OPTIMIZATION STUDY ON AMINE ABSORPTION PROCESS

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ABSTRACT

Capturing CO_2 produced from large scale combustion plants such as fossil fuel power plant is becoming more favourable and feasible. One of the most common methods used to capture CO_2 is amine absorption process. An amine CO_2 capture plant can capture as much as 90% of the CO_2 emitted from the power plant and so has a real benefit for the environment. In this research, optimization is done to optimize the process operation of the absorber column. The parameters such as solvent flow rate, temperature of absorber, number of stages and height of absorber and absorber pressure were adjusted to obtain the optimum condition to maximize the CO_2 removal. A process model was developed using the Aspen Plus® simulation and compared with the base case. This was followed by validating the base case data with the simulation data, so that the result obtain in the simulation is valid with less than 10% of error. From the result obtain, it shows that error percentage obtain is less than 10% with 0.45% of error percentage. It shows that the data obtain from the simulation is valid. This was followed by doing the optimization for amine absorption. Two types of optimization were done which is optimization for operating process condition and optimization for process condition with absorber design. Through the optimization process, the best case found is case 1 and case 6. The suitable optimization parameters are 0.25 mol CO_2 / mol MEA of lean loading, 30 wt% of MEA concentration, 1 bar of absorber pressure, 303K of flue gas and solvent temperature, 1100 kg/s of solvent flow rate, number of stages is 10, 14 m of absorber height and 20 m of absorber diameter.

ABSTRAK

Pengumpulan CO_2 yang dihasilkan daripada pembakaran berskala besar seperti loji janakuasa bahan api fosil sedang menjadi lebih efektif dan boleh di kembangkan ke seluruh negara. Salah satu kaedah yang paling biasa digunakan untuk memerangkap CO_2 adalah proses penyerapan amina. Penyerapan CO_2 menggunakan pelarut amine boleh memerangkap sebanyak 90% daripada CO_2 yang dibebaskan dari loji janakuasa dan mempunyai manfaat sebenar untuk alam sekitar.Dalam kajian ini, pengoptimuman telah dilakukan untuk mengoptimumkan operasi proses ruangan penyerap. Parameter seperti kadar aliran pelarut, suhu penyerap, beberapa peringkat dan ketinggian penyerap dan tekanan penyerap telah diselaraskan untuk memberikan keadaan yang optimum untuk memaksimumkan penyingkiran CO_2. Model proses telah dibangunkan dengan mengguna simulasi Aspen Plus ® dan dibandingkan dengan kes asas. Ini diikuti dengan mengesahkan data kes asas dengan data simulasi, supaya hasilnya adalah sah dengan kurang daripada 10% daripada kesilapan.Keputusan yang diperoleh, menunjukkan bahawa peratusan kesilapan adalah kurang daripada 10% dengan purata preratusan kesilapan sebanyak 0.47%. Ini menunjukkan bahawa data yang diperolehi daripada simulasi adalah sah. Ini diikuti dengan melakukan pengoptimuman untuk penyerapan amina. Dua jenis pengoptimuman telah dilakukan iaitu pengoptimuman untuk keadaan proses operasi dan pengoptimuman bagi keadaan proses dengan reka bentuk penyerap. Melalui proses pengoptimuman, optimum terbaik yang ditemui adalah kes 1 dan kes 6. Parameter pengoptimuman sesuai adalah 0.25 mol CO2 / mol MEA muatan tanpa lemak, 30% berat tumpuan MEA, 1 bar tekanan penyerap, 303K gas serombong dan pelarut suhu, 1100 kg / s kadar aliran pelarut, 10 peringkat penyerap, 14 m ketinggian penyerap dan 20 m diameter penyerap.

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1 INTRODUCTION

1.1 Motivation and statement of problem

Global warming caused by greenhouse gases has been recognized as a worldwide issue. It has become an important issue and its increasing negative impacts on human lives and a sustainable environment are looming more urgently than ever before (Safire, 2007). The global average temperature has been increased by 0.74 K since the late 1800s, and would cause further warming by continued greenhouse gases emission at or above current rates by the end of the 21st century (IPCC, 2007). Example of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), emissions have a long-term influence on climate change. The largest contributor amongst the greenhouse gases is CO_2 gas which accounting for half of the greenhouse effect (Myers, 1989). The Figure 1.1 shows that the CO_2 emission form fossil fuels are increasing every year.

