HSN University College
of Southeast Norway

FMH606 Master's Thesis 2017

Energy and Environment Technology

Embryo research of a reactor to produce CO$_2$ hydrates

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Course: FMH606 Master's Thesis, 2017

Title: Embryo research of a reactor to produce CO₂ hydrates

Number of pages: 58

Keywords: CO₂ hydrate, Promoter, Apparatus development, Induction time, Transportation

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Approved for archiving: _____

(supervisor signature)

Summary:

The potential applications of carbon dioxide hydrate have attracted many interests over the past decade. CO₂ transmission in the form of hydrate is an alternative way of transportation in CCS chain, however, the CO₂ hydrate transportation might be challenging. Evolution of this concept is considered in the present work through developing hydrate formation reactor. The induction time and the initial hydrate formation temperature of CO₂ hydrate are measured within batch and semi-batch reactors. Moreover, the effect of adding various thermodynamic promoters on induction time is investigated at an isobaric procedure. The results show that semi-batch reactor initiates to form CO₂ hydrate faster than batch reactor. Also, increasing the pressure inside the reactor reduces the induction time. The experiments illustrated that THF and TBAF had a better effect on reduction of induction time compared with other studied promoters. In addition, a higher concentration of promoter facilitated the hydrate formation. Thus, an increase in promoter concentration decreased the induction time and also increased the initial hydrate formation temperature. Also, repetition of the CO₂ hydrate formation and dissociation cycle led to a reduction in induction time and an increase in the initial hydrate formation temperature. Observations from experiments approved the possibility of CO₂ hydrate transmission at the metastable condition.

Preface

This thesis has been written to fulfill the master degree in Energy and Environment Technology at University College of Southeast Norway in close cooperation with Tel-Tek in Norway.

The present work has been performed in CO_2 capture laboratory at University college of Southeast Norway in order to develop the hydrate formation reactor. The concept of utilizing CO_2 hydrate in transportation purposes is investigated through the experiments.

Besides the challenges of the embryo research, it was unique experience to be part of a well-known research group, which taught me valuable lessons.

I would like to thank my supervisor, Prof. Dag Eimer, for his great support and guidance throughout my work. His encouragement and advice during the thesis were a key component to fulfill this thesis. I would also like to appreciate Dr. Zulkifli Idris and Dr. Jiru Ying from Tel-Tek for their important advice during building the apparatus.

I sincerely wish to appreciate my parents, Ghader and Fakhri, and my brother, Behnam, for their infinite support and love during my life. Difficult situations became easier and memorable with their support.

Porsgrunn, 14 May 2017

Sayed Ebrahim Hashemi

Nomenclature

abbreviation

CCS	Carbon dioxide capture and storage
CH_4	Methane
CO_2	Carbon dioxide
DTAC	Dodecyl-trimethyl-ammonium-chloride
H_2	Hydrogen
HFR	Hydrate formation reactor
HN	Hydration number
IEA	International energy agency
IPCC	Intergovernmental panel on climate change
N_2	Nitrogen
N_2O	Nitrous oxide
O_3	Ozone
S.F.	Separation factor
S.Fr.	Split fraction
SC	Semi-clathrate
SDS	Sodium dodecyl sulphate
T-80	Tween-80
TBAB	Tetrabutylammonium bromide
TBAF	Tetrabutylammonium fluoride
$TBANO_3$	Tetrabutylammonium nitrate
TBPB	Tetrabutylphosphonium bromide
TBPC	Tetrabutylphosphonium chloride
THF	Tetrahydrofuran

Nomenclature

Symbol	Description	Unit
n	Number of mole	mol
P	Pressure	Pa
R	Universal gas constant	$J \cdot mol^{-1} \cdot K^{-1}$
T	Temperature	K
V	Volume	m^3
Z	Compressibility factor	
Δn	Number of gas mole consumed in hydrate formation	mol

Contents

1 Introduction

Changes in the climate system and global warming issue, which are mostly attributable to human activities are considered as the main concerns of the future. In other words, the average temperature in the globe has been continuously increasing as a result of human activities via the emission and accumulation of greenhouse gases (e.g. CH_4, N_2O, O_3, and CO_2) in the atmosphere for the past decades [1]. Based on the current emission rate of greenhouse gases, the earth's average temperature is estimated to increase by 3.2-7.2°C over the next 100 years [2].

Among all greenhouse gases, CO_2 is the most important greenhouse gas due to its high concentration in the atmosphere. The prominent sources of CO_2 have increased by about 90% since 1970 and are from industry, agriculture, transportation, electricity and heat production mainly due to the combustion of fossil fuels which essentially consist of carbon atoms [1].

CO_2 concentration was about 280 ppm before the industrial revolution, while today the CO_2 level in the atmosphere is above 380 ppm with an increase of approximately 2 ppm annually [1]. However, the Intergovernmental Panel on Climate Change (IPCC) reported that the CO_2 concentration could reach between 490 and 1260 ppm with respect to different emission scenarios by the end of the twenty-first century [3]. Therefore, the International Energy Agency (IEA) has proposed several mitigation action scenarios in order to limit the CO_2 concentration with an attention to the combustion of fossil fuels [4].

The release of CO_2 cannot be eliminated since the major of the CO_2 emission is as a result of necessary human activities. Although, different CO_2 capture methods from the combustion processes have been proposed in order to reduce the CO_2 concentration in the atmosphere.

In general, the CO_2 capture technology can be classified with respect to the combustion processes which emit the flue gases with different concentration of CO_2. Post-combustion, Pre-combustion and oxy-fuel combustion are the main capture technologies [5].

Post-combustion capture is an end-of-pipe solution where the CO_2 concentration is about 4-15% and the rest of the composition is assumed nitrogen (N_2). While in the pre-combustion capture primary fuels burn, which produce approximately 40% CO_2 and 60% H_2. However, fuel burns through approximately pure oxygen in the oxy-fuel combustion and the outlet gas consist of almost 90% CO_2.

On the other side, CO_2 separation from the flue gases as a part of CO_2 capture process is necessary. The conventional CO_2 separation methods are absorption, adsorption, membrane technology and cryogenic separation [5].

As the conventional CO_2 separation methods need high energy consumption and they are less environmentally friendly, researchers have focused on several new technologies in order to separate or capture CO_2 from the flue gases. One novel method that has attracted many interests is hydrate based CO_2 capture or separation.

The early attention regarding hydrate was because of line blockage in oil and gas transportation. Therefore, the first attempts were to prevent forming hydrates with assisting several inhibitors. However, promising potential of hydrates such as energy recovery, storage, transportation, and separation by hydrates contributes increasing interest in hydrate formation investigations over the past decade [6].

Since the volume of the same amount of gas molecules at hydrate form is 150-180 times less than the volume of gas molecules in standard condition, therefore, hydrate formation can be considered as an alternative for large-scale gas storage [7]. Moreover, hydrates have the possibility of self-preservation property that leads to remain in stable condition at atmospheric pressure and very low temperature. This property is also called metastable condition for hydrates, which allows transporting gas hydrates in solid phase [8].

In over past decade, the majority of investigations in gas hydrates have focused on the separation and CO_2 recovery applications. There are only a few investigations about storage and transportation by hydrates whereas most of them concentrated on natural gas hydrate storage and transportation.

Therefore, the focus on CO_2 hydrate formation seems to be necessary as a potential way for CO_2 storage and transportation utilizations in order to complete the carbon dioxide capture and storage (CCS) chain. The aim of this thesis is to provide a primary understanding of CO_2 hydrate formation in lab-scale studies that can employ in developing CO_2 hydrate storage and transportation concept.

In the present work, the initial effort was to develop the hydrate formation reactor and then the determination of CO_2 hydrate key parameters discussed in order to prepare better comprehension. In chapter 2, an overview of gas hydrate formation and its structure is done. Moreover, a brief literature review regarding CO_2 hydrate formation performed in this chapter.

Development of hydrate formation reactor is proposed in chapter 3. In addition, the experimental procedure and technical problem during the experiment have been explained. Eventually, the experimental results from CO_2 hydrate formation experiments have discussed in chapter 4.

The conclusion of this thesis is found in chapter 5 and also suggestions for further work are presented in chapter 6.

2 CO₂ hydrate formation

CO_2 hydrate formation has attracted many types of research for not only CO_2 capture but also other purposes such as transportation recently. The basic idea is that CO_2 hydrate can be produced by only water and CO_2 molecules, however forming hydrates requires relatively high pressure and low temperature .

A summary of scientific literature related to the CO_2 hydrate formation is given in this chapter in order to provide a brief description of the hydrate formation processes, the hydrate structure and key parameters affected on hydrate formation. Also, the influence of using different chemical additives in hydrate formation process is discussed.

2.1 Gas hydrate formation and its kinetics

Gas hydrates are comprised low molecular weight gases such as CO_2, N_2 and O_2 trapped within the cage-like lattice of water molecules in order to form non-stoichiometric and ice-like clathrate compounds [9]. In fact, cavities of the polyhedral structure through hydrogen bonding of water molecules, (host), are stabilised by enclosing guest molecules within the lattice of water molecules under suitable conditions where high pressure and relatively low temperature are required [10]. Despite the fact that there is no real chemical reaction and guest gas molecules only interact with the cage's walls of the polyhedral structure by van der Waals forces [11].

An overview of hydrate formation progress is shown in Figure 2-1. In the beginning of the progress, there are no gas molecules dissolved in the water while temperature and pressure are in hydrate formation region (A). When the gas molecules dissolve into water, unstable cluster forms (B). The size of dissolved gas molecules influences the number of water molecules participating in a cluster. Then agglomeration step occurs when clusters share faces to aggregate unstable clusters (C). However, this step is a metastable and microscopic process where hydrate nuclei are unstable and may dissolve again. Later the primary nucleation and growth step begins when the size of cluster agglomeration reaches a critical size (D) [12]. Also, the gas consumption during the hydrate progress is illustrated in Figure 2-2. The number of gas moles consumed in growth step in hydrate formation progress increases till there are no empty cavities or the size of vacant cavities is smaller than gas molecule size [12].

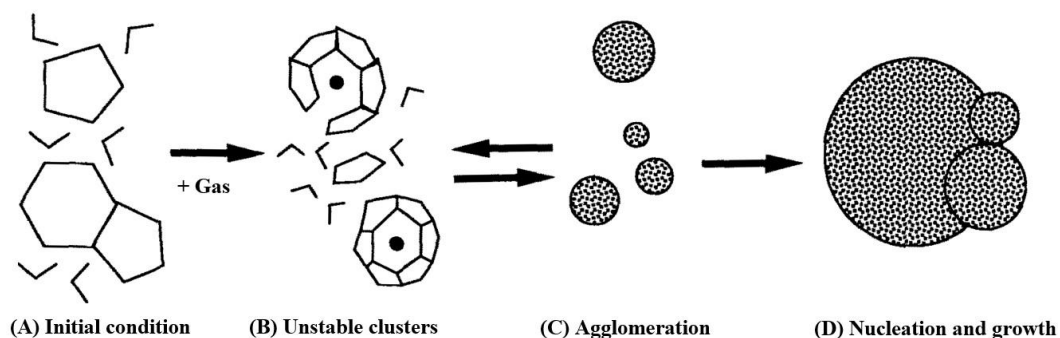(A) Initial condition   (B) Unstable clusters   (C) Agglomeration   (D) Nucleation and growth

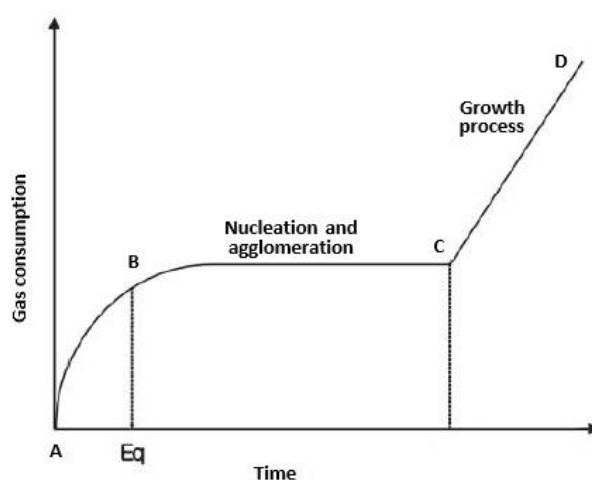Figure 2-1: Hydrate formation progress [12]

Figure 2-2: Gas consumption in hydrate formation progress [13]

In general, all gases will form hydrate at different temperature and pressure conditions. This phenomenon can be exploited as a separation method in a gas mixture. Different hydrate formation condition for several gases is illustrated in Figure 2-3. From Figure 2-3, it can be seen that CO_2 will form hydrate in much lower pressure compare to other gas molecules. Therefore, CO_2 capture by hydrate can be a novel alternative [14].
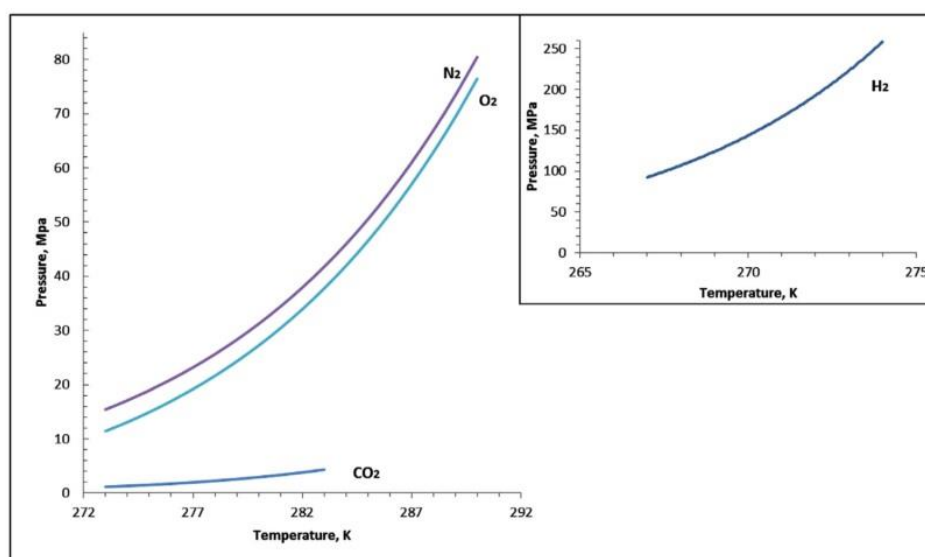

Figure 2-3: Hydrate formation condition for different gases [15]

2.2 Hydrate structure

The hydrate structure is stabilised only when the guest gas molecules occupy water cavities unless cages would collapse [16]. Generally, hydrates will be formed in three common structures; structure I (sI), structure II (sII) and structure H (sH) [15]. These structures are made from five different types of polyhedral i.e. 5^{12}, $5^{12}6^2$, $5^{12}6^4$, $4^35^66^3$ and $5^{12}6^8$ where the numbers

explain the shape of the faces while the superscript numbers are the number of such surfaces in cages. For instance, the cavity 5^{12} states that there are 12 pentagonal faces. An ideal schematic of different hydrate structures is shown in Figure 2-4. The number of water molecules required to form sI, sII and sH is 46, 136 and 34, respectively [17].
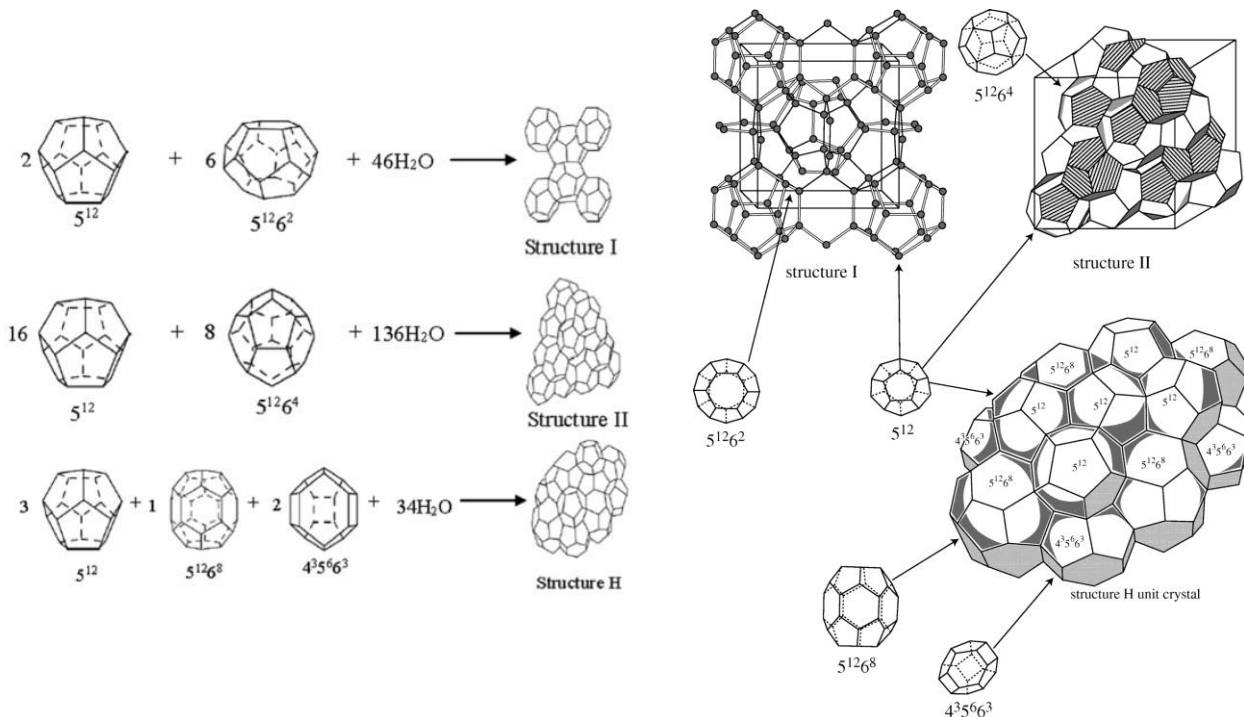

Figure 2-4: Ideal schematic of different hydrate structures [13]

As mentioned before, gas molecules particularly light molar weight gases can form a hydrate, however, the hydrate structure is highly dependent on guest gas molecule size and properties. The typical hydrate structure with respect to different gas molecule size is shown in Figure 2-5. For hydrate formed by only CO_2, the sI is the most common structure where adding chemicals such as tetrahydrofuran (THF) alters the hydrate structure to sII. Although structure sH may form in presence of a mixture of small and large molecules [13].

