].

$$Q_s = m * c_p * [T_m - T_i] + m * \Delta h + m * c_p * [T_f - T_m]$$

Where, T_m is the phase change temperature of the material in Kelvin and Δh is the enthalpy difference in joules (J).

2.2. Cold Thermal Energy Storage (CTES)

Storing thermal energy for cooling purposes is the main idea of cold thermal energy storage. The concept of storing the cooling thermal energy is not new. Researchers have worked on this concept since last century. A simple application for using cooling thermal energy is the usage of ice or chilled water for preserving food. During the summer season in most of the countries, cooling load usually increases. This increased load may lead to the power outage that can actually be a huge problem for the domestic and industrial users. In this situation, using cold TES becomes very important. Cooling energy can be stored at the off-peak load timings (usually the night time) when the system does not have a comparatively higher load. On-peak-hours load is then supplied by simply circulating the cooling medium rather than by using conventional compressors with high power demand. Here, it is worthy to note that storing the cold thermal energy medium is much cheaper as compared to storing electrical energy [9].

Cooling TES becomes really important on locations where there are more power generation charges or the weather situation requires extensive cooling loads. Locations with the less operation timings e.g. offices etc., cooling TES system works efficiently as it decreases the power consumption. Operation of cooling TES system can also be useful in some facility planning for further expansions. The cooling load for the new unit can be provided from an existing facility using this cold storage technology. The cooling energy can then be saved from the existing facility at off-peak hours. Then, it can be provided to the new unit without adding any additional burden on cooling loads.

2.2.1. Performance criteria. The performance of a cooling TES system is described by its coefficient of performance (COP). Coefficient of performance for a cooling TES system is basically the ratio of the refrigeration effect (system cooling capacity) produced to the total power consumed. In theoretical calculation, the chiller and compressor performances are used to calculate the COP of the CTES system. But

in actual practice, the refrigeration produced and total power consumption shall be measured [10].

2.2.2. Error sources affecting the performance. As explained through examples, this technology can be beneficial but there are still some issues that must be kept in mind for this technology.

- Sizing must be done carefully. Any error in the sizing of cooling TES system may lead to mismatching system components and then to the higher payback period.
- Malfunctioning in the equipment or any issue in the system may affect the desired results for saving.
- Inefficient operation of the system due to any human error may lead to a severe loss of all savings from cool TES system.

So, in order to have a better view and greater advantages from the applications of cold TES system, it is evident to take some recommendations from the user [2].

2.2.3. Classification of cold thermal energy storage systems. Generally all CTES systems have same basic configuration that includes chillers, storage tanks and pumps to provide the chilled medium to the space.

Today, they can be classified into three basic categories [11-12]:

- Chilled water storage system
- Ice storage system
- Eutectic salts

Details of the previous systems are explained in detail for a better conceptual view.

2.2.4. Chilled water storage system. In this system, water is stored in a tank at around 4-6°C based on its capability of making horizontal layers depending upon the temperature difference between consecutive layers of water. At the discharging time, the water is supplied through the bottom of storage tank in order to use it for the cooling purpose, which can be filled again in the tank from the top. It is important to store the tank with less flow rate in order to avoid mixing because mixing will reduce the temperature difference across the different layers of water which will reduce performance of the chilled water storage (CWS) system. In its general working, the

chilled water is stored at night and it is used at the time of requirement (usually in the morning) by passing the chilled water through the cooling coil which in turns cools the required space. In this way, the temperature of the chilled water decreases and this water is again stored in the cooling tank [2].

The CWS systems currently in use can be classified into labyrinth, baffle, tank series, multiple tanks with an empty tank, membrane and thermally stratified systems [13]. These types can be seen in Figure 2 [14-15]. In order to have broader views from literature, it is recommended to mention the advantages and disadvantages of the CWS system. Some notable advantages of CWS system are [2]:

- Higher operating efficiencies are observed for this system as the chilled water is stored at night when there is low outside ambient temperature resulting in higher performance of heat rejection system.
- Storage tank for the chilled water may also be used as the reservoir for the fire protection resulting in the economic benefits for the capital cost, etc. So, the capability of fire protection also increases especially in the plants dealing with inflammable products.
- CWS system operates under the same conditions as that of general cooling system with the conventional water chillers, which in result, gives the ease of maintenance and operation.

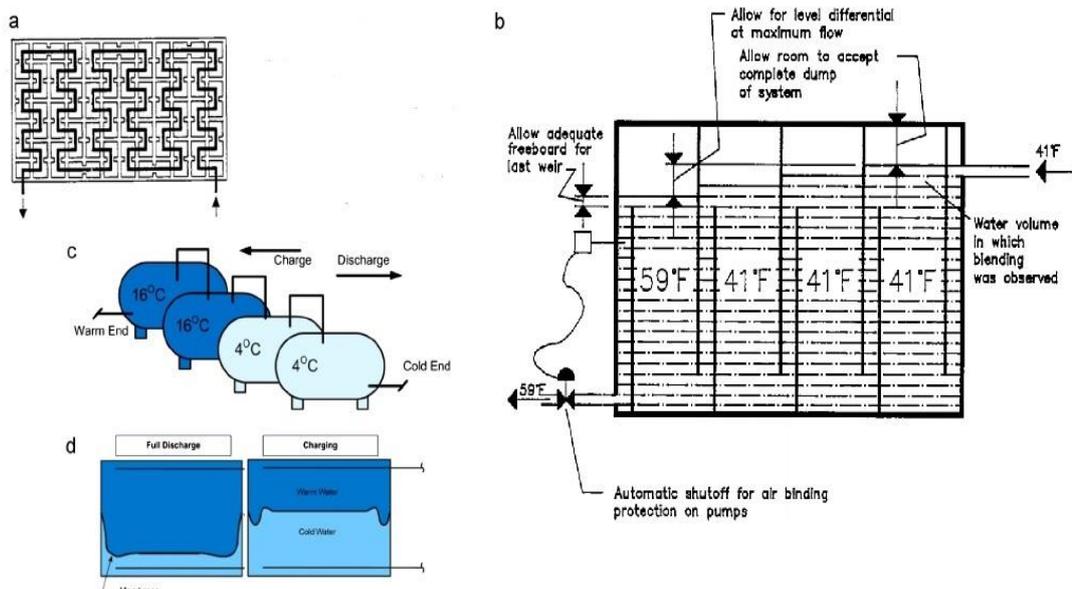


Figure 2: (a) Labyrinth tank [14],(b) Baffle tank [14], (c) Series tank [15] and (d) Membrane tank [15]

In practical situation while using CWS system, there are also some serious issues linked with CWS system. Some of them are mentioned below [2].

- The main problem while using CWS system is of storage capacity. Practically, each cubic meter of chilled water can only provide 5.8 KWh if temperature rises of 5°C is used. So, a huge volume requirement is essential for CWS systems.
- In order to have an efficient CWS system, there is a real need to separate the hot returning water from the chilled supplied water inside the tank. In case of mixing, the cooling capacity of the system will decrease. There are a lot of techniques with mixed results being used to avoid the mixing inside the storage tank. A few of them are tank membranes, compartmentalized tanks and multiple tanks, etc. [14-15].

2.2.5. Ice storage system. The basic principle of Ice Storage System (ISS) is to utilize electricity at night time in order to produce ice, and then to use this ice at on-peak hours (usually at the day time) to match the cooling load. Ice can be generated in many ways e.g. by using brine solutions, encapsulated ice storage systems or by direct expansion refrigeration unit, etc. [16]. The coefficient of performance of this system is specified by its cooling capacity which is directly linked to the amount of ice produced and the rate of melting of ice when it is used for air conditioning.

Ice storage systems are classified as static or dynamic. In the static systems, ice is generated on the coils which are already submerged inside the water tank, whereas in the dynamic system, the ice is produced on the coils, and is then removed from coils for storing in different tank. The issue for static system is its low chiller coefficient of performance. The surface of generated ice increases continuously on the cooling surface. This increasing surface also increases the resistance against the heat transfer which in turn decreases the evaporating temperature and hence decreasing COP of the system. This issue gets resolved in dynamic system as the ice is periodically removed from the heat transfer surface. However, it does not ensure the best performance either. The ice is removed from the surface using hot gas defrost which decreases the energy efficiency of the system by 10%.

The key advantage of using an ice storage system is its applications to any plant that has chilled water system. The main components of any ice storage system are the same as any other refrigeration plants and this (Ice storage) system can be attached to

any other conventional air conditioning system. Under normal working conditions, air can be supplied at (as minimum as) 13°C. While with using ice storage system, air can be supplied at about 6°C. By using ice storage systems, sometimes the environment becomes uncomfortable for people due to this much lower temperature (6°C) so the outside/ambient air must be mixed before supplying to any required conditioned space in order to supply the required air temperature [2]. Figure 3 shows a few examples of commercial ice storage systems heat exchangers used in cooling applications

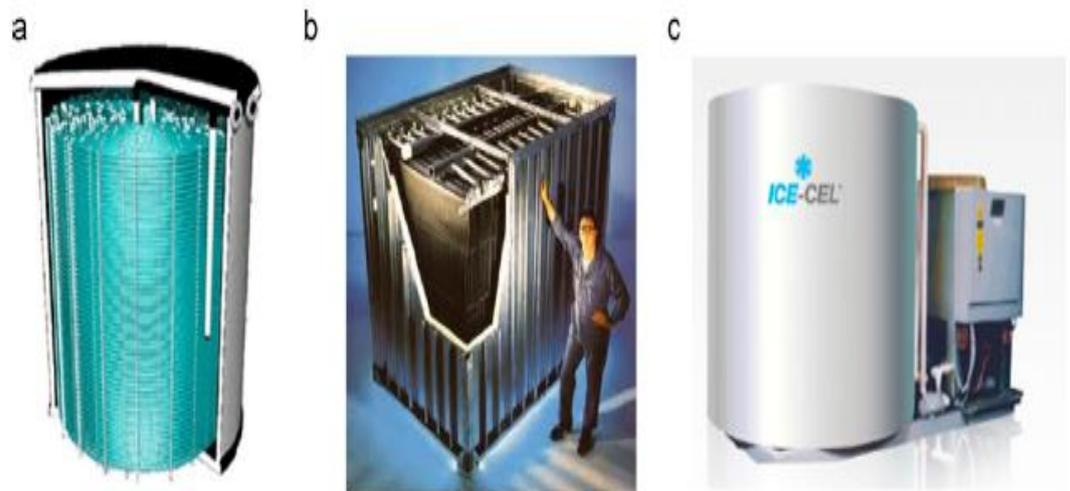


Figure 3: ISS heat exchangers (a) Calmac [17], (b) Fafco [18] and (c) Dunham–Bush [19]

2.2.6. Eutectic salts storage system. Eutectic salts are also considered to be one of the sources used for energy storage systems. Eutectic salts are the mixture of salts, water and stabilizing agents [20]. Same as in the case of ISS, the coefficient of performance for this system also depends upon the latent heat of fusion of salt and the total amount of frozen salt. Most of the salts used melt and freeze at 8°C. They also are easy to be used with conventional systems. The main benefit of using eutectic salt storage system lies in its quality of not expanding after getting melt which improves the efficiency of the system. Also, eutectic salts storage system usually has a higher density so that the floating problem inside the tank does not occur [2].

2.3. Operational Strategy of CTES System

Operational Strategies of CTES System can be classified between full storage and partial storage. These terms are derived from the air conditioning load needed to be shifted on the off peak hours energy storage. When integrated with systems, it is still possible to add different variations in operational capabilities. The details of full storage

and partial storage are given below. Figure 4 shows the basic operational strategies of CTES system [20].

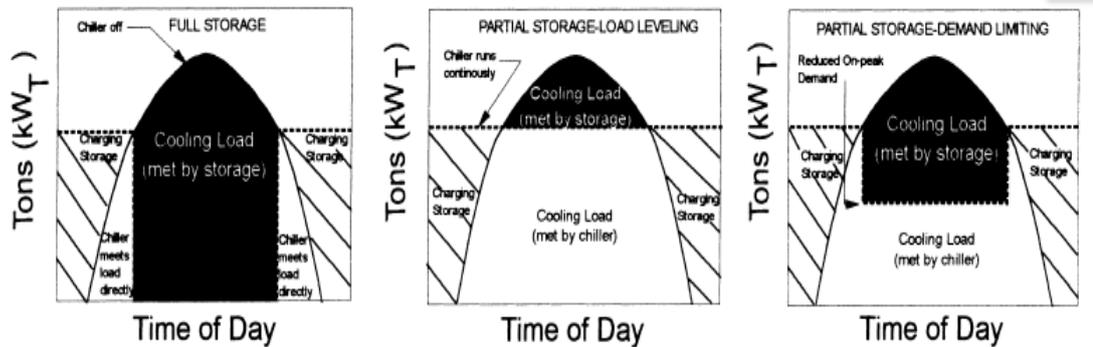


Figure 4: Basic thermal storage operating strategies [20]

2.3.1. Full storage. Full storage term is derived from the capability of the cool thermal energy storage systems to fulfill the full need of electricity for air conditioning purposes during the peak hours of usage. Strategy here is to shift the full peak hours load into the off peak hours load as can be seen in Figure 4. By effectively implementing the full storage system, the performance of integrated system results into the maximum possible savings. During the working mode of full storage, the compressors in air conditioning systems stop working during peak hours and the cooling load is supplied through the thermal energy storage system. Therefore, these systems require large storage tendency. By using full storage operational mode, peak load requirements could be reduced by 80-90% as compared to the conventional air conditioning systems [20].

2.3.2. Partial storage. Partial storage system provides only a part of the required air conditioning load utilizing the storage. The other portion of the required load still has to be provided through the conventional air conditioning system. In this mode, the required storage capabilities are lower as the chiller always keeps operating. At the time of lower cooling load than the chiller output, the system stores the excess cooling energy. This stored energy is utilized when there is a higher cooling load requirement as compared to the chiller output. So, it is recommended to use the load leveling mode at locations where the peak cooling load requirements are much higher as compared to the average load conditions. In the working of demand limited storage, the chillers of the air conditioning system keep operating except for the peak hours demand. The peak load shall be provided through the storage system. This application is mostly beneficial in case of higher demand charges and shorter occupancy timings in

order to have a higher storage timing. Using partial storage is not more efficient as compared to the full storage mode but it still saves 40-60% of peak cooling demand.

2.4. Phase Change Materials

In this section, a detailed view of the phase change materials (PCM) is given. In addition to the general concepts, its general classification and techniques for improvement in its working have also been discussed. A serious issue is emerging as the pressure is increasing on the natural resources for the power generation. The impact is not only on sources or financial but environmental as well. Using PCM for TES is one of the key solution results in efficient energy conservation and management. Storing energy in the form of latent heat is an efficient way as higher energy can be stored in less volume of material. Also, it works effectively as temperature swing between storing energy and releasing energy remains small. For using phase change materials in a specific application, it is always required that phase change temperatures of PCM shall be within the limits of operational temperature range of application [21]. While using PCM in TES systems, it is really important to know the specific heat capacity of the storage material whereas in cases where volume is important, density shall be considered [22].

2.4.1. Criteria for the selection of phase change materials. There are a number of factors that need to be checked during the selection of PCM's based on desired properties as shown in Figure 5.

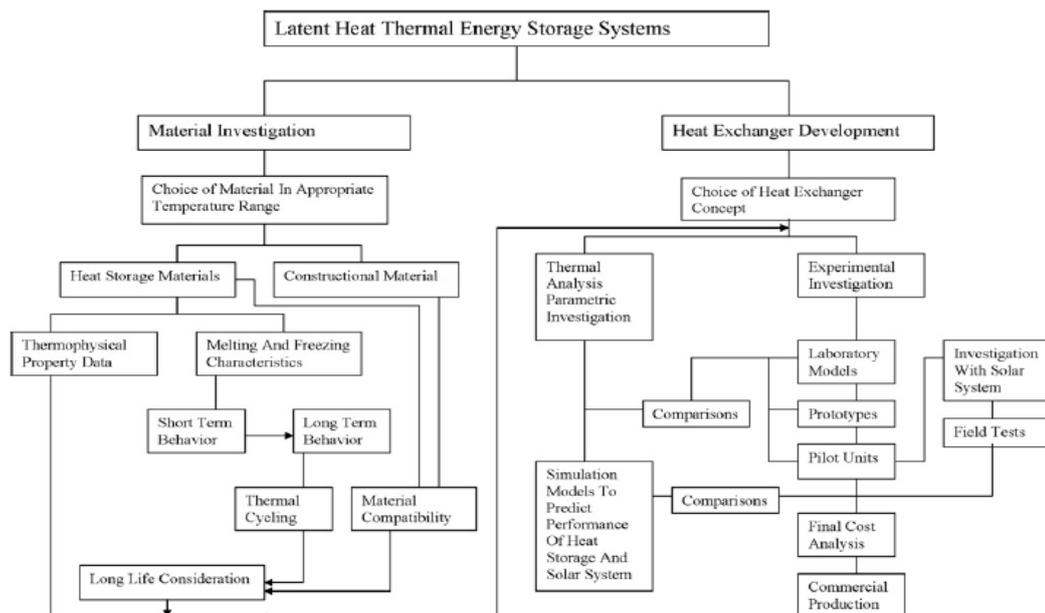


Figure 5: Flow chart for the development of latent heat TES system [23]

Main factors include their thermal properties, physical properties, kinetic properties and chemical properties. Thermal properties like phase transition latent heat per unit volume, melting temperature within the operating range of application, higher specific heat capacity and higher thermal conductivity are important ones to be taken care of. Also, the chemical properties like chemical stability, no corrosion effect, complete working cycle of melting and freezing processes and inflammability/no toxicity must be ensured before working with a material [8,23,24].

2.4.2. Classification of phase change materials. A wide range of organic and inorganic compounds can be categorized as PCMs. On the basis of their phase transition temperatures, PCMs can be classified into three main categories; low temperature PCM that melts below 15°C; high temperature PCMs that melt above 90°C; and mid-temperature PCMs having melt temperatures between 15°C-90°C [8,25]. PCMs are further sub grouped as organic, inorganic and eutectic materials (Figure 6). Comprehensive details about the classification of phase change materials are given below.

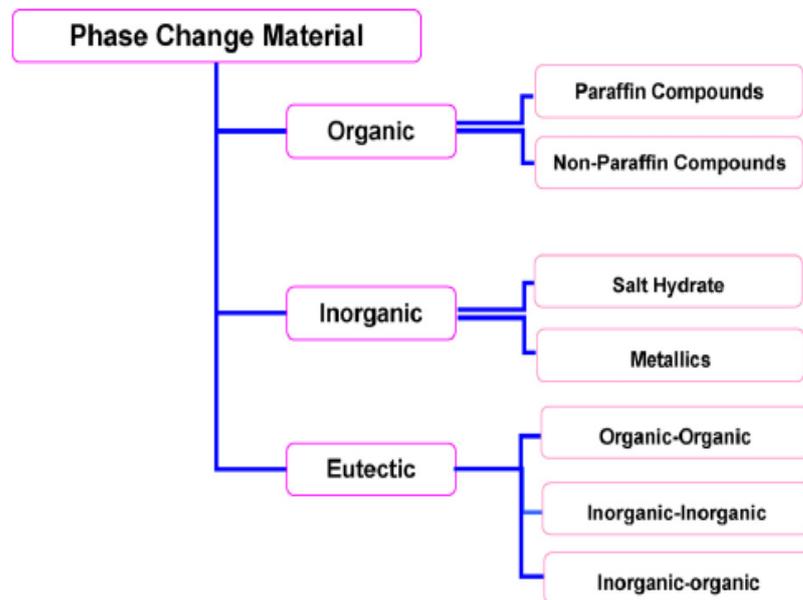


Figure 6: Classification of PCMs [8]

2.4.2.1. Organic phase change materials. Organic phase change materials absorb and release a large quantity of latent heat during transition. The key benefit of organic phase change materials is their property of getting melted and frozen repeatedly without any change in its phase characteristics and structure [26-28]. They are divided into two main categories i.e paraffins and non-paraffins.

2.4.2.1.1. Paraffins. Paraffins are straight chain alkanes carrying high latent heat storage capacity within a very limited scale of temperature. These are cheap, non-toxic and chemically inert materials that are stable below 500°C. Table 1 [3] shows the thermo-physical properties of paraffins. It illustrates that their melting point is directly proportional to the number of carbon atoms in the hydrocarbon chain. Alkanes between C5 and C15 have melting points ranging between 23°C and 67°C. [21,29].

Table 1: Thermo-physical properties of paraffins

Paraffin	No. of Carbon atoms	Melting temp (C)	Heat of fusion (J/kg)	Density (g/m³)
n-Pentadecane	15	9.9-10.0	206	0.771
n-Hexadecane	16	18.0-20.0	216-236	0.773
n-Heptadecane	17	22-22.6	164-214	0.778
n-Octadecane	18	28-28.4	200-244	0.776
n-Nonadecane	19	32.0	22.2	0.785
n-Eicozane	20	36.6	247	0.788
n-Heneicozane	21	40.2	213	0.791
n-Docozane	22	44.0	249	0.794
n-Trikozane	23	47.5	234	0.796
n-Tetracozane	24	50.6	255	0.799
n-Pentacozane	25	53.5	238	0.801

Pure paraffins are expensive and therefore commercial paraffins are produced by distillation of crude oil. They are safe, non-corrosive and are non-reactive, however chemical affinity with plastics can lead to infiltration and therefore requires careful handling [30].