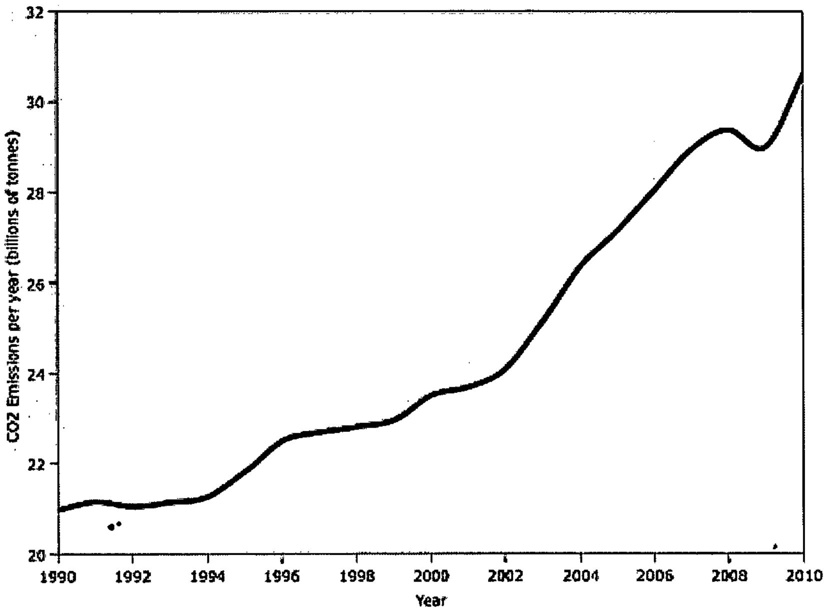

Figure 1.1: Observed CO_2 emissions from fossil fuels (Ahmadi et al., 2012).

The large emissions of CO_2 to the atmosphere cause the global warming issue to be more seriously concerned in the recent years worldwide. The CO_2 concentration in atmosphere now is close to 400 ppm which is significantly higher than the pre-industrial level of about 300 ppm (Oh, 2010). Figure 1.2 shows the contribution of greenhouse gases emissions to the atmosphere.

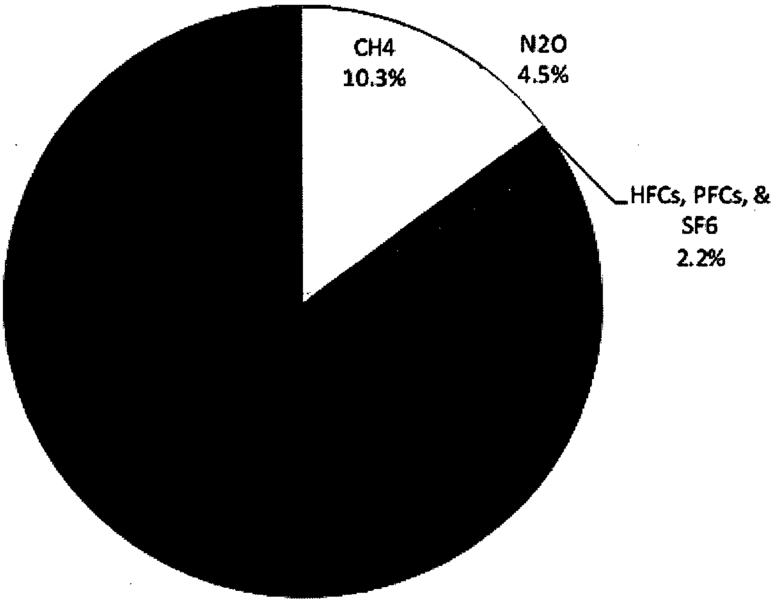

Figure 1.2: Greenhouse gas emissions by gas, 2009 (Ahmadi et al., 2012).

Among the human-related activities, the process of generating electricity through combustion of fossil fuels has been the largest source of CO_2 emissions to the atmosphere than the natural gas power plant (Lawal et al., 2009). Among the types of fossil fuel used, coal has the highest carbon content, resulting in coal-fired power plants having the highest output rate of CO_2 per kilowatt-hour produced (e.g., 743 g CO_2/kWh for pulverized coal, 379 g CO_2/kWh for natural gas combined cycle) (IPCC, 2007). The CO_2 concentration in power station flue gas, for coal-fired boilers is about 15% by volume, while for natural gas combined cycle power plants is 4% and for natural gas-fired boilers is around 8% (Viorica et al., 2010).

Fossil fuels are the dominant source of the global primary energy demand, and will likely remain so for the next decades. Currently, fossil fuels supply over 80% of all primary energy (Han et al., 2011). In the United States, energy–related carbon dioxide (CO_2) emissions alone constitute 83% of emissions from all sources on a CO_2 equivalent basis, and the process of generating electricity is the single largest source of CO_2 emissions from fossil fuel combustion, approximately 41 % in 2006 (EPA website, 2011). Based on IEA (2006), they have reported that the world energy-related carbon dioxide emissions will grow from 29.0 billion metric tons in 2006 to 33.1 billion metric tons in 2015 and 40.4 billion metric tons in 2030.

