COMPARISON OF CHEMICAL SOLVENT FOR CO_2 REMOVAL FROM POWER PLANT USING AMINE SCRUBBING PROCESS

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COMPARISON OF CHEMICAL SOLVENT FOR CO_2 REMOVAL FROM POWER PLANT USING AMINE SCRUBBING PROCESS

SITI NAJIBAH ABD RAHMAN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Pure)

Faculty of Chemical & Natural Resources Engineering
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JUNE 2013

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

Special thanks and love for:

My mother, Sarimah Marsan

My father, Abd Rahman Dullah

Beloved ones,

Ahmad Zaim Abu Bakar

and

My Lovely Friends

ACKNOWLEDGEMENT

I would like to express my gratitude to god, Allah S.W.T. for making me realize that dream is nowhere without efforts. For giving me such wonderful life and make me appreciate the knowledge that bestowed upon us. In particular, I wish to express my sincere appreciation to my only supervisor, Dr. Noorlisa Harun, for encouragement, guidance, critics and friendship. Without her continued support and interest, this thesis would not have been the same as presented here.

My praise and gratitude also extends to parents Abd Rahman bin Dullah and Sarimah binti Marsan, for lifetime love and support. Besides that, thank you to my colleagues and others who have provided assistance at various occasions. In particular, my sincere thankful is also extends to all lecturers and others who have provided assistance at various occasions. Their tips and views are useful indeed.

ABSTRACT

This research is aims to compare monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) solvents to achieve higher CO_2 removal efficiency in absorber column by varying some process parameters including amine concentration, lean solvent flow rate and temperature. Process model was developed using Aspen Plus v12.1 with the electrolyte property inserts for each amine using electrolyte-NRTL thermodynamic model. The rate-based Radfrac absorber column are model by using data adapted from pilot plant data Case 32 at University of Texas, Austin by Dugas (2006). From the results obtained, it showed shows that the CO_2 removal efficiency is increased with increasing of amine concentration for each amine. The CO_2 removal efficiency using the MEA solvent is the highest compared than DEA and MDEA solvent. Besides that, it is more realistic to used MEA concentration not more than 31.5 wt. % as it can achieved 99.8% CO_2 removal efficiency and to avoid corrosion effect to equipment in real plant. As the lean solvent flow rate increases, the CO_2 removal efficiency for studied amines increases that can be arranged as the following order: MEA > DEA > MDEA. MEA shows high CO_2 removal efficiency because MEA is primary amine which has high CO_2 absorption capacity and reactivity than to DEA and MDEA. However, CO_2 removal efficiency was decrease as lean solvent temperature increase for all amines. This is due to the reduction of amine in lean solvent since it were vaporised before entering the absorber. MEA solvent can achieved approximately 99% CO_2 removal at 1 kg/s lean solvent flow rate. While the DEA and MDEA can achieve 99% CO_2 removal efficiency around 133 kg/s and 110 kg/s lean solvent flow rate respectively. It proved that the MEA can achieve very high CO_2 removal efficiency at low lean solvent flow rate and concentration compared to DEA and MDEA.

Keywords: power plant, absorber model, CO_2 removal, amine solvent, Aspen Plus.

ABSTRAK

Kajian ini adalah bertujuan untuk membandingkan monoethanolamina (MEA), dietanolamina (DEA), dan N-methyldiethanolamina (MDEA) pelarut untuk mencapai kecekapan penyingkiran karbon dioksida (CO_2) yang lebih tinggi dengan mengubah beberapa parameter proses termasuk kepekatan amina, kadar aliran 'lean solvent' dan suhu. Simulasi proses dilakukankan menggunakan Aspen Plus v12.1 dengan memasukkan elektrolik bagi setiap amina yang model termodinamik elektrolik-NRTL. 'Radfrac absorber' simulasi dilakukan berdasarkan model dengan data disesuaikan dari 'pilot plant' kes data 32 di Universiti Texas, Austin oleh Dugas (2006). Daripada keputusan, ia menunjukkan bahawa kecekapan penyingkiran CO_2 telah meningkat dengan peningkatan tumpuan amina untuk setiap amina. Ia dilihat bahawa kecekapan penyingkiran CO_2 menggunakan pelarut MEA yang adalah yang tertinggi daripada pelarut DEA dan MDEA. Selain itu, adalah lebih realistik untuk MEA tidak kepekatan digunakan lebih daripada 31.5 wt.% kerana ia boleh dicapai 99.8% kecekapan penyingkiran CO_2 dan untuk mengelakkan kesan hakisan kepada peralatan di dalam loji kuasa sebenar. Apabila kadar aliran 'lean solvent' meningkat, kecekapan penyingkiran CO_2 untuk amina yang dikaji boleh disusun sepertiyang berikut: MEA > DEA > MDEA. MEA menunjukkan tinggi kecekapan penyingkiran CO_2 kerana MEA adalah 'primary amine' yang mempunyai kapasiti penyerapan CO_2 yang tinggi dan kereaktifan daripada DEA dan MDEA. Walau bagaimanapun, kecekapan penyingkiran CO_2 adalah menurun apabila suhu kadar aliran 'lean solvent' meningkat untuk semua amina. Ini adalah disebabkan oleh pengurangan amina dalam kadar aliran 'lean solvent' kerana ia telah diwapkan sebelum memasuki penyerap. MEA boleh pelarut mencapai kira-kira 99% penyingkiran CO_2 pada 1 kg / s kadar aliran 'lean solvent'. Walaupun DEA dan MDEA boleh mencapai 99% penyingkiran CO_2 kecekapan sekitar 133 kg / s dan 110 kg / s bersandar kadar aliran pelarut masing-masing. Ia membuktikan bahawa MEA boleh mencapai kecekapan penyingkiran CO_2 sangat tinggi pada rendah kadar aliran 'lean solvent' dan kepekatan berbanding dengan DEA dan MDEA.

Keywords: loji kuasa, model penyerap, penyingkiran CO_2, pelarut amina, Aspen Plus.

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LIST OF ABBREVIATIONS

$\dot{m}^{fluegas}$	flue gas flow rate
$\dot{m}^{solvent}$	solvent flow rate
$T^{fluegas}$	flue gas temparature
$T^{solvent}$	lean solvent temperature
wt.	weight
x_{amine}	amine concentration

LIST OF ABBREVIATIONS

CCS	Carbon capture and storage
CFC	Chlorofluorocarbon
CH_4	Methane
DEA	Diethanolamine
EOR	Enhances oil recovery
GHG	Greenhouse gases
IGCC	Integrated Coal Gasification Combined Cycle
IPCC	Intergovernment Panel on Climate Change
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
NRTL	Non-random-two-liquid
SFC	Sulfur hexafluoride
TWh	Terawat hours
USD	United Stated Dollar

1 INTRODUCTION

1.1 Background

The “Three E’s” stand for energy, economy and environment which are all societies concerned. People need energy particularly to generate electricity to improve standard quality of life, increase economic status and at the same time living in clean environment. Societies living with electricity, peoples drink cleaner water, live longer and have better education. Besides that, energy also can transform agrarian societies to modern industrial societies by increases their income and wealth. This can prove by industrial country such as in United States and Western Europe which use fuels to improve their socio-economic (IEA, 2012).There are four macro trends which are industrialisation, urbanization, modernisation and electric information revolution which are the criteria of modern industrial societies. These macros have required high demand for energy for transportation, manufacture products and transfer information. Urbanisation is the main factor that drives high demand of energy due to increase the proportion and population of people living in cities (IEA, 2012).

The energy supply, particularly electricity must be enough to fulfil the demand of electricity required for maintain socio-economic worldwide development. Fossil fuels including coal, natural gas and oil are contributed about 81% of world’s primary energy demand (IEA, 2012). Coal is main fossil fuels generating electricity compared to natural gas and oil over the past decades. Electricity produced by coal is over 8200 terawatt hours (TWh) annually which is about 41.3% of the world’s power as show in Figure 1.1. Furthermore, additional of 3800 TWh contribute 44% of coal generating electricity by 2035.

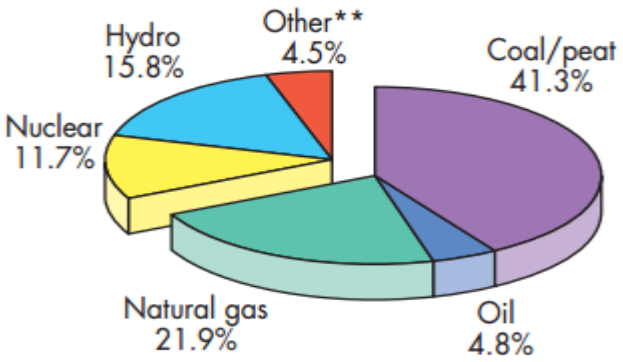


Figure 1-1: 2011 electricity generation by sources (IEA, 2013)

**Other includes geothermal, solar, wind, biofuels and waste, and heat

If compare among fossil fuels, coal give low energy prices which enables produce inexpensive electricity. In China, electricity generating from coal is the most affordable sources which costing USD 33/ MWh compared to USD 71 for wind, USD 50 for hydro and USD 53 for nuclear (IEA, 2010). Additionally, energy produced by coal have equivalency basis than natural gas and oil (IEA, 2012). Since coal is most abundant and widely distributed fossil fuel, the amount of electricity generated from coal is exceeds coal capacity compared to other fossil fuels.

Global climate changes know as global warming is a serious environmental issue which are most of people concern and become global problem. Global warming is caused by greenhouse gases (GHGs) in earth atmospheres that trap heat from reflected back to space. CO_2 is proven as the most abundant greenhouse gas that has caused increasing of earth's surface temperature and climate changes than others GHGs like CH_4, SF_6. N_2O, and CFC's (IPCC, 2005). The main source of CO_2 is from flue gases exhausts from burning of fossil fuels in boilers and furnaces that emitted from large exhaust stacks (Table 1.1). Besides that, large point sources of CO_2 are concentrated in proximity to major industrial and urban areas which use coal as generating electricity (IPCC, 2005).

Table 1-1: CO_2 emission by process (IPCC, 2005)

Process	Number of sources	Emissions ($MtCO2\ yr^{-2}$)
Fossil fuels		
Power	4,942	10,539
Cement production	1,175	932
Refineries	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas processing	Not available	50
Other sources	90	33
Biomass		
Bioethanol and bioenergy	303	91
Total	7,887	13,468

As the awareness and responsibility towards the environment, there are some options can be taken to reduce CO_2 emissions from power plant such as using advanced fossil-fuel technologies to increase coal-based generation efficiency and coupled with capturing and storing (CCS) CO_2 exhaust from combustion of fossil fuels. The benefits from these options can sustain coal as primary energy source and help reduce global warming. There are three types of CO_2 captured system for power plant such as post-combustion, pre-combustion and oxy-combustion. However, these technologies still in pilot plant stage and not applied yet in existing commercial power plant. There are several CO_2 capture technologies available such as chemical and physical absorption, adsorption, cryogenic and membrane separation. The key of selection for CO_2 system and technology are depending on energy efficiency, capital cost, and performance in plant.