2.3 CO$_2$ hydrate formation in different concentration

Various CO_2 capture configurations such as post-combustion or pre-combustion capture comprise different amount of CO_2. In general, the typical CO_2 concentration is about 3-15 mole% of the flue gas in post-combustion CO_2 capture and rest is mostly N_2, whereas the CO_2 concentration in pre-combustion is 35-45 mole% and the rest is H_2 [16]. Investigation of different CO_2 concentration became interesting as a wide range of CO_2 concentration in the industrial application has been faced. In fact, CO_2 concentration in gas mixtures influences the hydrate formation temperature and pressure condition. Hydrate phase equilibria for different CO_2 concentration is illustrated in Figure 2-6. Higher CO_2 concentration leads to moderate hydrate formation condition. Moreover, the gas separation efficiency in CO_2 capture process is improved in higher CO_2 concentration [18].
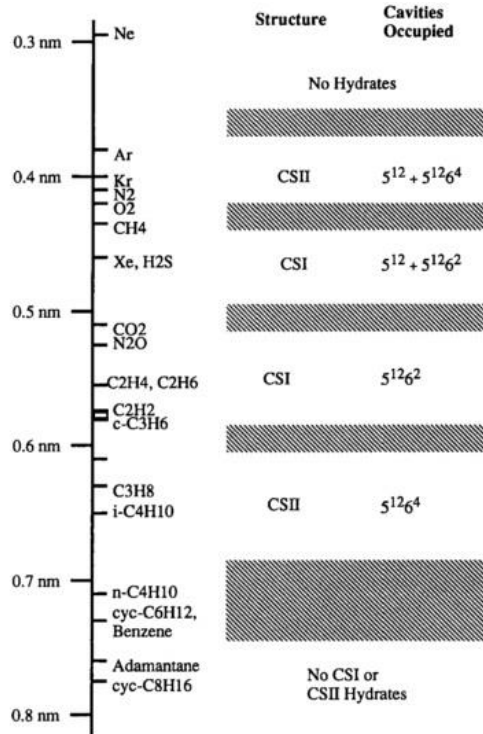
Figure 2-5: Typical hydrate structure for different gas molecules [12]

On the other hand, large-scale equipment is required to capture CO_2 in low concentration cases which result in high investment. The feasibility study of CO_2 capture by hydrate indicated when the high concentration of CO_2 is already available (e.g. treated flue gas from the combustion process), CO_2 hydrate technology would benefit to exploit solid transportation of CO_2 in a CCS chain [19].

Figure 2-6: Hydrate phase equilibria condition for different mixture of CO_2+ N_2 +water [18]

2.4 CO₂ hydrate parameters

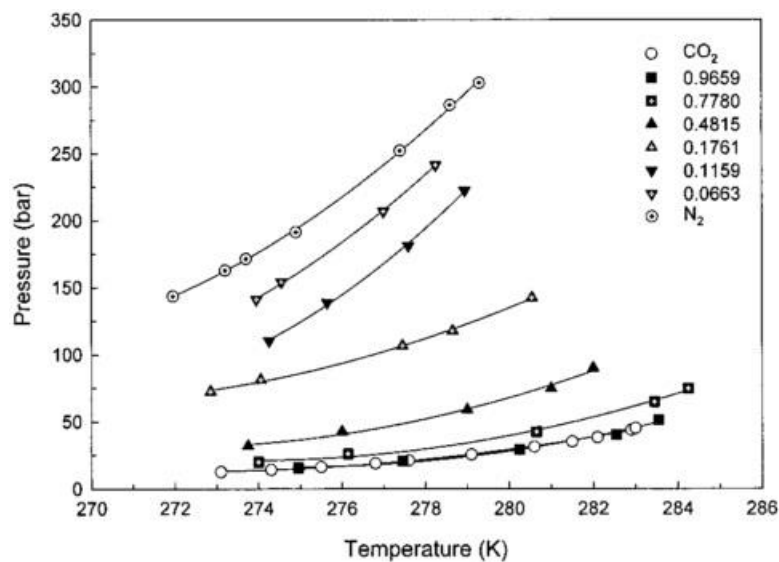The short explanation of important characteristics related to hydrate formation with especial emphasis on CO_2 hydrate is the main concern in this section. Generally, description of hydrate formation is basically based on several key features such as induction time, phase equilibrium condition, split fraction, separation factor. Most of the scientific research in the hydrate formation area have focused on determination of key features' impacts on hydrate formation [16].

The determination of the hydrate formation parameter has been achieved experimentally. Therefore, the value reported in different literature differs from each other due to different methods and equipment are used in experiments which account a difficulty in hydrate formation studies to find reliable and general values, particularly for induction time.

2.4.1 Induction time

The induction time is one of the main characteristics of hydrate formation which plays a significant role in the kinetic of hydrate progress. For instance, the induction time influences the type of hydrate formation reactor and the required residence time of gas and aqueous solution within the reactor directly. On the other side, when inhibition of hydrate formation is the main concern, induction time has a notable impact again as longer induction time facilitates transportation of fluid through the plant pipelines without crystallisation [20].

Several definitions exist for induction time in different literature. For example, Kashchiev et al. stated that *"The induction time is a measure of the ability of a supersaturated system to remain in the state of metastable equilibrium and has the physical significance of the system's lifetime in this state. The induction time is not a fundamental physical characteristic of the system, but is experimentally accessible and contains valuable information about the kinetics of new phase nucleation and/or growth"* [20]. However, the required time to appear the initial hydrate cluster at nucleus size which is able to continue hydrate growth is known as the common definition of induction time given by many research [17].

The lack of reproducibility in experimental procedures is accounted as one challenge with respect to induction time determination which has been reported in the literature [9, 21, 22]. Natarajan et al. [21] set a series of experiments to determine the induction time of hydrate formation. They showed that the reproducibility of experiments at low pressures did not give good results in comparison with experiments performed at higher pressure. However, the reproducibility of induction time has been increased in more recent scientific researches [23].

In general, both pressure and concentration of gas have inverse effects on induction time. Also adding the chemicals will prompt the induction time i.e. the induction time which lasts from a few minutes to few hours can be reduced by increasing the pressure of the CO_2 and/or by use of a promoter such as tetrahydrofuran (THF) [24].

2.4.2 Gas consumption

The number of moles of the gas is trapped in the water cages during the hydrate formation process is known as gas consumption. Gas molecules in two different stages are consumed during the hydrate formation that first stage is when the gas dissolved in aqueous solution and the second stage is about the nucleus and hydrate growth. However, in practice, the amount of

gas dissolved in the water is not taken into account by reason of assumption which the supersaturation condition exists throughout the hydrate process [24]. The number of CO_2 moles consumed during the hydrate formation for different initial pressure values is illustrated in Figure 2-7. It is seen from Figure 2-7 that the gas consumption depends on initial pressure which shows the initial gas moles within the reactor.
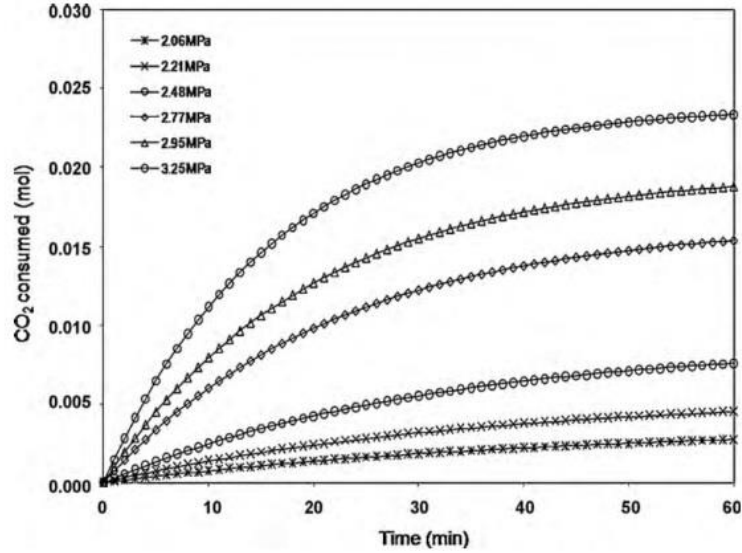

Figure 2-7: CO_2 consumption during hydrate formation at different pressure [24]

More recent work regarding hydrate formation has investigated the gas consumption during the hydrate formation in presence of chemical promoters [25-28]. Babu et al [26], performed a set of experiments to investigate the effect of adding THF to a mixture of $CO_2 + H_2$ on hydrate formation characteristics such as induction time and gas consumption. They showed that at lower experimental pressure, the induction time was longer while higher gas consumption was achieved in this condition because of longer dissolution period. Also, they attributed that the overall gas uptake raised by increasing pressure due to higher driving force.

A simple formula can be used to calculate the total amount gas consumption through the hydrate formation process between time =0 and time = t is given in Equation 2-1:

$$\Delta n = V\left(\frac{P}{zRT}\right)_0 - V\left(\frac{P}{zRT}\right)_t \qquad \text{Equation 2-1}$$

Where Δn [mol], P [Pa], T [K], V [m^3] and R [$J \cdot mol^{-1} \cdot K^{-1}$] are moles of gas consumed, pressure, temperature, the volume inside the reactor and universal gas constant, respectively. Furthermore, the compressibility factor, z, can be calculated by Pitzer's correlations [28].

2.4.3 Hydration number

The number of water moles is needed for one mole of CO_2 or other gas molecules to be caged is called hydration number (HN). Hydration number is mainly determined by the hydrate structure and the relative occupied cavities in the structures [12]. In large hydrate formation applications such as CO_2 capture or gas separation by hydrate formation from power plants,

the necessity of attention to the amount of required fresh water is important. Consequently, the determination of HN becomes essential in the design phase of plants and investments.

As mentioned former, CO_2 molecules with fresh water forms structure sI and according to the size of filled cavities in this structure, the value of 6.2 is suggested for HN of the mixture CO_2+water [29]. Nevertheless, if THF is used as a promoter to moderate the CO_2 hydrate formation condition, the hydrate structure would alter to structure sII. A stoichiometric CO_2 hydrate reaction in presence of THF is given by:

$$a\ CO_2 + b\ THF + c\ H_2O \rightarrow\ aCO_2 \cdot bTHF \cdot cH_2O$$

<div align="right">Equation 2-2</div>

Where a, b and C are 16, 8 and 136, respectively. Therefore, the HN increases to 8.5 [30]. Also, the use of, for example, TBAB as a promoter will form semi-clathrate structure and it contributes a higher hydration number of 12.7 [31].

Determination of HN can be done theoretically and experimentally, however, Herri et al [32], showed that the HN would have bigger value while it was determined by experiments compared to the theoretical calculation. In fact, the excess aqueous solution is needed to form maximum amount of hydrate through filling all possible empty cages. Moreover, utilising Clapeyron or Clausius-Clapeyron equations is the common way of HN determination theoretically [29].

2.4.4 Water memory

An important parameter regarding hydrate formation is the water memory. In fact, the water memory effect helps to form hydrates faster than the first crystalization when the hydrate formation progress is repeated several times with the same mixture. Various studies have reported this phenomenon but the detail information of the phnomenon is still under consideration. For instance, Wang et al [33], reported that the water memory led to reduce the hydrate formation time in further cycles. Moreover, the demand for cooling energy would reduce during the hydrate formation because of memory effect.

2.4.5 Phase equilibria condition

Phase equilibrium condition of hydrate refers to thermodynamic equilibrium point which satisfies the repeatability. Temperature and pressure in equilibrium point are favourite features to verify in research [34-36]. Relying on only hydrate formation condition is not an accurate and repeatable approach since hydrate formation condition depends on several factors such as water memory, the degree of subcooling and rate of cooling. Hence, the dissociation point of hydrate which is a thermodynamic equilibrium point is considered as phase equilibrium condition of hydrates [37].

The regular way to measure hydrate dissociation point is to form hydrate first either by reducing temperature (under isobaric and isochoric condition) or increasing pressure (in isothermal condition). Later, hydrate is brought to liquid form again by employing a reverse procedure for the hydrate formation until there is no crystalline in the aqueous solution [37].

The phase equilibrium condition for several gas molecules such as CO_2, N_2 and O_2 is demonstrated in Figure 2-8. In general, the formation of hydrate at higher temperature needs an increase in pressure.

It is worth mentioning that the gas consumption will increase through the higher pressure, however it does not necessarily mean a better CO_2 recovery due to the presence of other gases which may form hydrates contemporarily at these conditions. In real applications, lower pressure and higher temperature are favourable conditions which will influence cost directly.
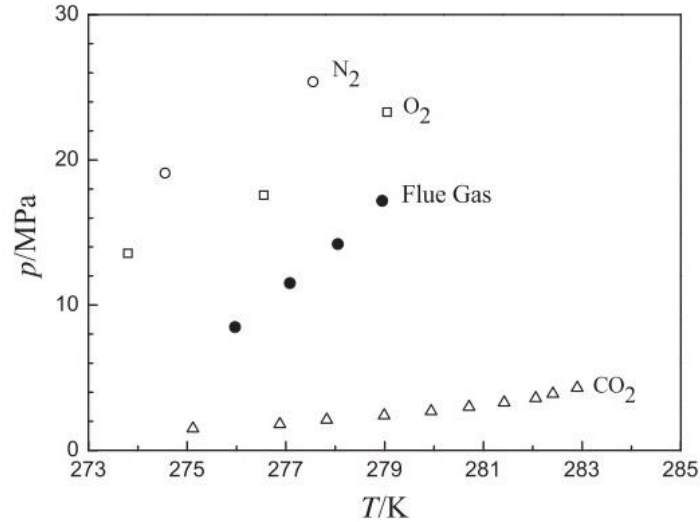
Figure 2-8: Hydrate phase equilibria for different gases [35]

2.4.6 Split fraction

One parameter related to CO_2 hydrate formation is addressed as split fraction (S.Fr) or CO_2 recovery. It is defined as the ration of CO_2 moles in hydrates ($n_{CO_2}^{H}$) to the number of CO_2 moles in feed gas ($n_{CO_2}^{feed}$) [38].

$$S.Fr = \frac{n_{CO_2}^{H}}{n_{CO_2}^{feed}} \qquad \text{Equation 2-3}$$

This parameter becomes important when a mixture of gases is used to formed hydrate and the aim of hydrate formation is to capture CO_2 from the feed gas. Linga et al [38], showed that the split fraction for a feed gas which consisted of 15-20% CO_2 was 42% while the hydrate formation experiment performed at 10 MPa and 0.6 °C. However, adding 1.0 mole% THF would improve CO_2 recovery by 46% in a mixture of 17% CO_2 and 83% N_2 while the hydrate formation process performed at moderate conditions (i.e. 2.5 MPa and 0.6 °C) [39]. Higher split fraction shows the more efficient approach to capture CO_2 by hydrate formation.