2.4.2.1.2. Non-paraffins. Unlike paraffins, non-paraffins have very diverse range of properties. These materials are further classified into fatty acids, alcohols, glycols and other non-paraffin organic compounds for energy storage purposes. Non paraffins qualify as desirable PCMs for latent heat thermal energy storage due to their favorable thermodynamic and kinetic characteristics for low temperature. As shown in Table 2 [8], they show higher melting point and latent heat behavior. They also possess relatively high melting and boiling points [31, 32]. Fatty acids are expensive materials, are slightly corrosive and have an unpleasant odor [8,3].

Table 2: Properties of non-paraffins

Material	Melting Point (C)	Latent Heat (kJ/kg)
Acetic acid	16.7	184
Polyethylene glycol 600	20-25	146
Capric acid	36	152
Eladic acid	47	218
Lauric acid	49	178
Pentadecanoic acid	52.5	178
Tristearin	56	191
Myristic acid	58	199
Palmatic acid	55	163
Stearic acid	69.4	199
Acetamide	81	241
Methyl fumarate	102	242

There are a few drawbacks of non-paraffin materials that need to be considered before choosing them for a specific application. Starting from the cost analysis; they are about 2-2.5 times expensive as compared to the technical grade paraffin. Some of the non-paraffins also show pro behavior towards corrosive properties.

2.4.2.2. Inorganic phase change materials. Key advantages of using inorganic phase change materials include lower super cooling and no decrease in their latent heat of fusion on repeated usage. They are categorized as salt-hydrates and metallic.

2.4.2.2.1. Salt hydrates. Salt hydrates possess certain favorable properties for thermal energy storage. They have high values of latent heat of fusion and possess relatively high thermal conductivity. They exhibit minimal volume changes on melting. They are non-corrosive and slightly toxic [3,8]. Salt hydrates have general formula $AB.nH_2O$ containing water of crystallization. There are few hydrated salts whose solid and liquid phase exists in equilibrium during phase change. Both phases have different composition due to formation of an anhydrous salt or a lesser salt hydrate [8]. Most salt hydrates supercool before crystallization due to poor nucleating at fusion temperature. Therefore a nucleating agent is added or otherwise some crystals are retained to act as nuclei to serve the purpose [8,3].

Most of the hydrated salts that qualify as suitable PCMs due to their favorable thermal storage show incongruent melting. As the water of hydration is not enough to dissolve the salt, the resulting solution is saturated at melting temperature due to differences in density. The salt collects at the bottom and therefore does not react with water during freezing process. This creates technical problems in practical applications. To tackle this problem, thickening agents are added which prevents settling of salts at the bottom by altering the viscosity of the salt hydrate [33]. Some use large amounts of water so that the saturated solution is not created [34]. The other key issue with salt hydrate is that of super cooling. The rate of nucleation remains really low at fusion temperature. It is important to get a reasonable rate of nucleation. For getting this rate, solution must be super cooled, so energy is discharged at much lower temperature.

Despite these drawbacks, salt hydrates are still considered as suitable PCMs for TES systems due to their high latent heat of fusion and cost effectiveness. Choosing a specific salt hydrate for a specific application is still not an easy task as it needs a comprehensive study of thermos-physical and chemical properties of different types of salt hydrates as per requirement. The most common low cost salt hydrate used is Calcium Chloride Hexa-hydrate [3].

2.4.2.2.2. Metallics. Metallics are considered as PCMs due to their high heat of fusion per unit volume. Metals and metal eutectics have unfavorable weight

characteristics which do not make them suitable PCMs. However, they are important when volume is in consideration. These materials have high thermal conductivity which distinguishes them from other PCMs. They have high conduction properties so they eliminate the requirement of other filler materials with added weight issues [8]. Lower specific heats of metallics are also one of the desirable property for their usage. Usually they are used in very smaller particular size, as of the order of micro and nano particles.

2.4.2.3. Eutectics. Eutectics are mixtures of two or more salts on the basis of which, they are classified as (i) organic-organic, (ii) inorganic- inorganic, (iii) inorganic-organic. Each of the constituent material exhibits congruent melting and freezing. There is no separation of the components during phase transition. During freezing, the components crystallize simultaneously forming a mixture containing crystals of each salt [35,36]. Similarly, there is no segregation between the liquid components when eutectics undergo melting.

2.5. Gas Hydrates

Cool thermal energy storage (CTES) systems, if used with proper designing and implementation; can give the maximum possible benefit. There are various CTES systems available for different sort of cooling storage mediums. Literature review has been explained previously about ice thermal energy storage (ITES). ITES systems are efficient in working. This technology provides a solution for the application of ITES systems in air conditioning systems. However, this system creates some complexity as working with ITES decreases the performance of refrigeration system. Freezing point of ice is 0°C whereas the evaporating temperature of ice for cool storage is -3°C to -9°C. This results in low performance of the cooling system [37]. Eutectic salts and organic PCM's can be used for the system but most of the eutectic salts are chemically unstable and they corrode, whereas most of the working organic PCM's have an issue of low thermal conductivity and latent heat while the expanding volume is with low change in temperature [38]. This troubled scenario led to the need for developing a phase change material suitable for the air conditioning systems. Tomlinson proposed to use Freon hydrate former as the cool storage medium in the air conditioning system [39]. Phase change temperature of gas hydrate (also known as Clathrate) is close to the air conditioning temperature by 5-15°C. Also, the latent heat of phase change condition is close to that of ice i.e. 302.4-464kJ/kg which makes it ideal for the heat exchange performance. These properties make it an efficient medium that can lead to the higher

performance of the system [40-41]. This also explains the reason why most of the refrigerants are considered as ideal cool storage medium in air conditioning systems [42].

Gas hydrates are formed when water molecules trap the molecules of a gas or volatile liquid at specific temperature and pressure and form a crystalline structure [43]. The development period of the gas hydrates starts from 1934 where, the clathrates were responsible for blockage in piping system. After the initial development, these clathrates were considered as the new renewable energy source due to their properties after they were found in abundance around the earth's crust. The high pressure and low temperature conditions make offshore locations, the most suitable areas for clathrate formation [44]. Applicability of clathrate was investigated in the air conditioning applications due to its phase change temperature being above the formation temperature of ice [45]. Now a days, there are a lot of refrigerants working as a cool storage medium such as R134a, R141b and R404.

2.5.1. Gas hydrates crystal growth. As mentioned before, gas hydrates are crystalline structure formed when the water molecules hold the molecules of a gas or volatile liquid at certain conditions. For the cool storage process, the refrigerants are used as volatile liquids. For the case of using R134a, when the water and refrigerant are filled in the storage tank, they actually form two immiscible phases with refrigerant in the lower side and the water in upper side. That happens because of their density difference. With the passage of time, crystals of gas hydrates start forming as the suitable conditions of low temperature and pressure are provided during the process [42]. During the process, the solution can be seen transforming from initially clear state to becoming non-transparent. That happens due to the formation of gas hydrates. The refrigerant molecules move upwards causing the turbulence at the interface of solution while filling the top surface by hydrate phase. As the process moves on, the crystals formation continues and the level of water keeps dropping while the solution again starts clearing. Finally, the crystals take all the place and the cool storage process stops [41]. The formation of crystals does have a key importance in the cool storage process as the conditions vary from refrigerant to refrigerant or by using different additives. The factors get affected by the temperature variation while the formation of crystalline structure and the time for the formation of crystals etc. So, additives can play a key role for the improvement of different factors. In our work, the formation of crystalline

structure has the key importance. The crystalline structure can be made using different refrigerants e.g. R134a and R404. The results then, can be compared and analyzed for the characteristics analysis.

2.5.2. Effect of additives on refrigerants. Mostly refrigerants are used with additives in any air conditioning systems. Additives are the compounds which are basically used to overcome the shortage of heat transfer issues in any refrigerant or to modify the characteristics of refrigerant in order to get the desired results. The selection of additives for any process is not an easy task. Most of the times, additives are selected on the basis of refrigerant used, system specifications and the desired characteristics of the additives.

Bi *et al.* [46-47] studied the effect of additives on the gas hydrate cool storage process and gas hydrate cool release process. In the former, experimental research was done on the crystallization process of gas hydrates using different concentrations of additives. Calcium hypochlorite or benzenesulfonic acid sodium salt were used as additives on the crystallization process of R-141b. Results proved the effect of additives as the reasonable concentrations of additives decreased the rate of subcooling and increased the formation rate of gas hydrates. Due to this ease in the formation of clathrates, the thermal energy can be stored effectively which increases the performance of air conditioning system. The research on the gas hydrate cool release process showed the corresponding effectiveness by the usage of additives. The results showed that the dissolution rate (which is responsible for the cool release process) was twice as much as the formation rate of clathrates. Also, the cool release per unit time was higher as compared to the cool storage process due to temperature difference of heat transfer during both processes. Here in both processes, the temperature difference between the hydrates and the provided cooling or heating process is the key factor that controls the cool storage and cool release processes. Additives also play their role in increasing the corresponding rates.

Literature review suggests that there has been a proactive research on different methodologies and additives in order to improve the effectiveness of different refrigerants. Zhang *et al.* [48] studied the effect of additives on the formation of gas hydrate by collecting the kinetic data of hydrate formation with different concentration of solutions of additives like alkylpolyglucoside, sodium dodecyl benzene sulfonate and

potassium oxalate monohydrate. The key factors about the characteristics of gas hydrates showed improvement e.g. the formation rate and storage capacity of gas hydrates were improved and the storage time was decreased. The results of the study also established that change was also visible by changing the concentration of solution of additives. A more comprehensive work on the effectiveness of additives on the cool storage and cool release process was done by Jianghong Wu and Shiping Wang [42]. They studied the characteristics of R134a gas hydrates using different concentrations of n-butanol as an additive. They studied that R134a is a good choice for air conditioning purposes due to its characteristics like boiling point temperature and condensation. But practically, using R134a in its pure form does have some issues attached. Due to lower density, it occupies the top upper surface in storage tank creating problems for both cool storage and release processes. Using n-butanol as an additive increases the cool storage rate while also increasing the total density. This results in solving the hydrate floating issue.

Chapter 3: Literature Review

3.1. Introduction to Crystal Growth

Crystal growth is an important factor not only for the practical science knowledge but also for the industries that depend on the functions of these materials. In order to make the processes more green and efficient, crystal engineering is required in materials like catalysts, semiconductors, pharmaceuticals, radio-active waste storage materials, and opto-electronic crystals. In fact, to get the best results, it is vital to control the properties of crystals like – geometry, crystal size intergrowths and synthesis cost. The issues of crystal growth for nano-porous materials are similar to that of all crystals, just like crystal habit and crystal size are important for the functioning of any crystal.

Every crystal may possess natural and unnatural defects, however, these may be controlled. To fix the defects, it is important to understand the defect through a method called transmission electron microscopy (TEM). Each crystal shows a unique defect and should be characterized individually like intergrowth and twin structure. Defects like such usually occur due to the imperfect crystal structure growth at some local dislocation and also occur during growth stage. A technique called atomic force microscopy (AFM) can be used to study the molecular events that take place during crystal growth and dissolution/recrystallization. There are some key concepts in order to understand the process of crystallization [48].

3.1.1. Nucleation. Nucleation is the process of formation of a new crystal from a solution. At this stage, atoms and molecules of the solution reposition themselves into the relatively big size formations of the product phase so that they can grow into a comparatively larger size. This size vary from case to case depending upon the molecules. Nucleation, also known as crystallization, can take place homogeneously as well as heterogeneously, i.e. in the absence/presence of impurity (also known as additive) in the solution, respectively. When the nucleation is done with the presence of crystals of same substance, it is called primary nucleation.

Supersaturation is the maximum amount of molecules in the solution above the chemical capacity of solution.

$$\Delta\mu = \mu_s - \mu_c$$

where μ_s is the chemical potential of molecule and μ_c is the chemical potential of the

molecule in the bulk crystal.

Also,

$$\Delta\mu = KT \ln S$$

where K is the Boltzmann constant, T is the absolute temperature and S is the supersaturation ratio. The form of the supersaturation ratio will change depending on the system. For the solutions, nucleation equation turns out to be as

$$S = \frac{\prod a_i^{n_i}}{\prod a_{i,e}^{n_i}}$$

where n_i is the number of i th ions in the molecule of the crystal, a_i and $a_{i,e}$ are the actual and equilibrium activities of the i th molecule in the crystal.

3.1.2. Energetics. The energetics basically present the system work that is required to form n number of molecule cluster. It is the energy difference of the system between complete stages. This can be presented as

$$\Delta G_T = -n\Delta\mu + 4\pi * r^2\sigma$$

where r is the assumed spherical radius of the nucleus and σ is the free energy as presented. Assuming that every molecule of the crystal takes a volume V , then following will be the expression for complete energetics

$$\Delta G_T = -\frac{4}{3}\pi * \frac{r^3}{V} * \Delta\mu + 4\pi * r^2\sigma$$

3.1.3 Nucleation rate. The rate of nuclei formed per unit time per unit volume is called the nucleation rate. This nucleation rate can be expressed with the help of an Arrhenius-type equation:

$$J = A * \exp\left(\frac{-\Delta G^*}{kT}\right)$$

where A and J are the function of supersaturation (S), K is the thermal conductivity and the T is the cooling temperature for the case of cooling process (clathrates formation process).

3.1.4. Induction time. The time element (difference) between the formation of a supersaturated solution and the start of formation of crystals is known as induction time. The induction time is calculated by different resources/ways. Obviously, there are a lot of factors which influence the formation of crystals like agitation in the solution, cooling temperature, rotational speed, solution properties etc. The equation for the induction was shown by Mullin [49] as

$$t_i = t_r + t_n + t_g$$

where t_r is the time required by the solution to reach a quasi-state equilibrium, t_n is the time required for nucleus formation and t_g is the growing time of crystal in the given solution.

3.2. Crystal Growth

It is the process in which atoms or molecules collaborate and meet together to form a crystal, and this attachment leads to the bigger crystal formation. The schematic presentation of crystal formation, as shown in Figure 7 [48], can be explained as in following steps

1. Transport of solute to a position near the crystal surface
2. Diffusion through boundary layer
3. Adsorption onto crystal surface
4. Diffusion over the surface
5. Attachment to an edge
6. Diffusion along the step
7. Incorporation into kink site

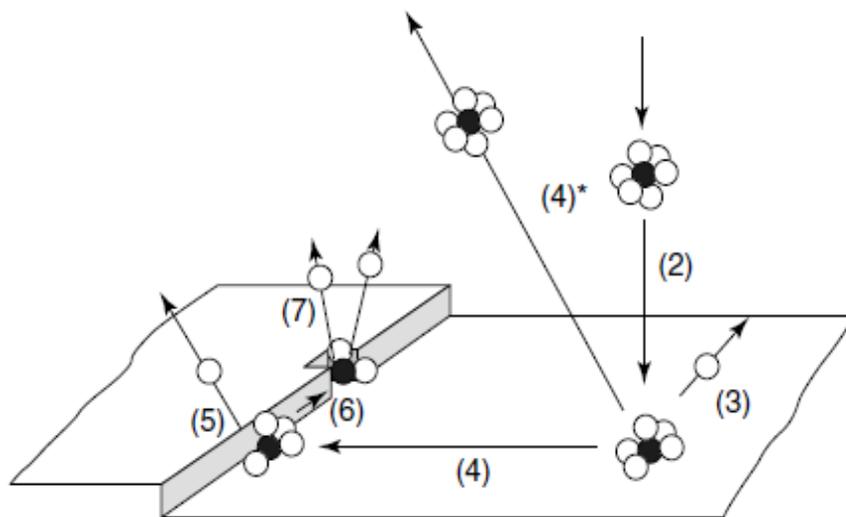


Figure 7: Schematic representation of crystal growth processes [48].

Basically, there are four main steps in any process of crystal growth starting from the movement of atoms or molecules within the solution. In the second step, these atoms or molecules get together and move towards the surface for joining. These atoms, then, start moving on the external top layer of solution and then finally they get attached to the crystal structure.

3.2.1. Mechanism of crystal growth. As mentioned before, gas hydrates are crystalline structures formed when the host molecules hold the guest molecules at certain conditions. For the cool storage process, the refrigerants are used as volatile liquids. The increase in the size of clathrate can be a systematic one or a haphazard one. This adsorption layer theory was presented by the Mullin which shows the orderly formation of crystal hydrates by layer upon layer with formation of new layer by the surface nucleation [49-50]. Before Mullin, this theory was proposed by the Volmer [51]. This relationship was presented by Mullin as

$$\frac{dM}{dt} = K_1 \Delta T^n + K_2 \Delta T^m$$

where M is the crystal mass, T is the time, K_1 is the constant of nucleation, K_2 is the constant of crystal growth, ΔT is the undercooling during the process, n is the nucleation exponent and m is the growth exponent.

As explained before the phenomenon of crystal growth, any imperfection in the geometry of crystal can lead to the spiral growth.

Tammann established a link between applied super cooling and the rate of freezing and his work is considered to be one of the most important in this field [50]. According to Tammann, the number of crystallization centers (KZ) developing per unit volume in unit time and linear rate of crystallization centers (KG) of nuclei is directly related to the rate of super cooling. Figure 8 [48] shows the super-cooling effect on nuclei formation.

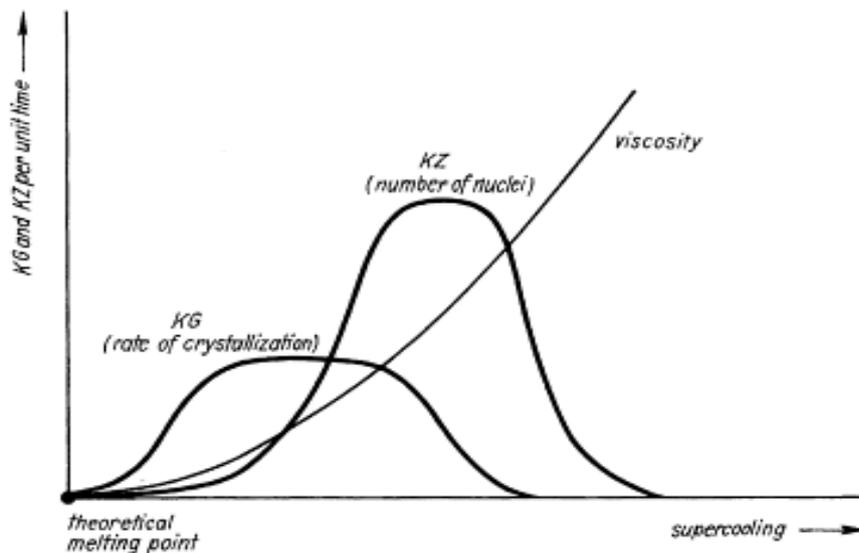


Figure 8: Super-cooling effect on nuclei formation [48]

3.2.2. Literature work. In the last few years, extensive work has been done by using different additives in formation of clathrates. Table 3 shows the summary of the literature work done.

Table 3: Summary of the literature work review

Title of Study	Year	Researcher	Materials under investigation
The study of impurities effect on the growth and nucleation	2002	J. Podder	Potassium di hydrogen phosphate, KCl, Urea
Effect of Surfactants on Hydrate Formation Kinetics	1993	N. Kalogerakis and A. Jamal	Sodium dodecyl sulfat
Research on cool storage and release characteristics of R134a gas hydrate with additive	2011	Jianghong Wu and Shiping Wang	R134a, Butanol
The crystallization kinetics of potassium chloride in the presence of common ions	2013	A. Abdullah and A. Nusret	KCl, K ₂ SO ₄ , CH ₃ COOK, NH ₄ Cl and BaCl ₂
The influence of impurities on phosphoric acid hemihydrate crystallization	2007	L. Dang,, H. Wei and Z. Zhu	Phosphoric Acid, Fe ₃ ⁺ , Al ₃ ⁺ , and F
Experimental testing and analysis of R134a clathrates based PCMs for cooling applications	2015	S. Zafar, I. Dincer and M. Gadalla	R134a, Cu, MgNO ₃ , NaCl, Al and C ₂ H ₅ OH,
Thermal conductivity and heat transfer enhancement of PCM containing C additives for heat storage application	2014	D. H. Choi, J. Lee and H. Hong,	Stearic Acid, Graphite

Podder et al. [52] worked on finding a new useful material with better non-linear optical properties for academic as well as industrial uses. They attempted to grow potassium dihydrogen phosphate (KDP) by doping with urea and with potassium chloride (KCl) in various molar ratios in aqueous solution using slow cooling method .According to Podder et al. [52], the presence of impurities affects the growth rate of KDP i.e. the growth rate of KDP increases with the increase in these impurity concentrations. Mobile impurity particles (inorganic species) move over the surface and reach the kinks. The absorption at kinks causes the suppression of the chemical activity of the metal ions impurities that are present in the solutions. On the other hand,

immobile impurity particles (organic species) mostly adsorb at the surface which causes inclusions. It was found that urea impurities promote faster growth rather than KCl impurities. In fact, KCl suppressed the metal ion impurities, also improved the crystal quality by giving it the highest transparency. Ultimately, KCl as well as urea doped crystals show better non-linear optical properties than pure KDP crystals. From the study, it is observed that urea merges in the framework of the KDP crystal whereas micro-hardness study showed that KDP crystal with urea is mechanically harder than crystal with KCl. Because of better optical properties, KCl doped crystals show good strength for colored signals than that of KDP doped ones. These colored signals confirm the second generation for both kind of doped crystals.

