Desorption of Dissolved Carbon Dioxide from Water by using Converging Nozzle: Effect of Pressure

By

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MIRZA TARMIZI BIN OTHMAN

ABSTRACT

Nowadays, the exploration of natural gas from oil rig is very important to support world's demand in many sector. However, natural gas that are obtained from offshore is not free from contaminants such as Carbon Dioxide. High concentration of Carbon Dioxide in natural gas cannot be allowed to be further process due its acidic property which can led to pipeline corrosion. Currently, there are many technologies that have overcome this problem such as by using chemical absorption, physical absorption and membrane technologies. However, most of the current technologies cannot help to remove Carbon Dioxide directly on offshore. Due to that, an efficient and compact separator need to be applied on there. The objectives of this study is to analyze desorption phenomenon and process of dissolved CO_2 from water across the converging nozzle by conducting an experiment in the laboratory. Effectiveness of the converging nozzle are also measured from that. Effect of pressure and pressure drop occur across the converging nozzle are the main parameters that affect the desorption rate of CO_2 from water. From the study conducted, it is shown that as the pressure set to the system is higher, the pressure drop across the converging nozzle also would be higher. It is also found that desorption process of dissolved CO_2 from water increase when the pressure of the system is set at higher value and the pressure drop occur across the converging nozzle is higher.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Natural gas can be characterized as a type of fossil fuels that are formed over a millions years ago. It is formed by the decomposition process of a living matter such as animals, plants and even microorganism after they exposed to a high amount of energy underground (Bakar, 2010). It is a type of non-renewable energy as it cannot be made by human.

With the continuous development of the world, the exploration for natural gas is very important to support human demands. Natural gas can be used and applied in many sector. According to Bakar (2010) 32% of natural gas has been applied for industrial purpose, 24% for electric generation, 22% for residential (cooking purpose), and 22% for commercial uses. Since it has a good market value, the exploration and production of natural gas is a very profitable business. However, most of natural gas extracted from oil rig is not free from contaminants especially CO_2. Currently, there are many technologies that help to overcome the problem such as physical absorption, chemical absorption, membrane technologies and cryogenic distillation. However, most of the technologies cost a lot of money and the process of CO_2 removal cannot be done directly on oil rig. Because of that problem, this project entitled “Desorption of Dissolved Carbon Dioxide from Water by using Converging Nozzle: Effect of Pressure” is develop.

Basically, the main focus area for this study is the regeneration process of physical solvent which is water from CO_2 through desorption process. Desorption of dissolved CO_2 from water occur through converging nozzle. The main parameter chosen for this study is the pressure of the system as the water content with CO_2 flows through the converging nozzle. The effect of pressure set to the system and how much pressure drop will occur across the converging nozzle will be investigated in this study to see how it will affect the process of desorption of dissolved CO_2 from water after it flows through the converging nozzle.

1.2 Problem Statement

Natural gas obtained from offshore usually will have a high concentration of Carbon Dioxide. Even in Malaysia the composition of Carbon Dioxide in natural gas is greater than 20 wt % (Mokhatab et al. 2007). Due to its acidic property, removal Carbon Dioxide from gas stream is very crucial. Pre-treatment of natural gas usually involves two process which are absorption and desorption. Currently, most of the techniques used to remove CO_2 from natural gas cannot be done directly on offshore. This is because most of the techniques might require a huge amount of area for the construction of an equipment such as desorption column. There is low possibility to build such a tower in the middle of the sea. Due to that constraint, natural gas needed to be transport to onshore to be treated. During the transportation process of natural gas from oil wells to onshore, Carbon Dioxide content which has acidic property in natural gas may cause corrosion and damage to the pipeline system (Mukhtar, 2012). This will lead to loss for a company as pipeline might cost a million tons of money.

Other than that, most of the techniques used to extract CO_2 from natural gas might consume a large amount of energy. T.Yeh et al (2006) state that even the current technology of Carbon Dioxide removal will reduce energy efficiency of utility steam plants by about 30% and will increase the cost of electricity by 80%. Apart from that, most of the current researches only focus on how to enhance desorption process of dissolved Carbon Dioxide from solvent by using several type of columns or membranes as a separator mechanism. There are a very limited researches focus on desorption process of dissolved Carbon Dioxide from water by using converging nozzle as a separator mechanism.

Since that, a compact and efficient separator for desorption purpose is needed to be applied at offshore platform. By using converging nozzle, the removal of Carbon

Dioxide also can be done directly in offshore in a most cost effective way. This is because the size of converging nozzle is compact when compare to size of other equipment such as desorption column which suits the purpose. So, it will not consume a large area and it is applicable to be install in the middle of the sea. Since its size is smaller, the cost of installing it might be cheaper compare to other technologies. Other than that, this technology does not required complexity such in membrane technology. The process is quite simple and straight forward.

Desorption of dissolved Carbon Dioxide from water is important as water used for absorption process of Carbon Dioxide need to be regenerated to be used again in a recycle process routes. This will help to reduce cost of utility. Other than that, water with high concentration of Carbon Dioxide cannot be flow straight away to environment as some of the Carbon Dioxide molecules will react with water molecules to form a weak solution of Carbonic acid. High value of Carbonic acid will increase the acidity of soil and sea and hence it will disturb the natural balance of aquatic life.

1.3 Objectives

The main aim of this project is to;

- To measure the effectiveness of converging nozzle on desorption process of dissolved CO_2 from water at different pressure based on the amount of CO_2 desorbed from water.
- To investigate the effect of pressure and pressure drop across converging nozzle on desorption process of CO_2 from water after flowing through the converging nozzle.

1.4 Scope of Study

The study of this project will cover in several area of study which are:

- Thermodynamic solubility theory of dissolvability of Carbon Dioxide in water
- Fluid hydrodynamic in converging nozzle
- Effect of pressure and pressure drop across converging nozzle on desorption rate of dissolve Carbon Dioxide from water.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Gas

Natural gas is a type of fossil fuels that are formed over a thousands or millions years ago by the decomposition process of a compressed living matters such as plants, animals and micro-organisms when the layers of this things are exposed to a great amount of light, heat and pressure (Bakar, 2010). It is a type of non-renewable energy as it cannot be made by human. Some other theory said that the natural gas is formed by a biogenic processes where it occurs deep under the earth crusts as deep under the earth crust there are contained rich amount of hydrogen and carbon molecules (NaturalGas.com 2010). These gases may react with the minerals contain deep under the crusts and by time the gases will rise to the surface of the earth. From the reaction it will form a gaseous molecules which contain several type of gases such as nitrogen, carbon dioxide, oxygen, and sometimes inert gases (NaturalGas.com 2010). This natural gas have properties like colorless, shapeless and odorless in its pure form. Natural gases is largely used as a source of energy in many application such as cooking, as a fuels for furnace in plant and many more.

Natural gas is divided into two, sour gas and sweet gas. Sour gas is a natural gas which contain significant amount of Hydrogen Sulfide (H_2S) and Carbon Dioxide (CO_2) while Sweet gas is a natural gas which does not contain significant amount of Hydrogen Sulfide (H_2S) and Carbon Dioxide. Determination of sour gas is determine if the natural gas contain more than 4 ppm of H_2S and CO_2 by volume in a room temperature and pressure (NaturalGas.com 2010).

Usually in oil wells, natural gas that being process will have different composition of components depending on the depth, location and geology of oil wells (Sapkal, 2013). During the process of oil rig, usually crude oil and natural gas are found together and since natural gas is far lighter than crude oil, natural gas will be extracted first. However, according to Mukhtar et al (2012) the composition of component in natural gas may be different with the time. This is because some small hydrocarbon molecules within the range from two until eight will react with methane which in gaseous state to form heavier component which in liquid state (Mukhtar et al, 2012). This component also known as natural gas liquid (NGLs). Table 1 shows the composition of component in natural gas in some part of the world including Malaysia.

Table 1: Chemical composition of natural gas in some part of world in volume (%)

Component	Groningen (Netherlands)	Laeq (France)	Uch (Pakistan)	Uthmaniyah (Saudi Arabia)	Ardjuna (Indonesia)	Terengganu (Malaysia)
Methane	81.3	69	27.3	55.5	65.7	50
Ethane	2.9	3	0.7	18	8.5	10
Propane	0.4	0.9	0.3	9.8	14.5	5
Butane	0.1	0.5	0.3	4.5	5.1	unknown
Heavy Component	0.1	0.5	-	1.6	0.8	unknown
Nitrogen	14.3	1.5	25.2	0.2	1.3	unknown
Hydrogen Sulfide	-	15.3	-	1.5	-	1
Carbon Dioxide	0.9	9.3	46.2	8.9	4.1	20

(Mokhatab et al. 2007; Bakar and Ali 2010)

2.2 Importance of Carbon Dioxide Removal

From table 1, it is observe that composition of Carbon Dioxide is quite high for most kind of natural gas including in Malaysia. Carbon dioxide should be removed from natural gas at offshore as it will affect natural gas market and selling price. This is because carbon dioxide has acidic and corrosive property. If natural gas which contain large amount of carbon dioxide and flow through a pipeline, it will cause corrosion and damaging the pipeline and equipment. This may result loss of a company as the pipeline used may cost a millions of Ringgit or Dollars.

According to Mukhtar (2012), in Liquefied Natural Gas (LNG) process plant, Carbon Dioxide may be frozen and block the flows in pipeline system during the process of cooling natural gas to a very low temperature to let the natural gas to condense to liquid. This may cause a huge problem because gas or liquid cannot flow through pipeline and sometimes high pressure air also cannot remove the frozen carbon dioxide. If this case occurs, the only things to troubleshoot the problem is to shut down the plant and cut the pipeline. This problem will cause a loss of millions of money.

2.3 Current Techniques of Carbon Dioxide Removal

Since Carbon Dioxide removal is very significant for the sake of the plant system, many oil and gas company had invest their money to the technologies that will help the process. The technologies develop is very important in order to keep the quality of the natural gas follows the specification required to be further process. In this section author will explain some of the technologies that world has develop to help the process of Carbon Dioxide removal

2.3.1 Chemical Absorption and Desorption Technique

For chemical absorption, sorbent are used to absorb and separate Carbon Dioxide from natural gas. The relativities and selectivity of the sorbent is very significant for this process as it will determine how much carbon dioxide can be absorbed. The reaction between the sorbent and the Carbon Dioxide molecules need to be a reversible as spent sorbent need to be regenerate to be used again. There are many type of sorbent can be used for the process such as MEA, alkali carbonate, alkanolamines, and aqueous ammonia. As the binding interaction between the sorbent molecules and carbon dioxide is very strong, the process of the carbon dioxide removal could be very effective and efficient. However, due to that cause, there is a rise concern on the regeneration of the sorbent. Because the binding force is too strong, regeneration of the sorbent may be very difficult and the energy consumption to regenerate the sorbent may be very high. When the energy consumption is very high, more cost are needed to done the process. There are also concern about the other acidic impurities in natural gas such as oxygen and hydrogen sulfide that may attach the sorbent and cause the sorbent to degrade (Chen, 2010). Other than that, because of the property of the common sorbent are corrosive, only a diluted solution of the sorbent usually around 18% for MEA are suitable for the process purpose (Chen, 2010).