2.4.7 Separation factor

Employing separation factor (S.F) is one way to measure the selectivity of one gas component among other components in hydrate formation process. In presence of a feed gas containing other gases different from CO_2, the separation factor is defined as the split fraction of CO_2 divided by the split fraction of all other components [38].

$$S.F = \frac{\dfrac{n_{CO_2}^{H}}{n_{CO_2}^{gas}}}{\dfrac{n_{A}^{H}}{n_{A}^{gas}}} = \frac{n_{CO_2}^{H} \times n_{A}^{gas}}{n_{CO_2}^{gas} \times n_{A}^{H}} \qquad\qquad \text{Equation 2-4}$$

Where $n_{CO_2}^{H}$ and $n_{CO_2}^{gas}$ are the moles of CO_2 in hydrate phase and gas phase, respectively. Also n_{A}^{H} and n_{A}^{gas} are the number of other molecules in hydrate phase and gas phase, respectively. Linga et al [38], reported that the separation factor for a feed gas which consisted of 15-20% CO_2 was 13.7 while the hydrate formation experiment performed at 10 MPa and 0.6 °C. However, adding 1.0 mole% THF would reduce the separation factor to 7.6 in a mixture of 17% CO_2 and 83% N_2 [39].

Practically, high separation factor is favourable for a more efficient hydrate formation since it shows an increase in the number of CO_2 molecules in the hydrate form.

The ideal condition for CO_2 hydrate formation for the purpose of recovery or gas separation is achieved when the gas consumption and separation factor are high while the induction time is very low [40]. Furthermore, favourable phase equilibrium condition are at low pressure coupled with high temperature. In practice, this is a very challenging task since high gas consumption means having a feed at high pressures and hence, extra cost associated with the compression of the feed gas. In addition, a high gas consumption may not necessarily mean high recovery or separation factor due to the presence of other gases in the feed.

2.5 Chemical promoters

Aforementioned challenges can be solved by using chemical additives for hydrate formations. In general, chemical additives which are known as hydrate promoters are exploited to shorten induction time, increase the hydrate formation rate and the selectivity of specific gas such as CO_2 in the hydrate. Although, the ability of reduction in the equilibrium hydrate formation pressure has attracted most interests.

The effect of adding different promoters is widely investigated in the literature. The chemical additives are divided into two types; Kinetic and thermodynamic promoters. Kinetic promoters which are also known as surfactants mostly enhance the hydrate formation rate and decrease the induction time without participating in the hydrate formation process [15]. Most reviewed surfactants for hydrate formation in scientific works are Tween-80 (T-80), dodecyl-trimethyl-ammonium chloride (DTAC) and sodium dodecyl sulphate (SDS) where SDS has been studied extensively [15].

While the other type of promoters will take part in hydrate formation procedure via competing to fill the empty cages within the hydrate structure. Thermodynamic promoters are mainly used to improve the hydrate formation condition at lower pressure and higher temperature [15]. Also, this kind of promoters can be categorised into two groups. The first group of thermodynamic promoters does not change the structure of clathrates, however, it might affect like surfactants. Well-known examples of this group are tetrahydrofuran (THF), cyclopetane and acetone [15].

Whereas the second group alters the hydrate structure through changing the shape of cavities or forming semi-clathrate. In fact, the second group of thermodynamic promoters fills the water cages first and then it is easier for other gas molecules such as CO_2 to put in the neighbour cages in order to form hydrates. There are several examples of this group which are mostly made by tetraalkylammonium salts such as TBAB (tetrabutylammonium bromide) and TBAF (tetrabutylammonium fluoride) [16]. The overall gas consumption reduces by using this group of promoters since additives should occupy cages first.
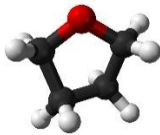
In this work, the focus will be on CO_2 hydrate formation and the use of promoters in order to enhance the CO_2 hydrate formation conditions. THF, TBAB, TBPB, TBAF and $TBANO_3$ are the chemical promoters which are studied in this work. Thus, the results of literature related to employed promoters in CO_2 capture by hydrate formation will be given briefly in following sections.

2.5.1 Hydrate formation by THF

Tetrahydrofuran (THF) is a colourless and ether-like odour, which is mostly used in industry as a solvent for various polymers and resins. THF is highly flammable which concentrated THF will form peroxide and becoming explosive. Also, THF may cause serious eyes and respiratory irritation and it is suspected to cause cancer in the long period [41].

The physical properties of THF are given in Table 2-1. THF is the most investigated promoter in hydrate formation procedure in the literature [15]. As mentioned before, CO_2 will form structure sI hydrate while the structure of crystalline will be structure sII in presence of THF [42]. The main influence of using THF in hydrate formation is to reduce hydrate formation pressure and also induction time. Daraboina et al [43], reported that the CO_2 recovery might raise while the separation factor may decrease. It means the gas consumption of mixture is reduced. In fact, an excess amount of THF will occupy the large cages within water lattice. Hence, the availability of vacant cavities for CO_2 or other gases reduces. Therefore, there should be a proper balance between reduction in hydration pressure and an increase in gas separation. Kang and lee [18], stated that 1 mole % THF might be the optimal value for CO_2 separation from the mixture of CO_2 and N_2. Ma et al [16], summarised the phase equilibrium data from the different literature for CO_2+water+THF systems. The results are shown in Figure 2-9.

Table 2-1: Physical properties of THF

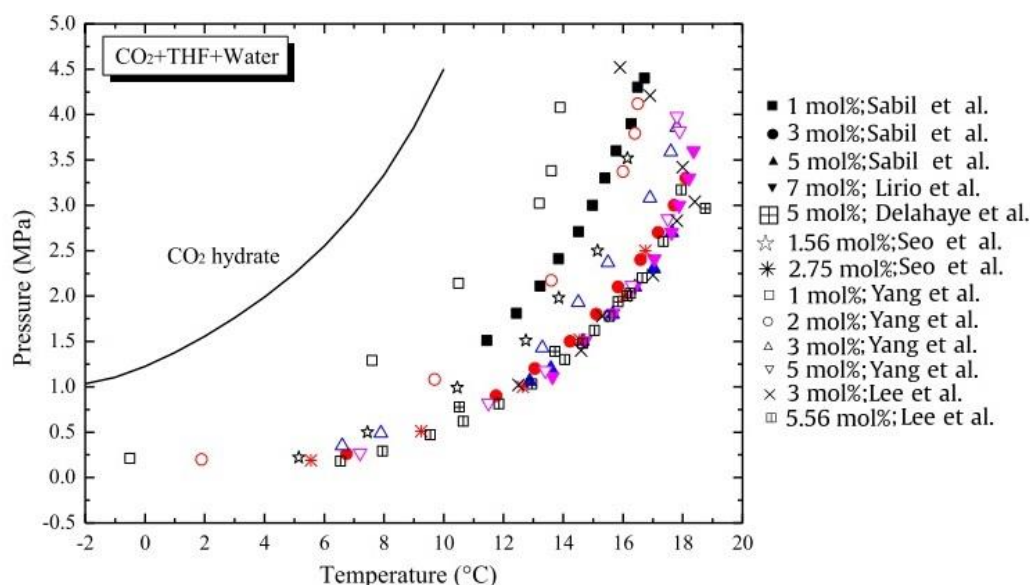| Chemical Structure	
Formula	C_4H_8O
Molar weight	72.11 g/mol
Density	889 kg/m³
Boiling point	66 °C
Melting point	-108.4 °C

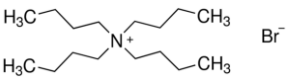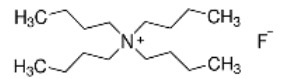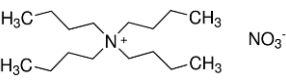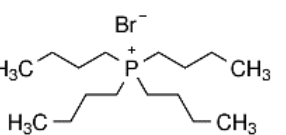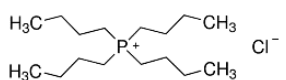Figure 2-9: Phase equilibrium data for CO2+THF+water system [13]

2.5.2 Hydrate formation by tetraalkylammonium/phosphonium salts

Tetraalkylammonium/phosphonium salts are categorised in the second group of thermodynamic promoters. This group forms a semi-clathrate (SC) hydrate because cages within the hydrate are formed by both water molecules and salt molecules. The relatively large size of salt molecules in tetraalkylammonium salt causes to form cavities within hydrate structure. Better stability at atmospheric pressure and higher gas consumption in water cages are the advantages of SC hydrates, meanwhile, the using of these promoters will reduce the pressure of hydrate formation [44].

The use of different tetraalkylammonium salts has been investigated in researches related to hydrate formation and gas separation [15]. However, among all promoters belonged to this group, TBAB (tetrabutylammonium bromide) is well studied and its thermos-physical properties are investigated extensively. Different promoters can be used to form SC hydrates but in the present work, the main attention will be on using of TBAB, TBAF (tetrabutylammonium Flouride), TBANO$_3$ (tetrabutylammonium Nitrate), TBPB (tetrabutylphosphonium Bromide) and TBPC (tetrabutylphosphonium Chloride) form CO$_2$ hydrate. A brief description of different tetraalkylammonium/phosphonium salts which would have been used in this report is given in Table 2-2.

The morphology of semi-clathrate showed that they formed two kind of hydrates named type A and type B [44]. Ye et al [45], reported that type A had columnar shape whereas type B was like undefined shape with a rougher surface. The hydration number for each type is different. In general, the hydration number of tetraalkylammonium/phosphonium salts is greater than other promoters like THF.

Table 2-2: Brief description of different tetraalkylammonium/phosphonium salts

Promoters	Chemical Structure	Molar weight g/mol	Formula	Melting point
TBAB		322.37	$C_{16}H_{36}BrN$	103°C
TBAF		261.46	$[CH_3(CH_2)_3]_4NF$	58 to 60 °C
TBANO$_3$		304.47	$(CH_3CH_2CH_2CH_2)_4N(NO_3)$	116-118 °C
TBPB		339.33	$(CH_3CH_2CH_2CH_2)_4P(Br)$	100-103 °C
TBPC		294.88	$(CH_3CH_2CH_2CH_2)_4P(Cl)$	62-66 °C

Ma et al [16], summarised the results achieved in different scientific articles. For instance, the phase equilibrium data for CO_2+water with different tetraalkylammonium salts systems are given in Figure 2-10 to Figure 2-13. They showed that the hydrate formation condition would improve by increasing the concentration of promoters in aqueous solution however, this improvement stops when the additive's concentration reaches to an optimal value. Afterwards, adding extra promoters deteriorates the hydrate formation condition.

The optimum concentration of TBAB in aqueous solution to achieved better hydrate formation pressure was around 30 wt% [45]. Though the concentration of 20-25 wt% of TBPB considers being sufficient amount in order to enhance hydrate formation pressure [46]. Moreover, Studies show that TBAF provides better hydrate formation conditions compared to other thermodynamic promoters [16].

The addition of promoters has been investigated widely and most of the research focused on the determination of the phase equilibrium data. Although thermo-physical properties of other thermodynamic promoters such as TBANO$_3$ are not reported sufficiently. Particularly, there is a few research on the determination of induction time of hydrate formation where those research are limited to well-known promoters such as THF and TBAB.

Therefore, investigation of induction time and also the initial hydrate formation temperature in presence of different thermodynamic promoters is one of the goals of this thesis. Moreover, CO_2 hydrate formation at different pressures will study in this work.
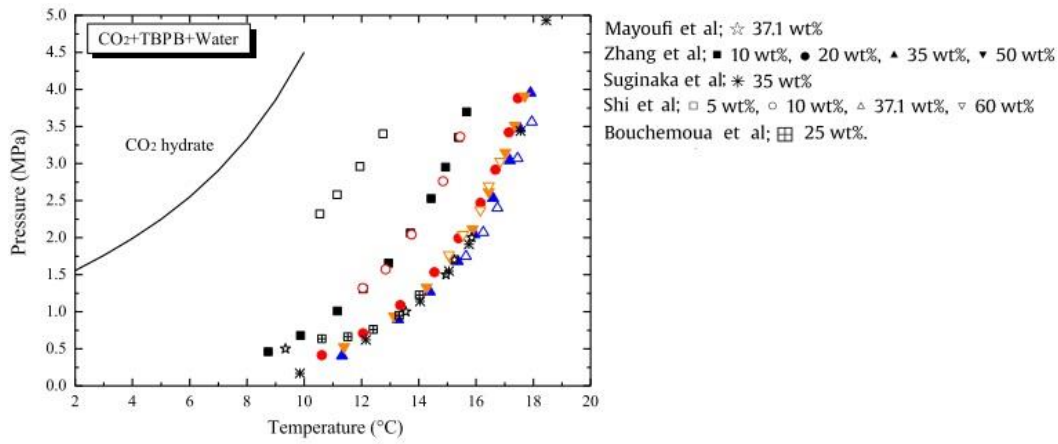
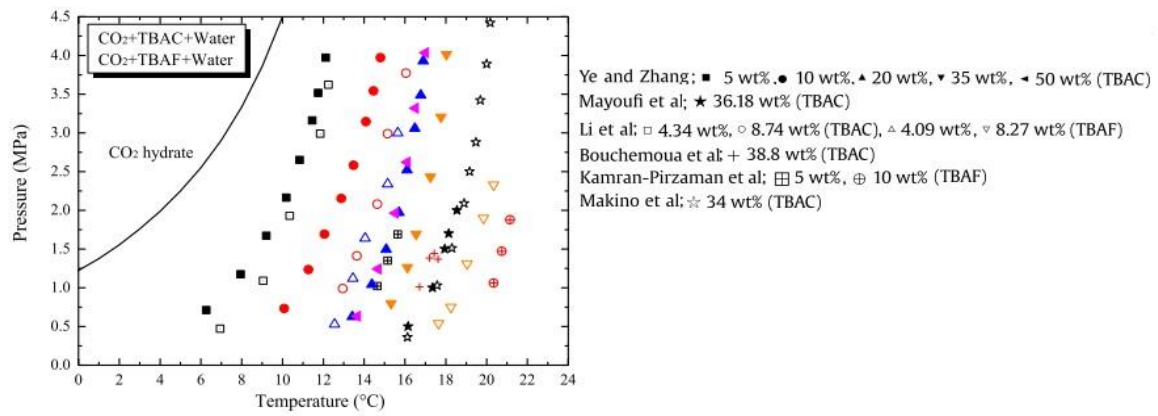Figure 2-10: Phase equilibrium data for CO$_2$+TBPB+water system [16]