Larsen et al. [53] developed a physical theory for growth inhibition. Single crystals of clathrates can for quick branching in addition of different polymeric additives with suitable properties. The solution used was the aqueous solution of tetrahydrofuran and ethylene oxide. Yet, the results also showed that more than a specific amount of concentration can result into the stoppage of crystal growth. Aqueous solution of tetrahydrofuran at specific conditions was formed and analyzed. Different types of additives can be considered according to the various characteristics. The growth of crystal hydrates can be affected by different kinetic additives. No growth took place after the transfer of crystal to an additives added solution which showed the fast adsorption process. Yet, polymer molecules take some time due to being slow in their nature. Additives also stake some time for their effect. On the other hand, the results also explained why the molecules without any kind of additives are not enough for their action as barriers to diffusion. The results of the experiment show that adsorption is a non-reversible process where natural crystals were shifted to the additives added solution.

Kalogerakis et al. [54] examined some surface active agents as additives. Results showed their pro behavior for crystal growth. Interestingly, they were looking for the additives in order to prevent the hydrates formation in oil field. The basic purpose of experimentation and analysis was to see whether these additives had any effect on hydrates in practical field. There are few key factors that indulge in this analysis for the better understanding of the influence of hydrates in crystal formation which are: the molecular size, the quantity of soluble ethane in the molecule, the amount of water in molecular formation and the effective volume of molecules available for solutes. A solution having sodium dodecyl sulfate as additive of the similar additives

tries to increase the gas hydrates formation phenomenon. Instead of these additives, the usage of a metal container for the formation of crystals, also varies the properties of the crystals hydrate growth. With the process continuation, the surface of water tends to decrease along with the crystals sticking to the metal surface of the container. In this way, the gas hydrates tends to form layers at the top surface, and this surface increases with the passage of time. The water molecules trap the gas molecules making the gas hydrates. The results showed the high formation rate of gas hydrates in the presence of metal container at the specific conditions (at a gauge pressure of 3.89 MPa and a temperature of 275.4 K) within three hours. On a larger scale, these results can be implemented to get the gas storage properties of gas hydrates.

N. Zaitseva et al. [55] showed the experimental results on the impact of supersaturation along with the addition of additives or impurities during the crystal hydrates formation [55]. The basic purpose for the experiments was to find the suitable conditions for the uniformly and homogeneous growth of hydrate crystals. Crystals were grown by using the lower temperature techniques. A spectrometer was used for the ultraviolet absorption measurements and the results were obtained in the form of topo-graph. Results showed that

- Stability of the solutions to fast nucleation process was not affected by the additives/impurities at the supersaturating conditions during the fast nucleation process of crystal growth
- Effect of the additives on crystal growth is less obvious when the growth starts at high σ_{reg} outside the dead zone.
- Rapid growth of KDP crystals should be done at the supersaturated conditions which relates to the linear part of the dependencies.

Maekawa et al did the numerical analysis for the crystal growth of binary semiconductors and analyzed the possibility of comparatively bigger crystal with feasible properties. In this analysis, they determined the flow field of solution, temperature of both solution and crystals and the interface movement between the liquid-clathrates [56]. The analysis also focused on the effect of super-cooling for the bigger crystal structure. The study found that crystal growth can be affected by controlling the solution zone width and the temperature distribution at the proper location inside the solution. A new crystal growth method was introduced in the backlight of the uniform composition issue in the growth of binary semiconductor

crystals. In this analysis, the solution was filled between the solvent and the solute molecules. The results found that as the solution zone width increases, the velocity of the convection increases. The results were encouraging as the temperature distribution and the liquid-crystals interface were not deformed with this method. The crystal growth was also proportional.

Ayhan Abdullah et al. worked on the dynamics such as temperature super saturation and mixing rate that affect the process of crystallization [57]. However, one vital factor that influences crystal growth behavior on multiple levels is the presence of impurities in the crystallization medium. This research study systematically explored the growth and dispersion rates of potassium chloride in the presence of impurities added in the form of additives with common cation. The effects of K_2SO_4 , CH_3COOK , NH_4Cl and $BaCl_2$ anions were investigated on potassium chloride crystals electrostatically separated on the basis of their surface potential. In order to do so, three different concentrations (10 ppm, 100 ppm and 1000 ppm), separated using dings electrodynamic separator. Each additive was tested in an isolated crystal cell. The experiment results indicated that the growth behavior of KCl crystals is altered in the presence of additives with common ions that are not surface potential dominating ions. However, the studied system did not point to either excessive surface nucleation or any other growth behavior as both are characteristics of crystal's surface potential. Increase in the concentration of (K_2SO_4 and CH_3COOK) led to a minor increase in the surface nucleation and the increase in concentration of additives with common anions (NH_4Cl and $BaCl_2$) resulted in decrease of surface potential of KCl. However, further increase led to neutralization and then increased the surface potential again by donating opposite charges to the surface. But these effects were weak. The study further revealed that the formation of dead zones was constant in the presence of additives at all concentrations. The additives did however; specifically NH_4Cl and $BaCl_2$ decreased the width of these zones. The results of these experiments were later compared with the growth and dispersion rate values of the same crystals obtained in pure solutions. As suggested earlier, dead zone formation results from the impurity affect the results of this study which suggests that dead zone formation in pure solutions is a result of surface potential dominating ion which acts as an impurity.

Da Hee Choi et al. worked on the effects of thermal conductivity in phase change material by using additives [58]. For that purpose, multi-walled carbon

nanotube, graphite and graphene were made and the thermal conductivity of the phase change material was measured with the help of transient hot-wire technique. Furthermore, thermal conductivity of the PCM was improved by including the carbon substances and poly vinyl pyrrolidone as a scattering stabilizer. Impact on thermal conductivity was assessed. Findings showed that the heat exchange rate improves up to 3.35 times on account of graphite at 5.0% volume which concluded that graphite is the most effective agent for heat exchange upgrade of stearic acid among three carbon substances despite the fact that graphene gives the most astounding thermal conductivity improvements. Further, followed by the phase change materials prepared to improve the thermal conductivity of stearic acid (SA) as the phase change materials; the scattering stability was assessed and the thermal conductivity of the PCMs was measured by the transient hotwire.

Moreover, the impact of carbon substances on the thermal exchange rate was assessed and the outcomes from the present study were the dispersion stability of PCM was maintained for 10 days by adding poly vinyl pyrrolidone as a dispersion stabilizer. Graphite dispersion lasted for 3 days and Graphene for 8 days while not undermining the further good dispersion stability by adding poly vinyl pyrrolidone. Findings also predicted that at liquid state, thermal conductivity of the nano-phase change materials increases with increasing the concentrations of multi-walled carbon nanotube in graphite and graphene particles. Particularly graphene particles of 0.1% volume, the thermal conductivity was enhanced up to 21.5%. In conclusion, it was found that graphite is the most effective additive for heat transfer enhancement of stearic acid while graphene gives the highest thermal conductivity enhancement.

Leping Dang et al. quantitatively investigated the effects of impurities on the crystallization kinetics of $\text{H}_3\text{PO}_4 \cdot 5\text{H}_2\text{O}$ [59]. The nucleation and the concentration of Fe_3^+ , Al_3^+ , and F^- were controlled under 500, 500, and 2000 ppm, correspondingly for the accuracy of quantification of crystal growth rate. The experiment results revealed that if Fe_3^+ , Al_3^+ , and F^- (450 ppm) are added, the metastable zone for phosphoric acid crystallization increased slightly. It was further discovered that adding small amounts of H_2SO_4 (150 ppm) can increase metastable zone width but higher level of H_2SO_4 has little influence on this zone. The effect of cations is much stronger on nucleation rate that decreases as compared to anions. It was found that all impurities have strong effect on the growth rates of phosphoric crystals. Adding SO_4^{2-} leads to an increase in the

acid crystal growth rates in a wide concentration range with the extreme growth rate at 5000 ppm. Introducing minor quantity of HF leads to the rapid growth of crystal. However, $\text{H}_3\text{PO}_4 \cdot 5\text{H}_2\text{O}$ crystal growth rates were observed to reduce by increasing the concentration of HF to 2000 ppm. Similarly, the addition of Fe_3+ , Al_3+ can intensify crystal growth rate until it reaches a maximum at 50 and 100 ppm respectively, after which it starts to decline. Anions such as SO_4^{2-} and F do not affect phosphoric crystal morphology even though they do influence growth rate. However, cations such as Fe_3+ , Al_3+ considerably transform the crystal formation.

Sayem et al. [60] worked on the formation of water R134a gas hydrates using different additives. They also performed energy and exergy analysis of the clathrates formation. The work covered using different percentages of refrigerant and the usage of different percentages of copper, magnesium nitrate, sodium chloride, aluminum and ethanol. The results showed that copper reduces the onset time while magnesium nitrate reduces the endset time, while 35% of the refrigerant is the optimum amount for the formation of clathrates. The results also showed that out of all mentioned additives, ethanol forms the clathrates with higher density ensuring good heat transfer.

Chapter 4: Experimental Work

This chapter consists of the details about the experimental apparatus used and the experiments done using different additives.

4.1. Experimental Apparatus

The experimental apparatus is clifton range refrigerated water bath (temperature control chiller circulator). This system is basically designed for the circulating temperature controlled liquid and it is also used for the immersion of laboratory samples at low (controlled) temperatures. This system has its specifications and working instructions. It needs to be used for the inside applications where the ambient conditions must be in between 5°C-40°C, whereas the cleanliness is important and the surrounding must be non-explosive.

4.1.1. System configuration. The refrigerated cooling bath (RCB) system basically consists of a stainless steel tank that is fitted inside an outer casing. The insulation is also placed in order to achieve maximum working efficiency. The system is user friendly as the water filling can easily be done and this water can also be emptied in order to clean the system as well as for the refilling purpose. The assembly is fitted with a pipe for these purposes. Just under the stainless steel tank, a refrigeration compressor is fitted in order to provide cooling to the system. As the compressor serves as a cooling component, a heater is also at place in order to control the overall temperature of the liquid. Temperature of the liquid keeps getting checked throughout the time by the temperature control unit and if there is a need to raise the temperature, heater increases the temperature with an increment of 0.1°C. The whole system is moveable as well.

One of the very important parts of the system is thermos-stirrer. The purpose of this stirrer is to make sure the uniform temperature (cooling) distribution throughout the liquid is inside the stainless steel tank. This thermos-stirrer is also made up of stainless steel and is coated with corrosion resistant material. This material helps especially when using the system for longer periods while being in contact with the liquid. The level of the liquid inside the tank continuously remains checked and if the liquid surface decreases, the heater stops working until the surface temperature of liquid is restored. The system has a maximum capacity of 18 litre. Complete specifications of the system are given below in the Table 4.

Table 4: Complete specifications of the refrigerated water bath

Dimensions	External: 423w x 469d x 672h mm Internal: 295w x 300d x 200h mm Bath opening: 295w x 210d mm Water level: Maximum 180mm
Operating Temperature Range	-30°C to 99°C
Temperature Control	4 digit LED Display (PID Digital)
Sensitivity	±0.1°C @ 10°C
Pump Capacity	10 litres/min
Pressure	150mbar
Cooling Power	+20°C: 900W 0°C: 660W -10°C: 380W -20°C: 220W Refrigerant: R134a
Voltage	230V
Packed Weight	55kg
Heater Power	1250W
Cooling Power Consumption	2800W
Model	NE7-18
Compressor	Danfoss

4.2. Operation of the System

Before using the system for experimental purpose, the cleanliness of the system is important. The Thermocirculator can simply be cleaned by any soft cleaning material. While for the cleaning of the stainless steel tank, simple water can be used. The cleaning water can be emptied from the tank using the same exit water pipe. If the tank is being cleaned after a long time, nitric acid can be used on a cloth. At the start of the operation, this stainless steel tank must be filled with the suitable liquid to the desired level of

operation. Once the liquid is filled, the surface of the tank must be covered by the given lid. Now for the start of operation, the compressor is started using the button given at the side bottom of the system. This starts cooling the liquid inside the tank. In order to get the desired temperature, thermo-circulator is also switched on using the backside button of it. After switching on, the apparent temperature of the water gets visible at the surface of light emitting diode (LED) display. And from this stage, the desired temperature can be inserted using the up and down button on the thermo-circulator. Although, thermo-circulator itself keeps measuring the temperature for constant cooling conditions, yet any external circulation can be added/fitted [61]. Figure 9 shows the configuration of the system.

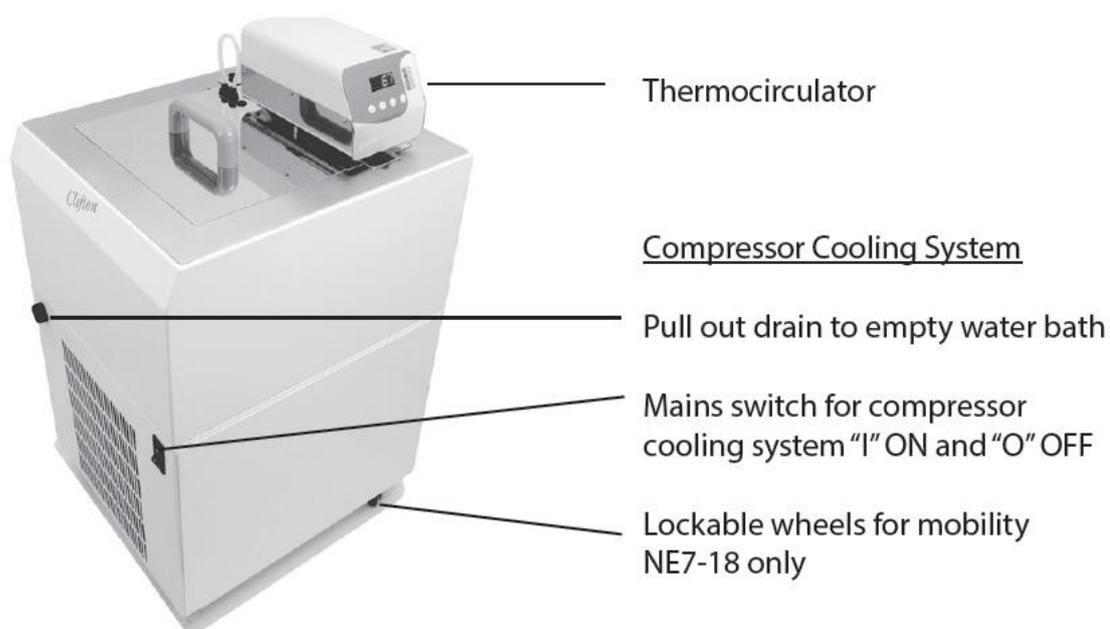


Figure 9: Configuration of refrigerated cooling bath [61]

4.3. Using R134 as Refrigerant

While using refrigerated water bath as the experimental apparatus, refrigerant R134a (Tetrafluoroethane) is used with water in order to form the clathrates. Chemical formula of the refrigerant R134a is CH_2FCF_3 . This refrigerant is widely used as a substitute of R12 whose usage has widely been stopped due to the damaging effect of R12 for the environment. R134 is a far better choice because of its safe usage and non-toxic behavior. It has been widely used in air conditioning applications. As has been already discussed in the literature, the clathrates form when the water molecules act as

the host molecules and capture the refrigerant molecules which act as the guest molecules. For different experimental analysis, the ratio of water and the refrigerant may vary from case to case. This ratio of refrigerant and water depends upon the desired results and the nature of clathrates formation. Table 5 shows some of the other key properties of refrigerant R134a.

Table 5: Properties of refrigerant R134a

Ozone Depletion	0
Water Solubility	0.11% by weight at the ambient conditions (25°C temperature)
Boiling Point	-26.1°C
Color	Light Blue
Auto-ignition Temperature	770°C

4.4. Additives Used

Although the usage and effect of the selected additives for the clathrates formation have been discussed previously in details, for current experimental work, the focus is to use commonly available, easily usable and efficient additives. The experimental has been focused on four additives.

- i. Ethylene Glycol
- ii. Glycerol (Glycerin)
- iii. Ethanol
- iv. Butanol

All of these candidate additives have their different respective chemical properties. Yet, all of these three have higher thermal conductivity. This property along with their stability makes them a suitable additive for clathrates formation. Before discussing the results of every individual case of additives, it is important to discuss the process of clathrates formation in the lab using refrigerated cooling bath.

4.5. Process of Clathrates Formation Using Refrigerated Cooling Bath

Process of clathrates formation using refrigerated cooling bath consists of proper measurements of water, refrigerant and the additives. The apparatus used in this

regard is available in the air conditioning lab. Cleaning of all the using apparatus is of higher importance since any impurity may affect the output. The basic apparatus used in this process consists of a high pressure glass tube, ceiling assembly, mass balance, refrigerated cooling bath, insulation and a vacuum pump. Before using the glass tube, it is really important to wash the glass tube. This glass tube is then fitted with its ceiling assembly. Now, the initial mass of the glass tube (with ceiling assembly) is measured to get the estimate of tube mass without any liquid inside it. Once the mass of glass tube gets measured, the reading gets noted. After removing the glass tube from mass balance, the required amount of distilled water gets measured very carefully (by removing the mass of the dropper or a cup). This water is then poured inside the glass tube. The ceiling of glass tube is tightened once again after filling the water and the new mass of



Figure 10: High pressure glass tube

glass tube gets measured. After this step, the required amount of additive is measured the same way as that of water using a dropper or a cup. The glass tube is shown in Figure 10.

This additive is then poured inside the glass tube and the ceiling assembly is tightened again. The new mass of the glass tube is measured. The glass tube is fitted with the vacuum pump in order to remove all the air from inside. The vacuum pump is shown in Figure 11. The glass tube is fitted with the external pipe of the vacuum pump. The valve of the glass tube is opened and vacuum pump gets started in order to remove



Figure 11: Vacuum pump

all the vapors/air molecules from inside the tube. The vacuum inside the tube can be confirmed by noticing the pressure gauge attached with the ceiling assembly. Once there is vacuum inside the tube, the valve at the ceiling assembly is carefully closed and the external pipe of the vacuum pump is disconnected.

Finally, the refrigerant R134a is filled inside the glass tube. This refrigerant is available in the cylinder. This cylinder is fitted with an external assembly of two valves. This assembly is shown in Figure 12. First of all, the cylinder of the refrigerant is turned upside so that the vapor of refrigerant inside the cylinder remains on the top of the liquid refrigerant and the liquid will flow out of the cylinder. One of the two valves (say valve 1) of external assembly attached to the cylinder is fitted directly whereas the other valve (say valve 2) has an external pipe attached. This pipe is used to fit with the valve of glass tube. At the start of filling the refrigerant, valve 2 is closed and only the valve 1 is opened to the safe amount. Before attaching pipe of the valve 2 with the valve of glass tube, the valve 2 is slowly opened so that the air inside the pipe may be removed. The pipe of valve 2 is then attached with the valve of glass tube. This valve of glass tube is then opened slowly and the valve 2 is also opened systematically. The refrigerant then enters inside the glass tube in the form of the liquid. This can also be noticed by looking at the pressure gauge. These glass tubes are designed for a maximum pressure of around 120 bar. Once the desired amount of refrigerant gets filled inside the glass



Figure 12: Valve assembly for the refrigerant tank

tube, the valve of the glass tube is closed. Before removing the external pipe of valve 2, the valve 2 is closed and then the pipe is slowly removed from the valve of glass tube. In this way, the refrigerant present inside the tube gets released which is also

important for the safety of glass tube and the refrigerant valve. Once the refrigerant inside the tube gets released, the external pipe of valve 2 is removed. The new mass of the glass tube (which now has Refrigerant R134a, distilled water and the additive) is measured. These readings are also noted and compared with the desired ratio of distilled water, refrigerant R134a and additive.

While doing all this filling, the refrigerated cooling bath is switched on and the desired temperature can be achieved parallel to the process. Once the desired temperature is achieved, the glass tube is then immersed inside the cooling bath. It is important that the surface of liquid inside the glass tube must be completely submerged below the surface of liquid inside the cooling bath so the amount and ratio of the distilled water, refrigerant and the additive must be accordingly calculated at the start of the experiment. Once the glass tube is submerged inside the cooling bath, the time is measured for the formation of clathrates. This time is also divided into two categories.

1. Onset time
2. End set time

The onset time is the time, at which clathrates start formation. The End set time is the time when the process of clathrates formation gets completed. Depending upon the used additive, the clathrates formation time varies. It also depends upon the temperature of refrigerated cooling bath. System during the operation can be seen in Figure 13.



Figure 13: System during operation with insulation

4.6. Ethylene Glycol as an Additive

Ethylene glycol (chemically $C_2H_6O_2$) is commercially used as the coolant in automobiles along with the water. The water is mixed with the ethylene glycol generally in the ratio of fifty-fifty in order to improve the heat transfer properties, which in

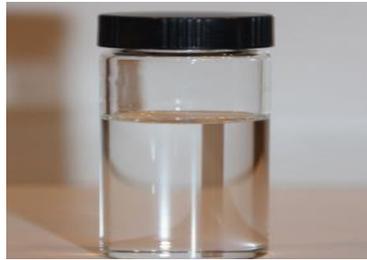


Figure 14: Ethylene glycol additive

automobiles, increases the boiling point of water and also lowers the freezing point. Ethylene glycol when added with the water as an additive, it improves its thermal properties as it also has good thermal properties. The sample of ethylene glycol additive is shown in Figure 14.

4.6.1. Experimental process and calculations. Numerous experimental runs for the clathrates formation were performed in details while using ethylene glycol. The experiments cover the usage of different percentages of the ethylene glycol additive at different operating cooling temperatures.