Since the Industrial Revolution, the emissions of CO_2 from fossil fuel combustion dramatically increased. In 2007, about 29 billion tonnes of CO_2 were from fossil fuel combustion (more than 47% as compared to 1990). As seen in Figure 1.3, energy sector produced nearly 41% of the global CO_2 emissions in 2007, followed by transport and industry. Fossil fuels provided over 70% of the world electricity and heat generation, of which coal supplied 41% of the generation (Viorica et al., 2010).

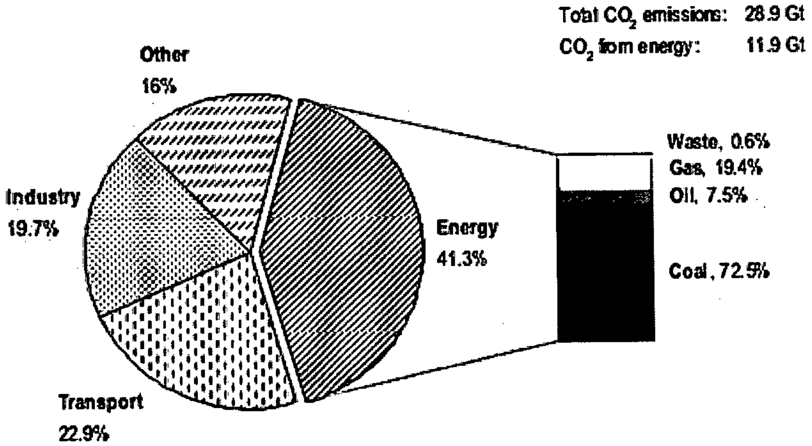

Figure 1.3 – World CO_2 emissions by sector in year 2007 (Viorica et al., 2010).

Therefore the control of CO_2 emission is very important as it is one of the most challenging environmental issues faced by many countries today. Emissions of CO_2 resulting from fossil fuels can be reduced by means of several measures (Viorica et al., 2010):-

(i) To improve/increase the efficiency of power plants and production processes;
(ii) To reduce the energy demand;
(iii) To use low carbon content fuels and to increase the use of renewable energy source;
(iv) To apply CO_2 capture and storage.

The capture of CO_2 from fossil fuel-fired power plants offers the possibility to reduce the CO_2 emissions on a medium time scale. CO_2 capture and storage, which involves capture, transport and long-term storage of CO_2, is now widely recognized as one of feasible methods that could contribute significantly to the reduction of CO_2 emissions. It was reported that it is possible for the European electricity generation system to meet an 85 % CO_2 reduction target by 2050 with a potentially large contribution from CO_2 capture (Odenberger and Johnsson, 2010).

Therefore, to reduce the emission of CO_2 to the atmosphere, there are a few technologies that have been introduced. The methods that can be used to remove CO_2 are absorption process, adsorption process, cryogenics separation and membranes. Among these technologies, chemical absorption using aqueous alkanolamine solutions is proposed to be the most applicable technology for CO_2 capture (Rochelle, 2009). The advantage of a chemical absorption technology is that it is the most matured technology for CO_2 capture and it has been commercialized for many decades. The process involves absorption-reaction of CO_2 with an amine solution followed by regeneration of the amine.

Monoethanolamine (MEA) has been the preferred choice due to its high absorption efficiency (Øi, 2007).Currently, nearly all large commercial plants use the monoethanolamine (MEA) based solvent to capture CO_2. There are several benefits to using MEA to capture CO_2 at low partial pressures. Three key advantages to using this approach include:-

i. The low molecular weight of MEA results in a high solution capacity at high concentrations on a weight basis.
ii. In the MEA molecule, the nitrogen functional group produces a high alkalinity for this primary amine.
iii. MEA has a high reaction rate with CO_2, which is especially important when the CO_2 concentration is low as is the case in power plant post-combustion flue gas.

However, the energy requirement for MEA regeneration is very high (Veawab et al., 2003). Furthermore, MEA is known to be very corrosive. Therefore, there is a considerable incentive for using an alternative solvent such as diethanolamine (DEA), which is comparable to MEA in terms of performance and cost.

The basic separation unit that functions to remove CO_2 using chemical absorption technique is absorber and stripper. Figure 1.4 demonstrates the typical schematic diagram of the CO_2 capture process using re-generable absorbent.