Figure 2-11: Phase equilibrium data for CO$_2$+TBAC/TBAF+water system [13]
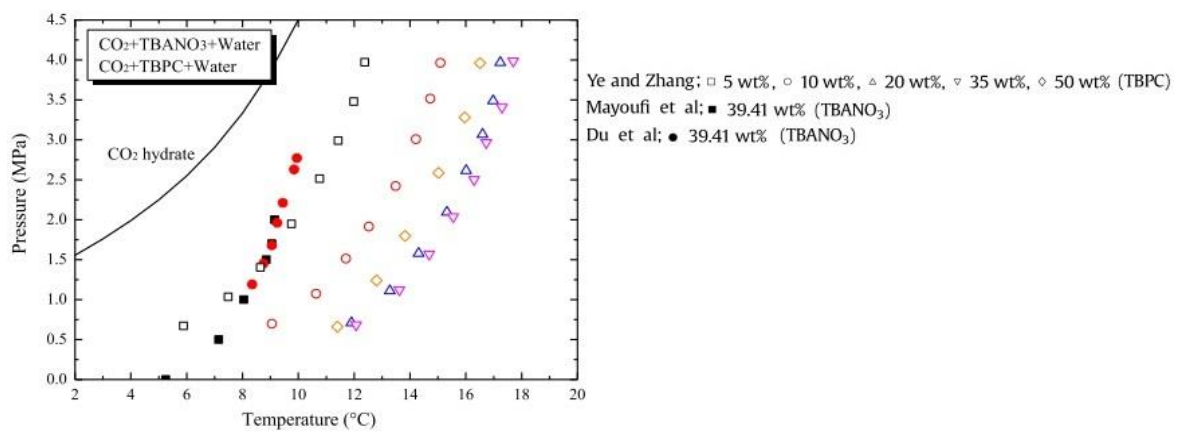
Figure 2-12: Phase equilibrium data for CO$_2$+TBANO$_3$/TBPC+water system [13]
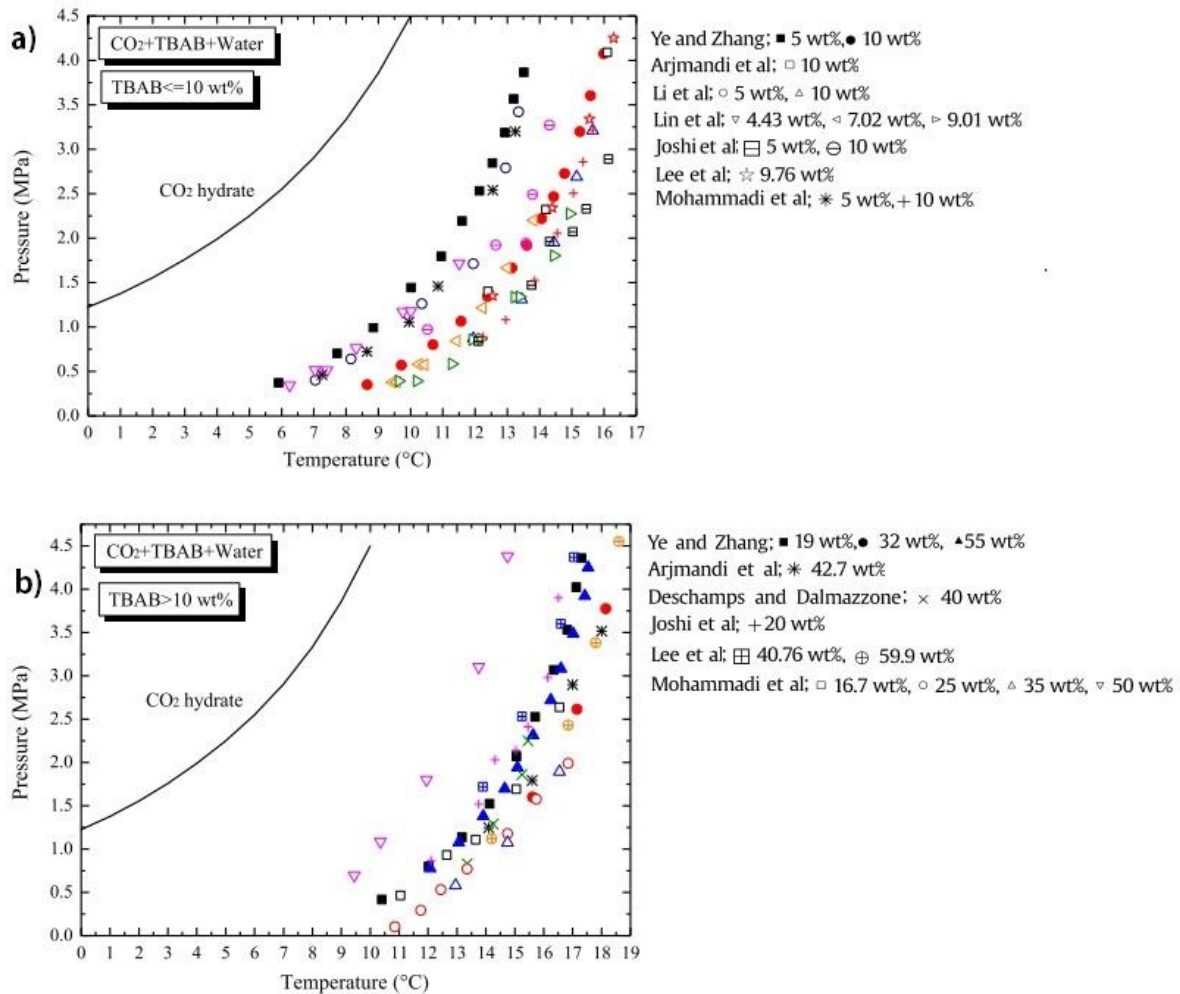
Figure 2-13: Phase equilibrium data for CO_2+TBAB+water system a) concentration less than 10% b) concentration more than 10% [13]

2.6 Hydrate storage and transportation

Gas hydrates have been investigated in many fields like gas separation [47, 48], energy source [49], gas storage and transmission [7, 8, 50]. Among all application of gas hydrate, the number of studies in gas storage and transportation is less. However, those studies have focused on natural gas storage and transmission.

There are two main reasons that make gas storage and transportation in the form of hydrates as an alternative approach in a large-scale application; firstly, the volume of gas hydrate is 150-170 times less than the volume of the same amount of gas [7]. Secondly, the hydrate can be transported by the metastable nature of the hydrates which gives the possibility of solid-phase transportation.

The metastable condition of hydrates means that hydrates can be preserved for a long time at atmospheric pressure and below zero degrees while the hydrates are frozen in a metastable

condition. In fact, a thin ice-like film surrounds the hydrates at below zero degree and atmospheric pressure when the hydrates start dissociating. The external ice layer serves a protective shield [51]. This unusual behaviour is also named as "anomalous" because the unstable condition is expected when the hydrate begin to decompose, while the self-preservation of ice-like shield due to gas decomposition in hydrates leads to prevention of further dissociation [51].

Transmission and storage of CO_2 have similar priority as CO_2 capturing in order to have a feasible CCS chain. The possibility of employing CO_2 hydrate in a complete CCS chain needs several considerations in transportations. Therefore, an essential effort on solid-phase CO_2 hydrate transportation is required while the lack of information about CO_2 hydrate transmission requires a wide range of studies in the field of CO_2 hydrate formation.

In the present thesis, primary attempts are to develop the idea of CO_2 hydrate formation which can be employed in a complete CCS chain by hydrates. Moreover, the reduction in induction time of CO_2 hydrate formation is the focus of the present study since shorter induction time makes the CCS chain by hydrates more feasible and it will provide useful information for further investigation of CO_2 hydrate transportation.

3 Development of hydrate formation reactor

Embryo research on hydrate formation in lab scale in this thesis includes several stages: experiment apparatus and its development, finding proper experimental procedure with respect to available apparatus, measuring and analysing the achieved data.

As it was the first experience related to hydrate formation in CO_2 capture laboratory, the effort was to develop the set-up to achieve a primary understanding of CO_2 hydrate formation. However, only CO_2 gas molecules were introduced into the reactor to form hydrate due to the fact that forming CO_2 hydrate took place in milder conditions in comparison with a mixture of different gases.

In order to be able to form CO_2 hydrate and later to determine the important hydrate parameters, a proposal development of hydrate formation reactor (HFR) aimed in this master thesis. For this purpose, two different types of HFR were considered: batch HFR and continuous gas flow reactor (semi-batch HFR). A detailed information and technical problems during the experiments of each type will be discussed in this chapter.

Furthermore, an appropriate method which was matched to available rig should be utilised in hydrate formation experiments. Thus, a brief explanation of different experimental procedures related to the hydrate formation is given in this chapter. Eventually, reasons of the selected method and its specific aspects will be part of this chapter.

3.1 Batch reactor with magnetic stirrer

In the beginning of this work, the idea was just to form hydrate from CO_2 with a primary facility in CO_2 capture laboratory. Consequently, the first HFR rig was designed as a batch reactor. Since the reactor was filled with gas and aqueous solution initially and there was no gas or liquid flow into/from the reactor, it is called batch reactor.

The batch HFR have been widely used in different researches [52]. For instance, zhang et al [53], employed a high-pressure vessel to investigate the phase equilibrium data for a mixture of CO_2+N_2 in presence of THF and SDS. Operational experiences have illustrated that the batch HFR is suitable reactor type to determine the phase equilibrium data point of hydrates.

The batch set-up consists of three main elements; pressurised reactor, thermostat and data acquisition. A schematic of batch HFR is shown in Figure 3-1. A mini autoclave with a volume of 200 mL is used as a reactor which tolerates the pressure up to 10 bars. Two needle valves are installed at top of the reactor to regulate the gas inflow and outflow. Also, the needle valve gives the possibility of keeping the pressure inside the reactor almost constant in experiments running time.

The reactor sinks in cooling bath linked to an adjustable thermostat. Therefore, the temperature of the reactor could be controlled just by adjusting the bath temperature which was connected to the thermostat. Moreover, the cooling bath is designed to work in the temperature range of -15 to 40°C by employing the mixture of water+ethylene glycol as cooling fluid.
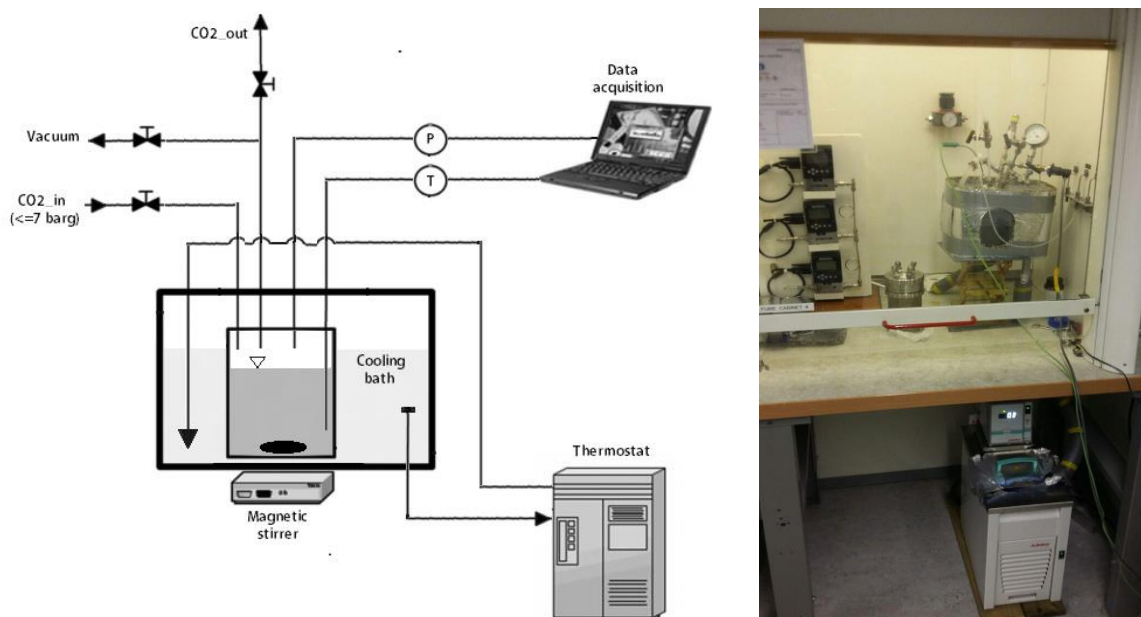
Figure 3-1: A schematic of batch hydrate formation apparatus

In order to record the pressure and temperature within the reactor during the hydrate formation experiments, the pressure sensor and PT100 (platinum resistance thermometer) installed inside the reactor. The accuracy of temperature and pressure sensors are $\pm0.1°C$ and ±0.1 bar, respectively. All data was collected in the computer (data acquisition) to further analysis.

Acceleration of hydrate formation rate in experiments is an important issue that it can be done in several ways such as using porous media and stirrer. The idea is to increase the contact surfaces between gas and liquid phases within the reactor. Hence, the growth rate of hydrate and consequently the gas consumption increases. In batch HFR, a magnetic stirrer where located at the bottom of the mini autoclave is used to agitate the mixing of gas and liquid phases in experiments.

Some operational experience with batch HFR and technical problems of this rig are reported in the following:

- Good insulation for the cooling bath is an important element, particularly at low temperature. The temperature differences between bath and room contribute a large heat loss at the time of experiments. Moreover, if the size of cooling bath is greater than necessary size then it takes a longer time to cool down or heat the reactor while the hydrate formation occurred. Therefore, it was necessary to insulate the cooling bath as much as possible.
- There is usually a deviation of $0.3°C$ between the set temperature in thermostat and the temperature inside the reactor after obtaining stable condition.
- In addition, the available thermostat in CO_2 capture laboratory circulates the cooling fluid in a closed system whereas the batch HFR rig was not the completely close system. This problem was solved by placing thermostat at a lower level than the cooling bath and by the use of gravity. Hence, it was necessary to place the cooling fluid outflow at

bottom of cooling bath. However, the control of sufficient level of cooling medium within the bath remained crucial especially when long time operation was favourable. In this case, the level of cooling liquid in bath reduces and then the thermostat and its circulation pump would stop working.

- According to the hydrate formation procedures, the constant pressure inside the reactor was required. Needle valves were the only instrument in order to manipulate the pressure. Consequently, a needle valve was mounted in the main CO_2 supply line to keep the pressure within the reactor stable. The needle valve was manipulated manually when there was a deviation of $\pm\ 0.04$ bar from the desired pressure inside the reactor.

- It is worth mentioning that all pressure values in this thesis are considered in bar gage.

- Additionally, the main CO_2 supply line could be controlled up to 9 bar, which was enough and it satisfied the safety aspects inside the reactor. Even though, the safety valve in the rig set at 7 bars.

- As mentioned above, a magnetic stirrer is used in the batch HFR in order to improve the contact surfaces between gas and liquid phases. Although using magnetic stirrer turns to a problem when the CO_2 hydrate formed. Since the density of CO_2 hydrate slurry is higher than aqueous solution, the magnetic stirring bar would be stuck between CO_2 hydrates that it will result in insufficient mixing inside the reactor. Therefore, the hydrate growth rate within the reactor decreases.

Since construction and operation of a stirrer reactor are quite easy in laboratory scale, most of the studies relating to hydrates have been carried out by this type of reactor. Nevertheless, the stirrer reactor is not the favourite type of reactor in an industrial utilisation due to its drawbacks related to the hydrate formation process.

Some of the disadvantages of the stirrer reactor for industrial utilisation are stated below:
- Difficulty of sealing the stirrer reactor at high-pressure operation
- Higher energy consumption compared to other mechanical methods like bubbling
- The viscosity of hydrate slurry increases quickly while the hydrate fraction in the reactor raises, therefore, more power needed to keep the turbulence of reactant system.
- The batch stirrer reactor is not suitable for continuous gas separation where endless contact between gas and liquid phase desired in the industrial application.

Therefore, this type of reactor is suitable for lab scale hydrate formation and determination of hydrate formation parameters such as phase equilibrium data [54].

Measurement of the induction time and other hydrate formation parameters such as hydrate formation temperature was possible with batch HFR. However, other parameters such as gas consumption were not possible to measure due to the fact that the flowmeter was not installed in the rig. The problem with flowmeter installation was because of high pressure inside the reactor. The discharge gas from the available flowmeter should be at atmospheric pressure whereas the pressure within the reactor reached up to 7 bars.

One of the priorities in this thesis was to find a superior rig which could be used as HFR in order to reduce the induction time. According to the agitating issues related to the magnetic stirrer, few modifications were required to the set-up. These modifications led to a new HFR which will be described in the following subchapter.