According to Herzog et al. (2000). shown that absorption process based on chemical solvents are currently the preferred option for post-combustion CO_2 capture and suitable for fossil fuels power plant. Advantage of post combustion process technology is it can retrofitted to existing fossil-fuel power plant with less capital investment compare to pre-combustion and oxy-combustion. Besides, this process is suitable for treating high-volume gas stream containing H_2S and CO_2 at low partial pressure (Kohl and Nielsen,

1997). Amine solution is chemical solvents that used for many years for removal CO_2 from natural and synthesis gases because the maximum removal CO_2 can be achieved.

1.2 Motivation and problem statement

Amine scrubbing process had proven as most preferred technology used to CO_2 removal in post combustion for many reasons. Amine solvent can achieve high CO_2 absorption about 90% when the gas is to be treated at low pressure, typically 3-15kPa (Kohl and Nielsen, 1997; Rao and Rubin, 2002). Additionally, amine solvent has low capacity and high alkalinity.

However, the existing chemical solvent used in this process give contribute to some drawback to such as high corrosion rate to equipment, low CO_2 loading capacity , and chemical losses. Corrosive is serious problem when using amine solvent in gas purification which gets most of the attention and many extensively studied available to eliminate corrosion issued. MEA is proven as most corrosive chemical solvent than other amine-based solvents (Kohl and Nielsen, 1997). The corrosion in amine plant including; wet acid gas corrosion occur in overhead section of stripper and bottom section of absorber, amine solution carbon steel corrosion occur in the bottom section of stripper. Wet CO_2 corrosion happen when increase in hydrogen ion concentration in ionization of CO_2 dissolve in water. So, the rate of corrosive increase with increases CO_2 concentration in the water. Amine solution carbon steel corrosion is cause by amine type. Primary and secondary amine can give corrosive since they can form carbamate when react with CO_2 than tertiary amine (Kohl & Nielsen, 1997).

Chemical losses of existing amine solvent, especially MEA which has higher vapour pressure than other amine and volatility losses can happen in low pressure in absorber (Figure 1.2).Besides that, amine degradation is another factor of chemical losses in existing amine plant. Solvent degradation is around 10% of total cost of CO_2 capture (Rao and Rubin, 2002).There are two types of degradation occur in existing fossil-fuel power plant which are thermal degradation occur due to presence of CO_2 at high temperature and high pressure in stripper and oxidative degradation occur if high amount of O_2 present in flue gas in absorber. In case of MEA, ammonia, N-(2-hydroxyethyl)-2-(2-hyroxyethylamino)-acetamide (HEHEAA) and N-(2-hydroxyethyl)-

piperazin-3-one (HEPO) are main degradation product in pilot plant (Gouedard et al., 2012). Degradation products can give advantages such as increase solution viscosity, decrease amine solution absorption capacity and in some case can contribute amine corrosive (Kohl and Nielsen, 1997).

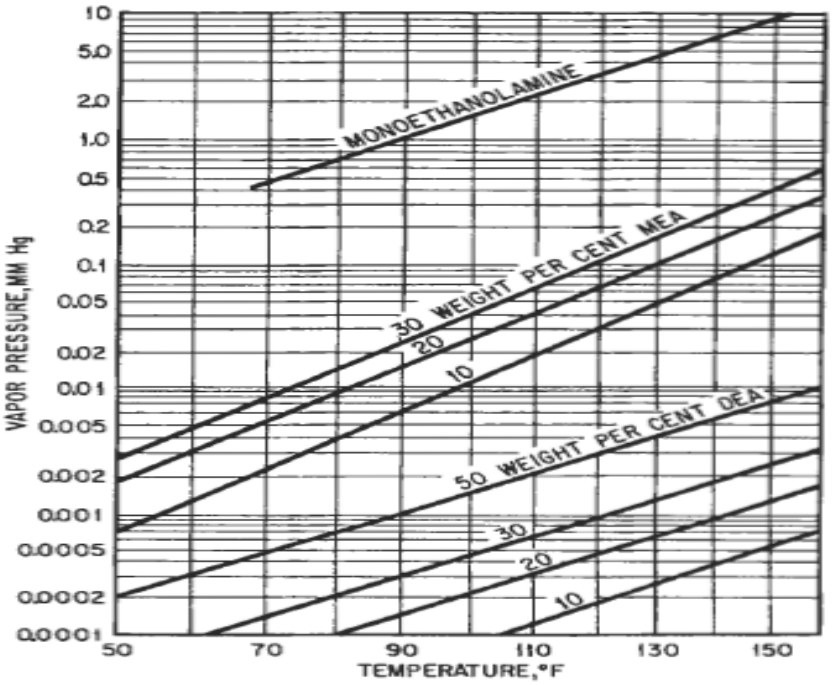


Figure 1-2: Vapor pressure of MEA and DEA at varies temperature
(Kohl and Nielsen, 1997)

All these problems will lead to high energy demand required for solvent regeneration which reduces the plant efficiency. Besides that, these problems will reduce the CO_2 removal efficiency in absorber and vented gases will increase GHG emission to atmospheres. Therefore, improvement in chemical solvent development is crucial for achieve higher CO_2 removal, reduce corrosive and decrease chemical losses. Besides, output from absorber can affect amount of energy required for amine degradation in stripper. Moreover, each of amine solvent has different reactivity at different parameter such as column pressure. Solvent flow rate and amine concentration also can give effect on efficiency of CO_2 removal in absorber. Thus, three types of chemical solvent which are alkanolamines; MEA, DEA and MDEA are chosen in this study to find which one is the best for higher CO_2 removal in post combustion. Main focus in this study is absorber column which to achieve higher efficiency of CO_2 removal by varying some process parameters (amine concentration, lean solvent flow rate and temperature).

1.3 Objectives

The following are the objectives of this research:

- To compare the performance of absorber column to remove CO_2 from power plant using different types of amine solvent using Aspen Plus® software.

1.4 Scope of this research

The following are the scope of this research:

i) Modeling of absorber for CO2 removal from coal power plant using amine scrubbing process based on the pilot plant study which done by Dugas (2006).

ii) Analyse the effect of amine concentration, lean solvent flow rate and temperature of MEA, DEA and MDEA on the efficiency of CO_2 removal.

The process flow diagram which stand-alone absorber is same as in Alie et al. (2005) and the flue gas flow rate and composition is used from Notz et al. (2012) based on the post combustion pilot plant study. Thermodynamics and transport properties were modelled by using amine concentration in Aspen Plus (Alie et al., 2005, Abu-Zahra et al., 2006). In this study, three difference types of amine solvents are used; MEA, DEA and MDEA to find the highest percentage of CO_2 removal in absorber. The concentration of amine solvent, lean solvent flow rate and temperature of each amine are set as process parameters variation used in this study. All these process parameter variations were used to find the efficiency of CO_2 removal in amine scrubbing process.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 present about review from previous literature related to CO_2 capture process in post-combustion technology. This chapter also describe in details about amine scrubbing process. Other than that, literature review about amine based-solvent and its chemistry and chemical kinetics also discussed in this chapter.

Chapter 3 describes the simulation algorithm used in this study. The operating conditions and column specification are including in this chapter. This chapter also gives overview about process parameter variation in this study.

Chapter 4 present the model validation for this simulation. Besides that, this chapter also shows the result and discussion based on the results obtained.

Chapter 5 gives a conclusion of the result and discussion which obtained from the Chapter 4.

2 LITERATURE REVIEW

2.1 Overview

This chapter are divided into six sections and organizes as follow: In Section 2.1 gives an overview of CO_2 emissions. Section 2.2 provides the potential of CO_2 capture technology for power plant including post combustion, oxy fuel combustion and pre combustion. While in Section 2.3 gives a description on advanced Post-combustion CO_2 capture. In section 2.4 an overview about amine scrubbing process. Meanwhile, section 2.5 briefly describes amine based-solvent and its chemistry and chemical kinetics. Lastly, section 2.6 provides overview about Aspen Plus simulator programme.

2.2 Carbon Dioxide Emission

Carbon Dioxide (CO_2) is proven as most abundant greenhouse gas that has caused increasing of earth's surface temperature and climate changes (Desideri and Poalucia, 1999; IPCC, 2005). About 77% of CO_2 emissions contribute to greenhouse gases composition and 74% from that are contribute from fossil fuel combustion (Figure 2.1).The increasing earth temperatures can result the world being affected by droughts and also harming agricultural production. According to United Framework Convention on Climate Change (UNFCCC, 2006) Conference, average global temperature increase must be held below 2 degrees Celsius (°C) to avoid worst impact of climate change .The maximum greenhouse gases concentration in earth atmospheres to achieve 2°C is 450 parts per million (ppm) of carbon-dioxide equivalent (IEA, 2013).

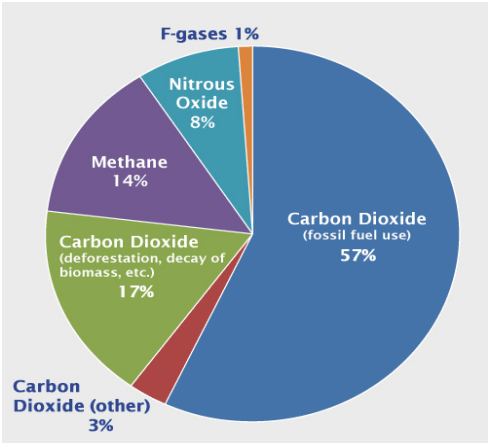


Figure 2-1: Global greenhouse gas (IPCC, 2007)

Combustion of fossil fuel power plant is main source of CO_2 emission to atmospheres compared than to industrial processes and natural gas processing. CO_2 emission contribute from coal fired power plant is higher than natural gas and oil combustion (Figure 2.2). The control of this greenhouse gases is the most concern in environmental policy issue in worldwide. Carbon capture and storage (CCS) is one of most suitable mitigation option to reduce CO_2 concentration in atmospheres and fulfil continual use of carbon-based fuels to meet the world's growing energy demand. CCS is possibly to decrease total energy related CO_2 emissions from 36 percent in 2005 to 34 percent in 2040 (IEA, 2013). CO_2 from flue gases produced by combustion of fossil fuels will extract using CO_2 recovery system. This system will produce concentrated CO_2 and will be stored in disposal site such as underground or used in food, chemical industries and enhances oil recovery (EOR) rather than emitted to atmosphere (Chapel et al., 1999; IPCC, 2005).