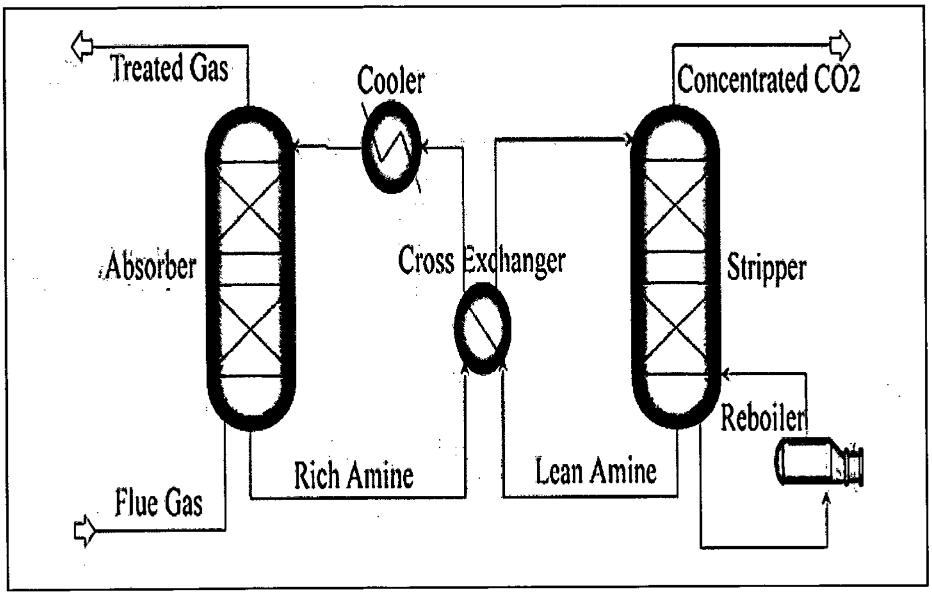

Figure 1.4: Process Flow of Chemical Absorption (Arachchige et al., 2012).

For a general description of the process, the liquid solution containing the chemical absorbent is supplied to the top of the absorber while the flue gas stream from the power plant process flows counter-currently from the bottom to the top of the absorber by passing through the absorber column. The absorber column contains internals such as tray or random packing or structured packing, each of which provides the surface area of contact between the liquid and the gas. This contact allows the desired component to be transferred from the gas phase to the liquid phase. In this process, the liquid chemical absorbent preferentially removes CO_2 from the gas stream while the other components of the gas stream that do not react with the chemical absorbent are vented to the atmosphere from the absorber top. The absorption of CO_2 with amine solvent relies on the reaction between the CO_2 and the MEA solvent in the absorber unit. The CO_2 rich liquid solution exits at the bottom of the absorber. Then, the CO_2 rich solution is pumped through the lean/rich heat exchanger before it enters the regenerator at the top for solvent regeneration and CO_2 stripping.

The carryover vapour stream of the solution is condensed back to the top of the regenerator, leaving mostly wet CO_2 out of the stripping process as the CO_2 product. The reboiler receiving the thermal heat primarily extracted from the steam-power cycle or other sources supplies the energy to the solution in the stripper. After regeneration, the lean solution carrying a lean amount of CO_2 from the reboiler is passed through the rich-lean heat exchanger to transfer heat to the CO_2 rich heat solution before the former is pumped through a cooler to cool the temperature before reintroducing into the absorber at the top. Based on the process, it can be seen that absorber unit is the most important unit to determine the performance of the CO_2 removal. Therefore by improving the design and process operation, it is expected that CO_2 absorption efficiency will be increased.

Besides that, as lean solvent flow rate is increased, more MEA is available to react with the absorbed CO_2 thus increase the absorption of CO_2 in the liquid phase of the absorber column (Harun, 2013). In certain cases, the solvent used in absorption process such as amines solution causes corrosion of the absorber units (Polasek and Bullin, 1984). When the solvent react with some corrosion inhibitors, it will cause erosion of the absorber unit therefore cause high tendency for foaming and solid suspension which can reduce the CO_2 solvent loading.

Hence, this studies aim to optimize the design and operation of the amine-based CO_2 capture process. The goal is to determine the operating conditions and design variables of the amine-based CO_2 capture plant which yields minimum solvent usage with optimum removal of CO_2. The parameters that can be varies to optimize the process are the solvent flow rate, temperature of absorber, number of stages and height of absorber and absorber pressure.Thus, this study will be conducted using Aspen Plus simulator.

Simulation is very useful if changes in an existing system are to be made, and the effects of the changes should be tested prior to implementation. Trying out the changes in the real system may not be a good option as the costs may be too high, the test may take too much time (weeks, months, years), and etc. In all these cases, a simulation model allows to test various scenarios in often only a couple of minutes or hours.Simulation using commercial process simulators such as HYSYS and Aspen Plus are advantageous as they offer good user-interface and reliable property packages for modeling and simulation of such complex process which may take shorter time (Halim and Srinivasan, 2009). Thus, in this research Aspen Plus® will be used as the simulation tool to develop the model as the HYSYS® has some limitations in modelling the absorber and stripper columns with large numbers of trays (Alie, 2004).