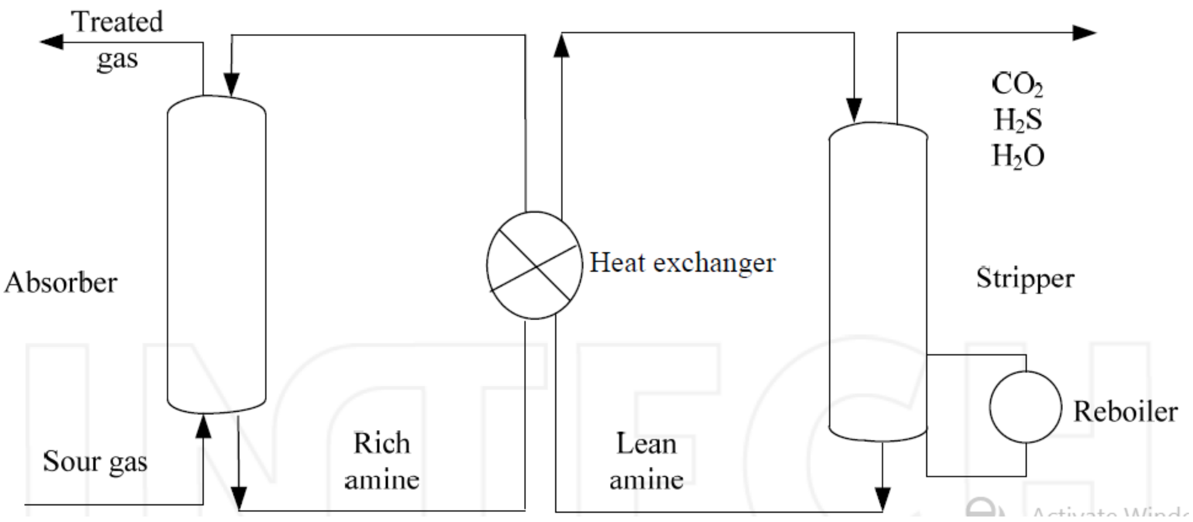


Figure 1: Process flow of the treating operation through chemical absorption by using amine as the sorbents (Al- Juaied, 2004)

2.3.2 Physical Adsorption and Desorption Technique

For physical adsorption process, Carbon Dioxide molecules are absorbed on the pore of the solid adsorbent pore surface. This process can be done by the help of the intermolecular force (Van der Waals force) of the adsorbent. Common type of adsorbent that are used for this process are zeolite, silica gel, and carbon (Mersmanm, 1988). The adsorption of the carbon dioxide is based on the gas molecule size (Steric Effect) and different binding forces between carbon dioxide gas and the adsorbent (Equilibrium Effect) (Mersmanm, 1988). Other than that, according to Gupta et al (2003), the adsorption process of carbon dioxide also will depends on the partial pressure, temperature and adsorbent pore size. Usually the solid adsorbents are arranged in a packed beds of spherical particles and the process are repeated in a cycle of adsorption and desorption (Mersmanm, 1988). For the adsorption part, Carbon Dioxide will be fed into a bed of adsorbent and other gasses such as oxygen will pass out the bed. When the concentration of carbon dioxide in the bed are high (no more carbon dioxide can be adsorb), the bed will be regenerate. Currently there are two established method to regenerate the adsorbent which are Pressure Swing Adsorption (PSA) and Themal Swing Adsorption (TSA). In Pressure Swing Adsorption (PSA), the process of regeneration is done by reducing the pressure until a certain value while in Thermal Swing Adsorption (TSA), the process of regeneration is done by increasing the temperature. This both processes applied Henry's Law as their basis as according to Henry's Law, the solubility of gas will be lower at low pressure and high temperature. Because of the high concentration of Carbon Dioxide in natural gas, physical adsorption might be not suitable and non-economical solution to counter the problem as the capacity of the adsorbent may not bear to load up the carbon dioxide (Meisen, 1997). Other than that, most of the adsorbent have low selectivity towards carbon dioxide gas molecules (Meisen, 1997). Due to this reason, currently physical adsorption is not an effective technique can be used to remove carbon dioxide from water.

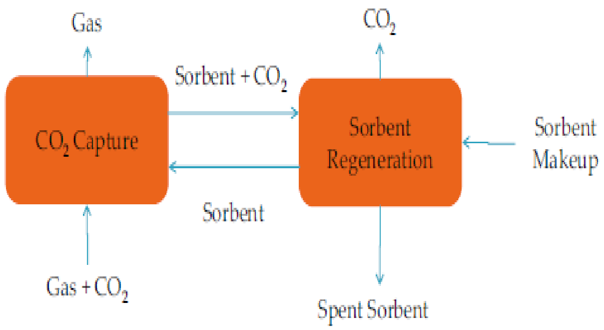


Figure 2: Process flow of the physical adsorption with regeneration (NaturalGas.com 2010)

2.3.3 Membrane Technologies Technique

Nowadays, the technologies of membrane are well known and well established for carbon dioxide removal purpose. Many membranes are made with the similar kind of material as physical adsorbent (Chen, 2010). There are many types of gas separation membrane such as porous inorganic membranes, palladium membranes, polymeric membranes and zeolites. This is because to make the membrane have a similar physical properties as the physical adsorbent to absorb Carbon Dioxide from natural case. The example of physical properties are like structure of the porous material and the Carbon Dioxide selectivity. According to Chen (2010), the membranes are microscopic sieves. When the natural gas flow through the membranes, some of the molecules may allow to pass and some of the molecules may not allow to pass the membrane. There are two important factors that determine the process. The first one is concentration gradient and the other one is the hydrostatic pressure (Chen, 2010).

Currently, according to Chen (2010), there are two types of membrane technologies that already been establish which are gas separation membranes and gas absorption membranes. For gas separation membranes case, separation can be done through a hydrostatic pressure applied to the system and the difference in the selectivity of carbon dioxide molecules species (Chen, 2010). For gas absorption membranes case, carbon dioxide molecules that diffuse in the membrane are carried away by the help of the liquid sorbent (Chen, 2010). For this case, low hydrostatic pressure are enough to carry the process. The membranes for this case can be made in the parallel hollow fibers, and the natural gas will enter this membranes in the opposite direction with the liquid sorbent. Although the carbon dioxide removal through membrane can achieved a very high degree of separation, the process is quite complex in term of selectivity and according to Meisen (1997), it required and consume a lot of cost.

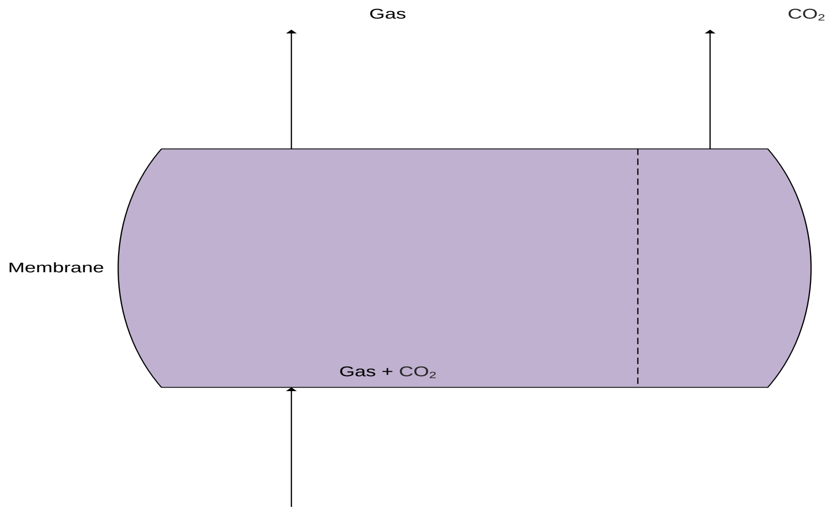


Figure 3: Separation with membrane (NaturalGas.com 2010)

2.3.3 Cryogenic Separation Technique

Besides that, separation of Carbon Dioxide also can be done in cryogenics distillation. This type of distillation will used a very low temperature to condense Carbon Dioxide (-73.30 °C). Usually, cryogenics distillation is used for stream that have high concentration of Carbon Dioxide (Zhang, 2014). Cryogenics distillation allows production of liquid carbon dioxide which can be used for some transport options such as ship. However, the amount of energy required to provide the refrigeration condition is quite high and the separation rate is poor for dilute Carbon Dioxide streams. It is a cost consuming method as it required to remove components which have higher freezing point than carbon dioxide to avoid blockage of a pipeline.

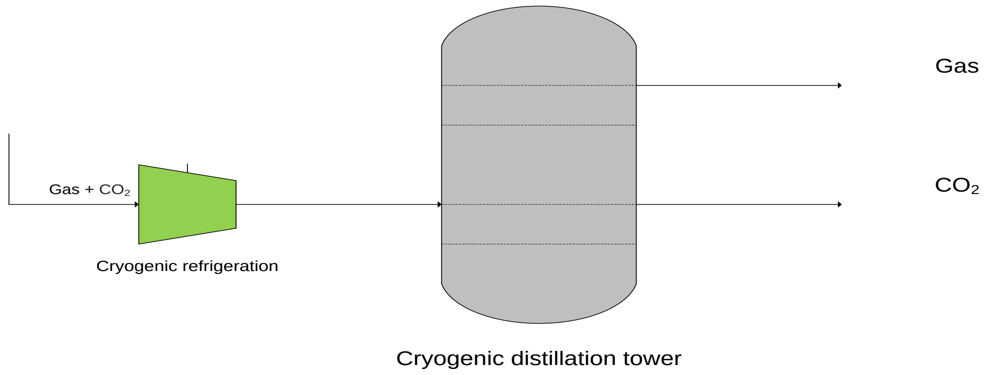


Figure 4: Separation by cryogenic distillation (NaturalGas.com 2010)

2.3.4 Physical Absorption and Desorption Technique

For physical absorption, the principle is quite the same as the chemical absorption. However, for physical absorption, there are no chemical reaction occur during the process. The interaction and the bond between the carbon dioxide molecules and the solvents are only cause by a weak force such as intermolecular force or electrostatic force which are weaker when compared to chemical bond in the chemical absorption. The amount of carbon dioxide absorb by the solvent is directly proportional to the partial pressure of the carbon dioxide. The higher the partial pressure of carbon dioxide, the higher the amount of carbon dioxide can be absorbed by the solvent. The higher the temperature of the solvent, the less carbon dioxide can be absorbed by the solvent. This theory is from Henry’s Law theory which state that at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid (Rubin et al, 1966).

Figure 2.5 shows the carbon dioxide loading in several sorbents against the partial pressure of carbon dioxide. From the graph it is shown that the curves shown a linear relationship for the physical solvents between the partial pressure and the amount of carbon dioxide while non-linear relationship for the chemical solvents between the partial pressure and the amount of carbon dioxide. Hence it can be concluded that the physical solvent is more effective compared to chemical solvents when the partial pressure of the carbon dioxide that need to be absorbed and removed is high. Carbon dioxide removal through physical absorption technique is very effective and save cost as we all know that the pressure of the natural gas which contain carbon dioxide as contaminant that just extracted from oil rig is high, so we can utilize the situation and can help to reduce the cost of carbon dioxide removal.

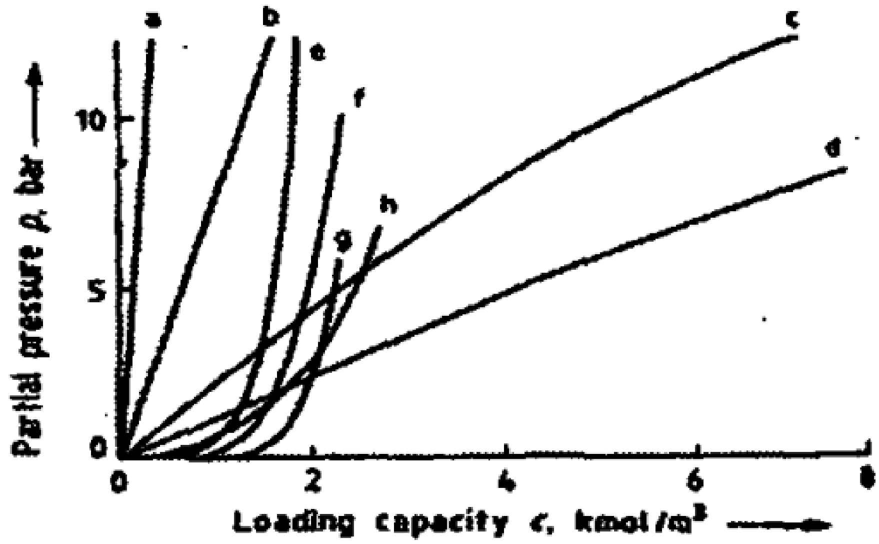


Figure 5: Equilibrium curve of Carbon Dioxide in various solvents (Hiller et al, 2009)

Physical absortion: a) Water (30 °C); b) N-methyl-2-pyrrolidone (110 °C); c) Methanol (-15 °C); d) Methanol (-30 °C); Chemical Absorption; e) Hot potassium carbonate solution (110 °C); f) Sulfinol solution (50 °C); g) Diethanolamine solution (50 °C); h) 3 molar Amisol DETA solution.