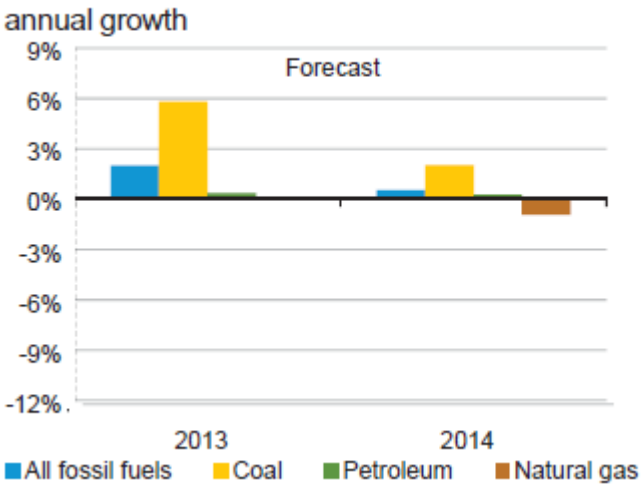


Figure 2-2: United Stated Carbon Dioxide emission by fossil fuel (Short-Term Energy outlook IEA, 2013)

2.3 CO2 capture technologies

Although the CO_2 technologies has not been applied at large-scale power plants, but there are wide range of technologies exits for CO_2 removal (IPCC, 2005). Figure 2.3 show four types of CO_2 capture system; post combustion, pre combustion and oxy-fuel combustion (Rao and Rubin, 2007; IPCC, 2005). The selections of CCS technology are based on performance of CCS technology used, the condition of flue gas which depends on the power plant technology and also the capital cost (Chakravarti et al., 2001). The

most cost-effective levels of CO_2 capture efficiency were estimated to be 81% for 1000 MWg power plant (Rao and Rubin,2006). The best practical use of CCS technology is by retrofitted or add-on to the existing power plants which without modify the current infrastructure.

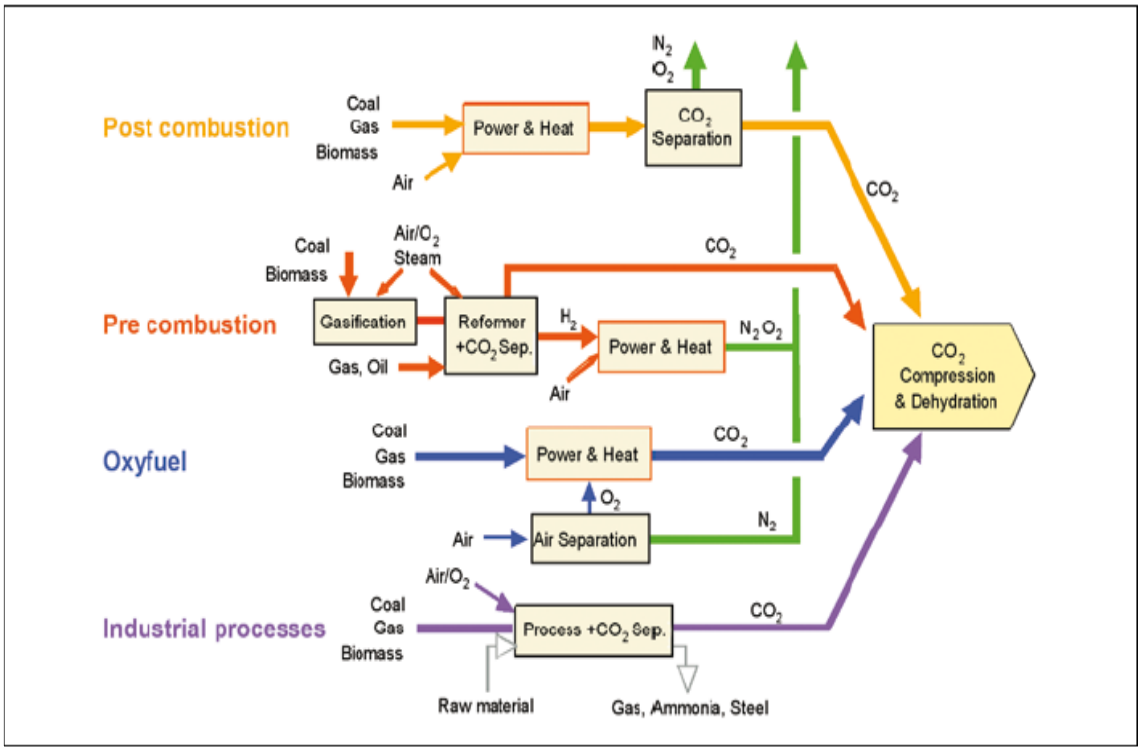


Figure 2-3: Carbon dioxide capture systems

2.3.1 Post combustion

In post combustion technology, CO_2 is captured from the flue gas exhaust by combustion of fossil-fuels in air (Figure 2.4). The CO_2 recovery system will absorbed CO_2 from flue gas that pass through it. The captured CO_2 is sequestration and the free CO_2 is discharged to atmosphere. The flue gases produced from combustion of fossil fuel is at atmospheric pressure which low pressure resulting large amount of nitrogen present in air. Hence, the large scale of CO_2 recovery unit needed which required higher capital cost. Chemical solvent process is commonly used for CO_2 removal in post combustion technology. A large amount of thermal energy required in this process to regenerate solvent and resulting reduction the efficiency of power plant. Even though the chemical solvent process in post combustion technology more problematic than other technology, it most common technology use which give high CO_2 capture

efficiency and selectivity (IPCC, 2005). Besides that, post combustion technology still preferred technology to remove CO_2 since this process is reliable and well proven.

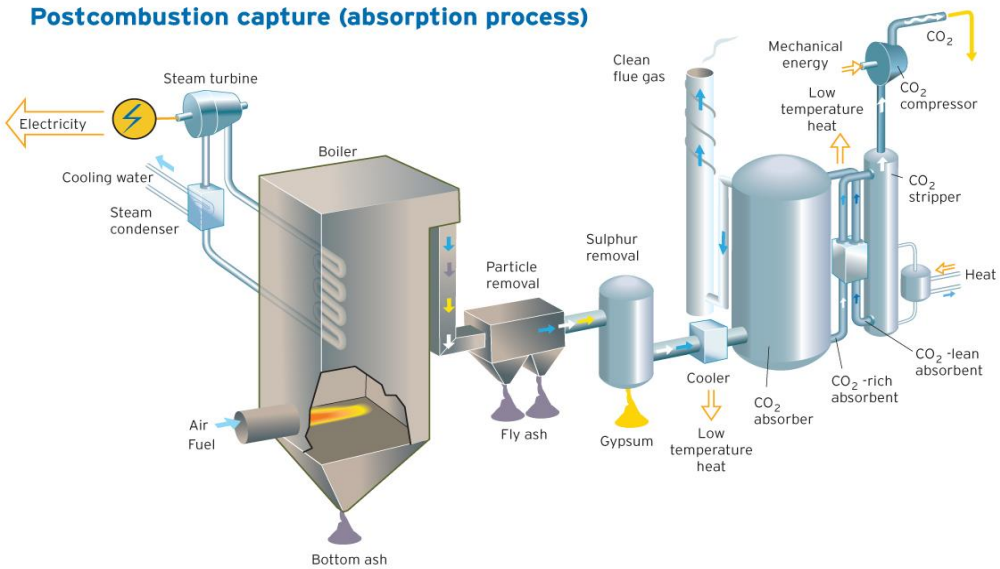


Figure 2-4: Post combustion technology

2.3.2 Oxy fuel combustion

Mechanism of oxy fuel combustion technology is same as in post combustion technology, but pure oxygen is used for combustion instead of air. By doing this, the composition of flue gas produced from combustion of fossil fuel mainly 80-98% CO_2 and H_20.Thus, CO_2 recovery system not required in this technology and CO_2 is directly to CO_2 compression process. Oxygen produced in air separation with low temperature which is cryogenic and other techniques including membranes and chemical looping cycles (IPCC, 2005). Disadvantages of this process is high temperature produced about 3500°C when combustion of fossil fuels and pure oxygen. Thus, the typical power plant material such as gas turbine cycle operates at 1300°C - 1400°C cannot be matched with the process. Water cooling is needed in the combustion chamber to control the temperature. CO_2 removal using oxy-fuel combustion is not commercial yet.

2.3.3 Pre combustion

In pre-combustion technology, fossil fuel is reforming to produce synthesis gas or syngas by reacting fossil fuel with oxygen or air and/or steam. The syngas is composed of hydrogen and carbon monoxide. Carbon monoxide is converted to CO_2 in a catalytic reactor by reacting CO with steam. Next, the CO_2 can be captured and storage, while

hydrogen is combusted to produce power. CO_2 in pre-combustion is captured and storage before the combustion process. Pre-combustion technology usually used physical and chemical absorption to remove CO_2 and high concentration hydrogen are used as fuel for gas turbines, boilers and furnaces. Integrated Coal Gasification Combined Cycle (IGCC) is technology for new power plants where coal is converted or gasified into CO_2 and H_2 before combustion. Advantages of IGCC are low levels of air-pollutant emission since the pollutants are captured before combustion, low process stream volume and can operate at high partial pressure. However, IGCC are not widely implemented in CCS because it only relevant to new power plant, not matured as post-combustion technologies and high capital cost than pulverized coal power plant (IPCC, 2005; Chakravarti et al., 2001).

2.4 Advanced Post-combustion CO2 Capture

Varieties of processes and improvement have been developed over the years to treat certain of gas with the aim of optimizing capital cost and operating cost and for environmental purpose. A lot of CO_2 recovery from flue gas technologies currently exists such as membranes, absorption, adsorption and cryogenic (Rao and Rubin, 2007; IPCC, 2005). Adsorption, membranes and cryogenics separation technologies are exist, but they not economically viable for CO_2 removal from flue gases in post combustion power plant. In adsorption process, CO_2 are adsorbed to activated carbon and desorbing of CO_2 by using pressure swing operation. This process not deployed in CO_2 removal from flue gas but commercial in hydrogen production from synthesis gas. Whereas, membrane process is operated at high CO_2 concentration and high pressure which not compatible with low partial pressure and low concentration of CO_2 from flue gas. This will reduce the driving force for CO_2 separation in membrane process (IPCC, 2005). There are two types of absorption available for CO_2 removal in post-combustion power plant which is chemical and physical absorption. The selection of separation process for CO2 removal is depend on the flue gas characteristics (Chakravarti et al., 2001).Typical composition of flue gas emitted from coal-fired power plant is 14% CO_2, 5% O_2 and 81% N_2 at low pressure which above atmospheric pressure (Chakravarti et al., 2001).Chemical absorption process is currently preferred process for CO_2 removal in post-combustion since the CO_2 from flue gases is diluted and low partial pressure (IPCC, 2005; Kohl and Nielsen, 1997).