The onset time presents the time at which clathrates formation starts while the endset time presents the time at which clathrates formation ends at specific temperatures. For the experimental purpose and analysis, different percentages of additives were used ranging from 1% to 4%. All of these percentages are given with respect to the mass basis. The experimental procedure was repeated for all the percentages (1%, 2%, 3% and 4%) at different operating temperatures of 2°C, 3°C and 4°C. The main reason to use three different temperatures was to compare and analyze the impact of the operating temperature on clathrates formation process. This variation of temperature was done to determine at what extent lower temperature may impact the crystallization process and does it worth to decrease the temperature below a certain limit at the cost of higher cooling energy.

A combination of 12 experimental results was compiled. For every experiment, total four glass tubes were used as the candidate apparatus to get the best possible results. For the experimental analysis, a sample calculation for 3% additive used (at the

cooling bath temperature of 3°C) is shown in Table 6.

Table 6: Sample Calculations with 3% additive at 3°C

Total mass of distilled water used	67g
Total mass of additive (Ethylene Glycol) added	3g
Total mass of Refrigerant R134a added	30g
Total mass of the mixture	100g

This calculation leads the percentage of 67% distilled water, 3% additive and 30% refrigerant in the glass tube. All of these percentages are given with respect to the mass. The total mass of this mixture (without glass tube) turns out to be 100g. Now, the temperature set for this refrigerated cooling bath was 3°C. The glass tube is then placed inside the stainless steel bath (filled with distilled water). In this way, the total and uniform distribution of cooling is assured since the water temperature of cooling bath remains checked and uniform by the thermo-circulator. This system is then covered with the foam based insulation above the whole system in order to minimize the effects of outside atmosphere. The holding glass cover is not opaque, the clathrate formation process can be seen with the passage of time.

4.6.2. Errors/Issues associated with experiments. It is really hard to do every experiment in one go, since there are too many factors involved in the experiments. Any mishandling or misreading can lead to the difference in the results. The biggest issue that was faced during the experiments was to control the leakages inside the tube. The ceiling assembly is basically made up of a cork in which a valve and pressure gauge are fitted. These assembly components gets leaked with a little extra pressure. At the same time, a little less or loose tightening of the glass tube also leads to the leakage of refrigerant which affects the results tremendously. While removing the air from the glass tube before filling the refrigerant, it is important to close the valve of the ceiling assembly before removing the external pipe of vacuum pump. At the same time, when the refrigerant is filled; it becomes important to close the valve of ceiling before removing the valve assembly of refrigerant tank to avoid the refrigerant leakage from glass tube. If there are some bubbles coming out of the water, it indicates the leakage of tube. In that case, it is important to separate the malfunctioned glass tube. In a case

when the bubbles are coming out of the valve opening, this opening can be closed using a cover and then using the glass tube. For the cases when the leakage is at the attachment of glass tube with the cork ceiling, a gasket may also prevent the leakage but sometimes extra pressure at the gasket may result in the worn-out gasket. In that case, it's important to use a new gasket. The system is really sensitive. The temperature inside the refrigerated cooling tank always needs to be cross checked by the external thermocouples as any external heat from the heater would also increase the temperature of the cooling water.

4.6.3. Experimental results. When experiments were completed, the results were analyzed. The below figures were obtained at the completion of experiments. The results are presented with their respective conditions.

4.6.3.1. Different percentages of additive at 2°C. The clathrates (using different additive percentage) at 2°C can be seen in Fig 15.

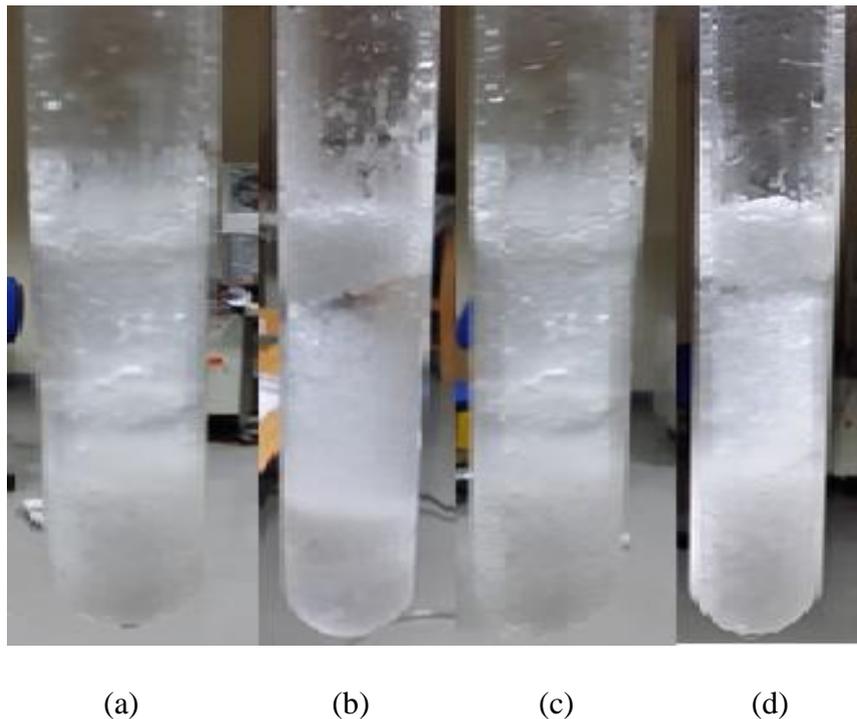


Figure 15: Clathrates formed with (a) 1%, (b) 2%, (c) 3% and (d) 4% additive (ethylene glycol) at bath temperature = 2°C, refrigerant = 30%

For the experiment of every percentage of additive e.g. 1% additive, 4 tubes were used. Out of these four tubes, one was found out to be malfunctioning so it had to be separated than the others in order to fix its leakages. At the end of the experiment, the average of the readings was taken in order to get the best result with least error.

Once the experiment is done, it is important to open the valve in order to get it emptied from the refrigerant R134a. Once the refrigerant is gone, the glass tube can be opened and washed completely. The average of the experimental results is plotted. The trend of the onset time and end set time can be seen in Figure 16. The graph is curve-fitted.

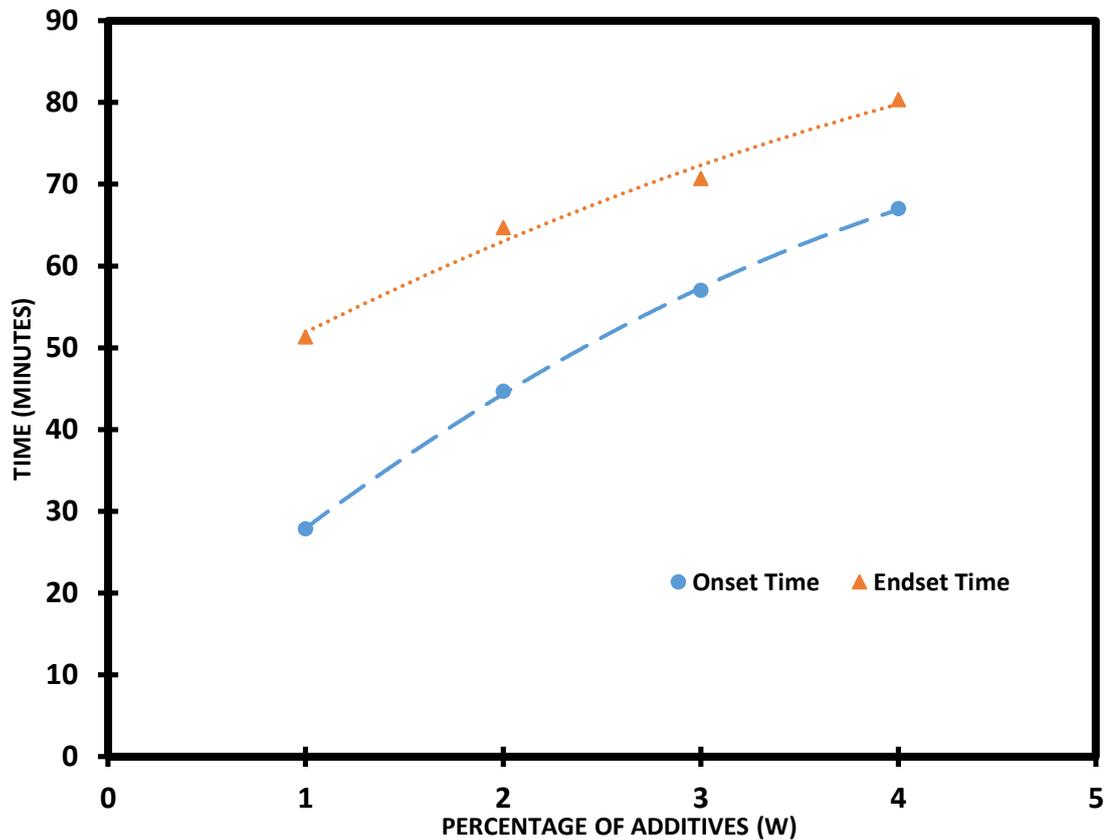


Figure 16: Variation of clathrates formation time with percentage of additive, bath temperature = 2°C, refrigerant = 30%

The equations of the onset time and the endset time after curve fitting were of second order polynomials. These equations show the general trend of onset and endset times at 2°C bath temperature. Whereas w presents the mass percentage of additive.

For onset time:
$$t = -1.7083w^2 + 21.525w + 8.125$$

For endset time:
$$t = -0.9167w^2 + 13.883w + 38.917$$

The detailed analysis of the results shows that as the percentage of additive increases, the onset time for the clathrates formation also increases. This can be explained as the thermal properties of the ethylene glycol are poor with respect to that of water and so onset time increases with increase in additive percentage. But it can be

seen that once the clathrates formation starts, more percentage of additive helps decreasing the endset time and total clathrates formation time.

4.6.3.2. Different percentages of additive at 3°C. In this second set of experiment, the cooling bath temperature was changed to the 3°C with the same varied percentages (1%, 2%, 3% and 4%) of additive. The formed clathrates at 3°C can be seen in the Figure 17.

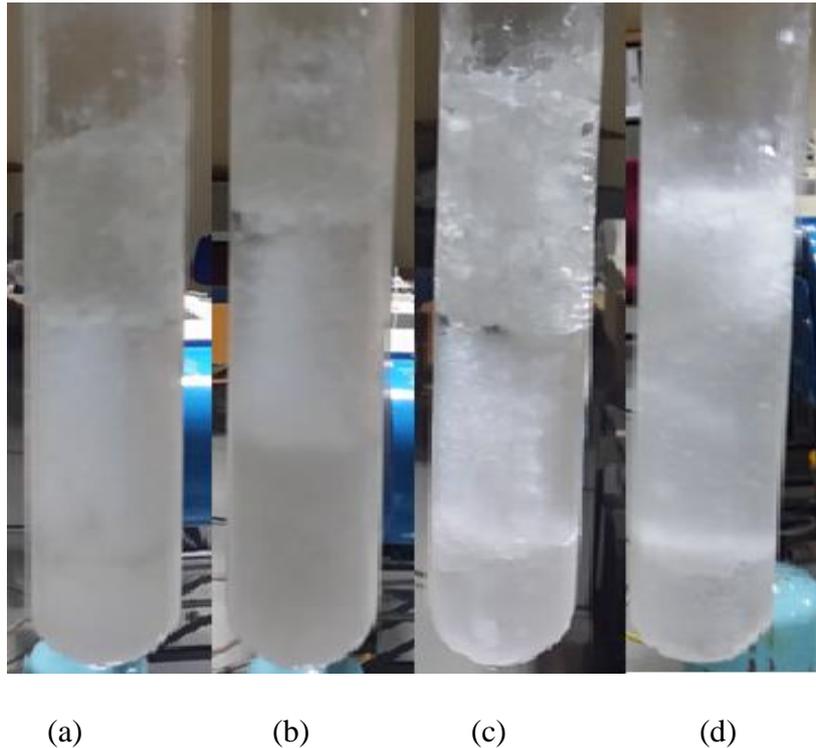


Figure 17: Clathrates formed with (a) 1%, (b) 2%, (c) 3% and (d) 4% additive (ethylene glycol) at bath temperature = 3°C, refrigerant = 30%

For the experiment of every percentage of additive e.g. 1% additive, 3 tubes were used as one of the ceiling was leaked and it had to get fixed. At the end of the experiment, the average of the readings was taken in order to get the best result with least error. These results are then plotted. The graph is curve-fitted.

The equations of the onset time and the endset time after curve fitting were of second order polynomials. These equations show the general trend of onset and endset times at 3°C bath temperature. Whereas, w presents the mass percentage of additive.

For onset time:
$$t = -1.1667w^2 + 18.033w + 16$$

For endset time:
$$t = 0.5w^2 + 2.7w + 64$$

The trend of the onset time and end set time can be seen in Figure 18.

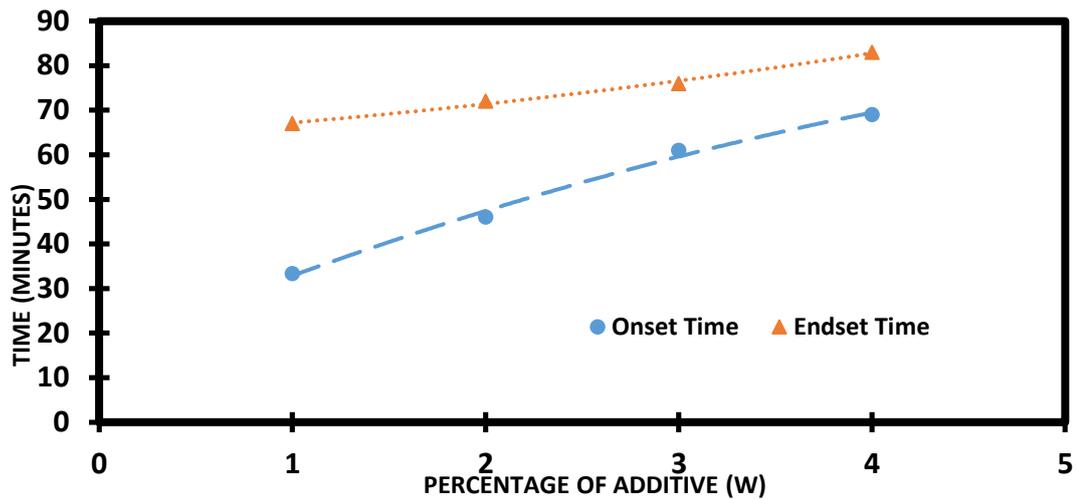


Figure 18: Variation of clathrates formation time with percentage of additive, bath temperature = 3°C, refrigerant = 30%

The results show the same behavior as that of the previous case. As the percentage of additive increases, it takes more onset time as the thermal properties of ethylene glycol are bad with respect to that of water. At the same time, we can see that the difference between onset time and the end set time decreases with the increment of additive percentage due to the better heat transfer rate effect by additives.

4.6.3.3. Different percentages of additive at 4°C. In this set of experiment, the cooling bath temperature was 4°C with the same varied percentages (1%, 2%, 3% and 4%) of additive. This can be seen in Figure 19.

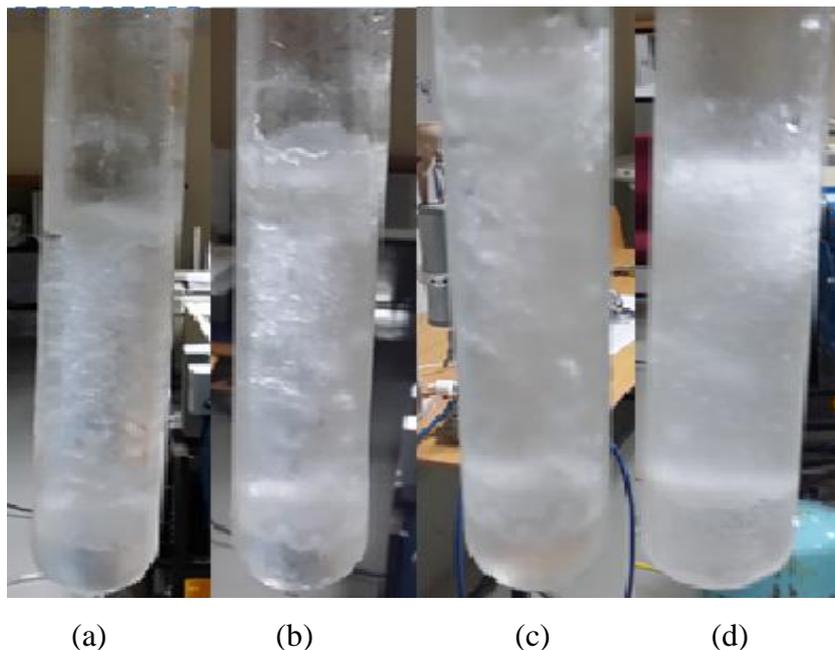


Figure 19: Clathrates formed with (a) 1%, (b) 2%, (c) 3% and (d) 4% additive at bath temperature = 4°C, refrigerant = 30%

The trend of the onset time and end set time can be seen in Figure 20.

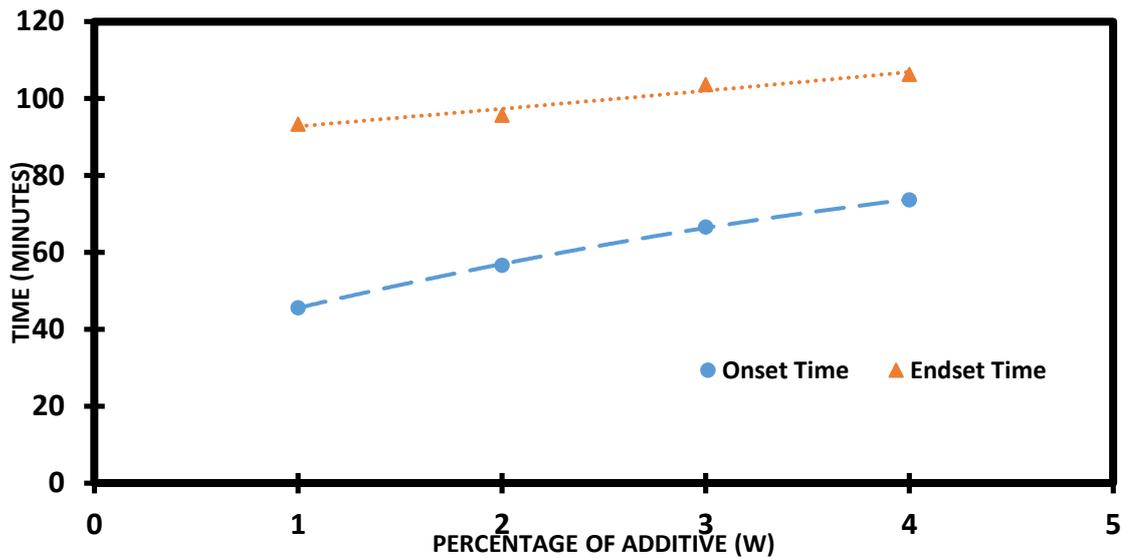


Figure 20: Variation of clathrates formation time with percentage of additive, bath temperature = 4°C, refrigerant = 30%

Again for this experiment, average of the results is taken and plotted. The equations of the onset time and the endset time after curve fitting were of second order polynomials. These equations show the general trend of onset and endset times at 4°C. Whereas w presents the mass percentage of additive.

For onset time: $t = -1w^2 + 14.4w + 32.167$

For endset time: $t = 0.0833w^2 + 4.2833w + 88.417$

A clear resemblance of all the trends of onset time, end set time and the clathrates formation time can be seen for the ethylene glycol. As explained earlier about the thermal properties of ethylene glycol, this trend is justified for the increment of onset time and endset time. But the clathrates formation time is clearly decreasing which indicates the effect of additive by improving the heat transfer rate, once the crystal growth starts.

4.6.4. Comparison between the cases of different temperature. The comparison of the results obtained at different temperatures (with different additive percentages) can be done by comparing the onset time and the endset time.

4.6.4.1. Onset time. Onset time means the time at which clathrates formation starts. The averages of all the candidate glass tubes are taken and then plotted in Figure 21.

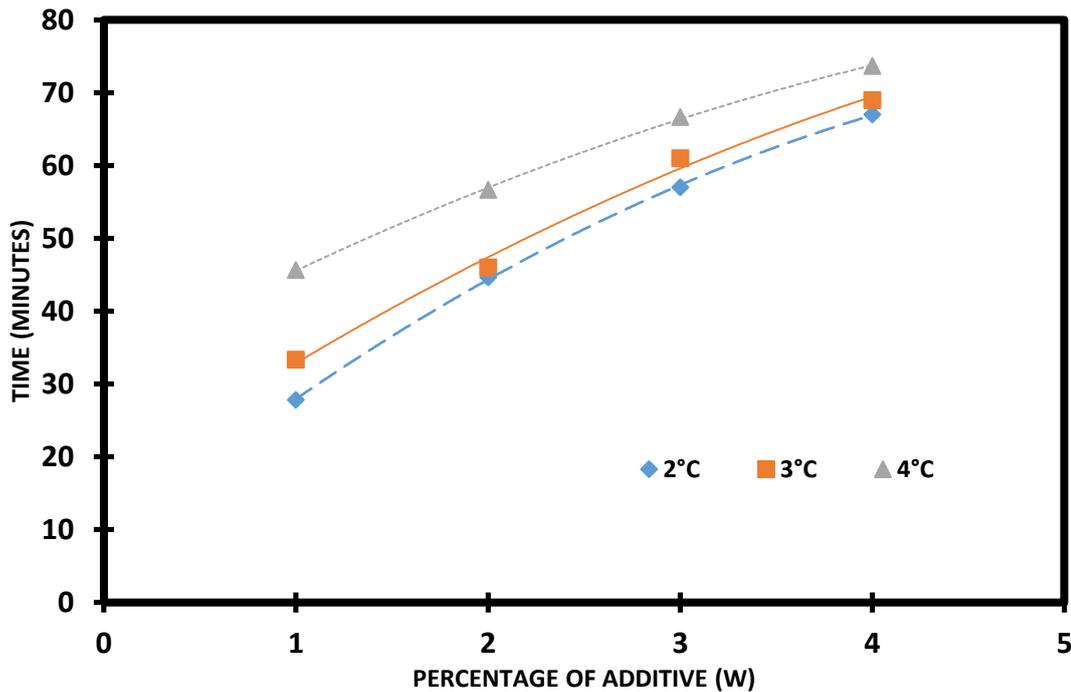


Figure 21: Comparison between the onset time obtained at different bath temperatures

The graph can be explained in light of the temperature effect. If we compare the results obtained at 2°C with results obtained with 3°C, we can see that there is minor increment (comparatively) in the onset time. The reason is the higher rate of heat removal with more cooling temperature. So, the trend curves go close to the parallel. This trend varies a bit when the results of 2°C and 3°C are compared with the results obtained at 4°C. There is a marked increment (comparatively) in the onset time at 4°C with respect to 3°C. It is worth mentioning that experiments were done for the 6°C as well but the clathrates formation time was so long that experiment had to be terminated. Providing cooling energy for longer duration would impact on the TES system performance in the negative way which also indicates and validates the impact of temperature for the clathrates formation process.