Since the process of physical absorption is quite similar to the chemical absorption, the process of regenerating the solvents are also similar to the chemical absorption. For physical absorption there are also two method to regenerate the solvent. The first one is Pressure Swing Absorption (PSA) and the second one is the Thermal Swing Absorption (TSA). For Pressure Swing Absorption (PSA), sorbent are regenerate by lowering the partial pressure to desorb carbon dioxide from solvent.

2.4 Summarization and Comparison for Current Carbon Dioxide Removal Technique

In this section, author will conclude some of the studies regarding the technologies of carbon dioxide removal from natural gas

Table 2: Summarization of current Carbon Dioxide removal techniques

Technique	Author	Year	Findings
Chemical Absorption and Desorption in a Packed Bed Column	Chen	2010	• The binding force of carbon dioxide with chemical sorbent makes the process of regeneration of the sorbent very difficult. • The energy consumption to regenerate the sorbent may be very high. • Some acidic impurities in natural gas such as oxygen and hydrogen sulfide that may attach the sorbent and cause the sorbent to become easier to degrade.
Physical Adsorption and Desorption by using adsorbent	Mersmanm, Gupta et al	1988, 2003	• The solid adsorbents are arranged in a packed beds of spherical particles and the process are repeated in a cycle of adsorption and desorption. • The regeneration of the adsorbent is done through Pressure Swing Adsorption (PSA) by reducing pressure until a certain value. • Because of the high concentration of carbon dioxide in natural gas, physical adsorption might be not suitable and non-economical solution to counter the problem as the capacity of the adsorbent may not bear to load up the carbon dioxide from natural gas.
Membrane Technologies	Chen, Meisen	2010, 1997	• Currently there are two types of membrane technologies that already been establish which are gas separation membranes and gas absorption membranes

			- Although the carbon dioxide removal through membrane can achieved a very high degree of separation, the process is quite complex in term of selectivity and it required and consume a lot of cost.
Cryogenic Separation using Column	Zhang	2014	- Cryogenics distillation can used for stream that have high concentration of carbon dioxide. - The amount of energy required to provide the refrigeration condition is quite high and the separation rate is poor for dilute carbon dioxide streams. - This technique is difficult in a way to remove component that have higher freezing point than carbon dioxide which may cause blockage in a pipeline.
Physical Absorption and Desorption in a Packed Column	Pennline et al	2009	- The amount of carbon dioxide absorb by the physical solvent is directly proportional to the partial pressure of the carbon dioxide - Physical solvent is more effective compared to chemical solvents when the partial pressure of the carbon dioxide that need to be absorbed and removed is high - Sorbent can be regenerated by heating up the sorbent and then the carbon dioxide lean sorbent is recycled back to the column for absorption

2.4 Desorption of Dissolved Carbon Dioxide from Water Previous Research Activities

This section will describe in general previous studies that have been done regarding desorption process of dissolved Carbon Dioxide from water. In contrast with gas absorption, desorption is employed when it is desired to transfer volatile component from liquid.

Table 3: Desorption process of dissolved Carbon Dioxide from water previous research activities

Author	Year	System	Findings
Sherwood et al, Sherwood and Holloway, Rixon	2000, 1997, 2008	Counter-current packed column	- Desorption rate was independent of the gas flow rate and increase with the increase of liquid flow rate and temperature.

Voyer et al	2005	Packed bed and unpacked cocurrent column	• Desorption rate was found to be higher for the packed configurations and it is increased as the liquid flow rate increased.
Shulman et al	2007	counter-current plate bubbled columns	• At constant liquid rate, 3 distinct region described the variation of desorption rate which are "streamline" region, "intermediate" region, and "turbulent" region. • Desorption rate was found to be highest in "turbulent" region.
Chaumat et al	2005	semi-industrial-sized co-current bubble column	• Desorption rate was found to increase with the increase in the gas velocity and to increase slightly with the increase liquid velocities.
Lisitsin et al	1994	Agitated pressurized vessel	• Desorption rate was tended to increase as the stirring speed in the agitated pressurized vessel is increased
Z.H Ban	2013	Venturi nozzle	• Desorption rate increased as the pressure drop occur across the nozzle increase.

Currently, most of the investigators used several type of column and tank to let and enhance the desorption process of dissolved Carbon Dioxide from water to occur which in real life situation, construction of column might be impossible to be built in the middle of the sea.

For parameters studies, most of the investigators focus more on the temperature, liquid and gas flow rate. All studies agree that a rise in temperature increase the rate of desorption because decrease in carbon dioxide solubility at higher temperature. Most of them also agree that increase in liquid (solvent) flow rate will increase desorption rate as at higher liquid flow rate, it would increase the energy dissipation rate in the system, which enhances bubble breakage and increase the desorption rate (Hindi et al, 2013). Increasing in the stirring speed also will lead to a finer dispersion and consequently enhance the rate of desorption (Lesitsin et al, 2008).

There are no studies that had been done on converging nozzle to let the desorption process to occur which is more compact and easy to handle. Another parameter which impact on the rate of desorption of dissolved Carbon Dioxide from water that still not well discuss in the literature is pressure. When using converging nozzle as a separator mechanism effect of pressure which will influence the pressure drop occur across the converging nozzle is a very crucial parameter that need to be determine its effect on the desorption process. Theoretically, desorption rate would be increase as the pressure of the system is increase as it will induced more pressure drop across the converging nozzle. Since there is still some gap between the studies, this project which entitle Desorption of Dissolved Carbon Dioxide in Water Using Converging Nozzle: Effect of Pressure is done.

2.5 Chemistry of Carbon Dioxide in Water

Water is used for this study as a physical solvent which acts as medium to absorb and desorb Carbon Dioxide from it. Past studies showed that carbon dioxide can dissolve in water. When mixing Carbon Dioxide and water, it will dissolve but some of the molecules will react to form a weak solution of carbonic acid and the remaining will stay as separated compound but in a same mixture. An example from our daily life is by drinking a soft drink. The bubbles in the soft drink is Carbon Dioxide and the 'tingly' taste on the tongue is the taste of carbonic acid (Carroll, 1991). During dissociation of Carbon Dioxide in water, Carbon Dioxide undergoes three chemical reaction involving four species: Carbon Dioxide, Carbonic acid, Bicarbonate ion, and carbonate ion.

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \quad (1) \qquad \text{(Carroll, 1991)}$$

$$H_2CO_3 \rightarrow H^+ + CHO_3^- \quad (2) \qquad \text{(Carroll, 1991).}$$

$$HCO_3^- \rightarrow H^+ + CHO_3^{2-} \quad (3) \qquad \text{(Carroll, 1991).}$$

From the reaction above, it is clearly shown that when there is carbon dioxide in water, there will be some reaction occur to produce Carbonic acid. However Carbonic acid produced are in a very small amount. The formation of the Carbonic acid will not affect the desorption process of Carbon Dioxide from water.

2.6 Solubility of Carbon Dioxide in Water Mathematical Model

Physical absorption is a process when liquid solvent absorbs a part of mass of gas into it. This process occurs naturally as we can see water that fall from waterfall may contain high concentration of oxygen because of physical absorption process (Hindi et al, 2013). While desorption is a process where substances are remove from the solvent through a surface (Hindi et al, 2013). This process is the inverse process of absorption. Both of this mass transfer process occurs at the interface between the liquid and gas. The transfer process of a component is affected by many factors such as temperature, pressure, concentration, flow rate, chemical reaction, mixing condition and many others (Azizi et al, 2012). In contrast with the absorption process, desorption of the gas is the process to move the gas out from liquid. For this project, the gas that author mean is Carbon Dioxide.

In this project, water is used as physical solvent because water is cheap, easy to get, environmental friendly and most importantly past studied showed that Carbon dioxide can dissolve in water. The solubility of carbon dioxide in water studied were early done by Wroblewski and Bohr (Hindi et al, 2013). After they succeed to prove the theory that Carbon Dioxide can dissolve in water, there are many studies done by other people based on experimental work. Other than that, people also published their work based on the thermodynamic models they develop to determine the solubility of Carbon Dioxide in water and phase equilibrium of the CO_2-water system (Feng et al, 2007).

According to Diamond et al (2003), Henry's law theory is used to determine and to study the behavior of the CO_2-water system. This model is used to determine the solubility of carbon dioxide in water when the system is in equilibrium condition.

$$x_{co2} = \frac{f_{co2} {y^*}_{co2}}{K_{Co2} y_{co2}} \qquad \text{Diamond et al (2003)}$$

Where,

$x_{co2} = mole\ fraction\ of\ carbon\ dioxide\ in\ water$

$f_{co2} = fugacity\ of\ carbon\ dioxide$

${y^*}_{co2} = activity\ coefficient$

$y_{co2} = mole\ fraction\ of\ carbon\ dioxide\ in\ gas$

$K_{C02} = Henry's\ coefficient$

By assuming ideal solution condition where pure water is used, assuming the activity coefficient is 1, mole fraction of carbon dioxide in gas is 1, and this equation can be used to determine the solubility of carbon dioxide in water over a range of low to moderate temperature and pressure (Diamond et al, 2003). Gas fugacity was determined from an appropriate EOS (RK approach).

$$\ln f = \ln \frac{RT}{V-b} + \frac{a}{bRT^{\frac{3}{2}}} \ln \frac{V}{V+b} + \frac{b}{V-b} - \frac{a}{RT^{\frac{3}{2}}(V+b)} \qquad \text{(L.Gainar, 2005)}$$

Where,

$a = 0.42748 \times R^2 \times \frac{T_C^2}{P_C}$ and $b = 0.08664 \times R^2 \times \frac{T_C^2}{P_C}$ (L.Gainar, 2005)

$for\ CO_2, T_C = 304.1\ K\ and\ P_C = 73.8\ atm$ (L.Gainar, 2005)

V is the molar volume which can be determined by using EOS RK approach;

$$V = \frac{ZRT}{P} \qquad \text{(Smith et al, 2005)}$$

Iteration need to be done in order to get Z value from RHS and LHS the same with initial value Z=1

$$Z = 1 + \beta - q\beta \frac{(Z-\beta)}{Z(Z+\beta)} \qquad \text{(Smith et al, 2005)}$$

$$\beta = \omega \frac{P_r}{T_r} \qquad \text{(Smith et al, 2005)}$$

$$q = \frac{\varphi T_r^{-\frac{3}{2}}}{\omega} \qquad \text{(Smith et al, 2005)}$$

Where,

$$P_r = \frac{P}{P_C}\ and\ T_r = \frac{T}{T_C} \qquad \text{(Smith et al, 2005)}$$

$$\omega = 0.08664 \; and \; \varphi = 0.42748 \text{ (Smith et al, 2005)}$$

Henry constant are calculated by using this equation;

$$\ln K_{C02} = -6.8346 + \frac{1.2817\times10^4}{T} - \frac{3.7668\times10^6}{T^2} + \frac{2.997\times10^8}{T^3} \text{ (Carroll, 1991)}$$

The solubility mathematical model develop is to only measure the amount of CO_2 in water in equilibrium at pressure of 1 bar and temperature of 40°C. This mathematical model are also compared to with the current literature to check its validation. The amount of excess CO_2 in water from experiment is calculated manually by taking sample from experiment added by the amount of CO_2 in water at equilibrium condition at 1 bar and 40°C.