1.2 Objectives

This study aims to optimize the amine absorption process mainly on absorber to maximize the percentage of CO_2 capture by using Aspen Plus®.

1.3 Scope of this research

The process flow diagram for amine absorption will be obtained from Arachchige, (2012). The parameters such as process operation and column specifications will be identified and specified in the simulator. In this study, the absorber parameters such as number of stages/ trays, height of absorber, absorber pressure, flow rate of MEA, flow rate of flue gas, temperature of absorber, lean solvent loading (mol CO_2/mol MEA) will be set as the input variables while the performance indicators will be CO_2 removal percentage which are proven to be important to show the efficiency of the CO_2 removal. All the data will be inserted into Aspen Plus® simulator. Pilot plant data from Arachchige et al. (2012) will be used as base case studies for model validation. The analysis on the performance will be done and the results comparison will be carried out.

1.4 Rationale and Significance

My research will focus on optimization study on amine absorption in order to reduce the CO_2 gas that escape to the environment. This is needed because the increasing amount of CO_2 to the atmosphere can cause the global warming issue to be more seriously concern. Therefore, optimization the amine absorption process using chemical absorption method may help to curb this problem. More investigation is being done on each separation unit and operating parameters until this present day to improve the CO_2 removal. This research will study on the optimization of amine absorption process mainly by manipulating the operating parameters such as flow rate of MEA solvent, concentration of the solvent. Besides that, Column Specification also will be manipulated to optimize the CO_2 removal. The separation unit that will be manipulated is absorption unit by changing the height, pressure, and number of stages of the absorption unit. The significant outcome that is expected from this research is improving the CO_2 removal by optimizing the condition in the amine absorption process.

2 LITERATURE REVIEW

2.1 Introduction

This paper presents on the general term of what is carbon dioxide removal and amine absorption. The methods to absorb CO_2 gas and types of solvent used are also explained. The various types of experimental work and how it affects the amine absorption process for capture CO_2 was discussed in this chapter.

2.2 Carbon dioxide removal

Carbon dioxide is one of the greenhouse gases that contribute to global warming and climate change in the environment. Among the greenhouse gases, CO_2 contributes more than 60% to global warming because of its huge emission amount (Albo et al., 2010). Based on Fruend, (2003), the major source of CO_2 emissions are from fossil fuel-fired power plants (e.g. coal and natural gas). Besides effecting the environment, there is also evidence of some harmful effects to public health and safety. Being exposed to higher concentrations of CO_2 can affects respiratory function and depression of the central nervous system. Moreover, high concentrations of CO_2 can also displace oxygen in the air, resulting in lower oxygen concentrations, which can cause suffocation (Smith et al., 2005).

Considering the mentioned effects of carbon dioxide to the atmospheric, several studies have been conducted to find the most efficient ways to prevent continual increase of Carbon dioxide gas to the environment. The CO_2 removal technique commercially available is (a) absorption; (b) adsorption; (c) cryogenics separation and (d) membranes. However, the most famous and popular method in CO_2 purification is chemical absorption because it absorbs and reacts with the gas efficiently.

2.2.1 Absorption Process

Absorption remains the most efficient and viable approach to mitigate CO_2 emissions (Ajibola, 2010). Absorption process can also know as extraction process by using liquid solvent. This solvent can be divided into two categories: chemical and physical solvents. Thus the process can be divide into two categories which is Chemical absorption and Physical absorption process. The current method for capturing CO_2 from flue gas is using a chemical absorption method.

2.2.1.1 Physical Absorption

Physical absorption is a process that utilizes solvent that cannot react with carbon dioxide such as water but is also rarely used because of its inefficiency. Mostly, physical solvent systems are used when the feed gas has high CO_2 partial pressure and low temperatures. The removal of CO_2 by physical solvent absorption is based on the solubility of CO_2 within the solvents. The partial pressure and the temperature of the feed gas are the two major factors that determine the solubility of CO_2 (Ebenezer and Gudmunsson, 2006). In physical absorption, the reaction between CO_2 and the absorbent is weak compare to chemical solvents. Besides that, it also decreases the energy requirement for regeneration. In addition, low CO_2 partial pressures and low outlet pressure of the product stream may also discourage the application of physical solvents method (Ebenezer and Gudmunsson, 2006).