4.6.4.2. Endset time. The endset time refers to the time at which the clathrates formation completes. Again for this case, the averages of all the candidate glass tubes are taken for their respective percentages of additive and then plotted on the same graph. For the end set time, the trend varies a little bit. The end set time for the 2°C and the 3°C has a visible difference for the 1% additive. But as the percentage of additive increases, the difference between the endset time decreases. And in the end when the percentage reaches maximum i.e. 4%, the difference between the endset time of 2°C and 3°C becomes very small which points out towards the minor impact of lower

temperatures in the presence of higher additive percentage. But the difference between the results of 3°C and 4°C is higher. This again, can be explained with the enhanced heat transfer rate or cooling at lower temperatures as explained earlier. Trend is shown in Figure 22.

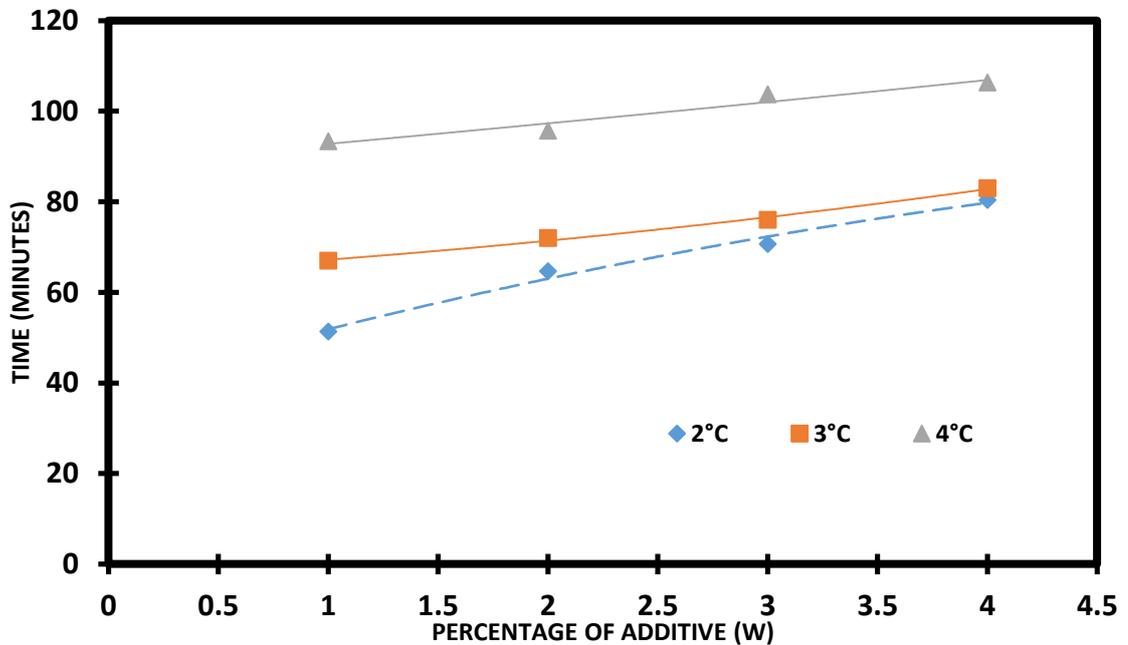


Figure 22: Comparison between the endset time obtained at different bath temperatures

This trend can also be seen as the clathrates formation time (the endset time minus onset time) as shown in Figure 23.

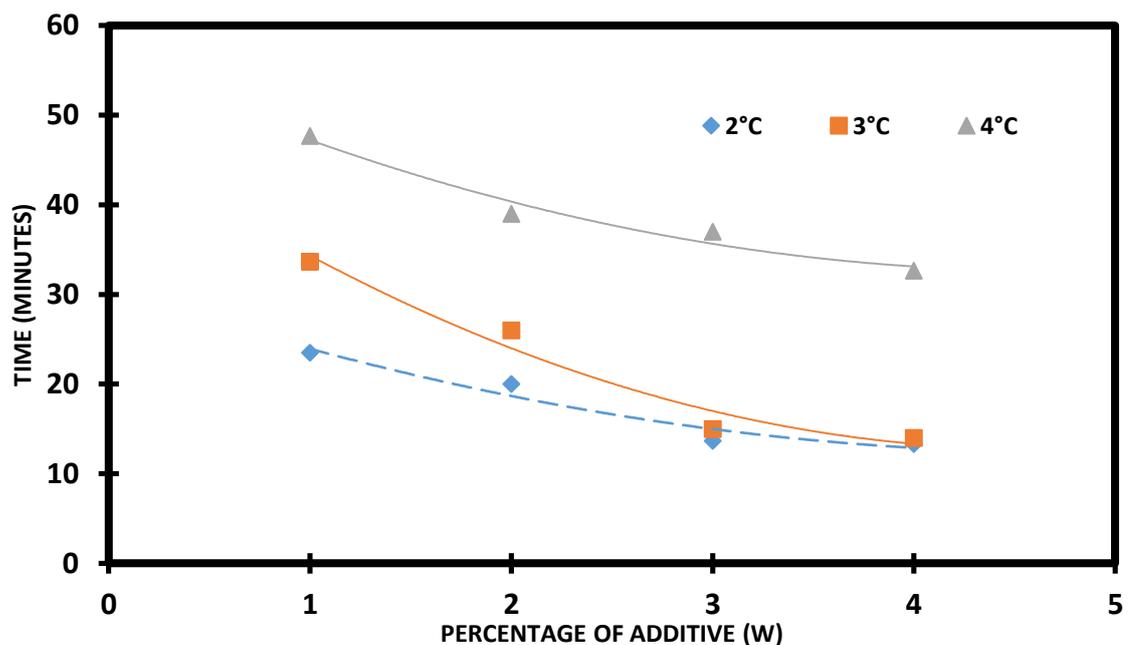


Figure 23: Clathrates formation time comparison for different bath temperatures

4.7. Butanol as Additive

Butanol (C_4H_9OH) is from the alcohol family of organic compounds with good thermal properties. Although relatively smaller amount of additive is used while using butanol, in this work, the percentage of additive is changed along with changing the percentage of refrigerant. It's less toxic in nature, yet the eyes and skin must be protected in its usage to avoid any hazardous effects. Butanol available in the lab is shown in Figure 24.



Figure 24: Butanol additive

4.7.1. Experimental results and calculations. The work in this regard covers using different percentages of butanol. The percentage of the refrigerant was also varied. The temperature of the refrigerated cooling tank was kept constant at $3^{\circ}C$. A total of 4 different percentages of butanol were used as an additive i.e. 1%, 2%, 3% and 4%. This was done in addition to using the different percentages of refrigerant R134a. The percentages used for refrigerant were 25%, 30% and 35%. Although, experiments were done for 25% and 40% as well, the results were not appreciative. The variation of refrigerant ratio is important in order to know the impact of the refrigerant on the clathrates formation. This is also important to know the optimum ratio between water and the refrigerant by comparison. For every experimental case, a total four glass tubes were used as the candidate apparatus. For the experimental analysis, a sample calculation for 3% additive with the 30% of refrigerant used is shown in Table 7.

Table 7: Sample calculation for 3% additive with 30% refrigerant.

Total mass of distilled water used	67g
Total mass of additive (Butanol) added	3g
Total mass of Refrigerant R134a added	30g
New total mass of tube	100g

Exactly the same methodology was used for these experiments as well and the variables (additive percentage and the refrigerant percentage) were changed for their respective cases. The clathrates formation in the case of butanol gave us solid ice like clathrates. So, apparently it gives us the view of stronger additive reaction and the higher heat transfer rate leading to the comparatively stronger clathrates.

4.7.2. Experimental results. When experiments were completed, the results were analyzed. The below figures were obtained at the completion of experiments. The results are presented with their respective conditions.

4.7.2.1. Different percentages of additive with 25% refrigerant. For this set of experiment, the percentage taken for the refrigerant was 25% and the refrigerated cooling tank temperature was 3°C. The only variable in these experiments was the percentage of additive. For the experiment of every percentage of additive e.g. 3% additive, 3 tubes were used. At the end of the experiment, the average of the readings was taken in order to get the best result with least error. These average values were then plotted. The formed clathrates can be seen in Figure 25.

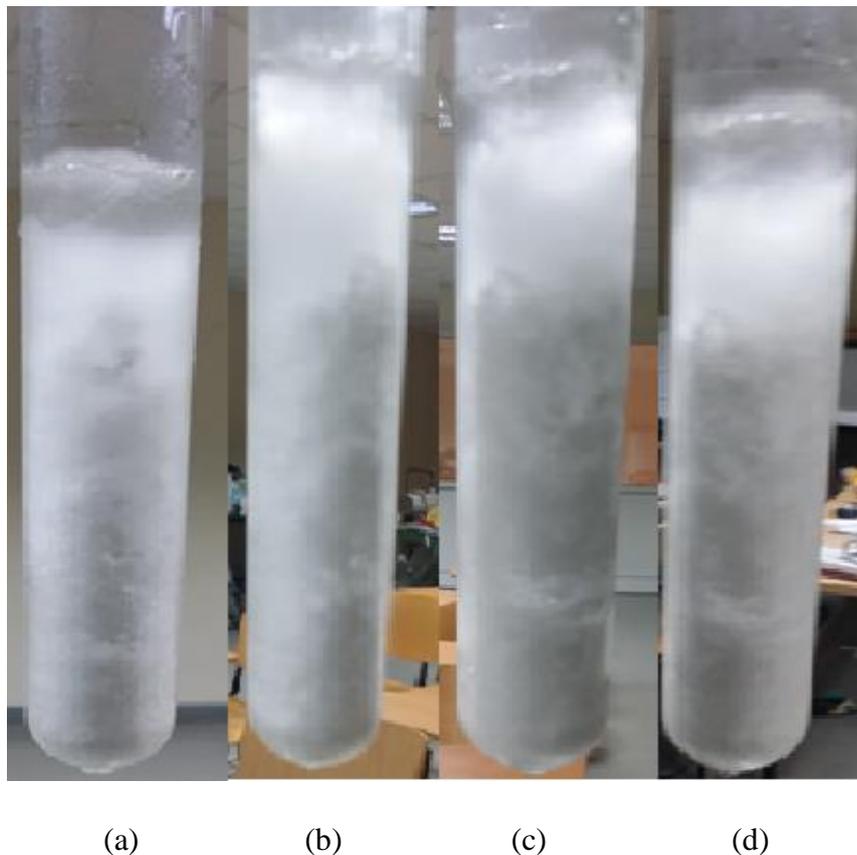


Figure 25: Clathrates formed with (a) 1%, (b) 2%, (c) 3% and (d) 4% additive (butanol) and 25% refrigerant at bath temperature = 3°C

The trend of the onset time and the endset time is shown in Figure 26. The data is curve fitted.

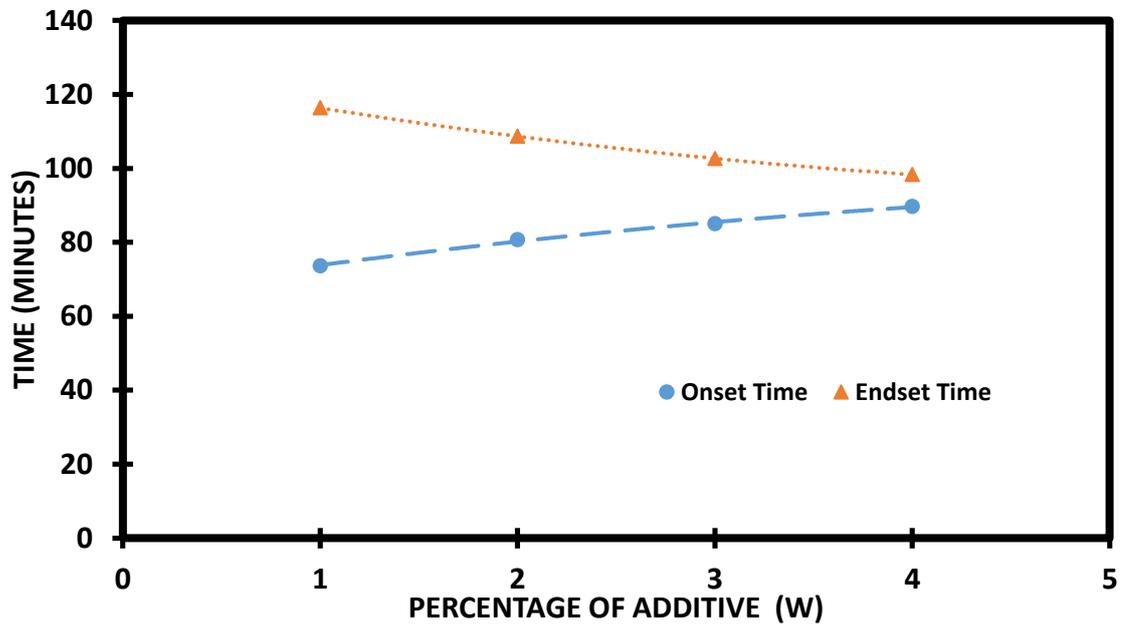


Figure 26: Variation of clathrates formation time with percentage of additive, bath temperature = 3°C, refrigerant = 25%

The equations of the onset time and the endset time after curve fitting were of second order polynomials. These equations show the general trend of onset and endset times at 3°C bath temperature and 25% refrigerant. Whereas w presents the mass percentage of additive.

For onset time: $t = -0.5833w^2 + 8.15w + 66.25$

For endset time: $t = 0.8333w^2 - 10.167w + 125.67$

The results show a clear trend of longer clathrates formation time at the start. This happens because of not having a perfectly balanced ratio between water and the refrigerant. But once the process of clathrates formation starts, it does not take long time to form clathrates especially with higher percentage of additive. The point to notice here is the remaining water. Since, with comparatively low percentage of refrigerant; not all water molecules form clathrates. The crystals in this case can be seen like hard solid crystal, unlike for the case of ethylene glycol where crystals were fluffy.

4.7.2.2. Different percentages of additive with 30% refrigerant. The formed clathrates (using different percentage of additive) with 30% refrigerant at 3°C can be seen in Figure 27.

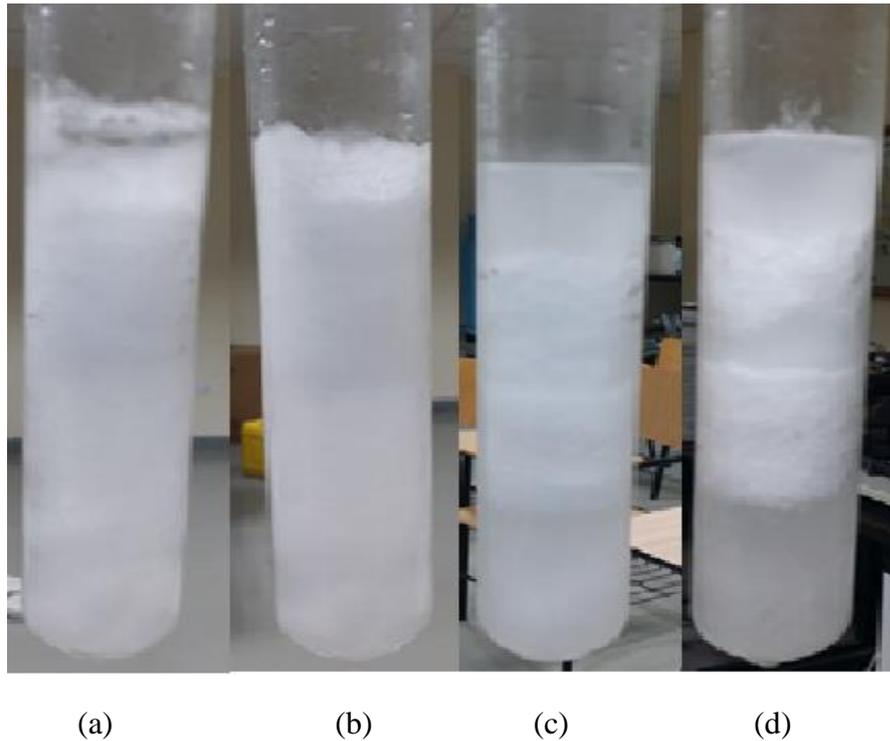


Figure 27: Clathrates formed with (a) 1%, (b) 2%, (c) 3%, (d) 4% additive (butanol) and 30% refrigerant at bath temperature = 3°C

The trend of the onset time and the endset time is shown in the Figure 28. The data is curve fitted.

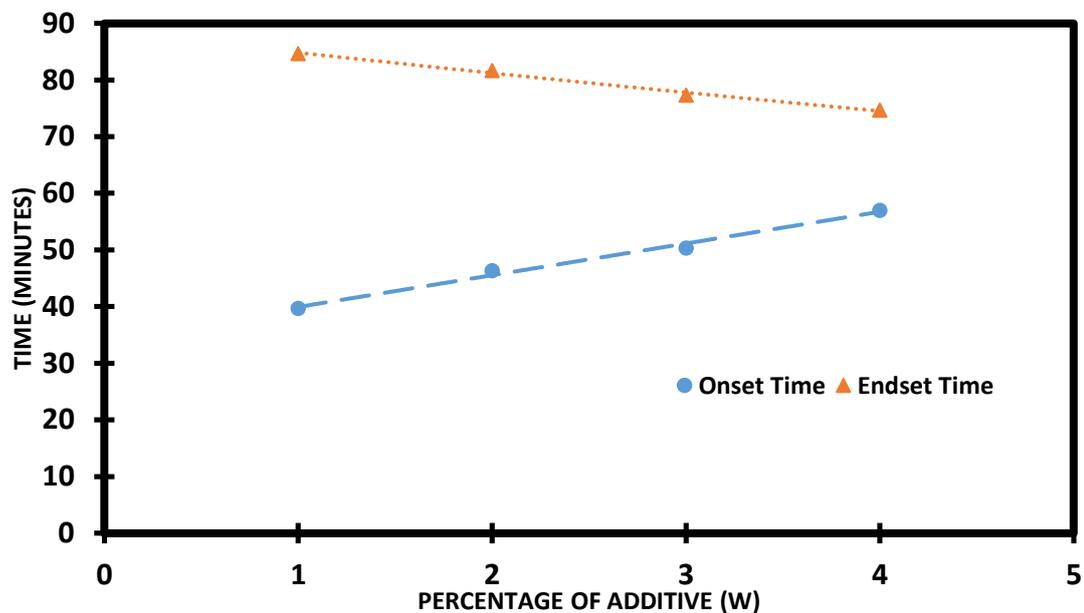


Figure 28: Variation of clathrates formation time with percentage of additive, bath temperature = 3°C, refrigerant = 30%

For this set of experiment, the percentage of refrigerant was 30% and the bath temperature was 3°C. The only variable in these experiments was the percentage of

additive. The average values of the experimental results were plotted. The equations of the onset time and the endset time after curve fitting were of second order polynomials. These equations show the general trend of onset and endset times at 3°C bath temperature and 30% refrigerant. Whereas w presents the mass percentage of additive.

For onset time:
$$t = 6 \times 10^{-14}w^2 + 5.6w + 34.333$$

For endset time:
$$t = 0.0833w^2 - 3.85w + 88.589$$

The results show that as the percentage of additive increases, onset time also increases which is because of poor thermal properties of the butanol as compared to water. But once the process starts, additive help decreasing clathrates formation time by improving the heat transfer rate. The crystals can be seen like hard solid.

4.7.2.3. Different percentages of additive with 35% refrigerant. The formed clathrates (using different percentage of additive) with 35% refrigerant at 3°C can be seen in Figure 29.