2.7 Hydrodynamic in Converging Nozzle

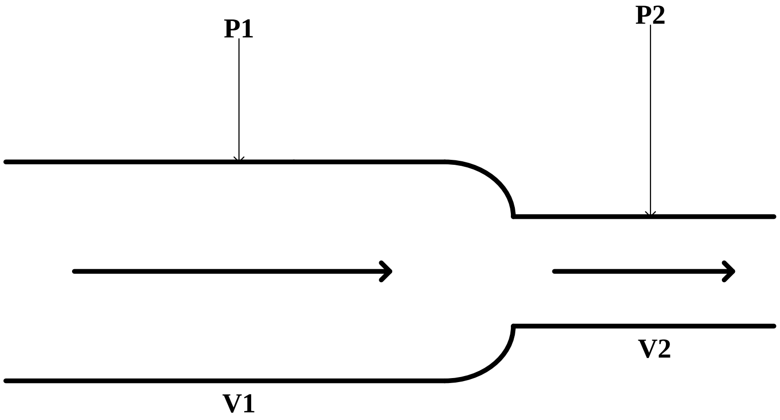


Figure 6: Illustration of converging nozzle

Energy cannot be created or destroyed. It only can change form to another form of energy. It is a principle of conservation of energy. Same can be applied to momentum as when the incompressible fluid flowing through the converging nozzle. When flowing through the nozzle energy that can be described is a mechanical energy which consist of potential and kinetic energy (Geankoplis, 2003). For an incompressible liquid, the general mechanical energy balance can be write as:

$$\frac{1}{2\alpha}(v_1^2 - v_2^2) + g(z_2 - z_1) + \frac{P_1 - P_2}{\rho} + \sum F + W_S$$
$$= 0 \qquad \text{(Geankoplis, 2003)}$$

Where,

$W_S = work\ added\ to\ system$ $\quad g = gravitational\ force$ $\quad \sum F = friction$

$\rho = density\ of\ fluid$ $\quad v = velocity\ of\ fluid$

$P = pressure\ at\ point$ $\quad z = pressure\ at\ point$

However, for this project there are no work added to the system and the friction is considered 0. The converging nozzle are also in a horizontal position. Because of this situation the mechanical energy above can be reduced to Bernoulli equation:

$$\frac{v_1^2}{2} + \frac{P_1}{\rho} = \frac{v_2^2}{2} + \frac{P_2}{\rho} \qquad \text{(Geankoplis, 2003)}$$

The continuity is also valid for this condition,

$$\mathrm{m} = \rho_1 A_1 v_1 = \rho_2 A_2 v_2 \qquad \text{(Geankoplis, 2003)}$$

Since the density of the water is constant the continuity equation can be reduced to:

$$A_1 v_1 = A_2 v_2 \qquad \text{(Geankoplis, 2003)}$$

From the equation above, it can be conclude that at when fluid flowing in the converging nozzle, there is a sudden increase in cross sectional area, the velocity of the fluid will be decrease and resulted some pressure build up at P_1. When the fluid transfer in the region P_2 which have a lower cross sectional area, the velocity of the fluid will be increase and will decrease the pressure at the region P_2. This occur due to the principle of conservation of energy which state that energy cannot be created or destroyed but it can form another form of energy. When increasing the pressure of the system, the pressure drop between the two regions will be increase at a constant cross sectional area from both side.

2.8 Bubble Nucleation Rate

Henry's Law state that at a constant temperature, the concentration of gas in liquid is directly proportional to the partial pressure of the gas above the liquid itself, (Enriquez et al, 2013).

$$c = k_H P \qquad \text{(Enriquez et al, 2013)}$$

Where c is the concentration of gas in liquid, k_H is the Henry's gas constant which dependence on the temperature and P is the partial pressure. In thermodynamic equilibrium point of view, supersaturated condition occur when the initial pressure of the system is decrease to a certain amount which lower than initial pressure (Enriquez et al, 2013). It also can be done when increase the temperature of the gas-liquid solution. Under supersaturated condition, it will create a new condition. Supersaturated ratio can be used to estimate the amount of excess gas in liquid.

$$S = \frac{c_0}{c_{vle}} \qquad \text{(Enriquez et al, 2013)}$$

Where S is the supersaturated ratio, c_0 is the concentration of gas in liquid at new condition and c_{vle} is the concentration of gas in liquid at equilibrium. From the formula above it can be say that at higher concentration of gas in liquid at new condition the supersaturated ratio also would be increase. Bubble formation occur under supersaturated condition.

Pressure plays a significant effect on the desorption rate of Carbon Dioxide from water. It has been agreed that the pressure will affect the solubility of Carbon Dioxide in water. Formation of bubble and nucleation of carbon dioxide from water occurs under supersaturated condition. Formation of bubbles are initiate by thermodynamic instability (Han et al, 2001). For example when there is a sudden drop of pressure. According to Baldwin et al (1995), under supersaturated condition the higher pressure drop occur when the fluid flowing through a nozzle will cause the higher the nucleation rate of Carbon Dioxide from water. This can be predicted through classical nucleation theory as shown below:

$$N_{nucl} = C_0 \exp\left(\frac{-\Delta G_{nucl}}{kT}\right) \qquad (Baldwin\ et\ al, 1995)$$

$$\Delta G_{nucl} = \frac{16\pi y_{bp}^3}{3\Delta P^2} \qquad (Baldwin\ et\ al, 1995)$$

Where ΔP the pressure drop is occur in the nozzle, ΔG_{nucl} is the free energy barrier, y_{bp} is the interfacial tension and N_{nucl} is the rate of nucleation. So it can be concluded that the higher pressure drop occurs, it will favored the desorption rate of Carbon Dioxide from water. This is because, at higher pressure drop it will result the free energy barrier to decrease. When the free energy barrier decrease, it will make carbon dioxide become easier to desorb from the water and hence desorption rate will also increase. However, in this project author did not calculate the nucleation rate of carbon dioxide from water due to limited knowledge constraint. In this project, author only study the phenomenon. From the concept mentioned above, it is expected the higher the pressure drop occur, the higher desorption rate of dissolved Carbon Dioxide from water will be.

CHAPTER 3

METHODOLOGY

3.1 Experiment Methodology

In order to achieve the objectives of this project, laboratory experiment is done. In a laboratory experiment, 2 water tanks with capacity of 100L is used to pump water to closed tank. One water tank is used to conduct the experiment and another one is used as standby equipment in case there is some technical damage occur. Converging Nozzle is used to let the desorption process of dissolve carbon dioxide from water. Six pressure transmitter are installed at the Converging Nozzle to show how much pressure value at the point.

Other than that, water is heat up by using water heater until achieve the required value. The heated water is also regulated by using pump to ensure that the heat distributed well throughout the system so that less error occur from the experiment. For pressure, it is regulate by the amount of Carbon Dioxide introduced in the closed tank. Carbon Dioxide is pumped to the pressure vessel by the compressor until it reach it reach 30 bar and wait for 30 minutes for each run of experiment to ensure that the amount of Carbon Dioxide contain in the water is the same for each run of experiment . The limitation of the pressure of this system is at 35 bar. Relief valve are also provided for safety purpose to prevent from any unwanted accident occur. Figure 3.1 shows the schematic diagram of overall process of the laboratory experiment.

Below is the simplified equipment set up for the experiment done in laboratory

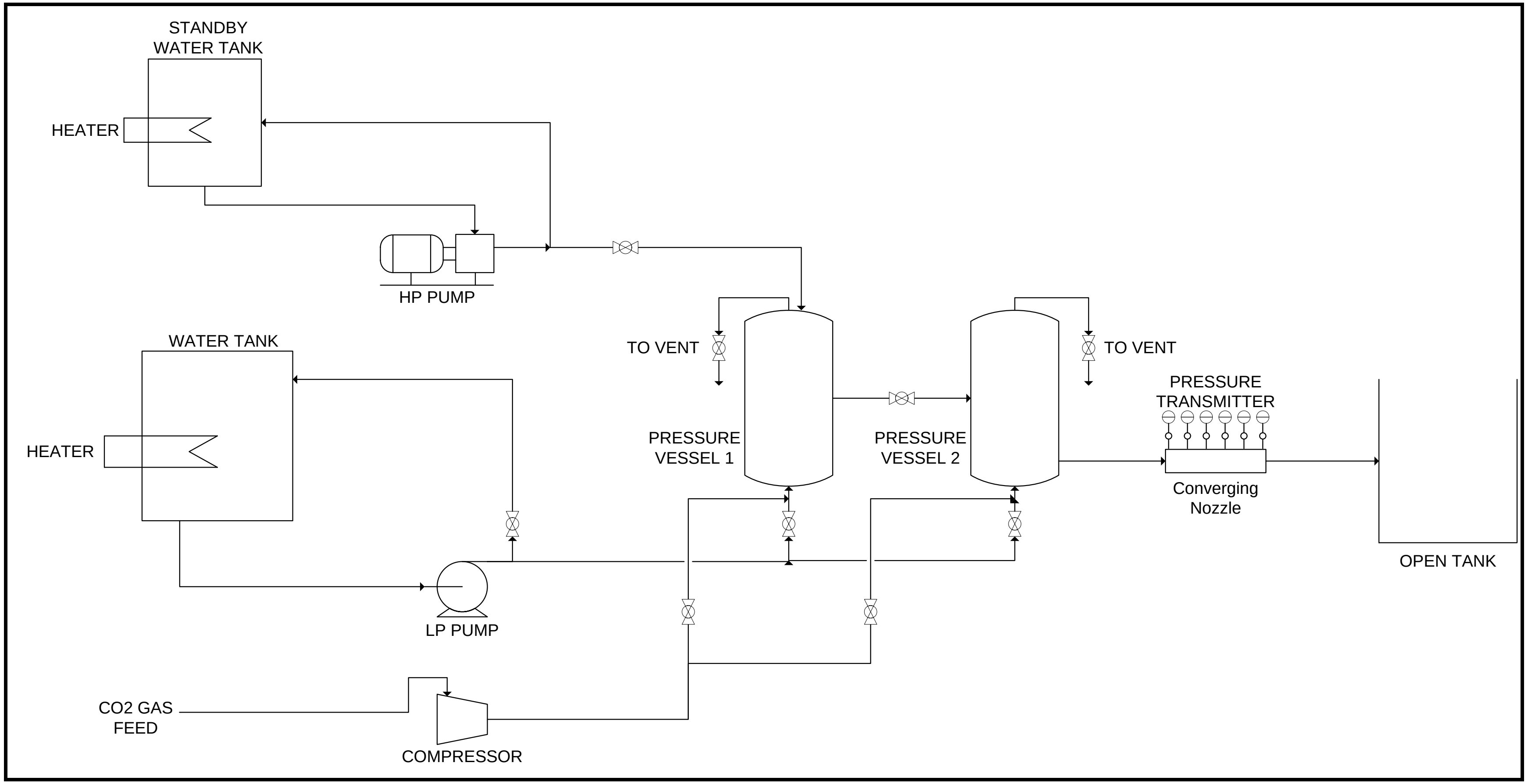


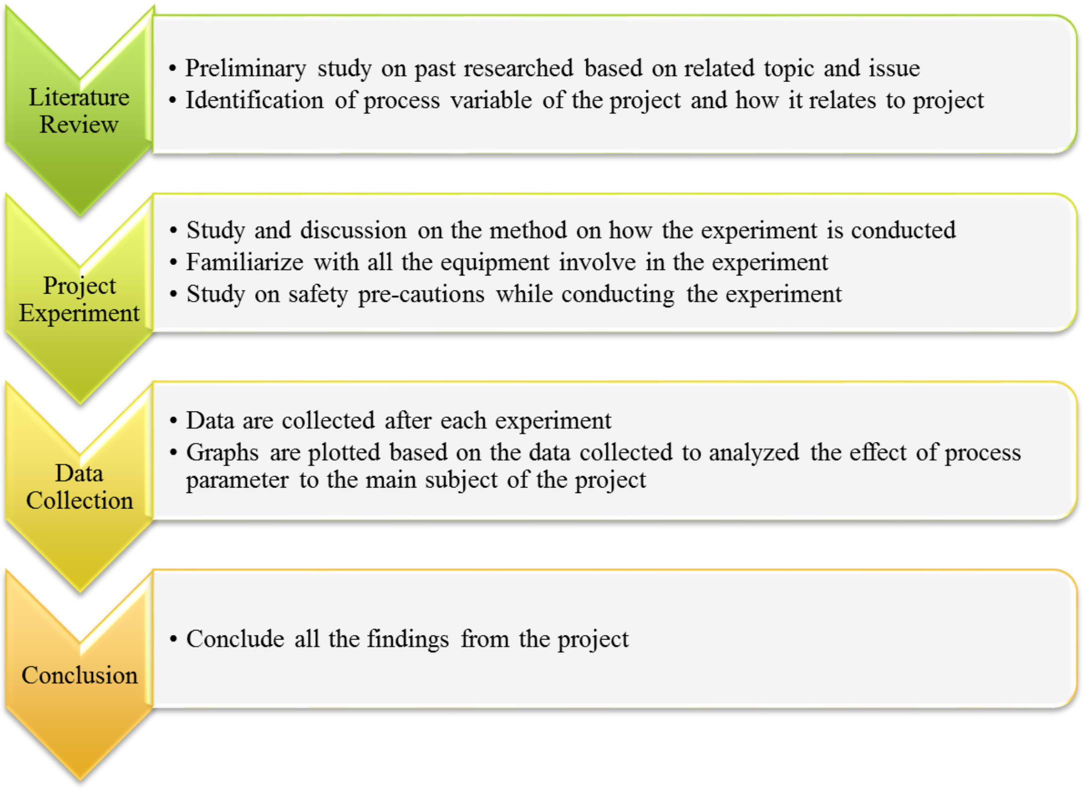
Figure 7: Simplified schematic diagram of laboratory experiment