2.2.1.2 Chemical absorption

Chemical absorption processes are used to remove CO_2 in the gas stream by exothermic reaction of the solvent with the gases. Alkanolamines are the most widely used as chemical solvent for CO_2 removal in the natural gas industries. The common amine based solvents used for the absorption process are monoethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA).This solvent reacts with CO_2 to form a complex bond. The hydroxyl groups which attach to the amine help to increase the solubility of amine in water. This helps reduces the vapour pressure of the amines which cause less amount of amine is being lost from the top of the absorber or stripper (Glasscock, 1990).Recently, 2-amino-2-methyl-1-propanol (AMP) which is another group of alkanolamines has become the main focus as it needs less energy for their regeneration (Rodriguez et al., 2011). The disadvantages of absorption are it can cause corrosion of the absorber units.

When the solvent react with corrosion inhibitors, it will cause erosion of the unit, high tendency for foaming and solid suspension. Moreover, since all of the solvents cannot be recycled back to the absorber column, the disposal of the solvents causes environmental hazards and thus showed the common disadvantages of using the absorption process (Bord, Cretier et al., 2004; Ebenezer and Gudmunsson, 2006).

2.2.2 Adsorption Process

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorptive gas separation process can be divided into two types: physical adsorption and chemisorption. The widely used adsorption processes are metal oxide (metal organic frame works) and molecular sieves (zeolites, activated carbon). The figure below shows the adsorption process.

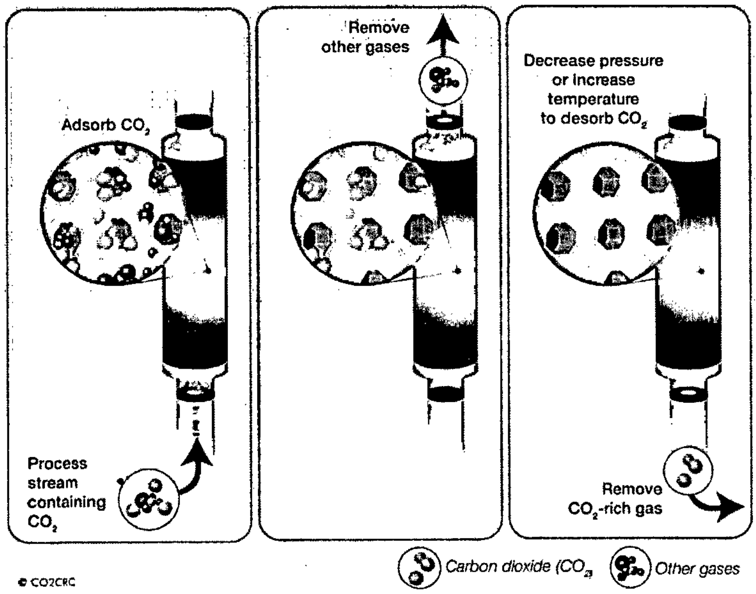

Figure 2.1: The adsorption process to remove CO_2.

2.2.2.1 Chemisorptions

Chemisorptions can be considered as the formation of a chemical bond between the sorbate and the solid surface (covalent interaction of CO_2 and the surface of the adsorbent) that gives scope for much larger increases in adsorption capacity. Such interactions are strong, highly specific, and often not easily reversible. Chemisorptions systems are sometimes used for removing trace concentrations of contaminants, but the difficulty of regeneration makes such systems unsuitable for most process applications (Meyers, 2001).

2.2.2.2 Physical adsorption

In most operations, adsorption processes depend on physical adsorption. The forces of physical adsorption are weaker (a combination of Van der Waals forces and electrostatic forces) than the forces of chemisorptions. Therefore, the heats of physical adsorption are lower and the adsorbent is more easily regenerated as no covalent bonds are formed and heat is released upon adsorption. Physical adsorption at a surface is so fast, and the kinetics of physical adsorption is usually controlled by mass or heat transfer rather than by the intrinsic rate of the surface process (Meyers, 2001). The main advantage of physical adsorption methods is its low energy requirement for the regeneration of the sorbent material with short period of time associated with the change in pressure.

2.2.3 Cryogenic Process

Cryogenic capture involves multiple compressions and cooling stages used directly to liquefy high purity carbon dioxide stream. However, this method requires enormous amount of energy though with high purity rate. Cryogenic separation (also known as low temperature distillation) uses a very low temperature for purifying gas mixtures in the separation process (Ebenezer and Gudmunsson, 2006).While cryogenic separation is used commercially to liquefy and purify CO_2 from streams that have high CO_2 concentrations, it has not been applied to large scale CO_2 capture from flue gas due to the low concentration of CO_2 that makes the application of this technique not economical. Cryogenic separation can separate CO_2 from other gases using pressure and temperature control resulting in solid or liquid CO_2 particulate matter and other contaminants are also removed in the process (Tobin J., Shambaugh P. et al., 2006). The advantages of this process are the suitability to liquefy and purify the liquid CO_2 which is ready for transportation by pipeline.