2.4.1 Physical Absorption

In physical absorption is occurring at low temperatures and high pressures (>200psia) and suitable for high partial pressure CO_2 from natural gas. Besides, CO_2 are absorbed into solvent on Henry's law (Lawal et al, 2009). The CO_2 absorb into soluble solvent and does not react chemically with solvent. This process is not convenient for flue gas because of low driving force of separation that gives low CO_2 removal. According to Chakravarti et al. (2001), high amount of energy required to compress which mostly composed of N_2 gas if physical absorption used in CO_2 removal from flue gas. Example of solvent used in physical absorption process is polyethylene glycol dimethyl ether in Seloxol Process (Kohl and Nielsen, 1997).

2.4.2 Chemical Absorption

Chemical reaction involve in chemical absorption is well applicable for CO_2 removal from flue gas. The chemical reaction can enhance the driving force of separation of CO_2 from flue gas to chemical solvent even at low CO2 partial pressure (60-100 psia). Besides that, the higher CO_2 removal efficiency can be achieved by this process. CO_2 purity (>99%) vapour can be obtain show that chemical absorption is most effective CO_2 removal from flue gas (Chakravarti et al., 2001). Chemical solvents which suitable for captured CO2 from flue gas at low partial pressure is aqueous solution chemicals. According to Kohl and Nielsen (1997), amines based solvent is most widely and reliable as chemical solvent known as amine absorbing or amine scrubbing process.

2.5 Amine scrubbing process

Amine scrubbing process is one of the chemical absorption processes which using amine liquid as solvent to remove CO_2. The high percentage of CO_2 removal can be achieved by this process between 80%-95%.The unit operations used in this technology consist of absorption packed and stripping column and the process is continuous (Figure 2.5).

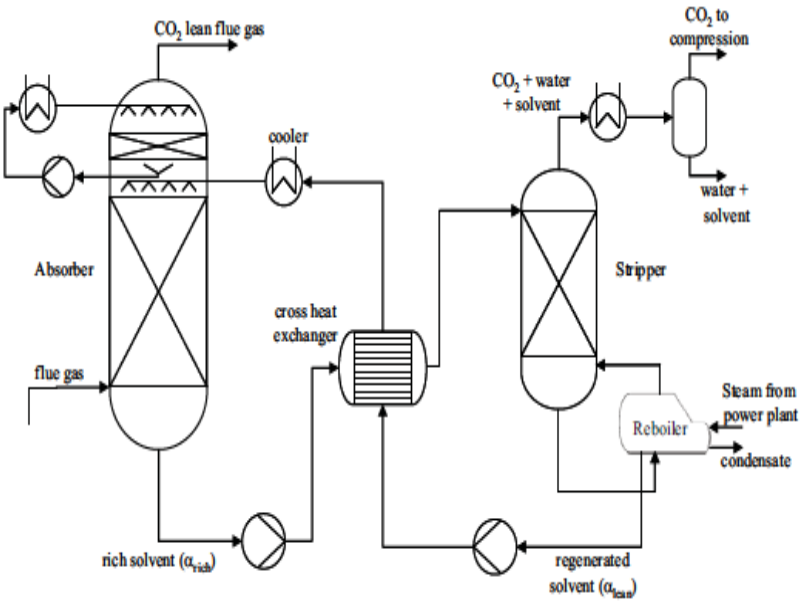


Figure 2-5: Typical process flow diagram for amine scrubbing process from flue gas

Treatment on flue gases is needed to remove acid gas such as NO_x and SO_x that can reduce absorption efficiency by forming heat stable salts with amine solvent (Lawal et al.,2009). Flue gas is cooled to 45-50°C before enter the absorber to increase CO_2 absorption and reduce solvent loss. Treated flue gas enters at the bottom of absorber and lean amine solvent enters from the top of absorber to allow counter-current flow. The temperature of solvent increase as absorbs CO_2 from flue gas which the reaction is exothermic. Temperature of top absorber is between 40-45°C and 50-60°C at the bottom absorber. CO_2 from flue gases absorbed and react chemically with lean amine solvent counter currently in the absorber. The absorption process is exothermic reaction and typical temperature of absorber is low between 40°C-60°C (IPCC, 2005; Cheng et al., 2012). Washing section at top absorber maybe required to reduce water loss and free CO_2 gases are vented to atmospheres.

2.6 Amine based Solvent

Amine compound are characteristic by presence of amino group (-NH_2) attach in hydrocarbon chain and water-soluble organic chemicals. Amines are divided into primary, secondary and tertiary amines which depend on hydrogen attached to nitrogen atom. Amine is solubility to acid gases because they are bases. Selection of amine solvent is important because it will affect percentage of CO_2 removal and its

regenerability. Many literatures are available study about the comparison performance between different amine solvent (Anita et al., 2013). The selection of amine solvent is based on low degradation, low corrosion, cheap, high reactivity and high absorption capacity (Davidson, 2007). Aqueous alkanolamines are widely used as solvents in gas cleaning for remove CO_2. Alkanolamines compound are consist of hydroxyl group (-OH) and amino group (-NH_2).

2.6.1 Monoethanolamine (MEA)

Monoethanolamine or 2-aminoethanol (often abbreviated ad MEA), is an organic compound which is primary amine due to two hydrogen atoms attached to nitrogen atom (Figure 2-6). Like other amines, MEA acts as a weak base. It is a toxic, flammable, corrosive, colorless with an odor like ammonia. Ethanolamine is commonly called as monoethanolamine (MEA) to differentiate it from diethanolamine (DEA) and triethanolamine (TEA). It is produced by reacting ethylene oxide with ammonia.

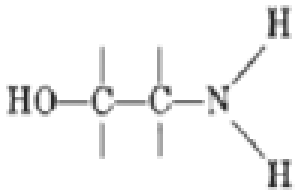


Figure 2-6: Molecular structure of MEA (Kohl and Nielsen, 1997)

Aqueous MEA solutions are first ethanolamines and have been used widely for many decades to remove CO_2 and hydrogen sulfide from natural gas stream (Kohl and Nielsen, 1997). Most of post-combustion power plant used MEA in chemical absorption process (Herzog et al. 2000). For example, Fluor Daniel Economine FG process is commercial process used 30 weight% concentrations of MEA in CO_2 recovery system that recover 95% CO_2 (Chapel et al., 1999). This solvent usually used as baseline to compare new solvents. One of advantages of MEA as chemical solvent is it has high alkalinity. MEA also has low molecular weight (61.09 kg/kmol) which produce high solution capacity at average concentrations. Besides that, MEA has proven as high absorption rate, fast and high reactivity to CO_2 than other amines solvent.

However, MEA has some of disadvantages such as corrosive than other amines resulting high costly materials of construction. MEA itself is not corrosion, but degradation by-product resulting corrosive. Conventional MEA concentration used is between ranges of 12 weight% to 32 weight%. Greater concentration of MEA than 32 weight% can give high corrosion rate (Kohl and Nielson, 1997). MEA concentration can be increased by added corrosion inhibitors which used in Fluor Daniel Economine FG process. Besides, MEA has higher vapour pressure than other amines lead to high volatility and high solvent losses in low pressure CO_2 recovery operation. Installing washing system at top column of absorber is needed to overcome amine loss. Heat of reaction of MEA with CO_2 is higher than other amines which create high thermal energy needed in stripper.

2.6.2 Diethanolamine (DEA)

Diethanolamine or 2,2'-Iminodiethanol often abbreviated as DEA is an organic compound, secondary amine consist of two hydroxyl group (-OH) and one hydrogen attached to nitrogen atom. DEA is colourless crystals, odourless, toxic, flammable and act as weak bases. DEA is produced by adding second equivalent ethylene oxide to reaction of ethylene oxide with ammonia.

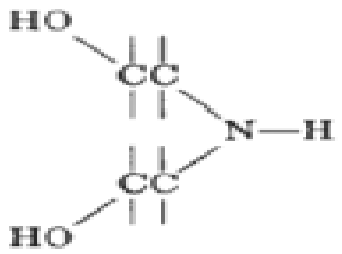


Figure 2-7: Molecular structure of DEA (Kohl and Nielsen, 1997)

Aqueous diethanolamine solutions is industrial chemical used in gas treating process such in treatment of refinery gas to remove CO_2 and H_2S for many years (Kohl and Nielsen, 1997). Typical DEA concentration used is between 20-25% for treatment refinering gases. Low vapour pressure of DEA (0.01 mmHg at 20°C) can give advantage to reduce loss of amine loss in absorption process. Heat of reaction of DEA is lower than MEA about 30%, which can reduce thermal energy require for amine regeneration. Besides, DEA is more basicity than MEA (Prachi Singh, 2011).

Furthermore, DEA is less corrosive than MEA because degradation product of DEA are no really corrosive and DEA also less reactive with CS_2 and COS.

However, aqueous DEA has slower absorption rate and had low absorption heat (70.44 kJ/mol at loading 0.658) than MEA (88.91 kJ/mol at loading 0.565) (Seok. and Hyung-Taek, 2004). Absorption rate is important in order to determine absorber dimension which can give effect on capital costs of post-combustion power plant (IEA GHG, 2004). Lower absorption rate give increased size of absorber column which give high capital cost.

2.6.3 Metylediethanolamine (MDEA)

Methyldiethanolamine often abbreviated as MDEA is a tertiary amine which has three hydroxyl group (-OH) and no hydrogen atom attached to nitrogen atom (Figure 2-8). MDEA is a colorless, with an ammonia odour. MDEA also act as bases like other amines.

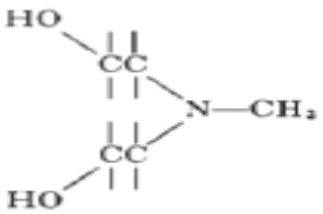


Figure 2-8: Molecular structure of MDEA (Kohl and Nielsen, 1997)

MDEA also is another amine solvent widely used in H_2S and CO_2 removal process and also alternative option to replace MEA solvent. Concentration of MDEA used in gas treating is between 30-55 weight percent (Kohl and Nielsen, 1997). Besides, MDEA is less corrosive than MEA. Advantages of the use aqueous MDEA solution include their high loading capacity (about 1.0 mol of CO2/mol of amine) and lowest heat of reaction than MEA and DEA (Pracci Singh, 2011). This will leads to positive effect which lower thermal energy used in stripper. However, MDEA is show lowest absorption rates than primary and secondary amines resulting less acid gas can be absorbed and increased the absorber size. This is because MDEA is lack of N-H bond than can form carbamate which cause CO_2 cannot react directly with MDEA.