General steps to conduct the laboratory experiment*:*

1. Water in the water tank is heat up until it reach 40 ºC by using water heater.
2. After the water in the tank reach 40 ºC, close all ball valve to both pressure vessel and switch ON LP pump at the control panel to let the water circulated in the tank so that the temperature of water in water tank is the same for 10 minutes.
3. To fill in the pressure vessel 1, circulation ball valve is close and ball valve to the pressure vessel 1 is open to fill in the pressure vessel 1 with heated water.
4. During fill in the pressure vessel 1, all venting valve is open to let the process occur faster and to ensure that the pressure vessel 1 is fully filled with water.
5. When water flows out from the venting line of pressure vessel 1, LP pump is switched OFF and all necessary ball valves are closed.
6. Steps (3 – 5) are repeated to fill in pressure vessel 2.
7. Compressor is switch ON and both ball valves for Carbon Dioxide line are open to inject Carbon Dioxide gas from its source into both pressure vessel.
8. Carbon Dioxide is pump to both pressure vessel until it reach 30 bar for each run of experiment.
9. The system is kept pressurize for 30 minutes to ensure that same amount of Carbon Dioxide dissolved in water for each run of experiment.
10. After 30 minutes, the 20 mL water sample from the pressure vessel 2 are taken to measure the amount of Carbon Dioxide absorbed in the water and the data is collected and recorded in the table.
11. Before flows the water to the converging nozzle, ensure that the pressure in the pressure vessel and HP pump is the same at 30 bar. The outlet pressure of this HP pump is adjusted by the load of the pump spring.
12. Without further delay, ball valve to the converging nozzle is open to let the water which contain Carbon Dioxide from the pressure vessel 2 to flow through it. Here, desorption process occur.

13. 6 pressure transmitters at 6 different points on converging nozzle show the pressure values at the control panel. The data of the pressure value are collected in the table.
14. 20 mL water sample is once again collected at the end of the converging nozzle just before it enters open tank to measure the amount of Carbon Dioxide left in the water. Data is once again recorded and collected in the table.
15. The constant initial amount of Carbon Dioxide in water is subtracted by the final amount of Carbon Dioxide in water to measure how much Carbon Dioxide is successfully desorb from water and to measure the effectiveness of the converging nozzle after water filled with Carbon Dioxide flowing through it.
16. After all data are collected, all the water left in the system are drained to the necessary place.
17. Experiment is repeated by using different value of pressure that applied to the HP Pump at a value of 10 bar, 15 bar, 20 bar and 25 bar.
18. Since the objective of this project is to study the effect of pressure, the temperature of the system is kept constant at 40 ºC.
19. Result will be analyze according to the amount of Carbon Dioxide desorb from water and how much pressure drop occur when water flowing through the contraction pipeline for different value of pressure.
20. Experiment is repeated for several times in order to get a better result.

3.2 Project Flow Chart



- Preliminary study on past researched based on related topic and issue
- Identification of process variable of the project and how it relates to project

- Study and discussion on the method on how the experiment is conducted
- Familiarize with all the equipment involve in the experiment
- Study on safety pre-cautions while conducting the experiment

- Data are collected after each experiment
- Graphs are plotted based on the data collected to analyzed the effect of process parameter to the main subject of the project

- Conclude all the findings from the project

Figure 8: Project Flow Chart

3.3 Key Milestones

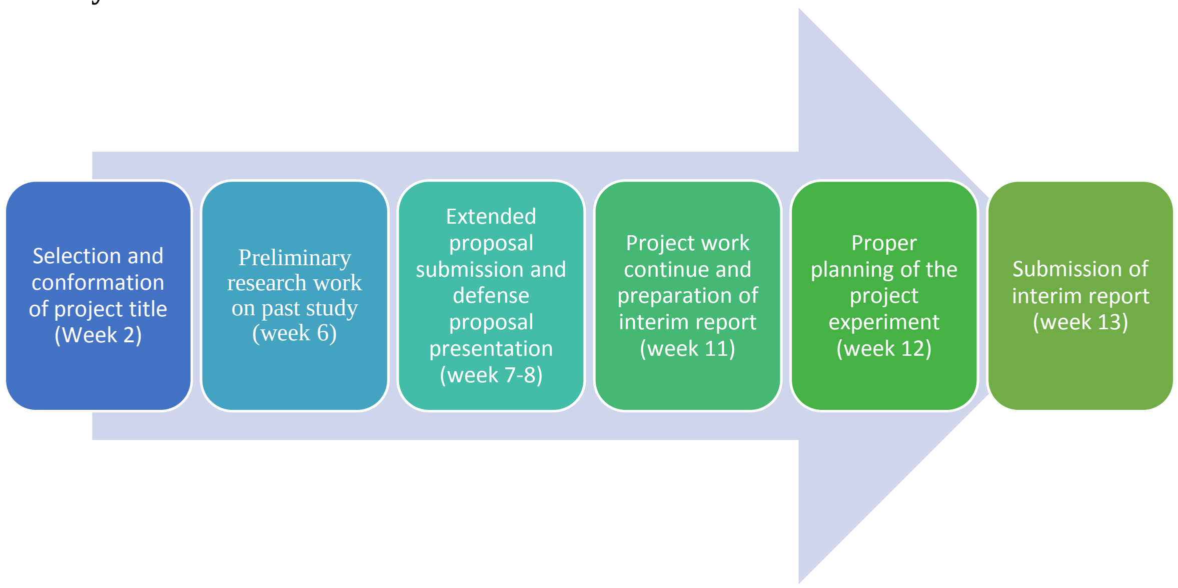


Figure 9: Key Milestone FYP 1

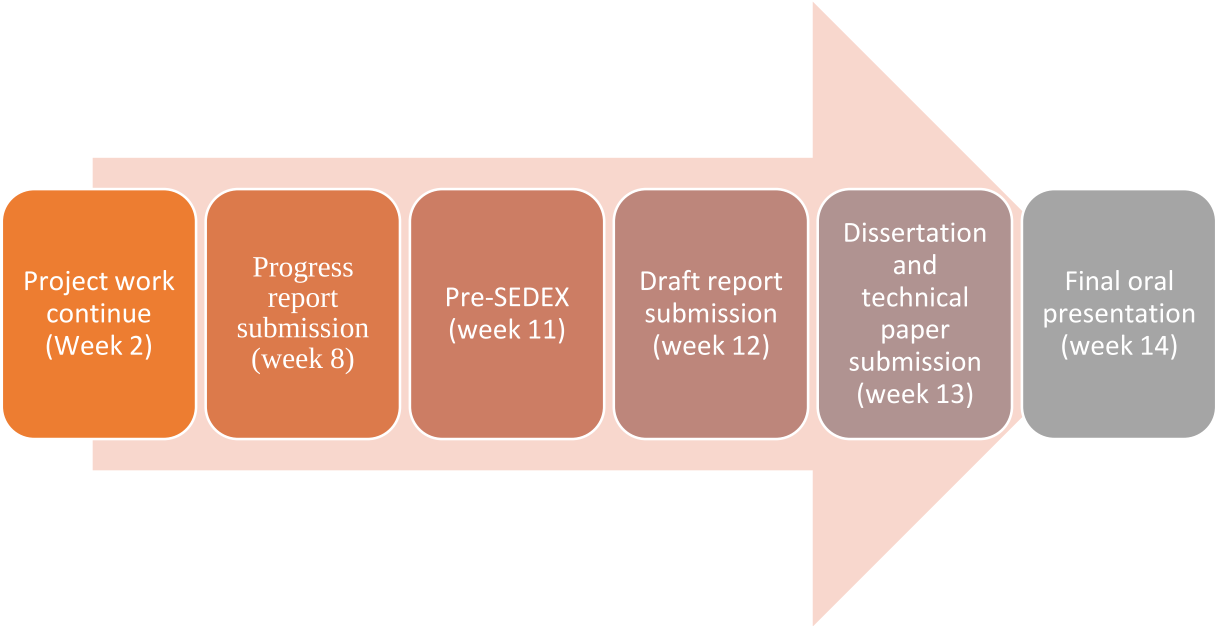


Figure 10: Key Milestone FYP 2

3.4 Gantt-chart

Table 4: Gantt-chart for FYP 1

FYP 1		Week													
No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of project title	🟨	🟨												
2	Preliminary research work and proposal preparation			🟨	🟨	🟨									
3	Extended proposal submission						🟨								
4	Proposal defense							🟨							
5	Project work continue								🟨	🟨	🟨	🟨			
6	Submission of interim draft report												🟨		
7	Submission of final interim report													🟨	🟨

Table 5: Gantt-chart for FYP 2

FYP 2		Week													
No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project work continues	🟥	🟥	🟥	🟥	🟥	🟥	🟥							
2	Submission of progress report								🟥						
3	Conducting experiment in lab								🟥	🟥	🟥	🟥	🟥		
4	Pre-SEDEX											🟥			
5	Project work continue												🟥		
6	Submission of draft report												🟥		
7	Submission dissertation (soft bound)													🟥	
8	Submission of technical paper													🟥	
9	Oral Presentation														🟥
10	Submission of project dissertation (hard bound)														🟥

CHAPTER 4

RESULT AND DISCUSSION

In this section, author will illustrate and show all the graphs plotted and data obtained from the experiment. From the graphs and data, discussion will be made based on the theory of the phenomenon. Discussion in this section will be divided into 2 parts. For the first part, author will discuss on the pressure profile across the converging nozzle as water enter the converging nozzle at different pressure. For the second part, author will discuss on the phenomenon of desorption of dissolved carbon dioxide from water at different pressure of the system.

4.1 Part A: Pressure Profile across the Converging Nozzle

As stated in methodology, all the data from the experiment are collected and recorded in the table. Table 6 shows the data of the pressure profile of the water when it flowing through the converging nozzle at certain point. This pressure profile data are collected at fixed temperature which is at 40 °C and at different pressure which ranging from 10 to 30 bar. This data are shown recorded at the main control panel.