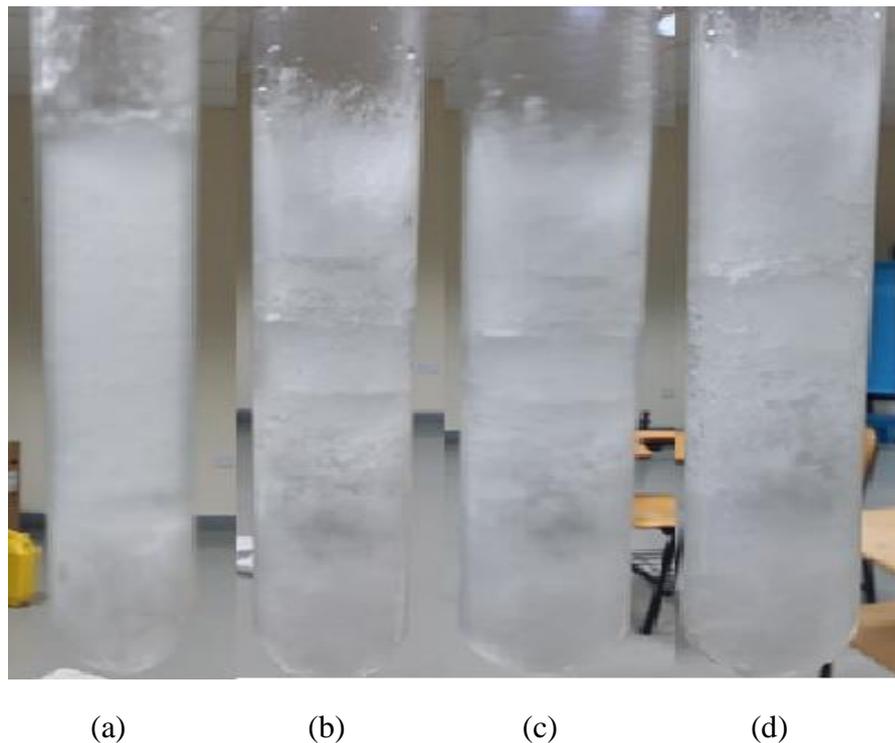


Figure 29: Clathrates formed with (a) 1%, (b) 2%, (c) 3%, (d) 4% additive (butanol) and 35% refrigerant at bath temperature = 3°C

For this set of experiment, the percentage taken for the refrigerant was 35% and the refrigerated cooling tank temperature was 3°C. It was same for all the glass tubes used in the experiment. The only variable in these experiments was the percentage of

additive. Same methodology was adopted as that of previous cases and the average values of experimental results were plotted. The trend of the onset time and the endset time is shown in Figure 30. The data is curve fitted.

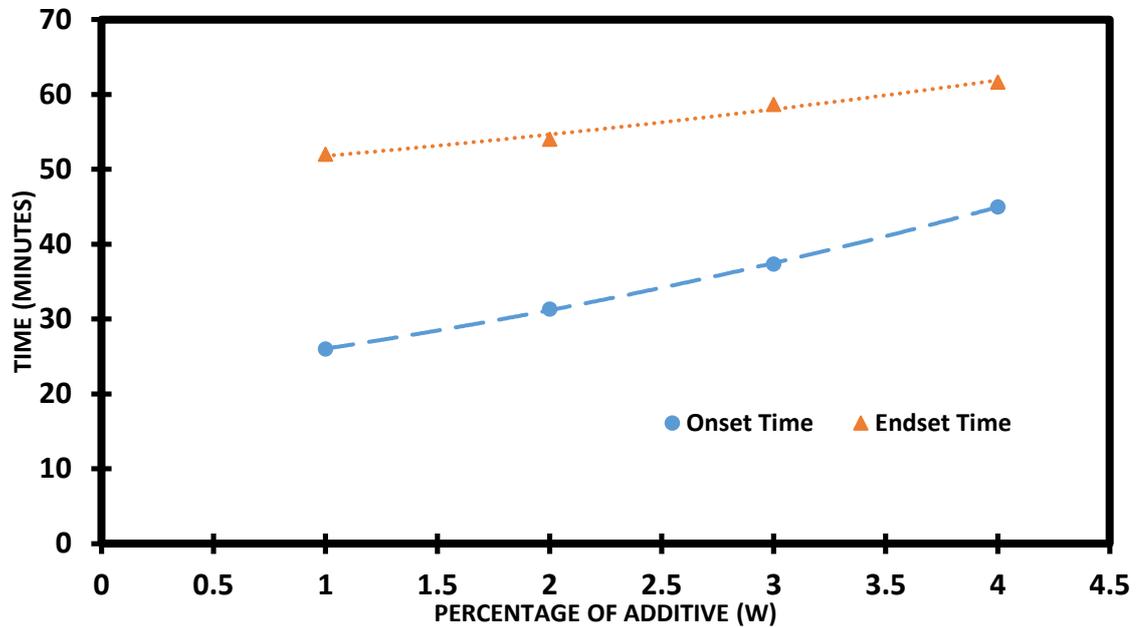


Figure 30: Variation of clathrates formation time with percentage of additive, bath temperature = 3°C, refrigerant = 35%

The equations of the onset time and the endset time after curve fitting were of second order polynomials. These equations show the general trend of onset and endset times at 3°C bath temperature and 30% refrigerant. Whereas w presents the mass percentage of additive.

For onset time:
$$t = 0.5833w^2 + 3.3833w + 22.083$$

For endset time:
$$t = 0.25w^2 + 2.1167w + 49.417$$

The plot shows that as the percentage of additive increases, the onset time also increases, whereas for the case of endset time, with the increment of additive the endset time is also increasing but this increment is very small. The onset time and the end set time difference is decreasing throughout. Reason being the poor thermal properties of butanol which impacts at the start but once the process starts, higher refrigerant percentage helps decreasing the charging. The crystals can be seen like rock solid.

4.7.3. Comparison of different percentages of refrigerant used. For the different percentages of refrigerant, the main variable that affects the onset time and the endset time is refrigerant. The comparison of the results obtained for onset time with

different percentages of refrigerant R134a is presented in Figure 31.

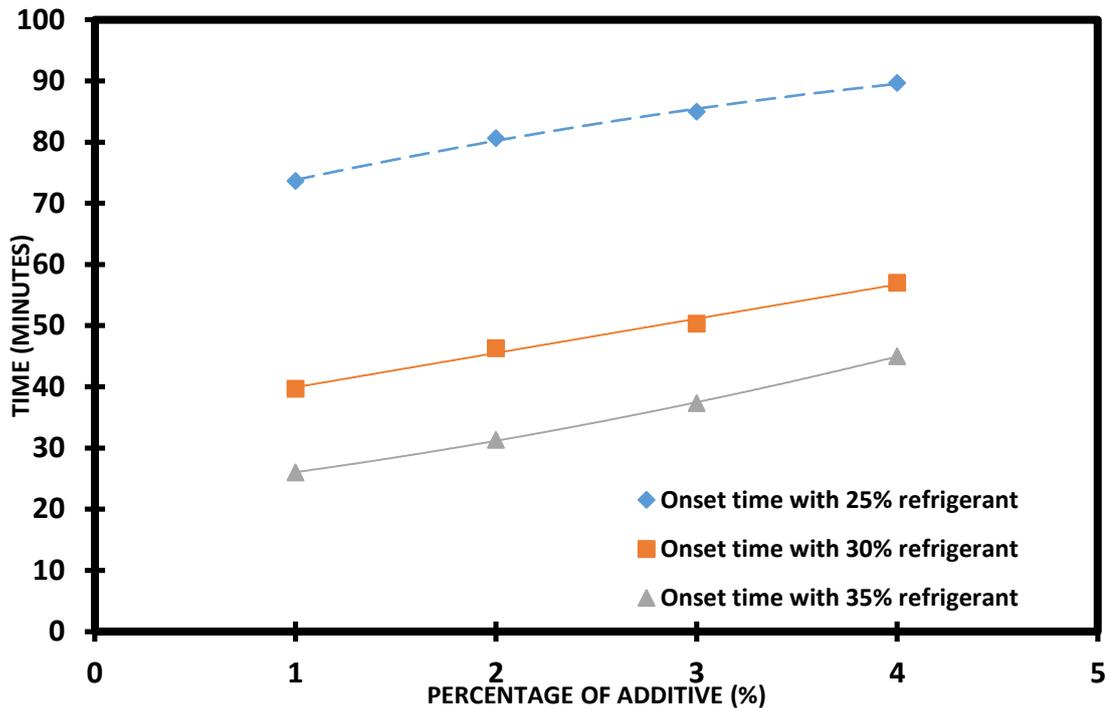


Figure 31: Onset time comparison with different percentages of refrigerant at 3°C

The detailed analysis of the experiments shows that the highest onset time is for the case of 25% refrigerant. It shows that there needs to be a perfect ratio for the refrigerant-distilled water mixture in order to form clathrates completely. With 25% refrigerant, it takes highest time to start forming the clathrates as the percentage of refrigerant is low. With increase in the refrigerant percentage, onset time for clathrates formation decreases and it is the minimum for 35% refrigerant in these three cases. An important point to be noted here is, there remains a certain amount of water left for the cases of 25% and 30%. Although, this amount of unused water (in clathrates formation) is very low, it points out towards a definite proportion of refrigerant and distilled water in order to completely form the clathrates. The results for the endset time comparison shows that as the refrigerant percentage increases, the endset time decreases which shows a bit different behavior for 35% refrigerant case. Yet, the endset time is minimum for the 35% refrigerant. Although, it appears to be showing the increase in endset time with increase in additive percentage, the difference between onset time and endset time is decreasing which shows that using more percentage of additive helps clathrates formation in lower time. So results show that the minimum clathrates formation time was for the 35% refrigerant. The comparative analysis for endset time is shown in Figure 32.

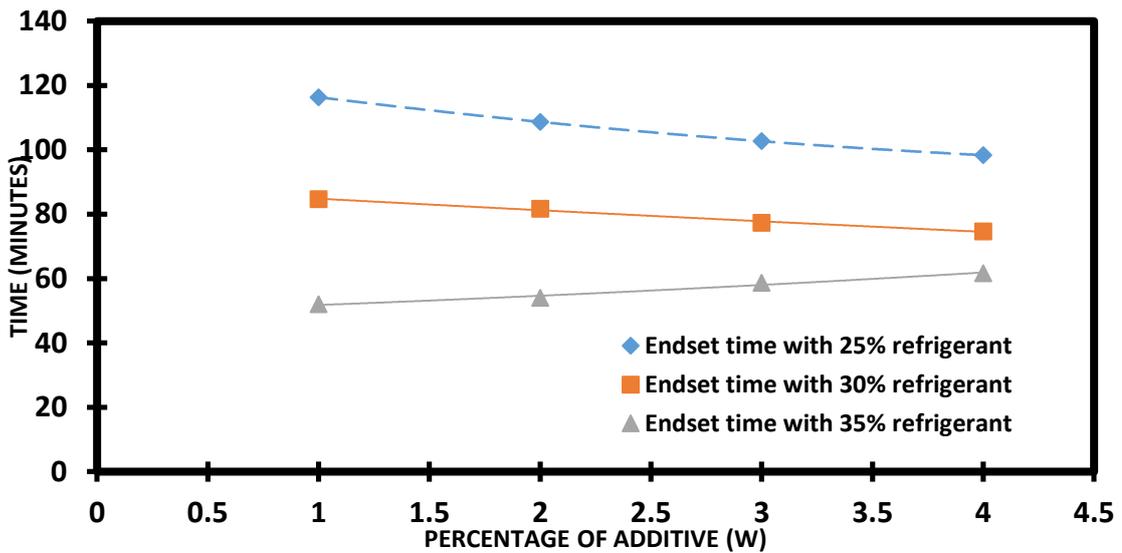


Figure 32: Endset time comparison with different percentages of refrigerant at 3°C

For the comparison of clathrates formation time with different percentages of refrigerant, the results showed an interesting scenario in which minimum clathrates formation time is for the 35% of the refrigerant for the lower percentages of butanol as additive. The clathrates formation time trends for 25% and 35% of the refrigerant intersects each other and the minimum clathrates formation time turns out to be for the 35% of the refrigerant. Now, this mainly happens because of the major impact of the refrigerant which is the main variable between these two cases. It points out towards a specific ratio between distilled water and the refrigerant for the optimum clathrates formation conditions. The percentage of the refrigerant for this optimum condition turns out to be close to 35%. Figure 33 shows the clathrates formation time comparison.

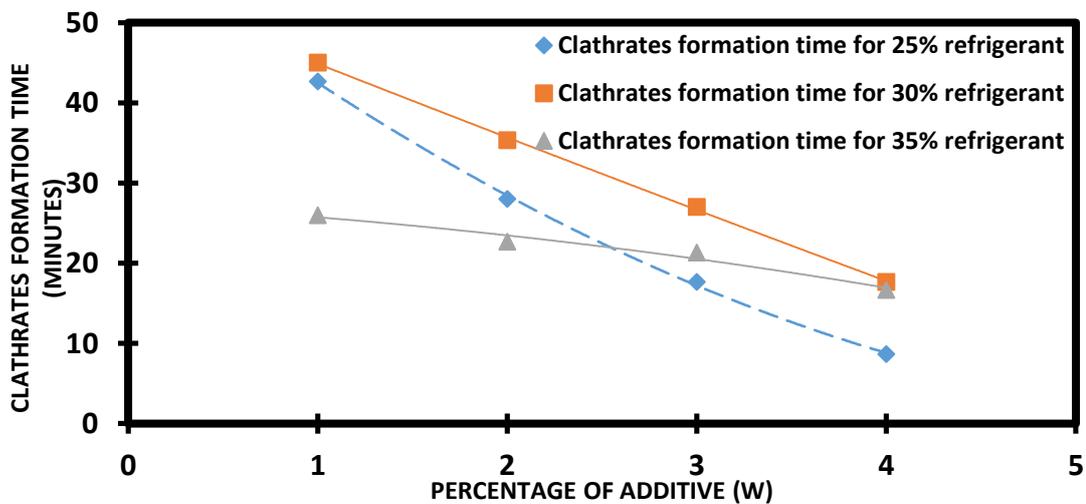


Figure 33: Clathrates formation time comparison with different refrigerant percentage at 3°C

4.7.3.1. Comments. It needs to be noted that the experiments were also done for the 40% refrigerant, but the onset time in this case was turning out to be maximum since the refrigerant percentage is really high and it does not have enough water molecules to form clathrates. On the other side, experiment was also repeated for the 20% refrigerant but it didn't form the complete clathrates since the percentage of refrigerant was really low as compared to that of water and in this case, refrigerant couldn't react completely with water resulting in the partial clathrates formation.

4.8. Ethanol as Additive

Ethanol (C_2H_5OH) is from the alcohol family of organic compounds with good thermal properties. It has a thermal conductivity of around 0.171W/mk. Although relatively smaller amount of additive is used while using ethanol, in this work, only the percentage of additive is changed. It is less toxic in nature, yet the eyes and skin must be protected in its usage to avoid any hazardous effects. Just like butanol, it has sharp odor. The sample of ethanol present in the lab is shown in Figure 34.

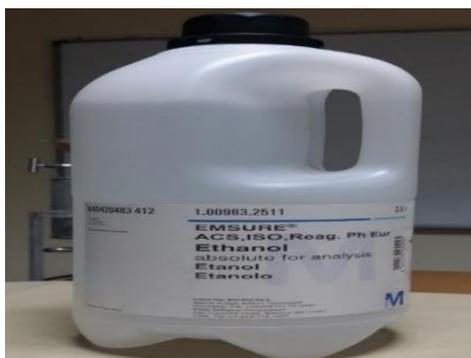


Figure 34: Ethanol additive

4.8.1. Experimental process and calculations. Detailed work was done using the Ethanol as an additive. The work in this regard covers using different percentages of ethanol. Unlike the case of butanol, only the percentage of ethanol was varied in this work. The temperature of the refrigerated cooling tank was kept constant at 3°C. A total of 4 different percentages of butanol was used as an additive i.e. 1.5%, 2.5%, 3.5% and 4.5%. The percentage of refrigerant used was 30%. A total of 4 set of experiments was done for this case. For every experimental case, a total of two glass tubes were used to minimize the risk of error. There were a little variation in the experimental results of the glass tubes but the average was taken in order to get the best optimum reading. For the experimental analysis, a sample calculation for 3.5% additive with 30% refrigerant

used is shown in Table 8.

Table 8: Sample calculation for 3.5% additive with 30% refrigerant

Total mass of distilled water used	66.5g
Total mass of additive (Butanol) added	3.5g
Total mass of Refrigerant R134a added	30g
New total mass of tube	100g

Exactly the same methodology was used for these experiments as well. The variable (additive percentage) was changed for the respective cases. The clathrates formation in the case of ethanol gave us solid ice like So, apparently it gives us the view of stronger additive reaction and the higher heat transfer rate leading to the comparatively stronger clathrates. The detailed results were compiled for the respective cases.

4.8.2. Experimental results using different percentage of additive with 30% refrigerant. The formed clathrates using different percentages of additive (1.5%, 2.5%, 3.5% and 4.5%) with 30% refrigerant at 3°C can be seen in Figure 35.

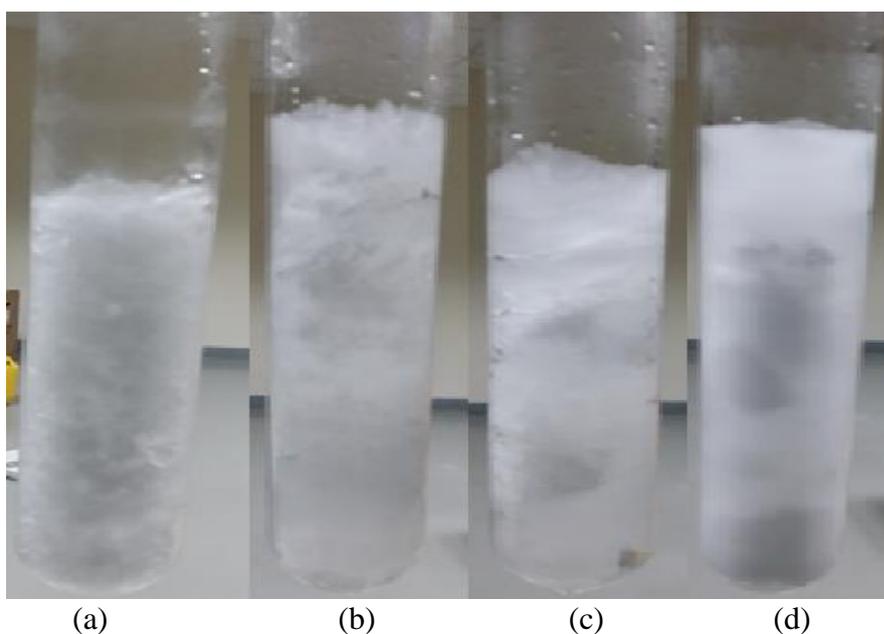


Figure 35: Clathrates formed with (a) 1.5%, (b) 2.5%, (c) 3.5% (d) 4.5% additive (ethanol) and 30% refrigerant at 3°C

For this set of experiment, the percentage taken for the refrigerant was 30% and the refrigerated cooling tank temperature was 3°C. It was same for the both glass tubes used in the experiment. The only variable in these experiments was the percentage of additive. In the end, the average of the both results was taken and plotted. The trend of the onset time and the endset time is shown in the Figure 36. The data is curve fitted.

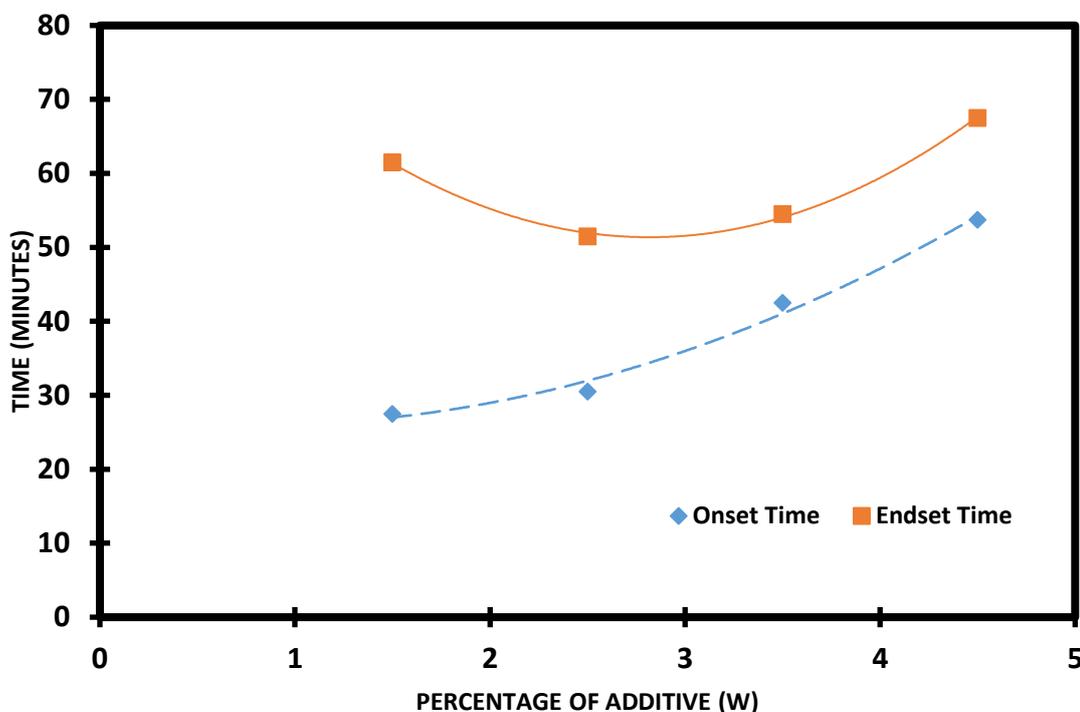


Figure 36: Variation of clathrates formation time with percentage of additive, bath temperature = 3°C, refrigerant = 30%

The equations of the onset time and the endset time after curve fitting were of second order polynomials. These equations show the general trend of onset and endset times at 3°C bath temperature and 30% refrigerant. Whereas w presents the mass percentage of additive.