2.6.4 Chemistry and chemical kinetics

Chemical properties of amines such as absorption capacity and reactivity to CO_2 are determining by molecular structure and chemical kinetics (Prachi Singh, 2011). Many previous researches available today that study chemical kinetics of amines to give understanding of relationship between amines structural and acid gases capture properties (Gouegard et al., 2012 : Prachi Singh, 2011). Gouegard et al. (2012) are study chemical kinetics of various amines for determine their oxidative and thermal degradation product in amine scrubbing process. Prachi Singh (2011) did research on how chain length, steric hindrance effect and side chain of amines can effect on absorption rates of absorbent to acid gases.

Amines are divided into primary, secondary and tertiary amines and each of categories have different reaction mechanism to CO_2. In general, primary and secondary amines react with CO_2 will produce carbamate as main product. Formation of carbamate had two proposed mechanisms which are zwitterion mechanism and termolecular mechanism. Caplow (1968) is first developed zwitterion mechanism and strengthen by Danckwerts (1970).In this mechanism, short-lived zwitterion formation as intermediate to the carbamate formation (equation 1).

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NH^+COO^- \quad \text{..... equation 1}$$

Where, R_1 and R_2 are substituted carbon chain; i.e, MEA: R_1=H, R_2=C_2H_4OH

Then, formation of zwitterion is deprotonated by base molecule, B such as water, amine molecule or water for carbamate formation (equation 2).

$$R_1R_2NH^+COO^- + B \leftrightarrow R_1R_2NCOO^- + BH^+ \text{.....equation 2}$$

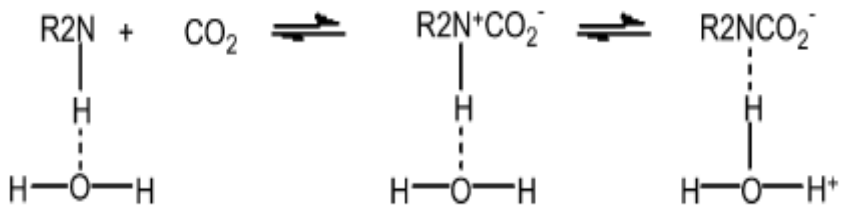


Figure 2-9: Zwitterion formation mechanism (Da Silva and Swendsen, 2007)

Termolecular mechanism was introduced by Crook and Donnellan (1989) proposed a single step mechanism of carbamate formation (Figure 2.5.4.2) (Equation 3).

$$B + R_1R_2NH + \ CO_2 \leftrightarrow R_1R_2NCOO^- + BH^+ \ldots\ldots\ldots\ldots \text{ equation 3}$$

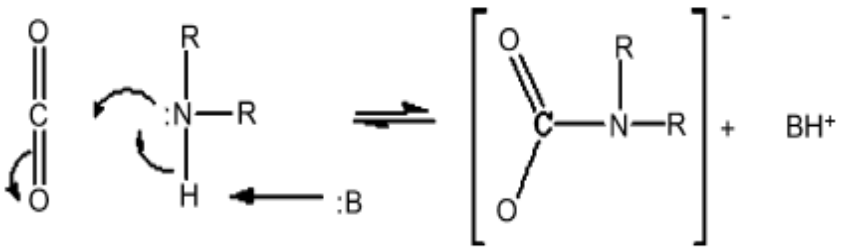


Figure 2-10: Single step mechanism (Da Silva and Swendsen, 2007)

The carbamate formed either from termolecular or zwitterion mechanism, tendency to form bicarbonate species by hydrolysis process (equation 4).

$$R_1R_2NCOO^- + H_20 \leftrightarrow R_1R_2NH + HCO_3^- \ldots\ldots\ldots\ldots\ldots\ldots\text{equation 4}$$

There is no hydrogen atom attached in nitrogen atom present in molecular structure of tertiary amine which carbamate in primary and secondary amines cannot be form. According to Da Silva and Svendsen (2007), bicarbonate formation usually featured by tertiary amines. The reaction of CO_2 with amine can occur after dissolving CO_2 with water for bicarbonate formation. The related equations of formation bicarbonates as follow (Da Silva and Svendsen, 2007):

$$CO_2 + OH^- \leftrightarrow HCO_3^-$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O$$

The bicarbonate ion is deprotonated with tertiary amine to yield the overall reaction of CO_2.The related equations of formation bicarbonates as follow (Da Silva and Svendsen, 2007):

$$H_2O + R_1R_2R_3N + CO_2 \leftrightarrow HCO_3^- + R_1R_2NH_2^+$$

The maximum loading capacity of primary and secondary amines for CO_2 is 0.5 mol of CO_2 /mol amine. The low CO_2 loading capacity is affected by hydrolysis rate to bicarbonate is low and carbamate stability is high (Kohl and Nielsen, 1997). CO_2 loading capacity of secondary amines is higher than primary amines because of its carbamate stability is low. Anita et al. (2013) research proved that the carbamate formation in DEA is six times less stable than MEA gives the higher CO_2 loading capacity. The tertiary amine that does not form carbamate has high loading than primary and secondary amine which is 1 mol of CO_2 /mol amine. However, bicarbonate formation without carbamate in tertiary amines is slower reaction than primary and secondary amines. Thus, absorption rates of CO_2 with tertiary amines are slower than primary and secondary amines.

Heat of enthalpy of CO_2 absorption with amine solvents is very important to determine energy required for regenerations in stripper. The high enthalpy value attributed to high energy demands in stripper. Factors that affect to CO_2 absorption enthalpy are carbamate stability and strength of bases. Primary and secondary amines have higher heat enthalpy of CO_2 absorption than tertiary amines. This is due to the exothermic carbamate formation reaction increase CO_2 absorption enthalpy and endothermic bicarbonate formation reaction decrease magnitude of CO_2 absorption enthalpy (McCann et al, 2011).

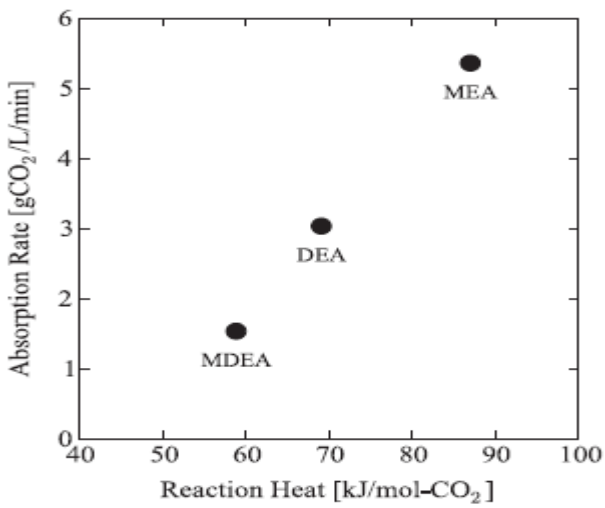


Figure 2-11: Absorption rates and reaction rates of amine-based solvent (Sartori and Savage, 1983)

2.7 Aspen plus

Simulation is the best alternatives to study about the performance of amine scrubbing process. This is because this process in large scale is taking a lot time to operate, expensive and difficult to operate (Dugas et al., 2009). Therefore it is reasonable to study this process by using simulation software. Besides that, the simulator programmes has proven suitable to running chemical process with all thermodynamics data base and also have been used for many years. However, not all simulator programmes are designed for the same purpose. A best way to find the suitable simulator programmes is knowledge the process behind the simulation (Henning Leifsen, 2007). Some of process simulators that been used in previous research such as ASPEN Plus, HYSYS, and FORTRAN 90 (Table 2.6).

Table 2-1: Simulator programmes for CO_2 removal processes from previous study

Author	Simulator programme
Dugas et al (2009)	ASPEN plus
Freguia (2002)	ASPEN plus
Alie et al. (2005)	ASPEN plus
Abu Zahra et al (2007a)	ASPEN plus
Plaza J. M (2011)	ASPEN plus
Lars Erik Oi (2007)	ASPEN HYSYS
Henning Leifsen (2007)	ASPEN HYSYS
Tobiesen et al. (2007)	FORTRAN 90

From the Table 2.6, ASPEN plus is simulator program that most of previous study used for. Besides that, ASPEN plus are widely used standard application for computerized flow sheet simulations in the chemical industry. So, this simulator will be used in this study in order to find best amine solvent of amine absorption process for post combustion CO_2 removal based on the efficiency of CO_2 removal.

2.8 Summary

This chapter reviews about CO_2 emission from fossil fuel power plant that leads to climate changes. CO_2 captured and storage (CCS) technology is alternative way to reduce CO_2 emission to atmospheres. Chemical absorption used in post combustion technology is best CCS technology that can be applied in fossil fuel power plant. CO_2 removal efficiency in amine scrubbing process is depending on performance of amine based solvent. The simulation is using Aspen Plus® can reduce the cost and time of the research while estimate the results accurately has brought much convenient to the researchers.

3 METHODOLOGY

3.1 Overview

This chapter is divided into four sections and organizes as follow: In Section 3.2 showed the flowchart of methodology for the simulation. Section 3.3 provides the operating conditions and column specification data from pilot plant at University of Texas, Austin by Dugas (2006). While in Section 3.3 gives an overview about process parameter variation in this study. In section 3.4 showed simulation algorithm with screenshot from Aspen plus.

3.2 Operating conditions and column specification

The pilot plant data from Dugas (2006) from University of Texas, Austin were adapted as input data to run this model. Out of 48 cases pilot plant data carried out in the research, case 32 was chosen. The model had been validated by Lawal et al. (2012) and Jayarathna et al. (2013). Table 3.1 shows the data of flue gases composition and flow rate. Meanwhile the absorber column parameters for amine scrubbing process are showed in Table 3.2.

Table 3-1: Flue gas flow rate and compositions by Dugas (2006)

Temperature (K)	319.71
Pressure (kPa)	103.5
Mass flow rate (kg/s)	0.13
Mass fraction (wt%)	
CO_2	0.0148
H_2O	0.2520
O_2	0.000
N_2	0.7332

Table 3-2: Absorber parameters for amine scrubbing process by Dugas (2006)

Operating Pressure (atm)	1
Number of stages	5
Column inside diameter, (m)	0.427
Packing	
Type	IMTP
Vendor	Norton
Material	Metal
Size	1.5 Inch or 38-mm

3.3 Process operating parameters

As mentioned previously, three difference types of amine solvents are used in this study which is MEA, DEA and MDEA. Besides, some of parameters affecting the efficiency of CO_2 removal in amine scrubbing process will be varied for each chosen amine solvent. These parameters are including amine concentration, lean solvent temperature and flow rate. Table 3.3 showed the summary of the process parameters variation that was discussed in this study. The amine concentration (wt %) were selected according to Kohl and Nielsen (1997).