Table 6: Experimental pressure profile data obtained from experiment ranging from 10 to 30 bar at 40 °C

Pressure (Bar)	10	15	20	25	30
Temperature (°C)	40	40	40	40	40
Pressure Point 1 (Bar)	10.6	15.3	20.2	25.4	29.5
Pressure Point 2 (Bar)	10.6	15.3	20.2	25.4	29.5
Pressure Point 3 (Bar)	10.6	15.3	20.2	25.4	29.5
Pressure Point 4 (Bar)	7.3	10.4	14.0	17.4	19.8
Pressure Point 5 (Bar)	6.9	8.4	11.3	14.0	15.8
Pressure Point 6 (Bsr)	4.5	6.3	8.7	10.6	11.5

Figure 11 shows the illustration of the converging nozzle from the test rig. The diameter of the converging nozzle from point 1 until point 3 are the same which is at ½ inch. The diameter of the nozzle from point 4 until point 3 are smaller compared to from point 1 until point 3 which is at ¼ inch. At each point as showed above, pressure transmitter are installed to show the current pressure at the respective point which can be recorded at main control panel.

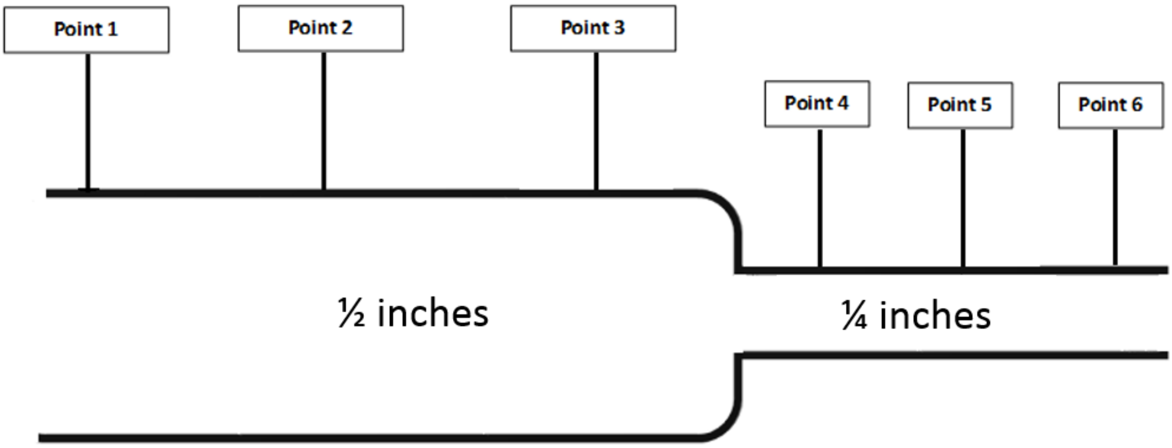


Figure 11: Illustration of Converging Nozzle of the experiment

Figure 4.2 shows the overall pressure profile of water when they flowing through the converging nozzle at different pressure of 10 bar, 15 bar, 20 bar, 25 bar and 30 bar at constant temperature of 40 °C. Based on the figure 4.7, is observed that as the water entering the converging nozzle, there is some pressure built up at point 1, point 2, and point 3. The pressure built up are not the same for each case. When the pressure of the system is set at 10 bar, the pressure built up is 10.6 bar. When the pressure of the system is set at 15 bar, the pressure built up is 15.3 bar. When the pressure of the system is set at 20 bar, the pressure built up is 20.2 bar. When the pressure of the system is set 25 bar, the pressure built up is 25.4 bar. However, when the pressure of the system is set at 30 bar, the pressure of system will be drop at point 1, point 2, and point 3 at a value of 29.5 bar.

The phenomenon of pressure built up occur because the diameter of the converging nozzle at point 1, point 2 and point 3 is slightly bigger which is at ½ inch when compared to the pipeline of water just before it enters the nozzle which have diameter of 3/8 inch. When the fluid transfer from a lower cross sectional area to a higher cross sectional area, the velocity of the fluid will be decrease and the pressure of the respective area would be increase according to continuity equation and Bernoulli’s equation (Geankoplis, 2003). The difference of the pressure is dependent on the change of the cross sectional area. The higher the changes of cross sectional area, the higher the different in pressure. However, when the pressure of the system is set at 30 bar, there is no pressure built up at point 1, point 2, and point 3. This is opposite from the theory. This phenomenon may occur because of the high pressure pump cannot sustain to maintain the pressure in the pipeline at 30 bar due to the pump constraint itself.

$$\frac{v_1^2}{2}+\frac{P_1}{\rho}=\frac{v_2^2}{2}+\frac{P_2}{\rho} \qquad (\text{Geankoplis}, 2003)$$

$$A_1v_1 = A_2v_2 \qquad (\text{Geankoplis}, 2003)$$

The pressure at point 1, point 2, and point 3 are observed same throughout the points because the cross-sectional area of the points are the same throughout the nozzle. This occur due to no changes in velocity of the fluid. When velocity of the fluid is the same, there is no changes in pressure as expected from theory of Bernoulli and continuity equation (Geankoplis, 2003).

However, as we can see when the fluid flowing from point 3 to point 4, it is observed that there is some pressure drop occur. The pressure drop occurs are not the same for each case. When the pressure of the system is set 10 bar, the sudden pressure drop occur from point 3 to point 4 is 3.3 bar. When the pressure of the system is set 15 bar, the sudden pressure drop occur from point 3 to point 4 is 4.9 bar. When the pressure of the system is set 20 bar, the sudden pressure drop occur from point 3 to point 4 is 6.2 bar. When the pressure of the system is set 25 bar, the sudden pressure drop occur from point 3 to point 4 is 8 bar. When the pressure of the system is set 30 bar, the sudden pressure drop occur from point 3 to point 4 is 9.7 bar.

This happen because of the different of cross sectional area which at point 3 has a diameter of ½ inch and at point 4 which has a diameter of ¼ inch. When the fluid transfer from bigger region to a smaller region, the velocity of the fluid will be increase and tend to decrease the pressure at the point due to the principle of conservation of momentum where the amount of momentum should be the same throughout the system and momentum same as energy which cannot be created or destroyed (Geankoplis, 2003). As mentioned above, the higher the different between cross sectional area, the higher the pressure different will be (Geankoplis, 2003).

From figure 12, it is also observed that at a higher pressure of the system, the pressure drop occur from point 3 and point 4 will also would be higher. This phenomenon happens as when the pressure of the system is set higher, the pressure at point 1, point 2 and point 3 would be higher. However they need to flow to point 4, point 5 and point 6 which have a smaller constant cross sectional area. So at higher pressure it will cause velocity of the fluid to point 4, point 5, and point 6 to increase more compared when at lower pressure. As the velocity of the fluid is higher at higher pressure, the change of pressure occur also would be higher resulted the pressure drop to increase. This can be related to the Bernoulli's equation (Geankoplis, 2003).

As the fluid flowing from point 4 to point 5 and point 6, it is observed that the pressure at the point will be decrease. However the trend of decrease is not the same for every case. When the pressure of the system is set at 10 bar. The average of decrease of pressure from point 4, point 5 and point 6 is 1.4 bar. When the pressure of the system is set at 15 bar. The average decrease of pressure from point 4, point 5 and point 6 is 2.1 bar. When the pressure of the system is set at 20 bar. The average decrease of pressure from point 4, point 5 and point 6 is 2.7 bar. When the pressure of the system is set at 25 bar. The average decrease of pressure from point 4, point 5 and point 6 is 3.4 bar. When the pressure of the system is set at 30 bar. The average changes of pressure from point 4, point 5 and point 6 is 4.2 bar.

The decrease in pressure at point 4, point 5, and point 6 occur because the velocity of the fluid increase as the converging nozzle is connected to open tank which operate at atmospheric pressure. Due to the principle conservation of momentum, when the velocity increase the pressure will be decrease (Geankoplis, 2003). So the nearer the pipe to the open tank, the lower the pressure in the pipe will be. The reason at higher pressure the average decrease in pressure from point 4, point 5 and point 6 is higher compared to lower pressure is because when at higher pressure, the initial pressure at point 4 is higher so they need to decrease its pressure more in order to have the same pressure with the connected open tank.

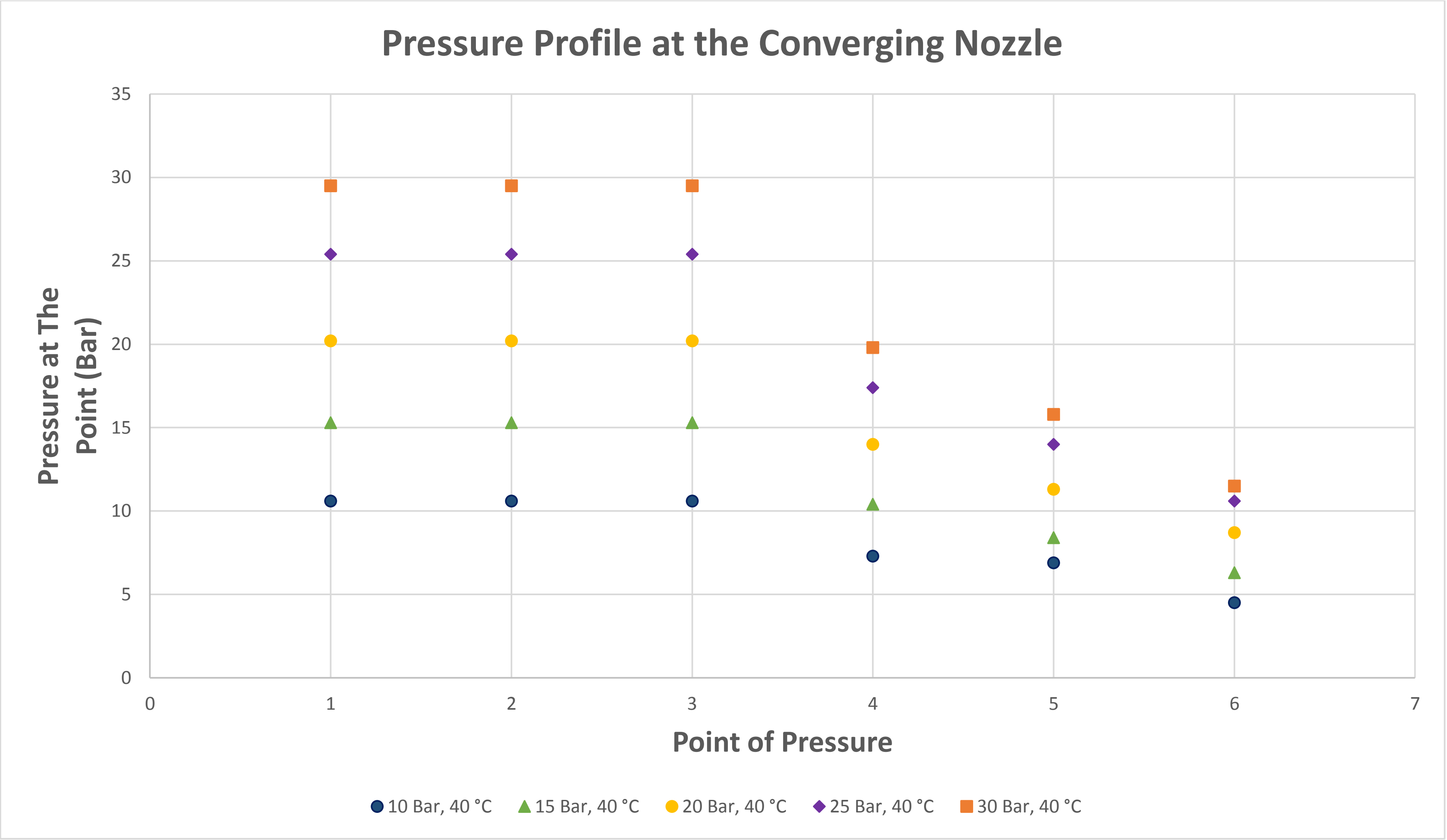


Figure 12: Graph of overall pressure profile of water flowing through the Converging Nozzle at pressure of 10, 15, 20, 25, and 30 bar and at constant temperature of 40 °C at respective point

4.2 Part B: Desorption of Carbon Dioxide from Water at Constant Temperature and Initial Concentration

Table 7 shows the experimental data of volume of CO_2 collected in measuring cylinder after water which contain same amount of Carbon Dioxide flowing through the converging nozzle. The amount of CO_2 contain in the water is constant for the absorption part in the pressure vessel for each experiment. To ensure that the amount of CO_2 contain in water is the same for each run of experiment, same number of mole and amount of carbon dioxide is introduced to the pressure vessel. For each experiment CO_2 is pump to the pressure vessel until the pressure in the pressure vessel reach 30 bar and then wait for 30 minutes. If the initial concentration of carbon dioxide in water is not the same, the experiment is repeated until get the same concentration. The initial amount of carbon dioxide in water is set constant at 0.001939 $mol\ CO_2 / mol\ H_2O$ (volume 43mL CO_2 per 20mL water sample).