3.2 Semi-batch reactor with bubble diffuser (continuous gas flow)

In an industrial and development point of view, one concern about the hydrate formation is how to form hydrate quickly and continuously. There are several ways to enhance the hydrate formation rate such as chemical methods (i.e. adding promoters) and mechanical methods (e.g. stirring, spraying and bubbling)[54]. However, if the hydrate formation takes into account as gas separation method or transportation purposes in large applications and industrial scale, the first concern is to form hydrate as fast as possible with lower energy consumptions.

Unlike the batch HFR which is widely investigated in lab-scale studies, the number of research about the bubbling or continuous HFR is limited [55-58]. Gudmundsson et al [55], built a pilot hydrate formation rig to investigate the natural gas hydrate formation kinetics. Both gas and liquid phase in their set-up flowed continuously. Also, Luo et al [59], investigated the hydrate formation kinetic by applying a bubbling tower for gas phase and flowing pressurised aqueous solution through the bubbling column.

The use of bubbling tower is a conventional way in industry sector especially when the gas-liquid interaction is in favour. Hence, the idea of bubbling within a HFR might benefit in industrial hydration process by reducing the induction time and increasing the hydrate formation rate. Moreover, the bubbling HFR might provide the possibility of continuous gas flow through the reactor.

According to the mentioned difficulties of batch HFR and benefits of a bubbling reactor, the efforts in the modification of the previous batch HFR led to the development of a new reactor. The available batch reactor in CO_2 capture laboratory developed to bubbling HFR. The second reactor is also called semi-batch hydrate formation reactor since the modified reactor had only continuous gas flow and the reactor was filled with aqueous solution former running the experiments.

A schematic of semi-batch HFR is shown in Figure 3-2. The principal of the new rig is similar to batch HFR. However, the main difference is about installing sintered plate at the bottom of the mini autoclave in order to create bubbles through the aqueous solution. The CO_2 gas flows through the liquid within the reactor and exits from the needle valve which is mounted above the reactor lid. Other elements such as pressure and temperature sensors, thermostat and cooling bath are the same as batch HFR.

From a technical point of view, running experiments in semi-batch HFR rig had few limitations which are explained in the following.

- The excess CO_2 from the reactor would release to the air. Therefore, continuous CO_2 gas flow in experiments led to limit the number of experiments because the amount of available CO_2 was limited in the storage hall.
- In fact, the consumed CO_2 gas for each experiment in semi-batch HFR was greater than the same experiment in the batch HFR. Therefore, it seems to be necessary to have a new configuration for later modifications in order to reuse excess CO_2 from the reactor.
- To keep the pressure constant inside the reactor, there were two needle valves mounted on the gas inflow and outflow lines. These valves were adjusted manually during the experiments to set pressure within the reactor stable at the desired pressure value.

However, a deviation of $\pm\ 0.04$ bar from the intended pressure in the experiment run assumed acceptable.

- In order to find the amount CO_2 hydrate formed within the reactor, several methods were tested but none of those yielded good results. One way was to measure the weight of the reactor just before and after hydrate formation. Due to the fact that hydrates attached to the sinter and temperature sensor rod, the results of weighting the reactor was not accurate. Moreover, the lack of flowmeters resulted in disability of hydrate formation calculations.
- Subsequently, to perform a complete hydrate formation experiments, installation of a proper flowmeter with respect to the type of reactor has to consider for more developments later. Because it gives measurement capability of several hydrate formation parameters such as hydrate formation rate and gas consumption.
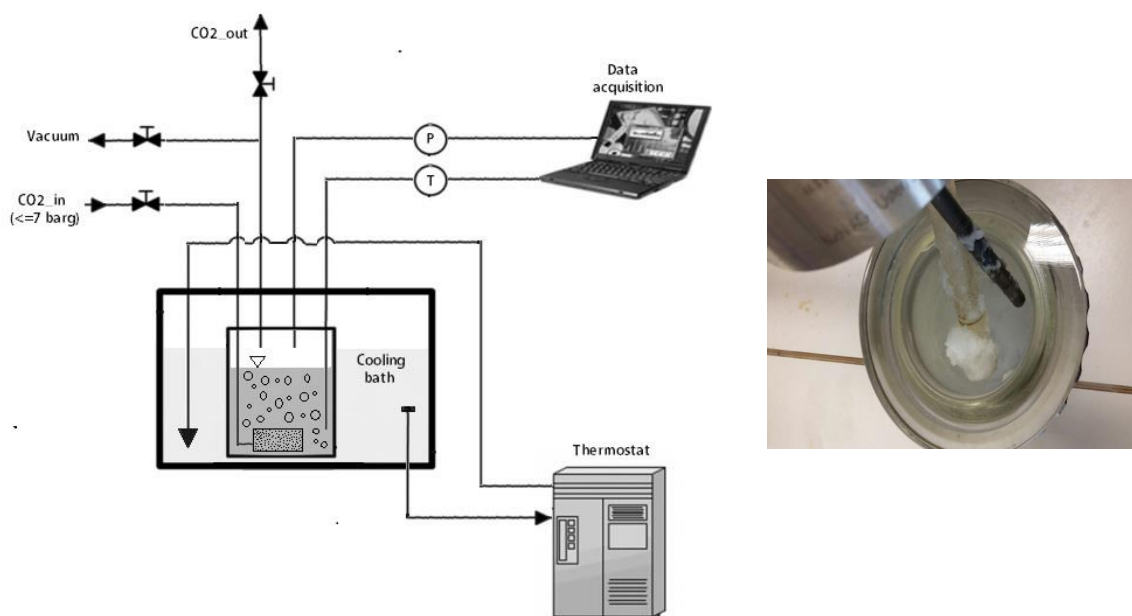
Figure 3-2: A schematic of semi-batch hydrate formation apparatus

The next step in the embryo CO_2 hydrate production research was to find an appropriate method not only to form CO_2 hydrate but also to be able to measure a few parameters of hydrate formation condition via available set-up in CO_2 capture laboratory. A brief explanation of possible ways of forming hydrates in a lab scale will be given in the following.

3.3 Different experimental procedure for hydrate production

In general, hydrate formation occurs at high pressure and low temperature condition. However, the gas hydrates can be formed in a milder condition in the presence of chemical additives. On the other side, finding a proper experimental procedure is important in terms of measuring hydrate parameters during the experiments.

Scientific investigations have employed different experimental approaches with respect to available apparatus and the favourite parameters which needed to be investigated. Three possible approaches in order to study the hydrate formation conditions are isothermal, isochoric and isobar methods.

Altering the pressure inside the HFR while the temperature is kept stable is the concept of an isothermal method to form hydrates. However, an isothermal method is not very interesting neither in lab scale experiments nor in industrial utilisation due to the fact that having a well-insulated system which does not transfer any heat from the system is absolutely ambitious. Therefore, this type of experiment has not been widely reported [39, 52, 60].

Among all experimental procedures related to the hydrate formation, isobar and isochoric methods have been extensively employed in the literature. An increase/reduction in temperature of the HFR to form/dissociate of gas hydrates is required in both methods. Principally, the hydrate formation can observe either from the reactor visually or sudden changes in pressure or temperature profiles that achieved from the data acquisition. Description of each method and their applications will be discussed below.

3.3.1 Isochoric method

If the purpose of the study is to find the phase equilibrium data of hydrate dissociation point, determination of CO_2 recovery and gas consumption, then employing the isochoric method would result in the most accurate results. This method is also known as isochoric pressure search method which is widely reported in the literature [61-65]. This method includes cooling step to form hydrate and heating step to dissociate hydrate. A typical graph of an isochoric method to find the dissociation equilibrium point is illustrated in Figure 3-3.

The typical procedure in isochoric procedure from Figure 3-3 is:
- Setting the reactor temperature far from the equilibrium point and then introducing the CO_2 or other gas mixture to obtain the desired pressure.
- Due to solving CO_2 into the liquid phase, the pressure inside the reactor decreases (dissolution curve)
- Reducing the temperature in order to cool down the reactor, the pressure within the reactor declines at the same time (cooling curve).
- Indicating hydrate formation by a sudden increase in temperature (due to the exothermic reaction of hydrate formation) and rapid decrease in pressure. (between point C and D).
- Heating the reactor in order to dissociate the hydrate (heating curve)
- The intersection between the cooling curve and heating curve in P-T diagram is the dissociation equilibrium point. (point F)

Moreover, pressure and temperature profiles versus time for a typical isochoric procedure are illustrated in Figure 3-4. The sudden increase in temperature or rapid decrease in pressure indicates the hydrate formation in Figure 3-4.
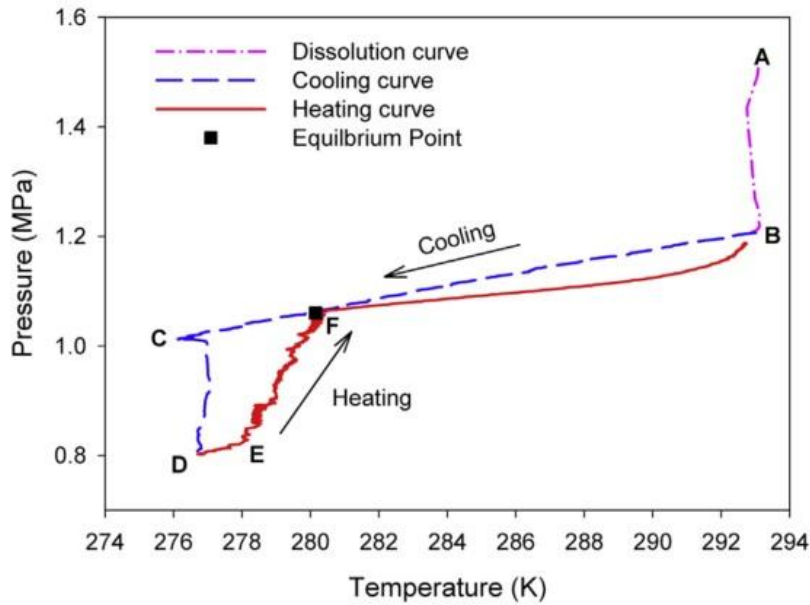
Figure 3-3: A typical P-T graph for isochoric method [64]
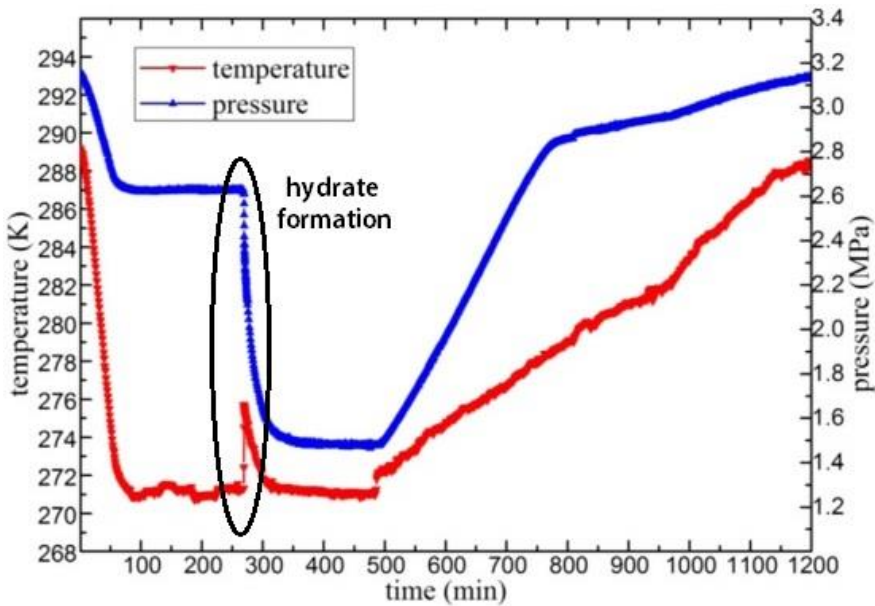
Figure 3-4: Pressure and temperature profiles versus time for a typical isochoric procedure [66]

Tohidi et al [63], reported that there were two ways of heating or cooling; continuous and stepwise methods. They claimed that the continuous heating used in increasing the temperature and dissociating gas hydrate led larger error compared to the stepwise method. However, a stepwise heating takes a long time to accomplish since the increase in temperature takes place in small temperature intervals and the system should be kept stable for a long time in order to reach equilibrium conditions.

Long time experiment considered a disadvantage of employing this method for an experimental procedure to form hydrates. However, the accurate phase equilibrium data and hydrate formation parameters outweigh the long-lasting time of experiments.

3.3.2 isobar method

Isobar method is one way to prevent consuming long time to perform hydrate formation experiments with assisting cooling step to form hydrate within the reactor. In fact, the application of isobar method benefits to prepare a good understanding of hydrate formation process and also it will provide some measurement abilities about the initial hydrate formation temperature, induction time and further analysis such as morphology of hydrate structure.

In comparison, the isobar method has not been used as common as an isochoric pressure research method in the literature. However, the recent interest of forming hydrates in the shorter time and finding induction time has attracted more attention to employ this method in lab scale studies [33, 67-70].

A typical temperature profile versus time during the hydrate formation experiments is demonstrated in Figure 3-5. In general, the hydrate formation reactor operates at constant, pre-set pressure by introducing CO_2 or other gas mixture inside the reactor. Then the pressurised reactor cools down. A sudden increase in temperature during the cooling step indicates hydrate formation as the hydrate formation is an exothermic reaction.
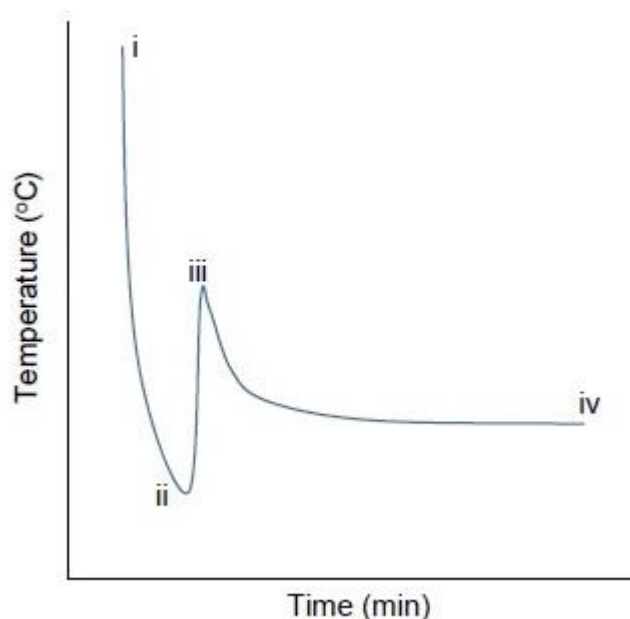
Figure 3-5: A typical temperature profile for isobar method i) initial temperature ii & iii) sudden increase in temperature indicates the hydrate formation iv) equilibrium temperature

In Figure 3-5, the temperature reaches a peak (point 'ii' in the figure) where the heat loss to the cooling bath equals the heat evolved by the hydrate formation. Eventually, the temperature is lowered back to the bath temperature as the hydrate formation diminishes [69].

The isobar method is capable of determining the induction time for hydrate formation even though, the incipient hydrate formation temperature (the temperature located at the valley in Figure 3-5) cannot expect to represent a thermodynamic equilibrium temperature.

Wang et al [33], reported that the stepwise cooling could improve measurements related to the hydrate formation temperature. Moreover, they stated that the repetition of experiments was still argued. Although, the results from the stepwise cooling was much better than a continuous cooling step.

Based on the short description of all possible experimental procedures in the lab scale application and available hydrate formation rig in the CO_2 capture laboratory, the isobaric method is selected as the proper experimental procedure in this thesis. A detailed experimental procedure of this work explains in the following.

3.4 Experimental procedures

Several experiments performed before deciding which experimental method was compatible with the available rig. In addition, the effort in this thesis was to measure some important parameters of hydrate formation.

In particular, attempts in this work were to determine better hydrate formation condition with shorter induction time because achieving these goals makes CO_2 hydrate production more feasible. Moreover, better hydrate formation condition and a good understanding of CO_2 hydrate formation boost the chance of using hydrates as a potential way of transportation. Therefore, it was necessary to form hydrate first and then trying to measure several important parameters.

3.4.1 Materials

The fluid and solid samples were used in the experiments are specified in Table 3-1. Also in Table 3-1, the supplier and purities of the samples are given.