Table 3-3: Summary of process variation studies

Varied parameter	Range of variation	Constant parameter
Amine concentration, x_{amine} (wt %) :		
MEA	20 - 35	$\dot{m}^{fluegas}$, $\dot{m}^{solvent}$, $T^{solvent}$, $T^{fluegas}$
DEA	25 - 40	
MDEA	35 - 55	
Lean solvent flow rate, $\dot{m}^{solvent}$ (kg/s)	0.6-5.0	$\dot{m}^{fluegas}$, x_{amine}, $T^{solvent}$, $T^{fluegas}$
Solvent temperature, $T^{solvent}$ (K)	303.15-323.15	$\dot{m}^{fluegas}$, $\dot{m}^{solvent}$, x_{amine}, $T^{fluegas}$
Amine concentration and lean solvent flow rate		
MEA	20 – 35 wt% ; 0.6 – 10 kg/s	$\dot{m}^{fluegas}$, $T^{fluegas}$
DEA	25 – 40 wt% ; 0.6 – 133 kg/s	
MDEA	35 – 55 wt% ; 0.72 – 110 kg/s	

Where; $\dot{m}^{fluegas}$ is flue gas flow rate, $T^{fluegas}$ is flue gas temperature

All these process parameter variations were used to find the efficiency of CO_2 removal in amine scrubbing process. Efficiency of CO2 removal is calculated by using following formula:

$$CO_2 \text{ removal efficiency, } \% = \left(\frac{Flow\ rate\ CO_2 \text{ removal}}{Flow\ rate\ CO_2\ measured\ in\ flue\ gases}\right) \times 100 \ldots\ldots \text{equation 5}$$

Where,

Flow rate CO_2 removal = Flow rate CO_2 measured in flue gases- Flow rate CO_2 measured in vent gas

3.4 Simulation algorithm

Figure 3.1 shows the simulation algorithm of absorber model in this study. Identified and gathered the data from pilot plant Dugas (2006) including column specification, flue gases flow rate and composition. The Physical Property method 'MEA Property Insert' in ASPEN plus v12.1to compute the NRTL thermodynamic model was chosen. Next, Radfrac absorber column was selected as standalone absorber as show in Figure

3.4 and inserted the data from Table 3.1 and Table 3.2. After that, the simulation was run and the result obtained was compared with temperature profile data from Dugas (2006). After the simulation model was validated, the simulation was run by changing some parameters (lean solvent flow rate, temperature and amine concentration) to obtain higher CO_2 removal efficiency as in Table 3.3. Before further analysing the results, the comparison was done to confirm that the similar and reasonable results were obtained. The steps were repeated for DEA and MDEA by chosen 'DEA Property Insert' and 'MDEA Property Insert' respectively. The results were tabulated and the graphs of the each changing parameter of each amine solvent against percentage CO_2 removal efficiency were plotted. The analysis and discussion were done after obtained the correct trends and conclusion was done based on of the findings.

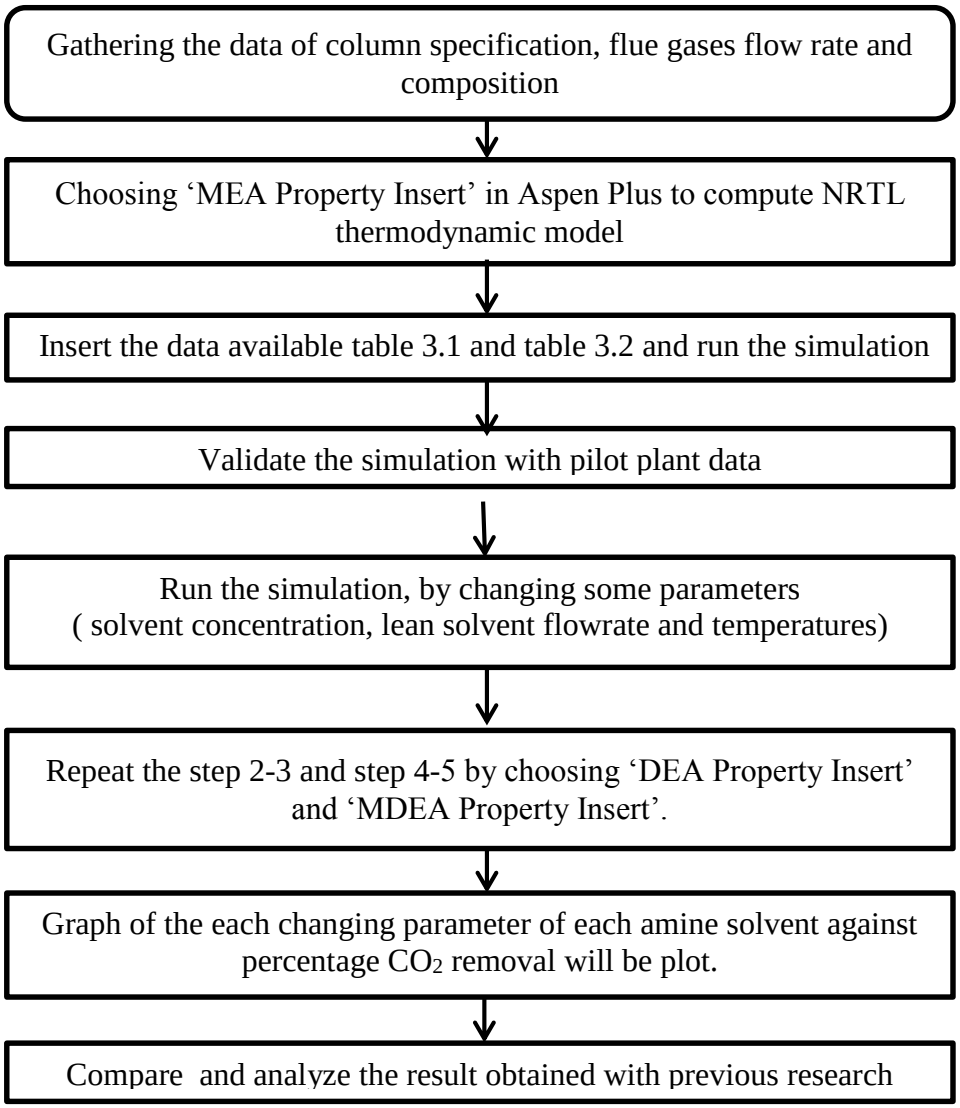


Figure 3-1: Simulation algorithm of this study

All the figures below had shown the detailed procedures where the simulation of stand-alone absorber for 32.5 wt. % MEA solvent was run with the Aspen plus version 12.1.The first step to run the simulation is the selection appropriate property method. For example, MEA is chosen as amine solvent, MEA electrolyte property insert.

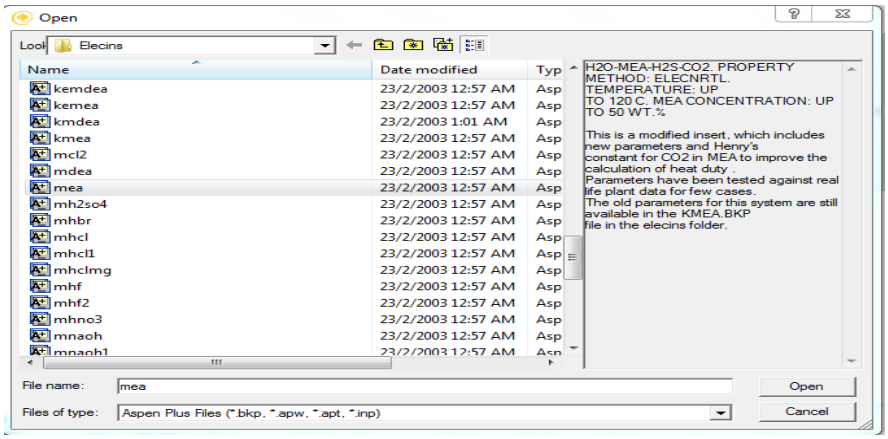


Figure 3-2: Property method insert selection

The next step is to put title of flow sheet for this simulation as in Figure 3.3.

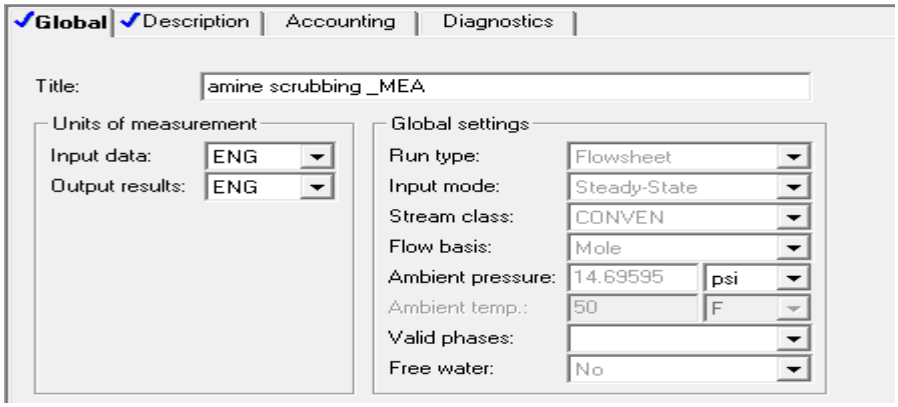


Figure 3-3: Setup description sheet

After the selection of MEA property method, built process flow diagram (PFD) in simulation flow sheet. In this study, Radfrac absorber is chosen to be inserted as standalone absorber in the flow sheet which is without the condenser and reboiler. All the streams are labelled as lean solvent, rich solvent, flue gas and vest gas as showed is Figure 3.4.