The main disadvantage of cryogenic separation is that the process is highly energy intensive for regeneration and can significantly decrease the overall plant efficiency (Ebenezer and Gudmunsson, 2006). This figure below shows the process for cryogenic process.

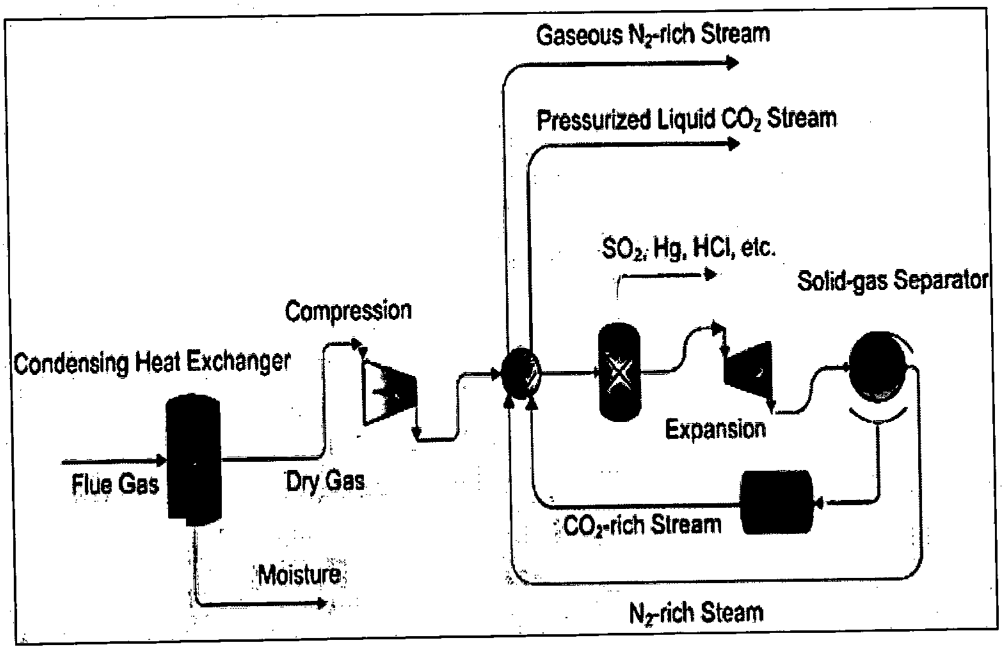

Figure 2.2: Cryogenic process for CO_2 removal.

2.2.4 Membrane Process

Membrane gas absorption is known as the process of membrane coupled with solvent to capture desired gas such as CO_2. In such process, the CO_2 diffuses between the pores in the membrane and is then absorbed by the solvent. The membrane maintains the surface area between gas and liquid phases. This type of membrane is used when the CO_2 has a low partial pressure, such as in flue gases. The advantages of the membranes process in removal of CO_2 are it enhanced weight and space efficiency which make it more applicable for off shore environment, high separation at low pressure and temperature, easy to combine with other separation process and use of other chemicals is not required, more environmental friendly, more flexible to operate, control and also easy to scale-up, low maintenance requirement, reduced energy consumption unless compression used, and low capital costs. However, it has some limitations as the separated CO_2 is at low pressure, it needs additional energy for compression of the feed gas to and meet pipeline pressure standard (Ebenezer and Gudmunsson, 2006).Membrane capture increases CO_2 purity as a multistage formation but decreases the final recovery.

The constrain that warrants the rare use in the industry is that it reduces the efficiency of the plant by eight to fourteen percent due to the compression of gas stream (Baker, 2004). The figures below show the process of CO_2 removal by membrane process.

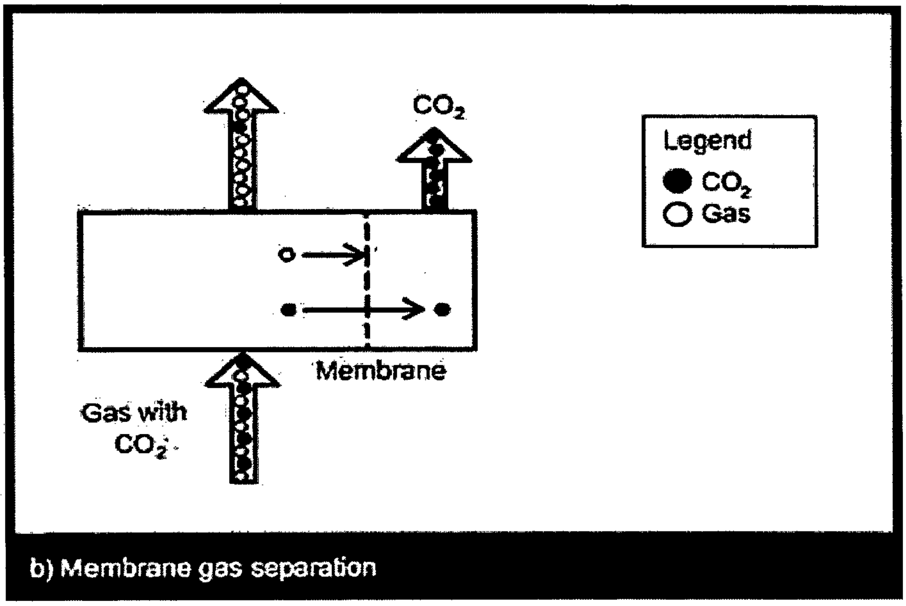

Figure 2.3: Membrane process for CO_2 removal.