For onset time:
$$t = 2.0625w^2 - 3.3w + 27.322$$

For endset time:
$$t = 5.75w^2 - 32.4w + 97.012$$

The plot shows that initially for the 1.5%, the difference between onset time and the endset time is higher and this difference decreases with increment in the additive percentage till it gets to 3%. After that till 4.5%, the endset time keeps increasing. The total clathrates formation time is decreasing due to better heat transfer properties by additive. The crystal structure and the pattern of growth resembles butanol crystals, which shows stronger effect of alcohol family of organic compounds as an additive.

4.9. Glycerin as an Additive

Glycerin (chemically $C_3H_8O_3$) is commercially used in a range of products. Its applications vary from cosmetic usage to the usage in food industry. It is non-toxic in nature and tastes sweet but doesn't really increase the sugar if used in cooking. Due to its good thermal conductive properties, it also makes a perfect combination with water as an additive. A sample is shown in Figure 37.

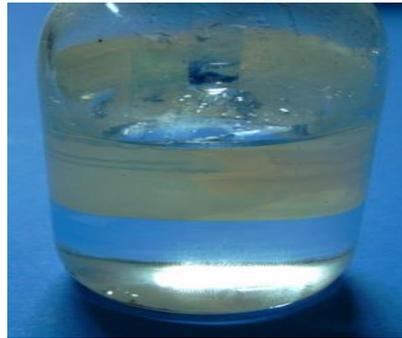


Figure 37: Glycerin additive

4.9.1. Experimental process and calculations. The work for glycerine was basically added to get to know the practical usage of glycerine to be used as additive. The work in this regard covers using different percentages of glycerin. The temperature of the refrigerated cooling tank was kept constant at $3^{\circ}C$. A total of 4 different percentages of butanol were used as an additive i.e. 1%, 2%, 3% and 4%. The percentage of refrigerant used was 30% for all the experiments. For every experimental case, a total of three glass tubes were used as the candidate. A sample calculation for 3% glycerin additive with the 30% of refrigerant is shown in Table 9.

Table 9: Sample calculation for 3% glycerin additive with 30% refrigerant

Total mass of distilled water used	67g
Total mass of additive (glycerin) added	3g
Total mass of Refrigerant R134a added	30g
New total mass of tube	100g

The clathrates formation in case of glycerine gave us fluffy structure clathrates comparative to the case of butanol and the ethanol. So, apparently it gives us the view of less stronger additive reaction and the comparatively lower heat transfer rate.

4.9.2. Experimental results using different percentages of additive with 30% refrigerant. The formed clathrates using different additive percentage with 30% refrigerant at 3°C can be seen in Figure 38.

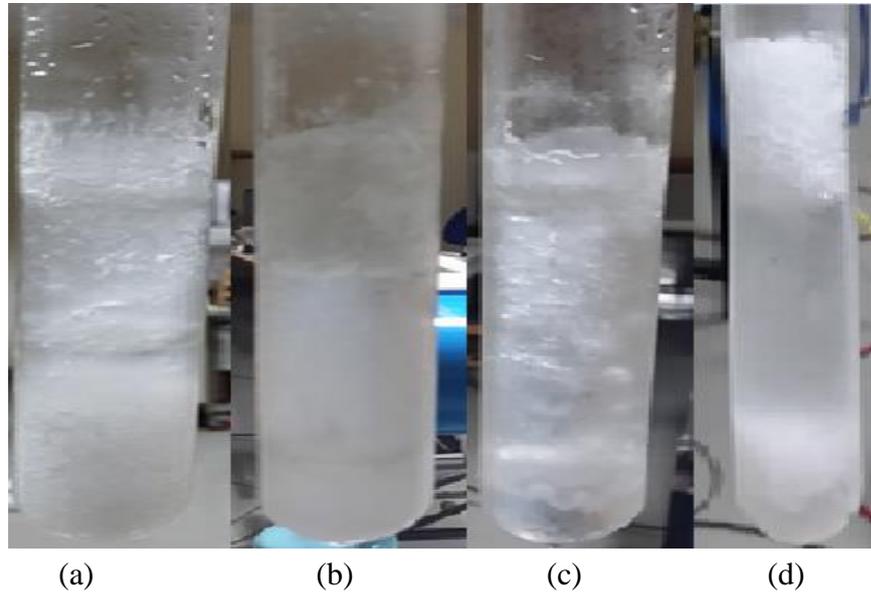


Figure 38: Clathrates formed with (a) 1%, (b) 2%, (c) 3%, (d) 4% additive (glycerin) with 30% refrigerant at bath temperature = 3°C

Same methodology was adopted for the compilation of results as that of previous cases. The average of experimental results obtained was plotted for onset time and endset time. The trend of the onset and the endset time is shown in the Figure 39.

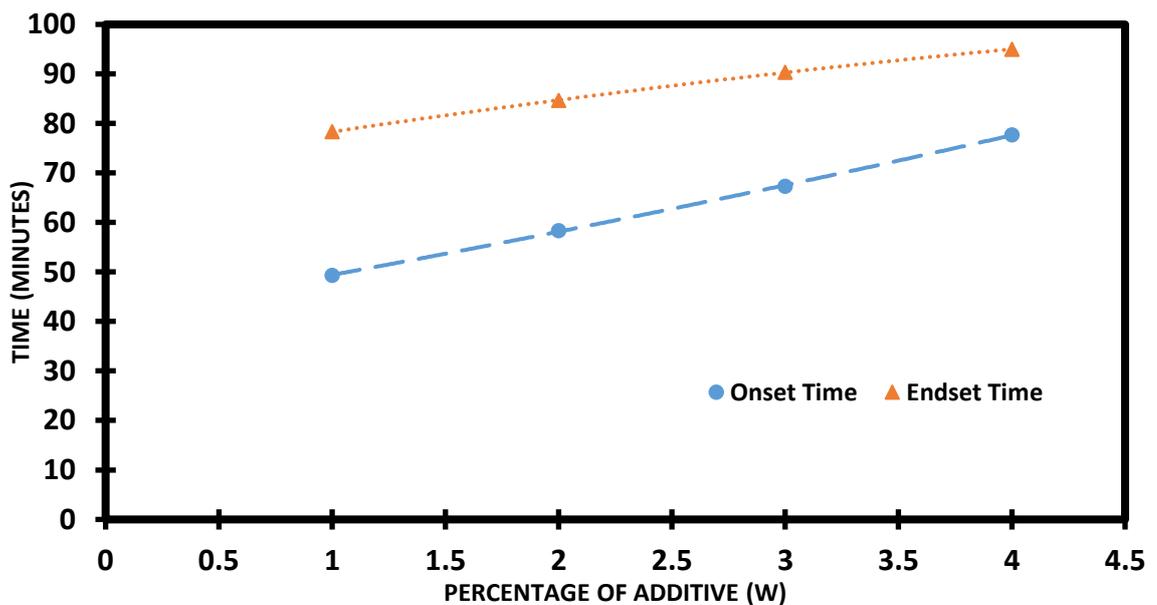


Figure 39: Variation of clathrates formation time with percentage of additive, bath temperature = 3°C, refrigerant = 30%

The equations of the onset time and the endset time after curve fitting curve fitting were of second order polynomials. These equations show the general trend of onset and endset times at 3°C bath temperature and 30% refrigerant. Whereas w presents the mass percentage of additive.

For onset time: $t = 0.3333w^2 + 7.7333w + 41.333$

For endset time: $t = -0.4167w^2 + 7.65w + 71.083$

Initially for the 1%, the difference between onset time and the endset time is considerably higher and this difference decreases with increment in the additive percentage. The comparison shows that glycerin as additive is not a favorable choice since there is a minor change in decreasing clathrates formation time. This case also resembles with ethylene glycol when it comes to the crystal structure and the pattern of growth which shows comparatively lower heat transfer rate and bonding.

4.10. Clathrates Formation without Additives

The clathrates were formed using distilled water and refrigerant R134a without any additive. The mass percentage of refrigerant used was 30%. The clathrates formed can be seen in the Figure 40. Same methodology was adopted for this case too. The onset time for the formation of clathrates was 61 minutes. Whereas, the endset time turned out to be 96 minutes. Which shows the total clathrates formation time of 35 minutes. The crystal characteristics showed the needle like dense clathrates formation. At the same time, this ratio of 70:30 between distilled water and the refrigerant R134a turns out to be the an optimum once since no refrigerant or water gets left behind. This was also one of the observation when the experiments were done for the different percentages of refrigerant using butanol as additive.

Now this experimental result can be compared to the work already done by the Sayem et al. [60] in which experimental work was done with different percentages of refrigerant in order to select the best ratio between water and the refrigerant R134a. That ratio, was then, used with different additives for the further experimental investigation of clathrates formation mainly with the metal additives. The comparison between this research and the already available work certifies the validity of the experimental work done in this research work as the results are comparable and can be explained in the same scenario. The comparative analysis of both experimental works is done below.

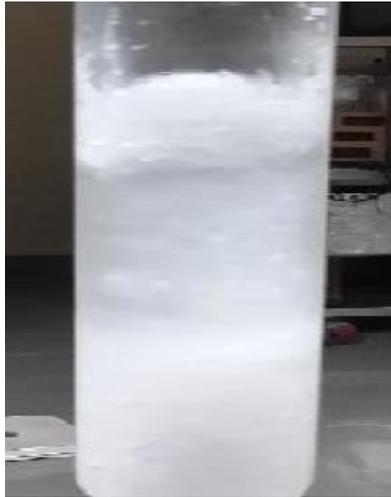
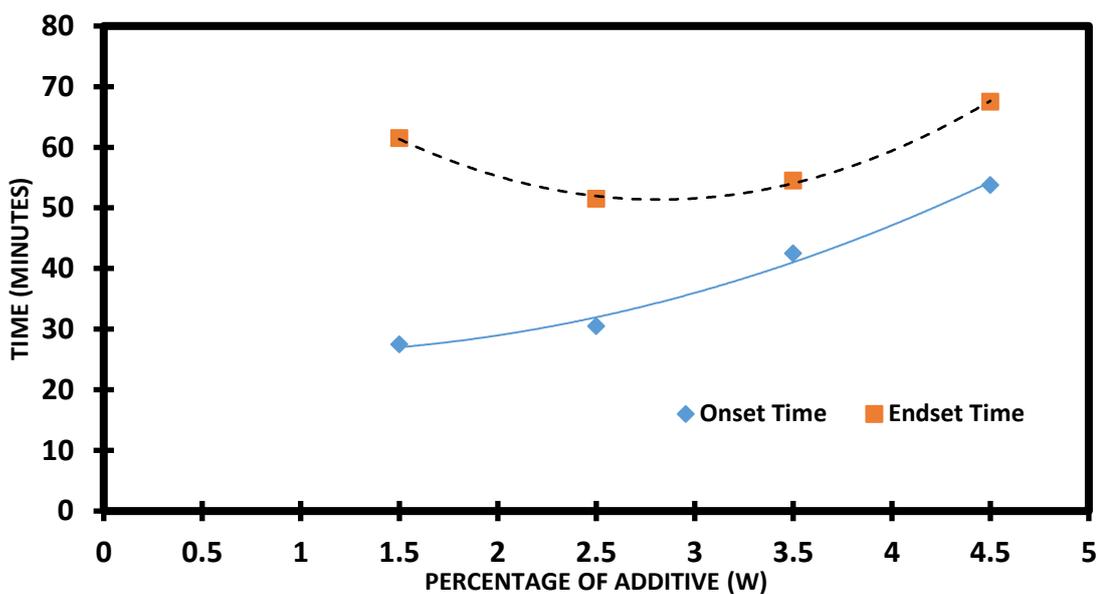


Figure 40: R134a Clathrates without additive

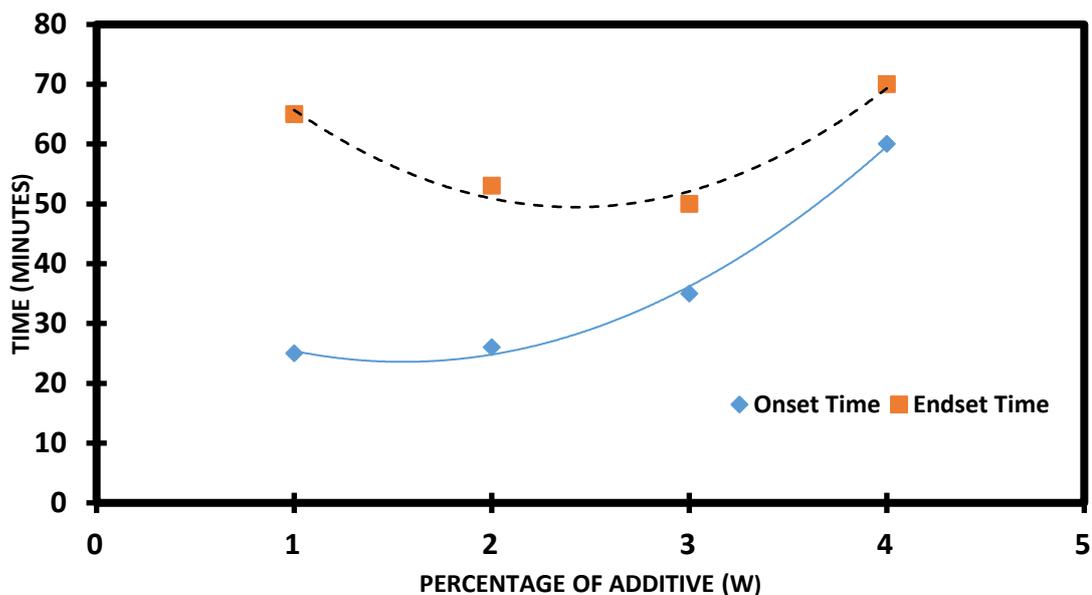
4.11. Comparison of Experiments with Available Literature

In this work, the focus was mainly on using different additives in their respective different percentages and the work also covered the effect of changing the refrigerant percentage. For the results validation, work needs to be compared with previously done research on it. In this work, ethylene glycol and glycerin were two new additives as no work has been done on these two additives. Ethanol and butanol are two additives on which research has been done before in a bit different way than this research. As previously described in the literature, the work has been done by Jianghong Wu and Shiping Wang [42] while using butanol as an additive for clathrates formation. That work mainly covered the effect of butanol on the geometry of clathrates, supercooling and the effect of using additive on the pressure and temperature during the clathrates formation. The work mentions using different percentages of additive (butanol) and the results showed 1.34% additive as the most effective percentage for supercooling. When that specific research work was compared with this experimental work, the analysis validates the results. The experiments show that using butanol as additive results in hard solid like geometry of clathrates. Most of the clathrates formation in the case of ethylene glycol and glycerin gives us needle like crystals formation. Similarly, the work has been done on the clathrates formation while using ethanol as an additive by Sayem et al. [60]. The work covers using different percentages of refrigerant and the usage of different percentages of ethanol as additive. The experimental analysis certifies the results obtained from this study. Two key points can be derived from the experimental analysis. First, with increase in the percentage of additive, onset time increases. The reason is that more percentage of additive results in

the more time required for the reaction, whereas the total difference between the onset time and the endset time decreases as once the process of clathrates formation starts, additive helps formation of clathrates. The second point can be compared with respect to the geometry of clathrates. The ethanol helps formation of clathrates with hard solid crystals. So, it can be derived that alcohol family chemicals (e.g. butanol and ethanol) help in the formation of stronger gas hydrates while ensuring uniform heat transfer. Figure 41 (a) shows the obtained experimental results of this research work. Figure 41 (b), however, shows the experimental results of work done by Sayem *et al.*



(a)



(b)

Figure 41: Comparative Analysis of different researches using ethanol as an additive

4.12. Concluding Comments

In the comparative analysis between different additives used in this experimental work, onset time and endset time can be compared for clathrates formation (while using all the additives). The important consideration must be to compare the results with same variables used in different researches. Since all the experiments were done for atleast one same temperature i.e. 3°C and the percentages of additive used were same for all except ethanol, we can compare additives (except ethanol). For the comparison, we can use 30% refrigerant as standard as it was used in at least all of the experiments.

Figure 42 shows the comparison done between the onset time while using all additives except ethanol because the percentage of ethanol additive used was different. This variation between different onset timings can be explained by their thermal properties and the class of organic compounds they belong to. Since, alcohol family (butanol) has good thermal properties and it also makes a homogeneous mixture with the refrigerant when used as additive, it helps crystal growth formation at the start of process.

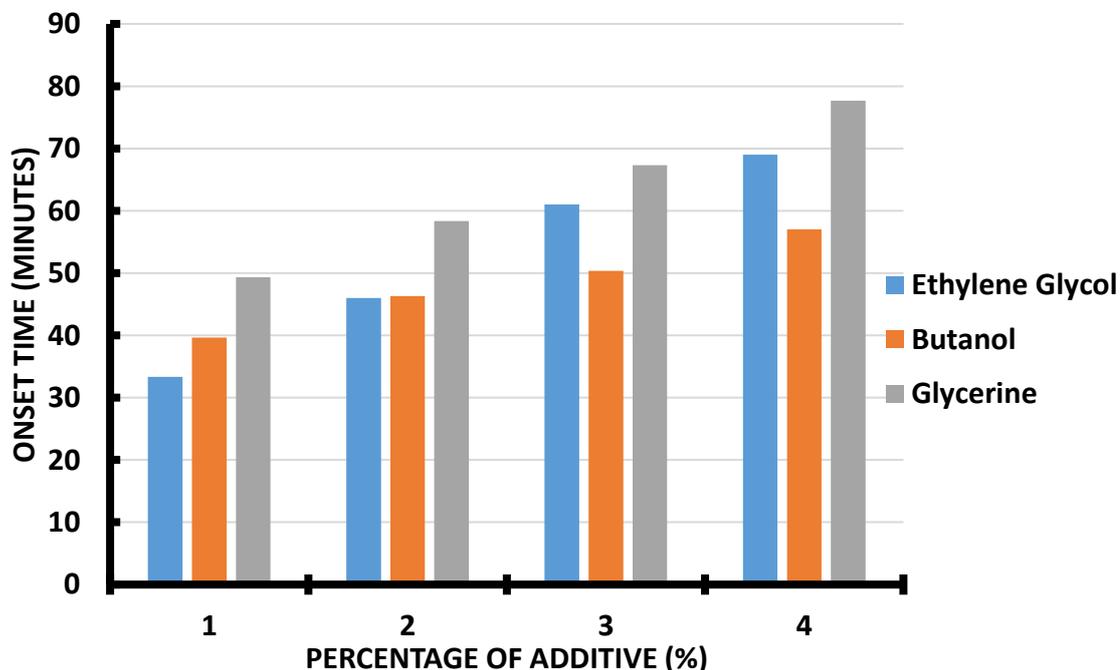


Figure 42: Onset time comparison b/w different additives at 3°C and 30% refrigerant

It can be seen from the bar graph that onset time is best for the butanol, whereas the ethylene glycol is comparatively better than glycerin. The comparison between the endset time can be seen in the Figure 43.

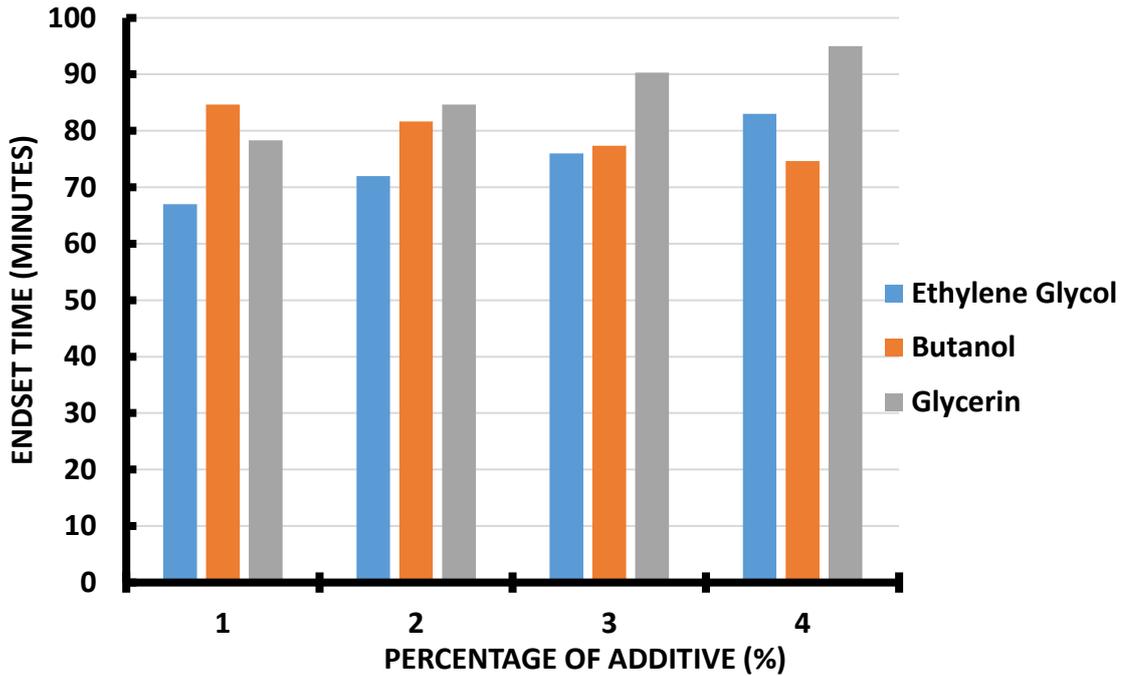


Figure 43: Endset time comparison b/w different additives at 3°C and 30% refrigerant

The total clathrates formation time can be compared for these three additives, i.e. Ethylene glycol, glycerin and butanol. Figure 44 shows the trend of clathrates formation time.