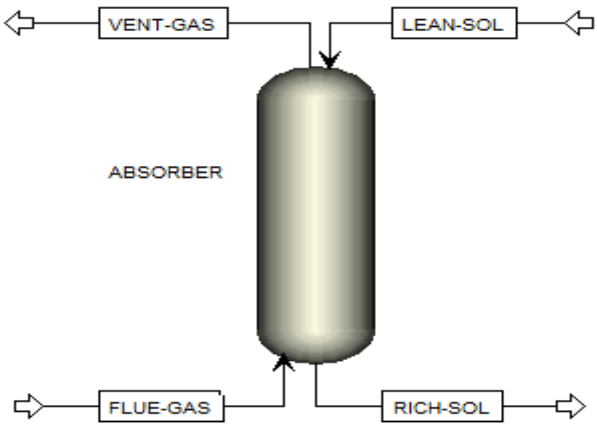
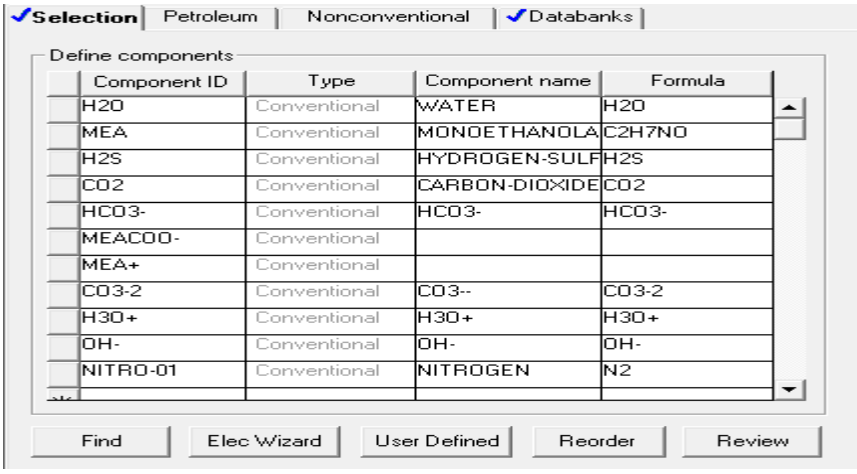


Figure 3-4: Stand-alone absorber

Then, selection of components provided when chosen the property method. As MEA package have been used the component for MEA solution is already on the component list of ASPEN Plus. The components consist of sulphur such as HS-and S-2 are removed because these components are absence in flue gas components. Nitrogen component is added manually followed Table 3.1.Figure 3.5 showed the components list that used in this study.



Component ID	Type	Component name	Formula
H2O	Conventional	WATER	H2O
MEA	Conventional	MONOETHANOLA	C2H7NO
H2S	Conventional	HYDROGEN-SULF	H2S
CO2	Conventional	CARBON-DIOXIDE	CO2
HCO3-	Conventional	HCO3-	HCO3-
MEACOO-	Conventional		
MEA+	Conventional		
CO3-2	Conventional	CO3--	CO3-2
H3O+	Conventional	H3O+	H3O+
OH-	Conventional	OH-	OH-
NITRO-01	Conventional	NITROGEN	N2

Figure 3-5: List of components of amine scrubbing process.

The next step is inserted specification stream (flue gases) such as temperature, pressure, composition and total flow rate after the completion of inserting the component based in Table 3.2 showed in Figure 3.6. Then, the specification stream of lean solvent is inserted showed in Figure 3.7.

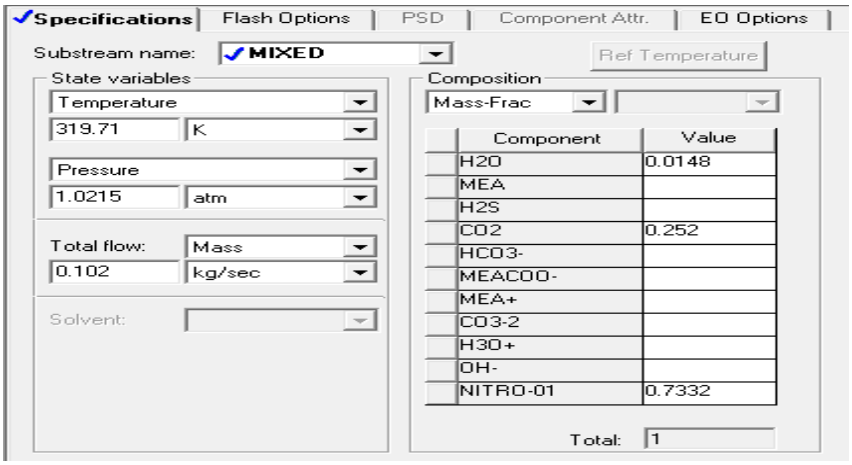


Figure 3-6: Flue gas stream specification

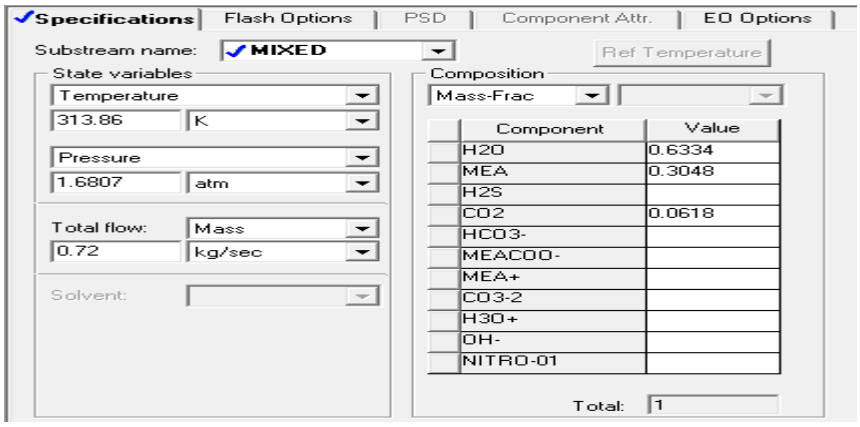


Figure 3-7: Lean solvent stream specification

After the completion inserted setup components streams (flue gas and lean solvent), inserting of column specification of the absorber is done with the completion of the configuration of the column, feed and product streams' stage, convention and phase as shown in Figure 3.8, Figure 3.9 and Figure 3.10.

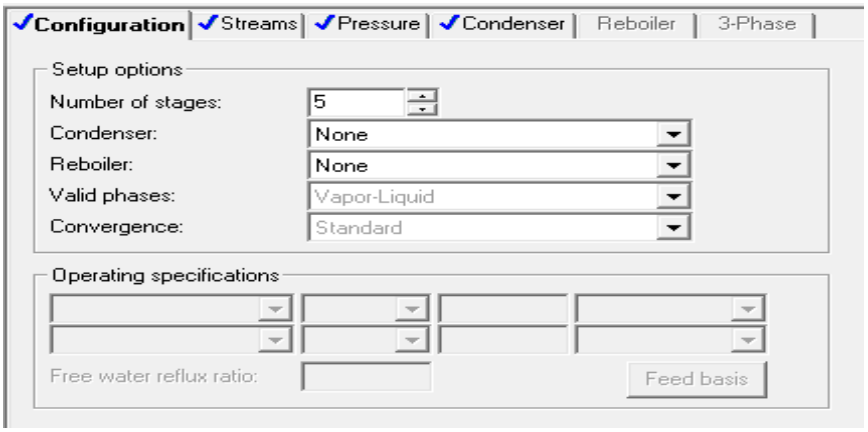


Figure 3-8: Configuration of column

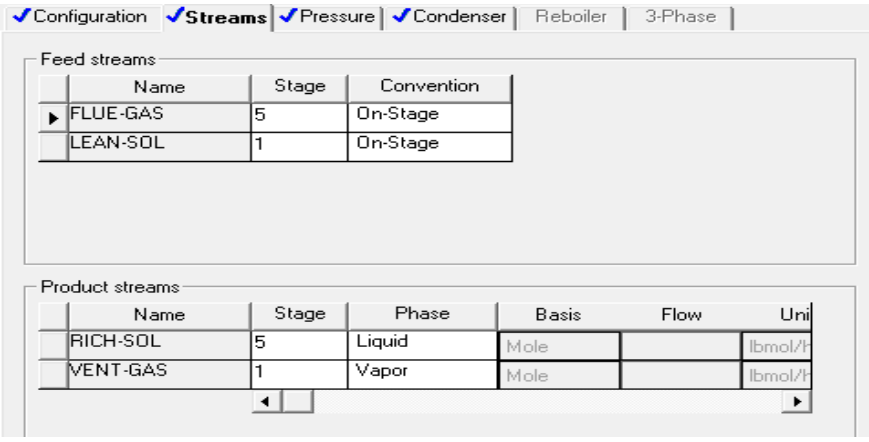


Figure 3-9: Configuration feed and product streams stages

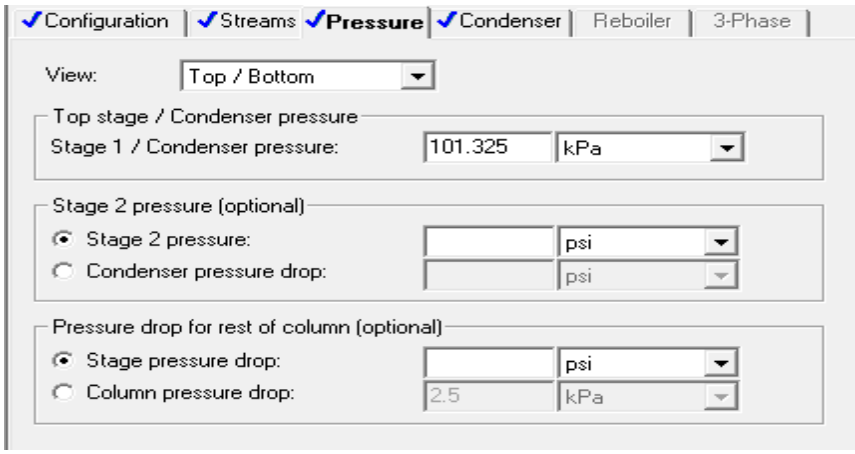


Figure 3-10: Configuration of pressure column

Next, the specification of packing rating of absorber is inserted into the system based on Table 3.2 as showed in Figure 3.11.