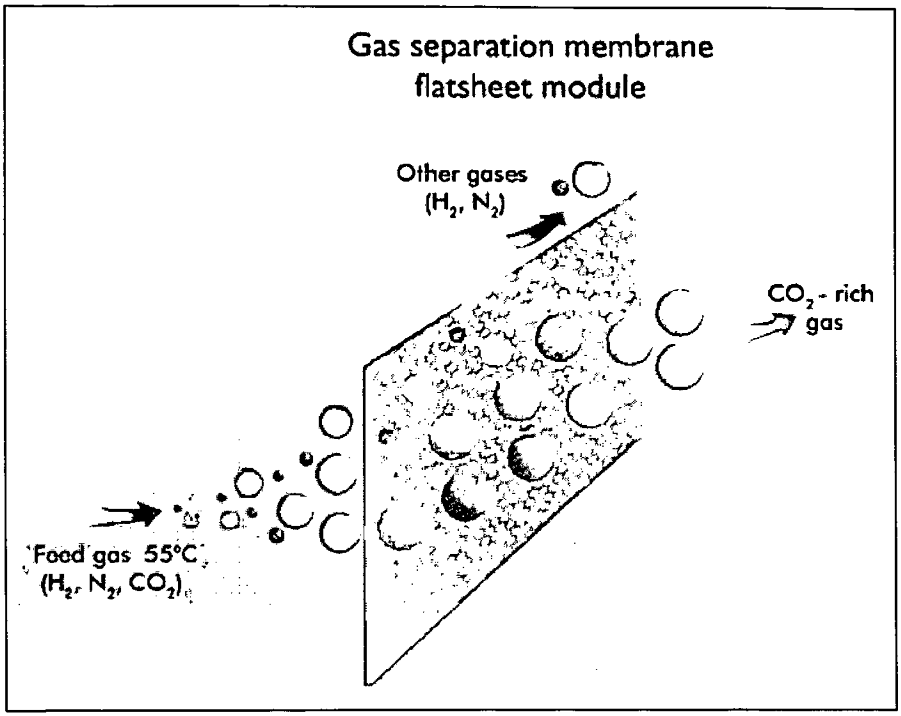

Figure 2.4: Gas separation membrane flat sheet module for CO_2 removal.

2.3 Suitable Method for CO_2 removal

Based on the available method above, it is preferable to use absorption method via chemical absorption as it has more advantages than other methods. The advantage of a chemical absorption technology is that it is the most matured technology for CO_2 capture and it has been commercialized for many decades (Rochelle, 2009). Another advantage of this technology is that it is suitable for retrofitting of the existing power plants (Yu et al. 2012) However, this technology also have several drawbacks such as low CO_2 loading capacity, high equipment corrosion rate, high energy consumption during high temperature absorbent regeneration, large equipment size (Resnik, 2004 and Haszeldine, 2009). The possible remedies to these drawbacks include the improvement of absorbents and operations have been done by many researches and still in progress. The table below show the advantages and disadvantages for different methods of CO_2 capture.

Table 2.1: Overall comparison of methods available for CO_2 captures (Ebenezer and Gudmunsson 2006).

Process	Advantages	Disadvantages
Absorption	• Widely used technology for efficient (50-100)% removal of acid gases (CO_2 and H_2S).	• Not economical as high partial pressure is needed while using physical solvents. • Long time requirement for purifying acid gas as low partial pressure is needed while using chemical solvents.
Adsorption	• High purity of the products can be achieved. • Ease of adsorbent relocation to remote fields when equipment size becomes a concern.	• Recovery of the products is lower. • Relatively single pure product.
Membrane	• Simplicity, versatility, low capital investment and operation. • Stability at high pressure. • Good weight and space efficiency. • Less environmental impact.	• Recompression of permeate. • Moderate purity.
Cryogenic	• Relatively higher recovery compared to other process. • Relatively high purity products.	• Highly energy intensive for regeneration. • Not economical to scale down to very small size. • Unease of operation under different feed stream as it consists of highly integrated, enclosed system.