Table 3-1: Material used in the experiments

Fluid and solid	Certified purity	Supplier
tetrabutylammonium bromide (TBAB)	0.99 mass fraction	Sigma-aldrich Co,Germany
tetrabutylammonium fluoride (TBAF)	0.98 mass fraction	Sigma-aldrich Co,Germany
tetrabutylammonium nitrate (TBANO$_3$)	0.97 mass fraction	Sigma-aldrich Co,Germany
tetrabutylphosphonium bromide (TBPB)	0.98 mass fraction	Sigma-aldrich Co,Germany
tetrabutylphosphonium Chloride (TBPC)	0.96 mass fraction	Sigma-aldrich Co,Germany
tetrahydrofuran (THF)	99.9 vol% contains 250 ppm BHT as inhibitor	Sigma-aldrich Co,Germany
water	Degassed and distilled	Laboratory-made

3.4.2 Experimental protocol

The experimental procedure for both batch and semi-batch hydrate formation rigs in the present work was the isobar method. The following steps carried out in order to prepare experiments:

1. Rinsing the cell with distilled water.
2. Degas water for 20 min up to 27 mbar by the use of vacuum machine.
3. Preparing an aqueous solution with different weight percent of additive and degas distilled water.
4. Flushing the reactor with CO_2 up to 2.5 bars to remove residual air from the reactor.

After preparation of the experiment, the isobar protocol was employed to perform experiments. First the temperature of the bath set to 15 °C. When the temperature within the reactor stabilised at 15 °C, CO_2 introduced into the reactor until the desired pressure of the experiment is reached and data acquisition starts recording at the same. Initially, the temperature within reactor increases due to pouring the pressurised cell by CO_2 and then it will go back to the set temperature.

In the next step, the temperature of the thermostat is then set to zero and the pressurised reactor cooled down. A sudden increase in temperature profile during the cooling step indicates hydrate formation as the hydrate formation is an exothermic reaction. The temperature reaches a peak where there is a balance between heat loss to the bath and the heat generated by the hydrate formation reaction. Finally, the temperature is lowered back to the bath temperature as the hydrate formation growth lowered.

Following comments are necessary to mention with respect to the hydrate formation process:

In the batch HFR:

- The magnetic stirrer turned on with a speed of 300 rpm as the CO_2 introduced into the pressurised cell.
- The needle valve mounted at CO_2 inlet line remained open at the pre-set pressure in order to keep the pressure inside the cell constant.
- For an aqueous solution with THF and TBAF, the thermostat temperature set at zero while for other promoters such TBAB, TBPB and TBANO$_3$, the temperature set at -2 °C. It is worth mentioning that the mixture of water and chemical additives in contact with CO_2 will not form ice at -2 °C and 6 bar. Therefore, the slurry components observed within the reactor are hydrates.

In the semi-batch HFR:

- The pressure inside the reactor kept constant by manipulating needle valves (where installed in both inlet and outlet CO_2 line) manually.
- The amount of flow rate of CO_2 controlled visually via looking at bubbles in the liquid phase in order to maintain the flow rate of CO_2 approximately constant in all experiments.

3.4.3 Experiment uncertainties

In order to make a better estimation of the results that have obtained in this thesis, the necessity of determination of experiment uncertainties seems to be unavoidable. However, measurement

of all uncertainties in experiments is not possible at this early stage study. The important factors, which can affect the results, are listed as below:

- Since the chemicals were used in the experiments are highly hydrophilic, therefore, the purity of chemicals would change after opening the cap of the chemical container.
- Setting the pressure at the specific value inside the reactor has been done manually, which led poor deviation from the pre-set pressure during the experiments.
- Employing cooling bath and thermostat led to a difficult adjustment of the temperature inside the hydrate formation reactor.

Beside mentioned factors, there are other parameters which influence the result of experiments. For example, operator mistakes such as delay in turning on the stirrer or cooling down the reactor temperature could make different results. Determination of exact uncertainty needs more investigation which was not in the scope of this works. Moreover, the number of similar studies about the induction time with the continuous flow at the range of studied pressure is limited in the literature. Therefore, the regression analysis at this early stage demands further experiments.

In the present work, the initial hydrate formation temperature and the induction time are studied. Also, the effect of adding thermodynamic promoters such as THF, TBAB, TBPB, TBAF and TBANO$_3$ on hydrate formation is investigated.

Both batch and semi-batch hydrate formation reactor at different pressure values (i.e. 4 and 6 bar) have been used in experiments. Also, the repeatability of the hydrate formation and the impact of adding sand in the reactor is also investigated. The results of experiments and analysis about the achieved data will discuss in the next chapter where all experiment data is reported.

For all experiments, the estimated time to form CO_2 hydrate was 2 hours and then the experiment would stop in order to prepare for next experiment. However, it might not form CO_2 hydrate in 2 hours in some cases.

4 Experiment results and discussion

In this chapter, experiment results of CO_2 hydrate production in the CO_2 capture laboratory will be discussed. The apparatus details and experimental procedure are described in chapter 3. Moreover, batch and semi-batch (continuous gas flow) hydrate formation reactors are employed in this thesis to form CO_2 hydrate in presence of chemical additives under isobaric procedure at 4 and 6 bar.

Investigation of formation properties of clathrates such as the formation temperature and induction time is the aim of this work. The influence of the different type of reactor, chemical promoters, working pressure and adding sand to the hydrate formation reactor will be discussed in the following subchapters.

Before representing the results, it might be a good idea to mention that this work employed an isobaric method for a semi-batch hydrate formation rig which has not been investigated in this way before according to the best knowledge from the literature review. However, a few modifications in available set-up and experimental procedure are required to achieve more accurate and reliable data.

Each experiment was performed twice and the average of results is represented in the tables and figures in this chapter. Also, a period of 2 hours (120 minutes) was considered to form hydrate otherwise the hydrate formation process stopped to perform next experiment. Because the idea in this thesis was to find better mixture which gives shorter induction time, then it could be employed in CCS chain and solid transportation of CO_2 by hydrates [19].

4.1 Comparison between batch and semi-batch reactor

In order to study the impact of reactor type on CO_2 hydrate formation, a mixture of water and different THF concentration was used in both batch and semi-batch reactors. Figure 4-1 and Figure 4-2 show the temperature profiles of CO_2 hydrate formation for a mixture of 5, 10 and 20 wt% of THF at 4 and 6 bar, respectively. In the figures, at the beginning, the temperature profiles declined due to the continuous cooling step. When the hydrate initiated to form a sudden increase in temperature profile occurs because of the exothermic reaction of hydrate formation. The time between starting the experiments and sudden temperature increase is identified as induction time. Then, the temperature would reach a peak where the heat loss to the bath equals the heat generated by the hydrate formation. Finally, the temperature was lowered back to the bath temperature as the hydrate formation rate diminished. Therefore, it is possible to determine the induction time and initial hydrate formation temperature from the Figure 4-1 and Figure 4-2. However, additional figures are concluded in order to interpret the hydrate formation key parameters more clearly.

Figure 4-1 and Figure 4-2 illustrate that employing the semi-batch HFR (continuous gas flow reactor) results in forming CO_2 hydrate faster compared with batch reactor results. Also, the hydrate formation is initiated at a higher temperature when the semi-batch reactor is used in the experiments. Moreover, higher pressure improves the induction time.
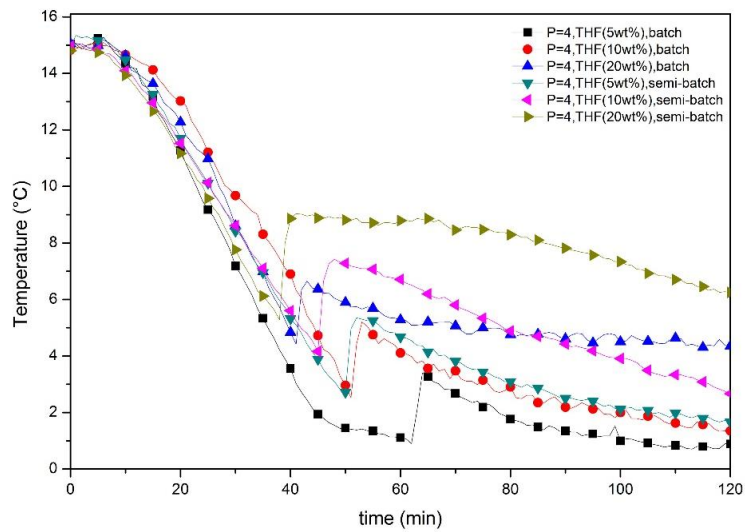
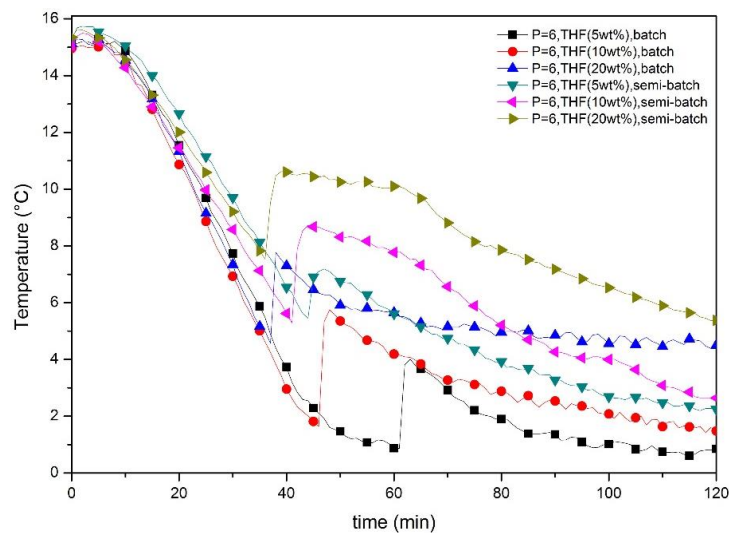Figure 4-1: Temperature profile of batch and semi-batch reactor at 4 bar for different THF concentration

Figure 4-2: Temperature profile for batch and semi-batch reactor at 6 bar for different THF concentration

It is seen from Figure 4-1 and Figure 4-2 that the induction time decreases when the THF concentration increased. This trend in CO_2 hydrate formation by THF was also investigated by other researchers. For instance, Choi et al [67], employed the isobaric method for a mixture of THF and water to form CO_2 hydrate at atmospheric pressure. They also reported that an increase in THF concentration shortened the induction time. Their results are shown in Figure 4-3. A comparison between Figure 4-1 to Figure 4-3 for batch reactors demonstrates that the CO_2 hydrate will be formed in shorter time and higher temperature when the pressure rises. For example, the induction time for 10wt% THF within the batch HFR at 1, 4 and 6 bar is 143, 51 and 47 minutes, respectively.
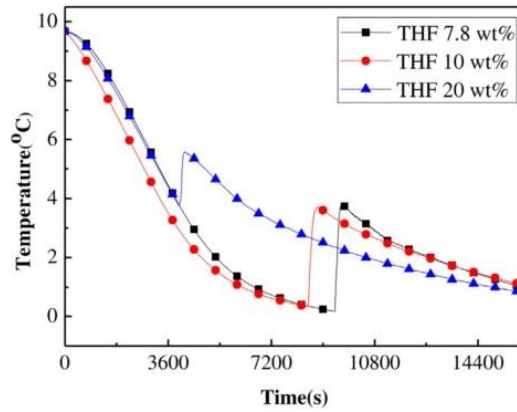
Figure 4-3: Temperature profile of CO_2 hydrate formation at atmospheric pressure for different THF concentration [67]

Figure 4-4 and Figure 4-5 can exploit from temperature profiles during the hydrate formation process in order to provide a better interpretation of the induction time and initial hydrate formation temperature for different types of hydrate formation reactors.

The induction time value for different types of the reactor at 4 and 6 bar is shown in Figure 4-4. From the figure, an increase in the concentration of THF reduces the induction time in both reactors. For instance, the results for 20 wt% of THF is shorter than 10 wt% for both types of reactor. However, CO_2 hydrate is formed faster in the semi-batch reactor in comparison with the batch reactor at the same condition. For example, the induction time of hydrate formation for 5 wt% of THF mixture at 4 bar through the batch reactor is 62 minutes whereas semi-batch HFR in similar condition would form CO_2 hydrate after 50 minutes. In addition, shorter induction time was achieved in the higher pressure and this attitude was similar to both reactors. In general, the shortest induction was obtained by semi-batch reactor at 6 bar with 20% THF concentration.
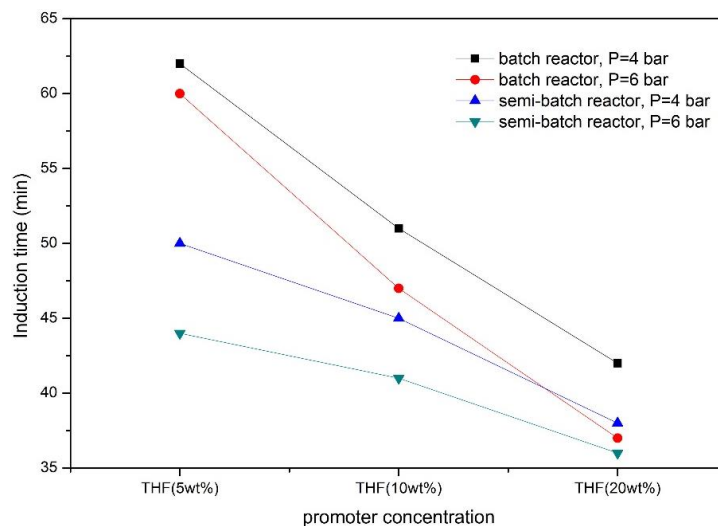

Figure 4-4: Induction time for different concentration of THF at 4 and 6 bar within batch and semi-batch reactor
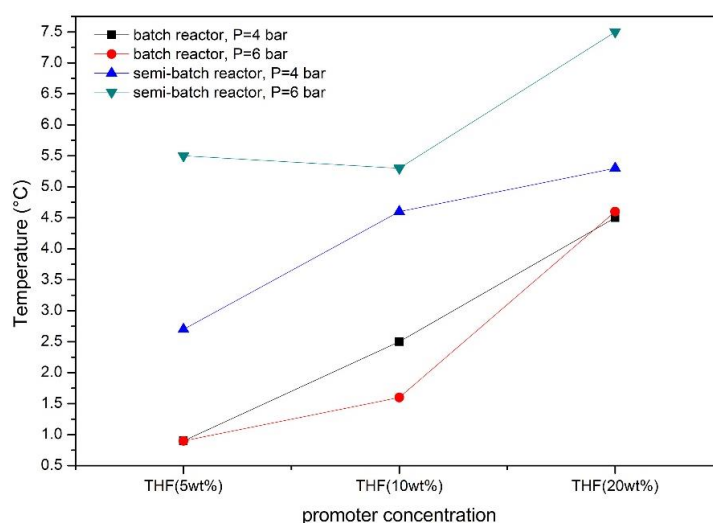
Figure 4-5: The initial hydrate formation temperature for different concentration of THF at 4 and 6 bar within batch and semi-batch reactor

In fact, the interaction between gas and liquid phase improves by CO_2 bubbles through the liquid phase. Thus, the hydrate formation becomes faster compared to the batch reactor which is only agitated via magnetic stirrer.

The initial hydrate formation temperature (the temperature of the valley in Figure 4-1 and Figure 4-2) within a batch and semi-batch reactors at 4 and 6 bar for different THF concentration is shown in Figure 4-5. The results show that CO_2 hydrate formation initiated at a higher temperature while semi-batch HFR was employed in the experiments. For instance, the initial hydrate formation temperature for 20 wt% of THF at 6 bar was 7.5 °C and 4.6 °C for semi-batch and batch reactor, respectively. An increase in a pressure enhances the initial hydrate formation temperature. On the other side, the effect of increasing THF concentration was the same for both reactors where the initial hydrate formation temperature increased at higher THF concentration.

4.2 Different chemical promoters within semi-batch reactor

In order to determine the effect of adding the promoters on CO_2 hydrate formation key parameters within the semi-batch reactor, different additives such as THF, TBAB, TBPB, TBAF, TBPC and $TBANO_3$ are investigated in this section.