(Note: Example calculation of mole fraction of CO_2 in water are shown in appendix 7)

Table 7: Experimental data obtained from experiment ranging from 10 to 30 bar at 40 °C after water flowing through the Converging Nozzle

Temperature (°C)	Pressure (bar)	Initial Mole Fraction of $C0_2$ in Water	Volume of $C0_2$ Collected after Converging Nozzle (ml)				Average Mole Fraction of $C0_2$ in Water after Converging Nozzle
			1st run	2nd run	3rd run	Average	
40	10	0.001939	18.0	18.0	17.5	17.8	0.001066
40	15	0.001939	15.0	14.0	14.5	14.5	0.000961
40	20	0.001939	14.0	13.0	13.0	13.3	0.000891
40	25	0.001939	11.0	11.0	11.0	11.0	0.000821
40	30	0.001939	8.0	8.5	7.0	7.8	0.000716

Figure 13 shows the comparison between the mole fraction of CO_2 in water during experiment (non-equilibrium) and the mole fraction of CO_2 in water at equilibrium condition after the water flowing through the converging nozzle against pressure of the system. Based on the graph, it is observed that the amount of CO_2 in water which is collected at the end of the nozzle for experimental data (non-equilibrium) is always higher compared to the amount of CO_2 during the equilibrium. The equilibrium condition is that at temperature of 40 °C and pressure of 1 bar.

In equilibrium condition means that there is no formation of bubbles that will release out from the water. All CO_2 gas are already dissolved in water. This can be simply understand by the analogy of carbonated drink. When carbonated drinks are exposed to the atmospheric environment and left for several hours or days, all the CO_2 bubbles will diffuse out from the water. However, when we drink the carbonated drinks that already exposed to atmospheric condition there is still a little bit taste of *CO* in the water. This mean that the CO_2 gases are already dissolve in the water at atmospheric condition.

From the figure, it can be say that no matter how much the value of pressure drop occur after the water filled with CO_2 flowing through the converging nozzle it still cannot desorb amount of CO_2 equal to the value of how much CO_2 can desorb during the equilibrium condition. To achieve the amount of value of CO_2 desorb same with the value at equilibrium is a quite impossible process when using converging nozzle. This is because at equilibrium condition, the process to remove all CO_2 in it until achieved an equilibrium may take a very long time. When water filled with CO_2 flowing through the converging nozzle, the process is fast and continuous. However, as the pressure of the system is increase the mole fraction of carbon dioxide in water become nearer to mole fraction of CO_2 in water at equilibrium condition.

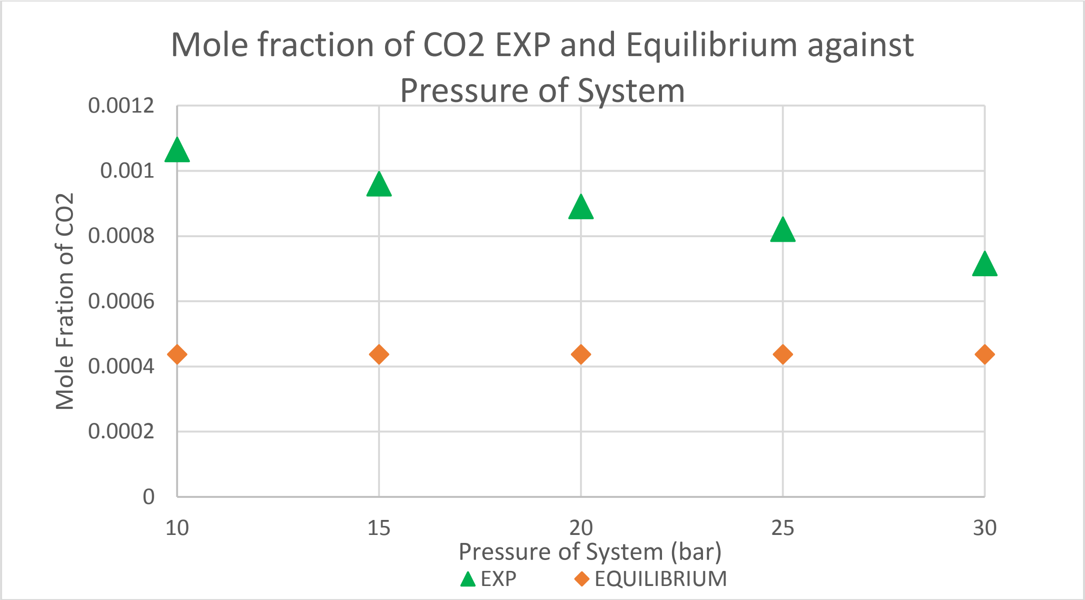


Figure 13: Graph of mole fraction of CO_2 in water from experiment and equilibrium (1 bar) against pressure of the system

Figure 14 shows the graph of efficiency of converging nozzle compare to equilibrium at 1 bar against pressure of the system. From the figure it is observe that when the pressure of the system is set at 10 bar, the efficiently of the converging nozzle calculated is 58.12 %. When the pressure of the system is set at 15 bar, the efficiently of the converging nozzle calculated is 65.11 %. When the pressure of the system is set at 20 bar, the efficiently of the converging nozzle calculated is 69.77 %. When the pressure of the system is set at 25 bar, the efficiently of the converging nozzle calculated is 74.43 %. When the pressure of the system is set at 30 bar, the efficiently of the converging nozzle calculated is 81.43 %.

The efficiency of the converging nozzle is calculated by the following equation:

$$Efficiency\ (\%) = \frac{initial - EXP}{initial - VLE} \times 100\%$$

The purpose of comparing the experimental value to equilibrium value (1 bar) is because at equilibrium value at 1 bar, it indicates the minimum amount of CO_2 can contain in the water. Thus it can be say it can desorb the maximum amount of CO_2 from water.

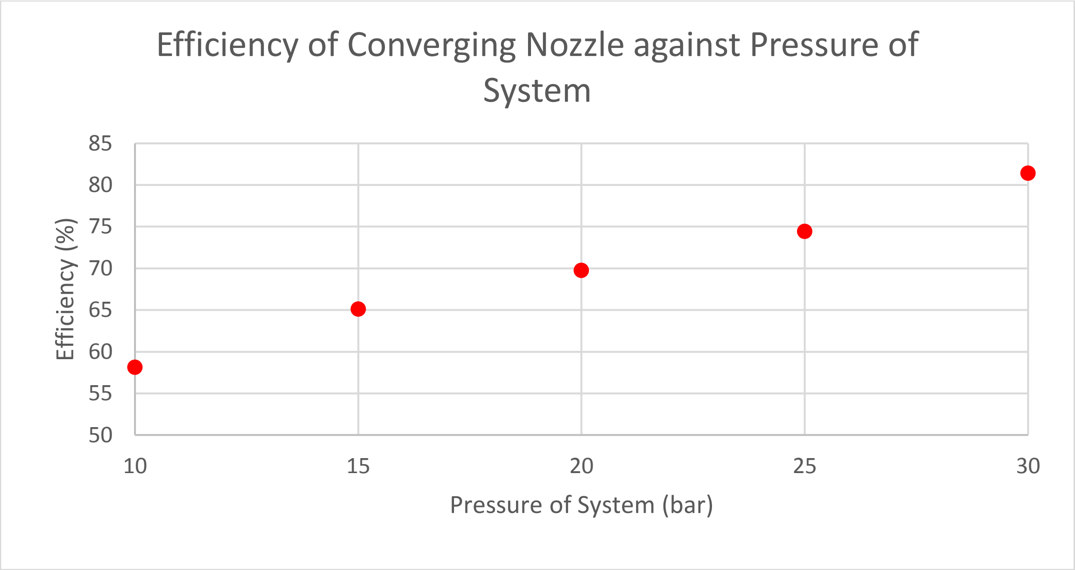


Figure 14: Graph of efficiency of Converging Nozzle compare to at Equilibrium at 1 bar against pressure of system

Figure 15 shows the mole fraction of the CO_2 successfully desorb from the water after it flows through the converging nozzle. Based on the graph it is observed that when the pressure of the system is set at a value of 10 bar, the mole fraction of CO_2 successfully desorb from water is 0.00087 (mol CO_2 / mol H_2O). When the system is set at a value of 15 bar, the mole fraction of CO_2 successfully desorb from water is 0.00098 (mol CO_2 / mol H_2O). When the system is set at a value of 20 bar, the mole fraction of CO_2 successfully desorb from water is 0.00105 (mol CO_2 / mol H_2O). When the system is set at a value of 25 bar, the mole fraction of CO_2 successfully desorb from water is 0.00112 (mol CO_2 / mol H_2O) and when the system is set at a value of 30 bar, the mole fraction of CO_2 successfully desorb from water is 0.00122 (mol CO_2 / mol H_2O). The total amount of CO_2 successfully desorbed from water is calculated by subtracting the initial amount of CO_2 in water which is constant for each run of experiment with the final amount of CO_2 contain in the water after flowing through the converging nozzle.

$$CO_2 \text{ successfully desorb} = \text{initial amount of } CO_2 \text{ in water} - \text{final amount of } CO_2 \text{ in water}$$

Desorption of CO_2 from water occur along the converging nozzle when there is a pressure drop. It is observed that when the pressure of the system is set at higher value, the amount of CO_2 successfully desorb from water also would be higher as expected.

The amount of CO_2 desorb from water is significantly depends on how much the pressure drop occur. Pressure drop occur across the converging nozzle will induced turbulence flow. Unlike laminar flow, turbulence flow is mean that the flow is disturbed. The higher the pressure drop occur across the converging nozzle, the more it will induced turbulence flow that will make the flow of water which contain CO_2 in it to be more disturbed. As this occur, the bubble nucleation rate will be increase resulted more CO_2 to be release out from the water in the form of bubbles which initiated by thermodynamic instability for this case is pressure drop under supersaturated condition. Hence desorption rate of dissolved CO_2 from water will be increase.

The simple analogy to understand this phenomenon is like carbonated drink in the bottle. When the flow of carbonated drink in the bottle is not disturbed, when the bottle is open less Carbon Dioxide will be released to atmosphere. However, when the flow of carbonated drink in the bottle is disturbed, more Carbon Dioxide will be released to atmosphere. According to Z.H Ban (2013), in order for formation of bubble to occur, there is some requirement of pressure drop needed to be achieved. From his study, he mentioned that the nucleation rate of dissolve Carbon Dioxide from water occur at its maximum rate at the throat of the venturi nozzle where the pressure drop occur is the largest.

For this case study, desorption rate of dissolved CO_2 from water is expected to occur at its maximum rate between point 3 and point 4 at the converging nozzle where the pressure drop occur is the highest. Desorption of dissolved CO_2 from water also expected to occur at point 5, point 6 and along the pipeline where there is pressure drop occur until it reach open tank.

Apart from that, Classical Nucleation Theory also improve the phenomenon. According to Baldwin et al (1995), based on the classical nucleation theory the higher the amount of pressure drop, the more it will promotes and favors the nucleation rate of dissolved CO_2 from water.

$$N_{nucl} = C_0 \exp\left(\frac{-\Delta G_{nucl}}{kT}\right) \quad (Baldwin\ et\ al, 1995)$$

$$\Delta G_{nucl} = \frac{16\pi y_{bp}^3}{3\Delta P^2} \qquad (Baldwin\ et\ al, 1995)$$

ΔG_{nucl} is the free energy barrier which is a function of pressure drop. Pressure drop also is a function of pressure. As when the pressure of the system is set high, it will create a larger amount of pressure drop across the converging nozzle which will cause the amount of free energy barrier to decrease. When the amount of free energy barrier is lower, the easier the dissolved CO_2 molecules to diffuse out through the surface of water in the form of bubbles. If the pressure drop across the converging nozzle is low, the free energy barrier, ΔG_{nucl} would be larger causing the probability of dissolve Carbon Dioxide molecules to be more difficult to diffuse out through the surface of water in the form of bubbles.