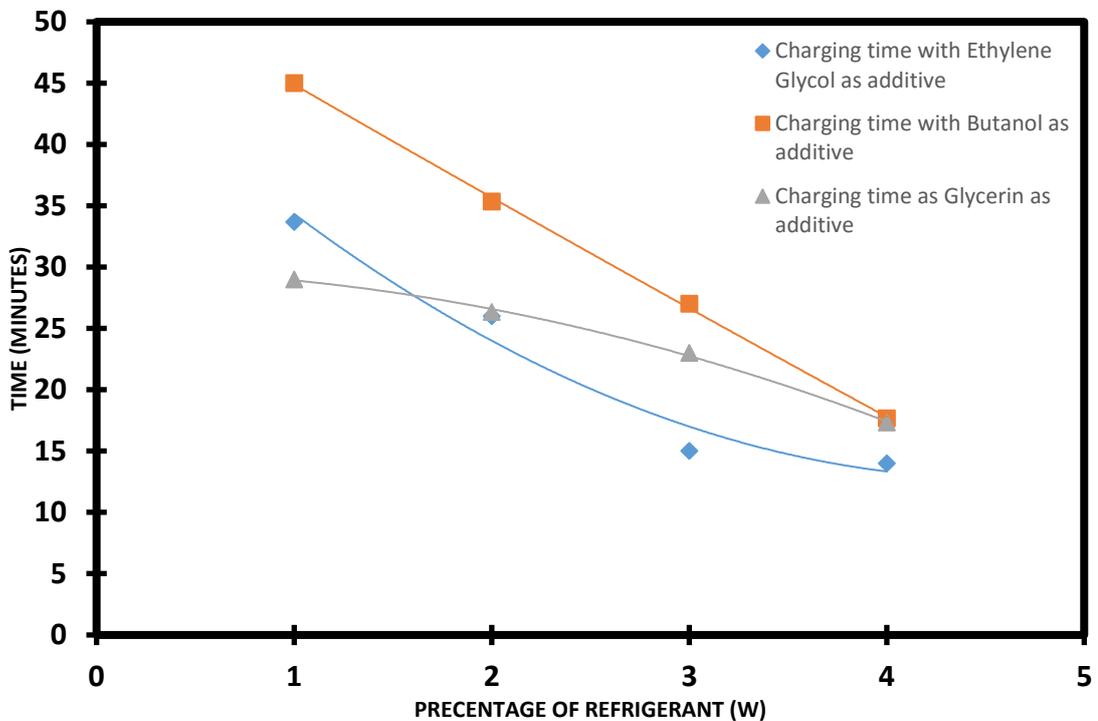


Figure 44: Total clathrates formation time comparison b/w different additives at 3°C and 30% refrigerant

The analysis of total clathrates formation time while using different additives shows that the maximum charging turns out to be for the butanol. While the minimum clathrates formation time turns out to be for the ethylene glycol (except 1% additive). This is in total correspondence with the thermal properties of these liquid additives where the thermal properties of the ethylene glycol are better than the thermal properties of butanol. One of the most important thermal property of these liquids is thermal conductivity and the ethylene glycol has higher value of thermal conductivity as compared to the butanol. But at the same time, the crystal structure turns out to be the better one for the butanol as compared to ethylene glycol and glycerin. This crystal structure may also be the deciding factor in some cases e.g. if some experimental work proves that the discharging time is better for the butanol and ethanol due to its crystal structure. The ethylene glycol turn out to be the right choice when it comes to the optimum clathrates formation time. While if we consider the better crystalline structure, butanol and ethanol has an edge over the other additives. This is also an indication of right heat transfer rate and the optimum time for the usage of cold energy in various applications. The results are in line with the goals identified in the thesis proposal which indicated the need to find an additive in order to have an optimum clathrates formation time. At the same time for the optimum results of crystal growth, it needs to have a right mixture of water and refrigerant. This amount is close to 35% refrigerant for the case of butanol as shown in this experimental work.

Chapter 5: Conclusions and Future Work

5.1. Conclusions

Clathrates using different additives were investigated and a comparative analysis was done with the present available research/work. Current work covered four different liquid additives like ethylene glycol, glycerin, ethanol and butanol. Current results for the ethanol were in agreement as they were comparable to some of the work already available in the open literature. Based on the experimental results, key outcomes of this experimental work were as follows:

- All the additives, when used with distilled water and R134a refrigerant, they increase the onset time and this behavior is in accordance to the fact that their thermal properties like thermal conductivity are bad as compared to those of water.
- Total clathrates formation time is smaller for ethylene glycol but that also results into the fluffy nature of crystals growth.
- Total clathrates formation time remains minimum for 35% of the refrigerant (when butanol was used as an additive). The experiments were also done for the 20% and 40% of the refrigerant (with butanol used as an additive) but the time for the clathrates formation was too long that it had to be ruled out which shows the need of a balanced ratio between water and refrigerant for the optimum crystal growth.
- For the case of ethylene glycol and glycerin, the structural analysis show that the clathrates are fluffy and loosely bound as compared to that of clathrates formed using butanol and ethanol as additives which points out towards better heat transfer rate in the presence of alcohol family of the organic compounds (when used as additives).
- Results also show that the additives do not only help decreasing the total clathrates formation time but also affect the nature of crystals formed.
- The results of butanol show that an additive may have more clathrates formation time as compared to other additives but we can't rule them out for the cooling applications due to the nature of crystals.
- 35% refrigerant shows the minimum clathrates formation time for clathrates formation and the temperature below 3°C doesn't really impact much on the

crystals growth clathrates formation time. Whereas, ethylene glycol and ethanol as the optimum additive choices among the used additives.

5.2. Future Recommendations

Again, based on the economic feasibility, structural and charging performance, the right choice can be used from these available options. Although, some of the work has been done on gas hydrate crystals, this field is really broad since it has immense potential to be used at industrial level. This work focused on using different additives and their effect on the charging of clathrates as well as on the geometry of those clathrates. For the future references, the researcher may look for different additives since, there is still need to have clathrates with optimum clathrates formation time while making sure for a reliable discharging time. The future work may also focus on the temperature and pressure changes while using these additives. There is another category of additives present in the nano-particles (of metals) form which can be used for the clathrates investigation while keeping in mind that they don't get mixed inside the mixture.

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Appendix (A) Tabulated Results Obtained for Ethylene Glycol

The results obtained for ethylene glycol at different temperatures are given below.

The collected data for onset time and end set time at 2°C is presented in the Table 10. Where w presents the mass percentage (%) of additive used.

Table 10: Experimental results for clathrates formation time (in minutes) for different tubes at 2°C

Run No	Percentage of additive	Mass of Refrigerant m_r (g)	Mass of Water m_w (g)	$r = \frac{m_w}{m_r}$	Operating Temp.	Clathrates formation time
Run No 1	1	30	69	2.3	2°C	23.5
Run No 2	2	30	68	2.26	2°C	20
Run No 3	3	30	67	2.23	2°C	13.66
Run No 4	4	30	66	2.2	2°C	13.33

The collected data for onset time and end set time at 3°C is presented in the Table 11. Where w presents the mass percentage (%) of additive.

Table 11: Experimental results for clathrates formation time (in minutes) for different tubes at 3°C

Run No	Percentage of additive	Mass of Refrigerant m_r (g)	Mass of Water m_w (g)	$r = \frac{m_w}{m_r}$	Operating Temp.	Clathrates formation time
Run No 1	1	30	69	2.3	3°C	33.67
Run No 2	2	30	68	2.26	3°C	26
Run No 3	3	30	67	2.23	3°C	15
Run No 4	4	30	66	2.2	3°C	14

The collected data for onset time and end set time at 4°C is presented in the Table 12. Where w presents the mass percentage (%) of additive used.

Table 12: Experimental results for clathrates formation time (in minutes) for different tubes at 4°C

Run No	Percentage of additive	Mass of Refrigerant m_r (g)	Mass of Water m_w (g)	$r = \frac{m_w}{m_r}$	Operating Temp.	Clathrates formation time
Run No 1	1	30	69	2.3	4°C	47.67
Run No 2	2	30	68	2.26	4°C	39
Run No 3	3	30	67	2.23	4°C	37
Run No 4	4	30	66	2.2	4°C	32.67

Table 13 shows the average onset time values at different bath temperatures. Where w presents the mass percentage (%) of additive used.

Table 13: Average onset time at 2°C, 3°C and 4°C with respective additive percentages

w	Average onset time at 2°C (30% refrigerant)	Average onset time at 3°C (30% refrigerant)	Average onset time at 4°C (30% refrigerant)
1	27.83	33.33	45.66
2	44.66	46	56.66
3	57	61	66.66
4	67	69	73.66

Table 14 consists of the average endset time at different bath temperatures. Where w presents the mass percentage (%) of additive used.

Table 14: Average endset time at 2°C, 3°C and 4°C with respective additive percentages

w	Average endset time at 2°C (30% refrigerant)	Average endset time at 3°C (30% refrigerant)	Average endset time at 4°C (30% refrigerant)
1	51.33	67	93.33
2	64.66	72	95.66
3	70.66	76	103.66
4	80.33	83	106.33

Appendix (B) Tabulated Results Obtained for Butanol

The results obtained for butanol are given below.

Table 15 gives us the details about the experimental results while using 25% refrigerant. Where, w shows the mass percentage (%) of the additive used.

Table 15: Experimental results for for clathrates formation time (in minutes) for different tubes with 25% refrigerant.

Run No	Percentage of additive	Mass of Refrigerant m_r (g)	Mass of Water m_w (g)	$r = \frac{m_w}{m_r}$	Operating Temp.	Clathrates formation time
Run No 1	1	25	74	2.96	3°C	42.66
Run No 2	2	25	73	2.92	3°C	28
Run No 3	3	25	72	2.88	3°C	17.67
Run No 4	4	25	71	2.84	3°C	8.66

Table 16 consists of the complete experimental results while using 30% refrigerant. Where w presents the mass percentage (%) of additive used.

Table 16: Experimental results for clathrates formation time (in minutes) for different tubes with 30% refrigerant.

Run No	Percentage of additive	Mass of Refrigerant m_r (g)	Mass of Water m_w (g)	$r = \frac{m_w}{m_r}$	Operating Temp.	Clathrates formation time
Run No 1	1	30	69	2.3	3°C	45
Run No 2	2	30	68	2.26	3°C	35.34
Run No 3	3	30	67	2.23	3°C	27
Run No 4	4	30	66	2.2	3°C	17.67

Table 17 consists of the experimental results obtained while using 35% refrigerant. Where w presents the mass percentage (%) of additive used.

Table 17: Experimental results for clathrates formation time (in minutes) for different tubes with 35% refrigerant.

Run No	Percentage of additive	Mass of Refrigerant m_r (g)	Mass of Water m_w (g)	$r = \frac{m_w}{m_r}$	Operating Temp.	Clathrates formation time
Run No 1	1	35	64	1.83	3°C	26
Run No 2	2	35	63	1.8	3°C	22.67
Run No 3	3	35	62	1.77	3°C	21.34
Run No 4	4	35	61	1.74	3°C	16.67

Appendix (C) Tabulated Results Obtained for Ethanol

Experimental results obtained for the ethanol are given below. Following Table 18 presents all the experimental results while using 30% refrigerant and different percentages of ethanol as additive. Where w presents the mass percentage (%) of additive used.

Table 18: Experimental results for clathrates formation time (in minutes) for different tubes.

Run No	Percentage of additive	Mass of Refrigerant m_r (g)	Mass of Water m_w (g)	$r = \frac{m_w}{m_r}$	Operating Temp.	Clathrates formation time (mins)
Run No 1	1.5	30	68.5	2.28	3°C	34
Run No 2	2.5	30	67.5	2.25	3°C	21
Run No 3	3.5	30	66.5	2.21	3°C	12
Run No 4	4.5	30	65.5	2.18	3°C	13.75

Appendix (D) Tabulated Results Obtained for Glycerin

Results obtained for the glycerin are given below. Following Table 19 shows the experimental results obtained while using 30% refrigerant and different percentages of glycerin as additive. Where, w presents the mass percentage (%) of additive used.

Table 19: Experimental results for clathrates formation time (in minutes) for different tubes.

Run No	Percentage of additive	Mass of Refrigerant m_r (g)	Mass of Water m_w (g)	$r = \frac{m_w}{m_r}$	Operating Temp.	Clathrates formation time (mins)
Run No 1	1	30	69	2.3	3°C	29
Run No 2	2	30	68	2.26	3°C	26.33
Run No 3	3	30	67	2.23	3°C	23
Run No 4	4	30	66	2.2	3°C	17.33

Appendix (E) Uncertainty Analysis of Experimental Results

This section includes the uncertainty analysis of the experimental results obtained. It consists of the error analysis resulting from the experimental apparatus. The standard deviation was also done for the clathrates formation time in order to know about the variation in the recorded time. There are a number of factors involved in the error analysis since the errors associated with the experimental readings are mainly because of the experimental reading errors, apparatus limitations/malfunctioning and approximation done while doing the experiments. Table 20 consists of the factors causing the error in the experimental value.

Table 20: Errors associated with the measured experimental results

Property	Error Margin	Comments
Temperature	0.05 K	Error associated with the thermocouple
Clathrates formation Time	20 seconds	Average interval for the visualization of crystals inside the tube
Mass of the variable (PCM, additive, water, Refrigerant)	0.5 g	Based on the limitation of digital weight balance

The standard deviation was also calculated and analyzed for all the additives in order to know the standard deviation of experimental results. The standard deviation for the sample set was calculated for every percentage since for every percentage of additive, 3 tubes were used except for the case of ethanol where 2 tubes were used for experimental analysis. The standard deviation associated with the phase change material clathrates formation time recorded for onset time and the endset time was calculated separately and then the comparative analysis was done for all the additives with the same operational conditions i.e. same temperature and the refrigerant ratio. The equation used for the standard deviation of samples of experiments was

$$S.D = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{mean})^2}{n}}$$

Where x is the sample value and n is the number of samples in the equation of standard deviation.

Following tables consist of the standard deviation values calculated using the experimental data obtained for the different additives.

Table 21: Standard deviation values of the ethylene glycol at 2°C and 30% refrigerant

Percentage	Standard Deviation value	
	Onset Time	Endset Time
1%	2.0	2.3
2%	4.7	1.5
3%	3.6	2.0
4%	2.6	2.5

Table 22: Standard deviation values of the ethylene glycol at 3°C and 30% refrigerant

Percentage	Standard Deviation value	
	Onset Time	Endset Time
1%	4.2	1
2%	2.6	1.7
3%	2	2.6
4%	4	3.6

Table 23: Standard deviation values of the ethylene glycol at 4°C and 30% refrigerant

Percentage	Standard Deviation value	
	Onset Time	Endset Time
1%	3.2	3.5
2%	1.1	0.9
3%	1.5	1.5
4%	3.5	2.5

Table 24: Standard deviation values of the butanol with 25% refrigerant at 3°C

Percentage	Standard Deviation value	
	Onset Time	Endset Time
1%	3.0	1.5
2%	2.1	1.5
3%	2	2.1
4%	1.5	1.2

Table 25: Standard deviation values of the butanol with 30% refrigerant at 3°C

Percentage	Standard Deviation value	
	Onset Time	Endset Time
1%	3.0	1.5
2%	4.0	1.5
3%	1.2	1.5
4%	3.6	1.5

Table 26: Standard deviation values of the butanol with 35% refrigerant at 3°C

Percentage	Standard Deviation value	
	Onset Time	Endset Time
1%	3.6	3.6
2%	2.5	5
3%	3.0	4.0
4%	3.6	4.7

Table 27: Standard deviation values of the ethanol

Percentage	Standard Deviation value	
	Onset Time	Endset Time
1%	1.5	3.5
2%	0.5	2.1
3%	1.5	3.5
4%	1.2	2.3

Table 28: Standard deviation values of the glycerin

Percentage	Standard Deviation value	
	Onset Time	Endset Time
1%	1.5	1.2
2%	2.1	1.5
3%	1.5	1.2
4%	2.5	2

The analysis is done for the standard deviation associated with the PCM clathrates formation time recorded for onset time is shown in the Figure 45. This analysis was done for all the additives except the ethanol since its percentage was different from other additives.

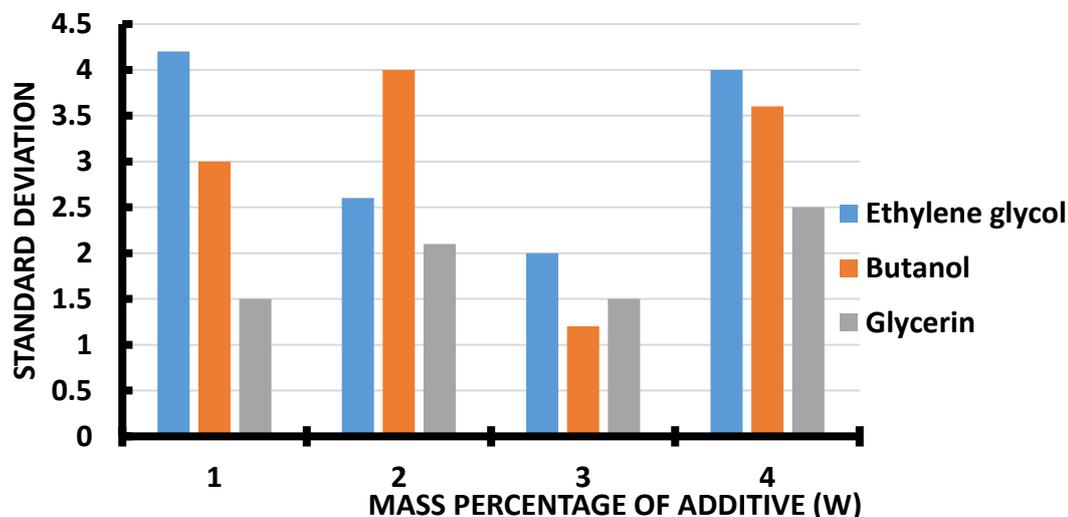


Figure 45: Standard deviation for PCM charging onset time.

The analysis is done for the standard deviation associated with the PCM clathrates formation time recorded for the endset time is shown in the following Figure 46.

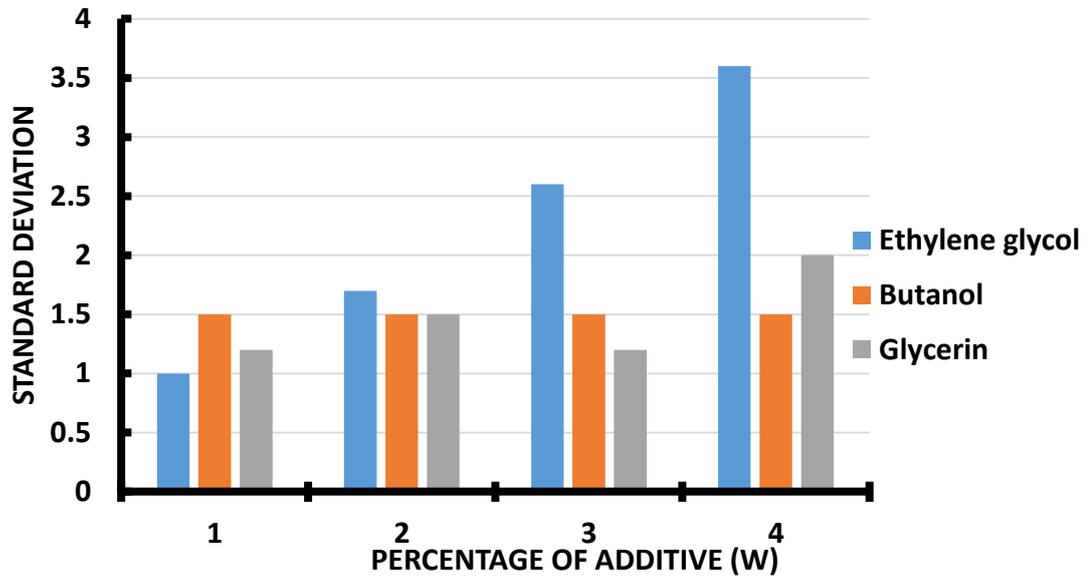


Figure 46: Standard deviation for PCM charging endset time.

VITA

Hafiz M. Ahmad was born on December 25, 1990, in Bahawalpur, Pakistan. After getting his early education in Jinnah Public School and Missali Pre-Cadet high school, he enrolled in and graduated from the Moon System of Education Bahawalpur with Academic Roll of Honor. He earned college scholarships and the shield of Honor because of his extra-ordinary academic results both at school and college level.

In 2007, he was selected in Pakistan Air Force (P.A.F). Mr. Hafiz chose a career in engineering over fighter pilot. He got admission in the Department of Mechanical Engineering at University of Engineering and Technology (UET), Lahore. During the period of bachelor studies, Mr. Hafiz was an active member of different co-curricular and extra-curricular societies. From the platform of American Society of Mechanical Engineers (ASME, UET Lahore Chapter), he actively participated in different projects and also presented a paper in All Pakistan Mechanical Engineering Conference, 2010 at GIKI. He also served in the capacity of Executive Head of UET Debating Society from 2009-2011 and finally graduated from university in 2011.

After spending a year working in the industry, Mr. Hafiz moved to UAE in 2013 and got enrolled in the MSME program at the American University of Sharjah. He also worked in the capacity of Graduate Teaching Assistant from 2013 to 2016. Mr. Hafiz has a deep interest in Debates, Current Affairs, Urdu poetry and Cricket.