In general, result presentations with respect to mole% of additives is preferable in scientific studies because of preparing a better comparison between different cases. However, a great difference between the molar weight of THF and other promoters (e.g. TBAB, TBPB,...) is a challenge. For example, in order to have an aqueous solution with 1 mole% of additive, the mass fraction of promoter would be 5 and 20wt% of the mixture for THF and TBAB,

respectively. Therefore, a greater amount of chemical is needed when TBAB, TBPB or other salts is used for CO_2 hydrate formation.

On the other hand, the amount of chemical in the lab was limited and it was not possible to have a wide range of mass fraction of promoters during the hydrate formation experiments. Thus, the results are presented in two parts where the first part is based on the different mass fraction of promoters and the second part is discussed with respect to mole% of various tetraalkyl ammonium/phosphonium salts.

The effect of adding a different concentration of THF, TBAB and TBPB within the semi-batch reactor at 4 and 6 bar on induction time is shown in Figure 4-6. The mass fraction of 5, 10 and 20 wt% of promoters was considered in CO_2 hydrate formation process. It should mention that Figure 4-6 is exploited from the temperature profiles of different THF, TBAB and TBPB concentration which is available in appendix 2.

Figure 4-6 shows when THF was employed as a promoter, the shortest induction time was obtained in comparison with TBPB and TBAB. However, it is noticed again that a certain mass fraction of promoters does not include the equal number of moles of a promoter which can affect the results. But the focus in this part is on mass fraction as comparison criterion.

Also, an increase in promoter concentration leads to a reduction in induction time. For example, the induction time for a mixture of 5 wt% of THF at 6 bar was 45 min whereas the induction time for 20 wt% of THF at 6 bar decreased to 35 min.

The common order of better reduction in induction time at the same condition (i.e. at a similar mass fraction of promoter and pressure condition) is THF, TBPB and TBAB, respectively. Moreover, the higher pressure, the shorter induction time would obtain. As an example, the induction time for a mixture of 10 wt% of TBPB at 4 and 6 bar had the induction time of 75 and 70 min, respectively. This behaviour is similar for THF, TBAB and TBPB.
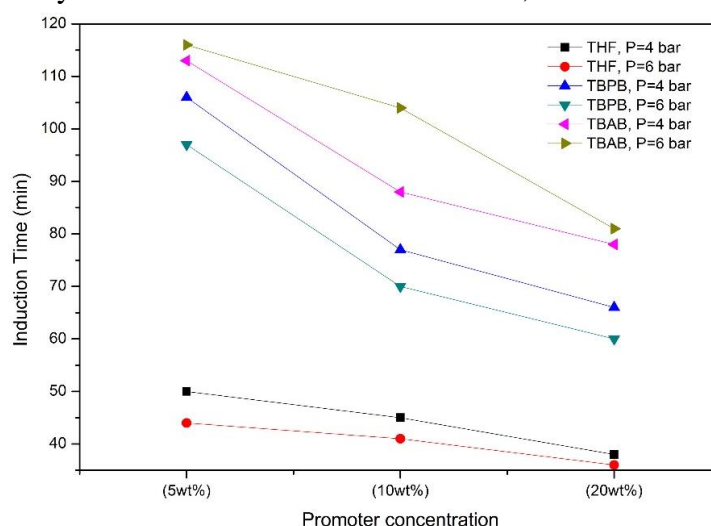

Figure 4-6: Induction time of different concentration of THF, TBAB and TBPB within the semi-batch reactor at 4 and 6 bar

The effect of adding different promoters within the semi-batch reactor at 4 and 6 bar on the initial hydrate formation temperature is demonstrated in Figure 4-7.

From Figure 4-7, THF initiated to form hydrate at a higher temperature than TBAB and TBPB at any specific promoter concentration. While the lowest initial hydrate formation temperature was observed in TBPB mixture. However, an increase in promoter concentration from 5 wt% to 20 wt% resulted in higher initial hydrate formation temperature for all promoters. For instance, the initial hydrate formation temperature at 6 bar for a mixture of 5, 10 and 20 wt% TBAB was -1.3, -0.2 and 2.3°C, respectively.

Also, the initial hydrate temperature was higher at 6 bar for a particular concentration of promoter compared with experiment result at 4 bar. Although, the pressure effect on the initial hydrate formation temperature was not considerable for all concentration of TBPB mixtures at 4 and 6 bar.
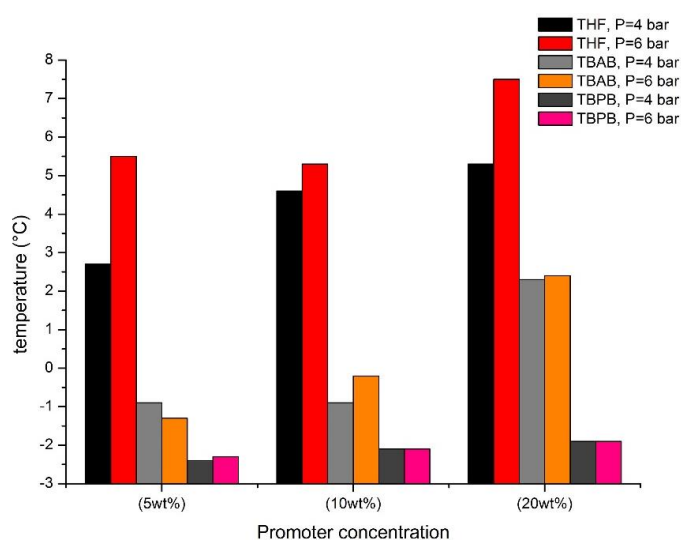

Figure 4-7: The initial hydrate formation temperature of different concentration of THF, TBAB and TBPB within the semi-batch reactor at 4 and 6 bar

The observations from Figure 4-6 and Figure 4-7 show that TBAB has longer induction time than TBPB, although the initial hydrate formation temperature of TBAB is lower than TBPB. In general, shorter induction time is obtained at a higher temperature of the initial hydrate formation. However, this general tendency was not followed by a mixture of TBAB.

In order to have a fair comparison between different tetraalkyl ammonium/phosphonium salts during the CO_2 hydrate formation process, 0.3 mole% of $TBANO_3$, TBAF, TBAB, TBPB and TBPC was employed to form hydrate at 4 and 6 bar. This mole fraction accounts as almost 5 wt% of the solution.

The temperature profile for 0.3 mole% of different chemical additives at 4 bar is shown in Figure 4-8. The main point in Figure 4-8 is that TBPC and $TBANO_3$ did not form CO_2 hydrate during 120 min. Therefore, there is no temperature peak for both of them in the temperature profiles. Moreover, TBAF had the shortest induction (i.e. 35 minutes) whereas the induction time for TBPB and TBAB at the similar condition was 105 and 115 min, respectively. On the other side, shorter induction time of a mixture of 0.3 mole% TBAF is coupled with higher initial hydrate formation of 4.8°C. While the initial hydrate formation temperature for a mixture of TBAB and TBPB is much lower that TBAF.
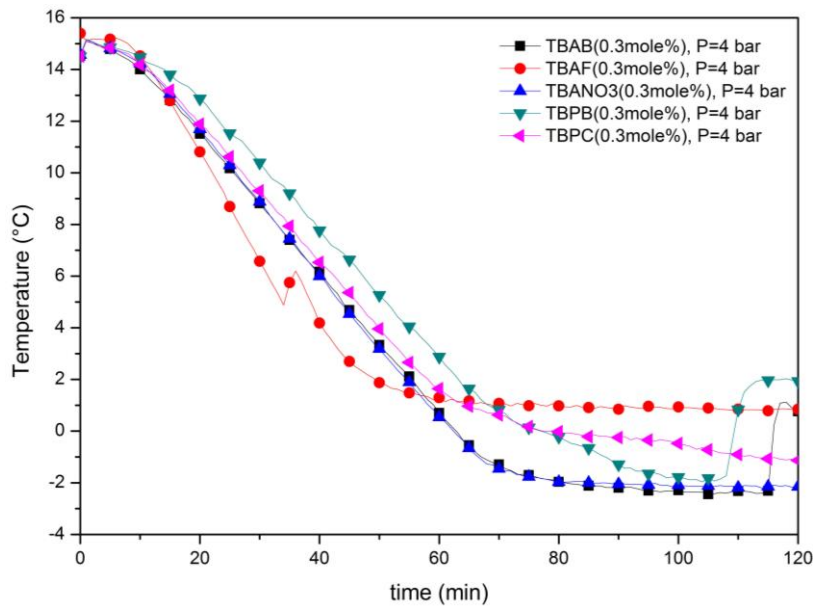
Figure 4-8: Temperature profile for 0.3 mole% of different chemical additives at 4 bar

The temperature profile for 0.3 mole% of different chemical additives at 6 bar is shown in Figure 4-9. Again a mixture of 0.3 mole% of TBANO$_3$ did not form CO_2 hydrate after 120 min while TBPC formed hydrate after 118 minutes. Increasing experiment pressure to 6 bar led to form CO_2 hydrate after 30 minutes in a mixture of 0.3 mole% of TBAF. Also, the induction time decreased in both 0.3 mole% of TBPB and TBAB solution at 6 bar compared with results in Figure 4-8. It means that the induction time reduces at higher pressure and also CO_2 hydrate formation is facilitated at higher pressure.
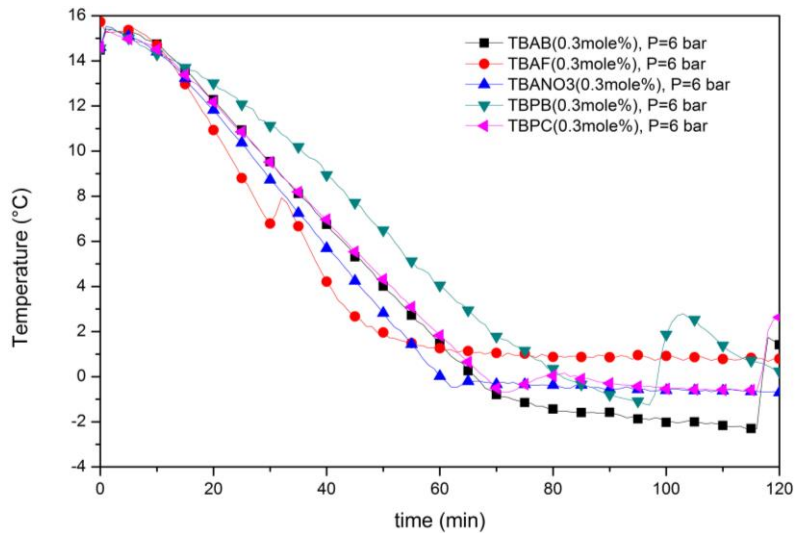

Figure 4-9: Temperature profile for 0.3 mole% of different chemical additives at 6 bar

From Figure 4-8 and Figure 4-9, it can be concluded that 0.3 mole% of TBAF has shortest induction time among all other promoters. In addition, 0.3 mole% of TBANO$_3$ is not sufficient

amount of promoter to form CO_2 hydrate before 120 minutes at both 4 and 6 bar. Therefore, a greater amount of $TBANO_3$ and TBPC should use to form hydrate at this range of pressure.

Since only one single mole fraction of the different promoter is used to form the CO_2 hydrate, so it is not possible to determine the best promoter here. However, it is clear that TBAF has a better effect on induction time and initial hydrate formation temperature.

4.3 Adding sand into the reactor

One idea to increase the initial hydrate formation temperature is to add fine particle like sand within the reactor. Generally, the existence of fine sand inside the reactor facilitate to reach the equilibrium condition of hydrate formation. In order to demonstrate this idea within the batch reactor, several experiments were performed with a mixture of 20 wt% of THF at 4 bar. In each experiment, 3 gr of sand with different size was placed at the bottom of the batch reactor.

The temperature profiles during the CO_2 hydrate formation for different sand size is illustrated in Figure 4-10. As it is seen in Figure 4-10, adding sand has a significant influence not only on the induction time but also on the initial hydrate formation temperature. In fact, the hydrate formation started in fairly same time and temperature in all size distribution of sand.
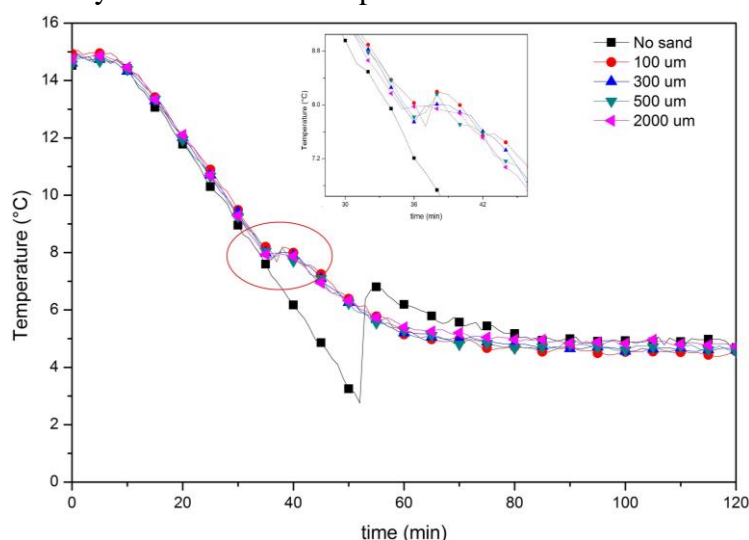
Figure 4-10: Temperature profiles for a mixture of 20 wt% THF at 4 bar by adding different sand size into the batch reactor

From Figure 4-10, it is seen that the peak temperature in temperature profiles are close to the initial hydrate formation temperature. It shows that adding sand into the reactor brings the initial hydrate formation temperature close to CO_2 hydrate equilibrium temperature since the hydrate formation does not generate very much heat due to the exothermic reaction of hydrate formation. Therefore, the temperature within the reactor did not increase significantly as the cooling bath was able to compensate the amount of evolved heat during the initial hydrate formation quickly.

Both the induction time and the initial hydrate formation temperature for different sand size is demonstrated in Figure 4-11. Adding sand into the batch reactor by itself causes to increase the initial hydrate temperature from 2.5°C to approximately 7.5°C (red plot in Figure 4-11).

However, the size of sand does not have a huge impact on the initial hydrate formation temperature. Although the bigger size of sand resulted in higher temperature but the temperature changes are not significant. In fact, sand particles help to reach the hydrate formation equilibrium faster.

Moreover, the induction time reduces from 55 minutes to almost 35 minutes when the sand was added to the reactor. The impact of adding sand on induction time is not dependent on sand size distribution where the induction time remained almost steady for different sand size. However, before running the experiments, it was expected that finer sand particles would result in shorter induction time while the results illustrated that the sand size does not have very much influence on induction time.
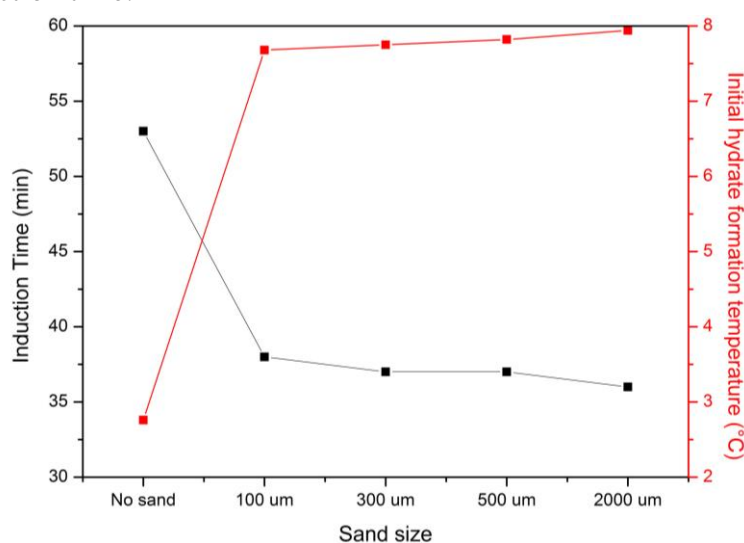
Figure 4-11: Induction time and initial hydrate formation temperature for a mixture of 20 wt% THF at 4 bar by adding different sand size into the batch reactor

4.4 Repeatability of CO_2 hydrate production

In this section, the effect of water memory on CO_2 hydrate formation parameters through repeatable cycles of the aqueous solution is investigated. To perform the repeatability experiments, a mixture of 20 wt% THF at 4 bar was employed within the batch reactor.