Hence, it can be said that the higher the pressure of the system introduced, the greater the pressure drop across the converging nozzle will occur. As this occur, it will promote more nucleation rate and desorption rate of dissolved Carbon Dioxide from water would be increase.

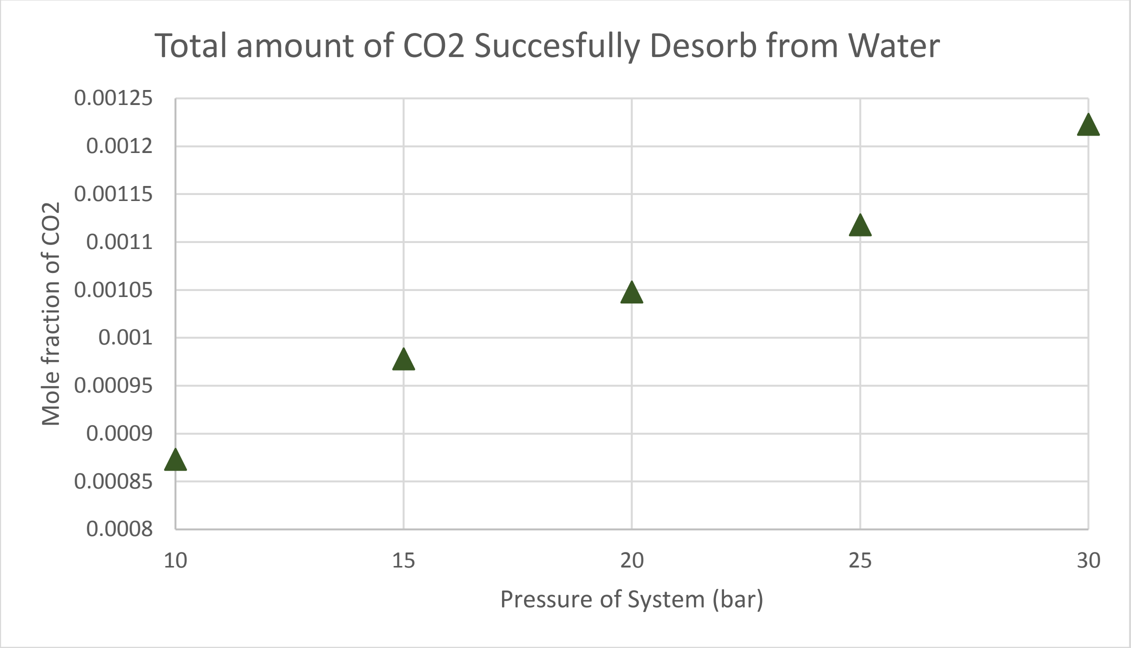


Figure 15: Graph of total mole fraction of CO_2 successfully desorbed from water against pressure of System

CHAPTER 5

CONCLUSION AND RECOMMENDATION

As a conclusion, the aim of the project is to measure the effectiveness of the converging nozzle and to investigate the effect of pressure and pressure drop across the converging nozzle on desorption of dissolved Carbon Dioxide from water are achieved. The development of this new technique is significant to make the process of Carbon Dioxide removal a lot easier and cost saving as we know that currently most of the techniques will cost a lot of money and far more complicated. By using this technique it will help to increase company's profit and indirectly it will increase country's economy. As the process is easier, the production of natural gas will also increase. This will help to increase and support demand for natural gas from user as natural gas can be categorized as one of the main energy source

From the result discussed, it can be said that the pressure of the system will greatly affect the pressure profile across the converging nozzle. It is found that as the pressure of the system is set at a higher value, the pressure drop occur across the converging nozzle also would be higher. This phenomenon occur due to the principle of conservation of momentum. The pressure drop across the converging nozzle played an important role in desorption rate. Pressure drop occur across the converging nozzle will induced turbulence flow for the fluid and promote the nucleation rate of CO2 to release out from water by the formation of bubbles.

It is observed that the amount of CO_2 desorb from water increase as the pressure drop increase. Thus, it can be conclude that to remove more CO_2 from water, a higher amount of pressure drop are required. In order to do that, a smaller size of tubing of the nozzle can be applied and used for future study. Other than that effect of different parameter such as different initial CO_2 loading, type of physical solvent used and different flow rate of the fluid should be further study in the future to improve the reliability of this converging nozzle as a separator mechanism. Apart from that, an improved sampling method are required to be implemented on the test rig to improve and reduce an experimental error from the experiment conducted.

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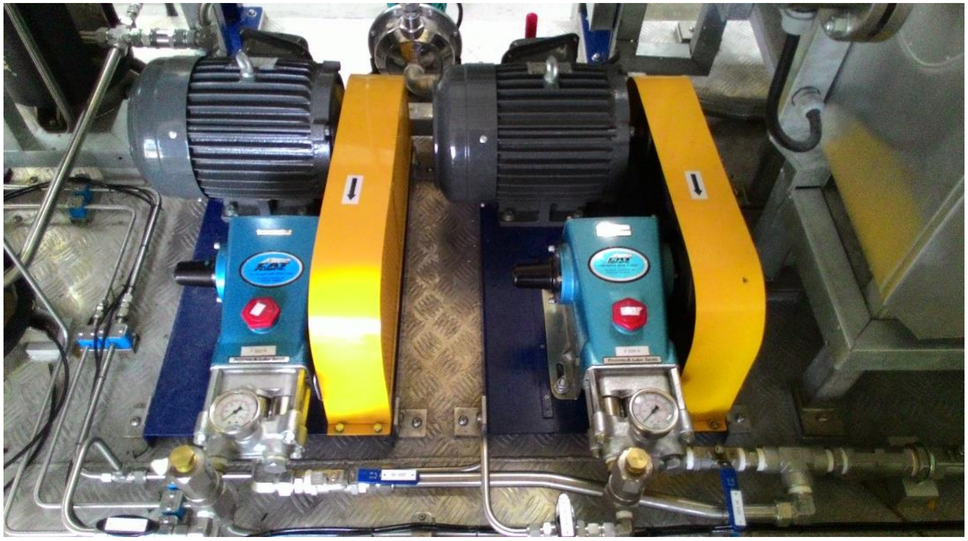
Appendices

Appendix 1: Two pressure vessel and the open tank of the test rig

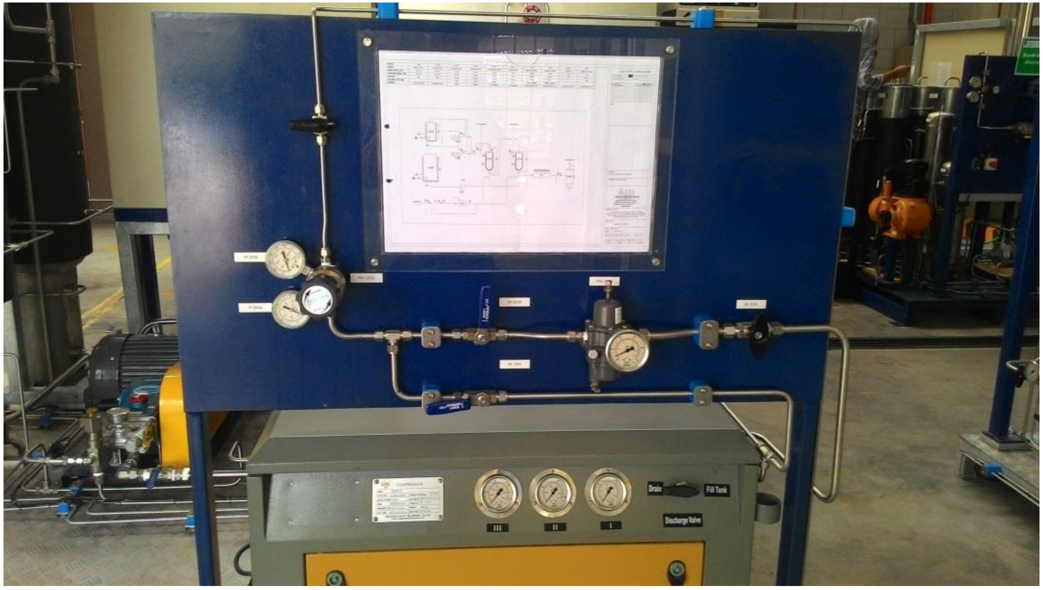
Appendix 1: High pressure pump of the test rig



Appendix 3: Water tank with heater of the test rig

Appendix 4: Converging nozzle of the test rig

Appendix 5: Carbon Dioxide gas compressor



Appendix 6: Main control panel of the system

Appendix 7: Example of calculation of mole fraction of CO_2 in water

This section will illustrate the method how to calculate mole fraction of CO_2 in water from experiment. For example the amount of CO_2 collected in measuring cylinder is 8 mL.

First, need to determine the amount of CO_2 in water at equilibrium at 1 bar and 40 °C by the solubility mathematical model develop.

<u>Molar volume calculation;</u>

$$P_r = \frac{1}{73.82} = 0.013546 \; and \; T_r = \frac{313}{304.19} = 1.02862$$

$$\beta = (0.08664)\frac{0.013546}{1.02862} = 0.001141$$

$$q = \frac{(0.42748)(1.02862^{-\frac{3}{2}})}{(0.08664)} = 4.727138$$

$$Z = 1 + \beta - q\beta \frac{(Z-\beta)}{Z(Z+\beta)}$$

From iteration;

$$Z = 0.995772$$

$$V = \frac{(0.995772)(8.314)(313)}{1} = 2591.278 \frac{cm^3}{mol}$$

Gas fugacity calculation;

$$\begin{aligned}\ln f = \ln &\frac{(8.314)(313)}{2591.278 - 29.6824} \\ &+ \frac{3703835}{(29.6824)(3703835)(313)^{\frac{3}{2}}} \ln \frac{25912.78}{2591.278 + 29.6824} \\ &+ \frac{29.6824}{2591.278 - 29.6824} - \frac{3703835}{(83.14)(313)^{\frac{3}{2}}(2591.278 + 29.6824)}\end{aligned}$$

$$f = 1.005927\ bar$$

Henry Constant calculation;

$$\ln K_{C02} = -6.8346 + \frac{1.2817 \times 10^4}{313} - \frac{3.7668 \times 10^6}{(313)^2} + \frac{2.997 \times 10^8}{(313)^3}$$

$$K_{C02} = \frac{2302.04}{bar}$$

Determine mole fraction of CO_2 in water;

$$x_{co2} = \frac{1.005927(1)}{(2302.04)(1)}$$

$$x_{co2} = 0.000437\ (\frac{mol\ CO_2}{mol\ H_2O})$$

<u>Convert 8 mL excess CO_2 gas collected in measuring cylinder to number of mole;</u>

$$n = \frac{101325 \times 8E - 6}{8.314 \times 313} = 0.000311\ mole$$

<u>Convert number of mole of CO_2 to mole fraction in 20ml (20g) water sample;</u>

$$mole\ fraction\ CO_2\ in\ water\ = \frac{0.000311\ mole \times 18\ g/mole}{20\ g}$$

$$mole\ fraction\ CO_2\ in\ water\ = 0.000279\ \frac{mol\ CO_2}{mol\ H_2O}$$

<u>Add the excess amount CO2 with the amount of CO2 that already dissolved in water</u>

$$total\ mole\ fraction\ CO_2\ in\ water\ = 0.000279 + 0.00437$$

$$total\ mole\ fraction\ CO_2\ in\ water = 0.000716\ (\frac{mol\ CO_2}{mol\ H_2O})$$