The variation of temperature was recorded during 7 cycles of CO_2 hydrate formation and dissociation. The 1st, 3rd and 7th CO_2 hydrate formation is demonstrated in Figure 4-12. As it is observed from Figure 4-12, the CO_2 hydrate formation initiated after 50 minutes. While the induction time decreased for the later cycles, for instance, the induction time for the 7th CO_2 hydrate formation reduced to 40 minutes. In other words, the time used for the 7th cycle to form CO_2 hydrate formation accounts as 80% of the time needed for the 1st cycle. Moreover, the initial hydrate formation temperature from almost 4.5°C for the 1st cycle to approximately 7°C for the 7th cycle of CO_2 hydrate formation.

Therefore, the repeatability of CO_2 hydrate formation and dissociation contributes not only a reduction in the induction time but also an increase in the initial hydrate formation temperature which both effects are in favour. In fact, the concept of recycling the CO_2 hydrate in a

formation/dissociation cycle enhances the applicability of CO_2 hydrate as a good alternative to CO_2 transportation in the solid-phase.
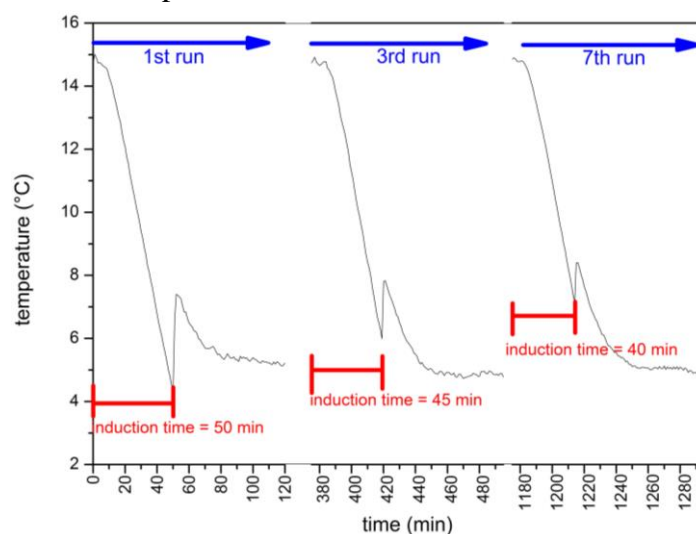

Figure 4-12: Temperature profile for a mixture of 20 wt% THF at 4 bar within the batch reactor.

4.5 Laboratory observation

In addition to described experiments, various tests have performed due to curiosity. However, measurement of observations was not in the scope of present thesis. Indeed, generating new concepts concerning CO_2 hydrate transportation needs the examination of different ideas, which can be appropriate to employ in CCS chain by hydrates.

4.5.1 CO_2 hydrate dissociation

The first examination attributed to the idea that the transported CO_2 hydrate can dissociate to a mixture of water + promoters through releasing the trapped CO_2 molecules. Thus, it prepares the possibility of recycling the mixture to the CO_2 hydrate production plant while the released CO_2 molecules utilised later.

An increase in temperature of hydrate is a typical method of hydrate dissociation. During the first examination, the produced CO_2 hydrate was kept at room temperature. The CO_2 hydrate dissociation progress at room temperature is shown in Figure 4-13. It is observed that the required time to dissociate CO_2 hydrate at room temperature was 70 minutes approximately. After 70 minutes, there were no visible hydrate nuclei within the mixture. In Figure 4-13, the released CO_2 molecules from the water lattice in form of bubbles are illustrated in part 'b'. Moreover, the degassed solution (part 'c' in Figure 4-13) was used in the next hydrate formation process and the mixture could form CO_2 hydrate again.

Observations from the test supported the idea of reusing the aqueous solution in CCS chain by hydrates, although, a deep understanding and measurement are required before any utilisation. For instance, determination of adequate temperature for hydrate dissociation or measurement of CO_2 losses during the CO_2 hydrate transportation and dissociation are attractive research topics in this field.
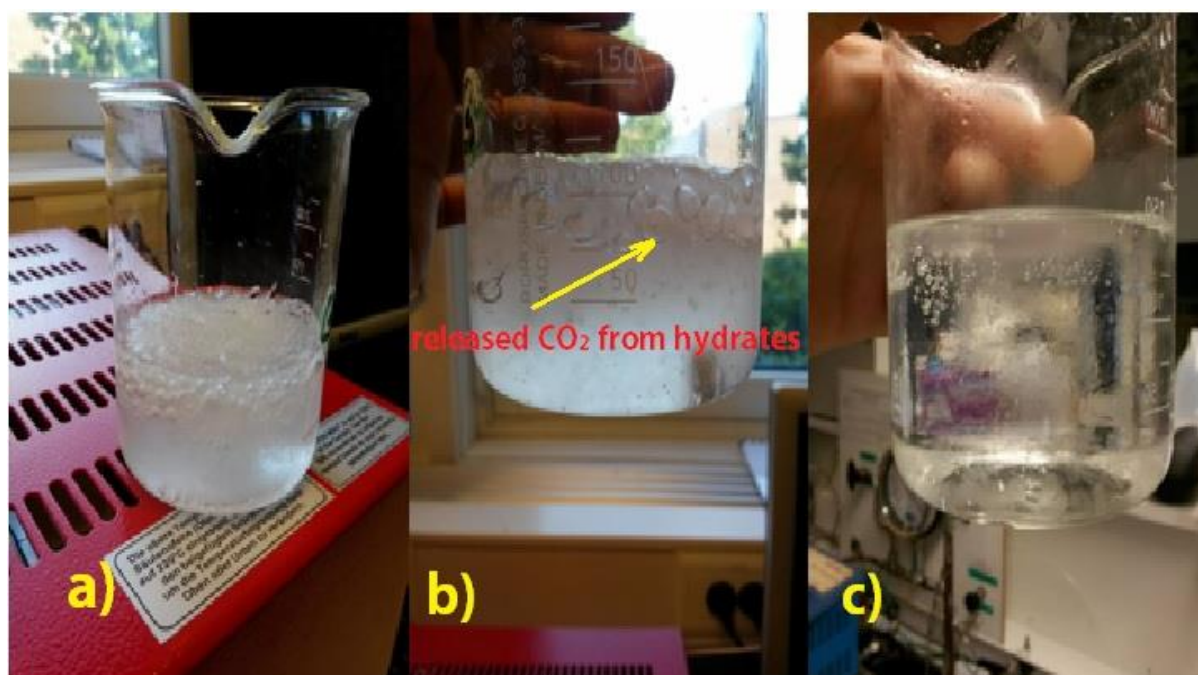
Figure 4-13: CO_2 hydrate dissociation progress at room temperature.

4.5.2 CO_2 hydrate squeezing

Packing the CO_2 hydrates in the purpose of solid-phase hydrate transportation seems to be essential particularly when the CO_2 hydrate transportation employs the ship cargo. The next tests examined the effect of squeezing CO_2 hydrates.

The visual observation indicates that the squeezed hydrate needs longer time to dissociation. For example, the time needed to dissociate the squeezed CO_2 hydrate at room temperature increased to 100 minutes.

In addition, compacting CO_2 hydrate resulted in very dense solid- phase hydrates whereas the excess water molecules removed from the hydrate. Therefore, the volume of CO_2 hydrate decreased significantly. However, the amount of CO_2 losses during the squeezing is not clear. The other observation regarding the squeezing of CO_2 hydrate is that produced hydrates by tetraalkylammonium/phosphonium salts such as TBAB was more compactable in comparison with hydrates formed in presence of THF. It means that the occupied volume by hydrates, which were produced in presence of tetraalkylammonium/phosphonium salts, is less after squeezing CO_2 hydrates. Observations showed that the transportation of solid-phase hydrates has the potential in CCS chain since handling the solid particles that can be compacted is always favorable at large scale applications.

4.5.3 Metastable condition of CO_2 hydrate

The utilisation of CO_2 hydrate in transportation requires proper conditions that give the possibility of solid from CO_2 hydrate handling. Transportation of natural gas hydrate at

metastable condition (i.e. at atmospheric pressure and below zero degrees) has been studied by literature. However, there is not enough data of CO_2 hydrate handling at the metastable condition.

In this part, tests performed in order to check the metastable condition for CO_2 hydrate. When the CO_2 hydrate formed within the reactor, the CO_2 gas released from the reactor to achieve atmospheric pressure. Then, the temperature inside the reactor reduced to -10°C and the reactor kept in this condition for one hour. The frozen CO_2 hydrate after the test is demonstrated in Figure 4-14.

Figure 4-14: The frozen CO_2 hydrate

Observations illustrate that the CO_2 hydrate will freeze at below zero degree temperature and it will form a solid-phase hydrate. However, the amount of CO_2 trapped in the frozen form of hydrate was not measured.

Forming frozen CO_2 hydrate vindicates the concept of transportation of CO_2 through hydrate formation at solid-phase, even though, there is still much unknown information about CO_2 hydrate at the metastable condition. This information includes a wide range of measurements such as CO_2 content in the frozen hydrate, the optimal temperature of achieving metastable condition for CO_2 hydrate, the formation of an ice-like shield surrounded the CO_2 hydrate and many other research topics, which have not been investigated yet.

5 Conclusion

In this study, a comparison between batch and semi-batch hydrate formation reactor has been performed. Moreover, the impact of different chemical promoters, operational pressure and adding sand to the hydrate formation reactor was discussed in order to measure the hydrate key parameters such as induction time and the initial hydrate formation temperature.

The results from different types of reactor showed that the required time in order to initiate CO_2 hydrate formation reduced as the semi-batch reactor was employed. In addition, the initial hydrate formation time was higher within the semi-batch reactor. On the other hand, an increase in chemical concentration or pressure inside the reactor decreased the induction time in both reactors. However, the amount of reduction in induction time was greater at the semi-batch reactor in comparison with the other reactor type when the pressure inside the reactor was 6 bar.

The temperature profiles during the hydrate formation progress illustrated that the induction time reduced while the concentration of chemical promoter increased (i.e. from 5 wt% to 20 wt% of mixture). At the same time, the shorter induction time resulted in higher the initial hydrate formation temperature. Nevertheless, THF could form CO_2 hydrate at shorter induction time compared with TBAB and TBPB whereas the common order of better reduction in induction time at the same condition (i.e. at a similar mass fraction of promoter and pressure condition) is THF, TBPB and TBAB, respectively.

Also, the experiments presented that salts the TBAF had the shortest induction time and the highest initial hydrate formation temperature among all studied promoters when the 0.3 mole% of tetraalkylammonium/ phosphonium salts was used. Even though, a mixture of 0.3 mole% of $TBANO_3$ did not form CO_2 hydrate at 4 and 6 bar after two hours. Therefore, the adequate mole fraction of TBANO3 to form CO_2 hydrate at 4 or 6 bar seemed to be greater than 0.3 mole%.

In general, it can be concluded that the semi-batch reactor forms CO_2 hydrate faster and at a higher temperature compared with the batch reactor. Furthermore, an increase in pressure or chemical concentration will reduce the induction time of hydrate formation.

Adding sand particles into the batch reactor showed that the induction time decreased significantly. In addition, the initial hydrate formation temperature approached to the hydrate equilibrium temperature. However, an alteration in the sand size within the reactor did not influence on the induction time and the initial hydrate formation temperature remarkably. Although, the larger size of sand performed better.

Repetition of hydrate formation/dissociation cycle showed that the induction time decreased about 20% after 7th cycle and the initial hydrate formation temperature increased. The temperature profiles of hydrate formation and dissociation progress after several cycles illustrated that the hydrate would form in a shorter time due to water memory effect of an aqueous solution.

Besides the experiments were designed to measure the hydrate formation parameters, observations in CO_2 capture laboratory from the arbitrary tests approved the capability of CO_2 hydrate as transportation method in CCS chain. Consideration of squeezing CO_2 hydrates,

repeatability of CO_2 hydrate formation/dissociation cycle and metastable condition of CO_2 hydrates encourages the utilisation of CO_2 hydrate as an alternative in CO_2 transportation.

6 Further work

The gas hydrate consists of a wide field of studies from the prevention of hydrate formation to the acceleration of hydrate formation. Further questions and modifications regarding the aim of every research are generated in the field of study. While responding to those questions will enhance the understandings in order to exploit in large-scale applications.

As mentioned in previous chapters, the CO_2 hydrate has the potentiality of handling CO_2 in CCS chain. The results in the present work approved the possibility of CO_2 hydrate formation at low pressure in presence of chemical promoters despite the fact that further experiments should perform in order to achieve data with high accuracy. Suggestions for future work can be categorised into two sections: development of experimental apparatus and investigation of important hydrate formation parameters.

The disability of measuring flow rates is the main shortage of the available apparatus. Therefore, the next modification of the hydrate formation rig should focus on determination of the gas flow rates and hydrate formation rate within the reactor. By possibility of measuring hydrate formation rate, measurement of the gas consumption during the hydrate formation is achievable. Moreover, the ability of in-situ gas analysis helps to determine the gas composition in the outflow from the reactor when a mixture of different gas is used in hydrate formation.

In fact, the modification regarding gas hydrate apparatus has to be compatible with the aim of the study. The ideal hydrate formation apparatus must have multiple units such as hydrate formation unit, hydrate dissociation unit, gas composition analysis unit, gas flow measurement unit and hydrate compactor unit. If continuous flow hydrate formation is favourable in the lab-scale studies, the possibility of recycling excess gas from the reactor should be considered because of prevention of releasing CO_2 from the rig. In addition, installation of appropriate valves seems to be necessary to control the pressure through the apparatus especially within the reactor. Consideration of heat removal from the hydrate reactor is vital which leads to select better equipment i.e. selection of better cooling bath and thermostat.

On the other side, spraying gas of liquid inside the hydrate formation reactor seems to be more efficient, however, this method has not been investigated widely. Therefore, the mechanical adjustment such as employing spray type of hydrate formation reactor can be considered in the future work.

Besides the apparatus modifications, there are several concepts that need to be perused in future work. The utilisation of CO_2 hydrate transportation in CCS chain is an alluring idea, but the lack of knowledge of CO_2 hydrate handling requires to design various experiments.

The future work must be able to provide practical information in order to obtain applicable condition regarding shorter induction time, lower hydrate formation pressure, higher CO_2 uptake in hydrate, optimal hydrate dissociation condition, the compressibility of CO_2 hydrate and metastable condition of CO_2 hydrate. Each one of these favourable conditions needs to be clarified in details with particular emphasise on CO_2 transmission by hydrates.

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Appendix

Appendix 1: Task description

Appendix 2: Temperature profiles of different THF, TBAB and TBPB concentration

Appendix 1: Task description

University College of Southeast Norway

Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: Embryo research of a reactor to produce CO_2 hydrates

USN supervisor: Dag Eimer

External partner: Tel-Tek

Task background:

This thesis is related to CO_2 as a greenhouse gas. CO_2 hydrates represent a potential way of transporting CO_2 that might otherwise be challenging to move. We are developing this as a concept for which we need to have information enabling the preliminary design of a reactor to produce said hydrates.

Task description:

There will be an apparatus available in our laboratories in which realistic experiments can be made to determine parameters important for the formation of said hydrates. The student is expected to make measurements and analyse the data, possibly using some regression analysis. The data should be put into context and a reactor proposal be developed. The work should be of such quality that publication of results are possible.

Student category: PT, EET

Practical arrangements:

Laboratory facilities are available. The student will become part of an active research group for the period with good access to tuition and help with troubleshooting from supervisors.

Signatures:

Student (date and signature):   1/2-2017   HASHEMI

Supervisor (date and signature):   Dag Eimer

Address: Kjølnes ring 56, NO-3918 Porsgrunn, Norway. **Phone**: 35 57 50 00. **Fax**: 35 55 75 47.

Appendix 2: Temperature profiles of different THF, TBAB and TBPB concentration

Appendix