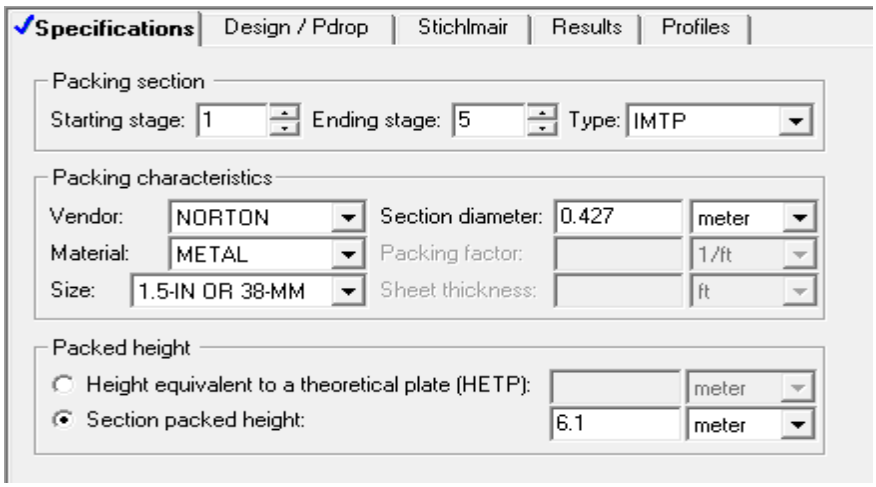


Figure 3-11: Packing rating

After completing all the steps, the simulation can be run and the results can be obtained from the stream table. However, the simulation needs to be converged before the result can be obtained. The simulation result obtained is compared with data from pilot plant by Dugas (2006) for validation. After the data was validated, the same steps are repeated with process parameters; amine concentration, lean solvent flow rate and temperature for MEA, DEA and MDEA.

3.5 Summary

This chapter presents data that will be used in this study and also process parameters variation that have been selected to achieve the objective of this study. This chapter also provides the simulation algorithm of this study.

4 RESULTS AND DISCUSSION

4.1 Overview

This chapter is present the results obtained from the simulation .The simulation results were validated using pilot plant data from Dugas (2006). The relationships between process operating conditions and carbon dioxide removal efficiency for different types of solvent; MEA, DEA and MDEA were discussed in this chapter.

4.2 Data validation

The simulation results validation was carried out using data obtained from the Separation Research Program from University of Texas, Austin. As mention in Chapter 3, case 32 from Dugas (2006) was selected as pilot plant data used for validation in this study. In order to validate the simulation results, liquid temperature profile inside the absorption column that obtained from the simulation was compared with the pilot plant as shown in Figure 4-1.

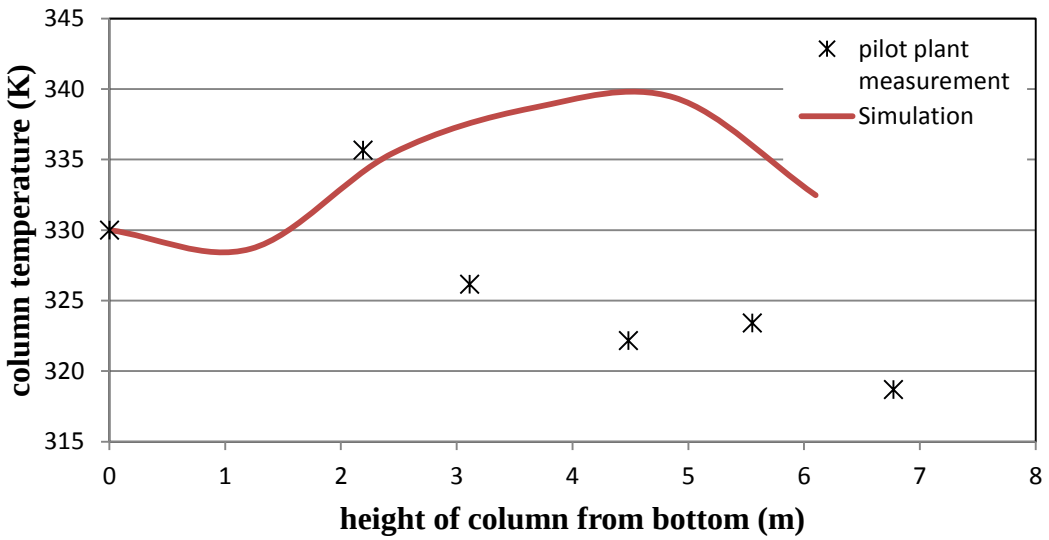


Figure 4-1: Stand-alone absorber liquid temperature profile of columns for Case 32.

Based on the absorber temperature profile in Figure 4-1, simulation results show poor prediction and high deviation from pilot plant data, which indicate that the simulation

results not satisfied with real pilot plant data. Therefore, inlet of flue gas flow rate was slightly reduce from 0.13 kg/s to 0.102 kg/s, so that the simulation can give good prediction with pilot plant measurement. Figure 4-2 shows better predictions for absorber temperature profile with adjusted inlet flue gas flow rate. However, this changes results higher CO_2 removal efficiency than pilot plant data as shown in Table 4-1.

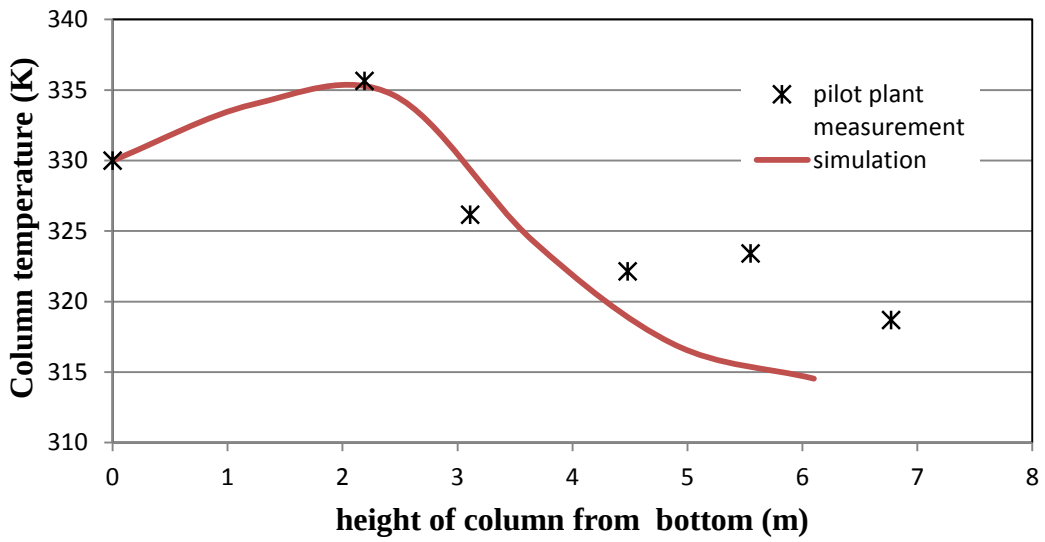


Figure 4-2: Stand-alone absorber liquid temperature profile for Case 32 for adjusted inlet flue gas flow rate.

Table 4-1: CO_2 removal efficiency for simulation and pilot plant measurement.

	Pilot plant measurements	**Simulation**
Flue gas flow rate (kg/s)	0.13	0.102*
CO2 removal efficiency (%)	95	99.6

*Adjusted inlet flue gas flow rate

4.3 Results and discussions

The simulations in this study were done by using same flow sheet in model validation since that simulation was respond satisfactorily. In order to indicate the relationship between process operating parameter that are precise to each amine, a single model was performed using the same operating conditions that led to the better CO_2 removal efficiency from the MEA analysis, substituting MEA with DEA and MDEA.

4.3.1 Amine solvent concentration

In order to find relationship between variation of amine solvent concentration with CO_2 removal efficiency, the solvent flow rate was held constant for every specific amine solvent while the amine solvent concentration were varied within the range suggested by Kohl and Nielsen (1997). Figure 4-3 shows the CO_2 removal efficiency as a function of MEA, DEA and MDEA solvent concentration.

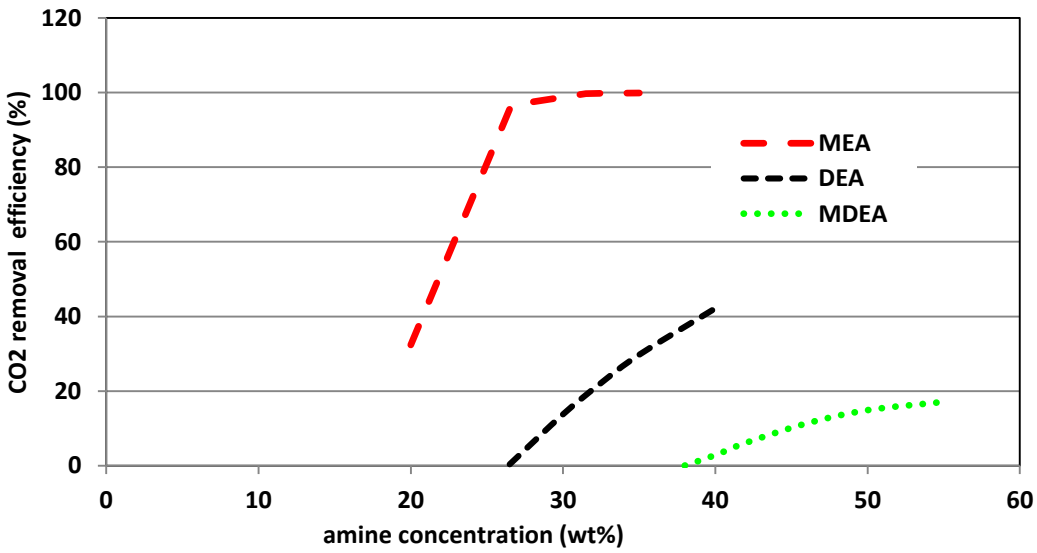


Figure 4-3: CO_2 removal efficiency of difference MEA, DEA and MDEA solvent concentration

The result presented in Figure 4-3, showed that the CO_2 removal efficiency was increased with increasing of amine concentration for each amine. It is seen that CO_2 removal efficiency using the MEA solvent was the highest compared to DEA and MDEA solvent. The simulations for MEA showed a very high CO_2 removal efficiency of 99.8% at low concentration of 31.5 wt. %. The increases of MEA concentration from

20 wt. % and 30 wt. % leads to increase CO_2 removal efficiency from 31.8% to 98% respectively. This is as expected because more MEA molecules available to react with CO_2 molecules resulting less unreacted CO_2 released to vent gases. Meanwhile, increases MEA concentration greater than 31.5 wt. % give maximum and constant CO_2 removal efficiency of 99.8%. Thus, it is more realistic to use 31.5 wt. % of MEA solvent concentration for achieving a high CO_2 removal efficiency. However, it should be noted increasing MEA solvent concentration up to 32 wt. % expected to give corrosive effect.

DEA and MDEA solvents were not able to achieved high CO_2 removal efficiency as MEA solvent. The highest CO_2 removal efficiency obtained using DEA solvent is 35% for DEA solvent concentration at 35 wt. %. Meanwhile, 23% is the highest CO_2 removal efficiency can be achieved using maximum 55 wt. % of MDEA solvent. This analysis reflects to their reactivity and absorption capacity of CO_2 (Adewale Adeosun et al., 2013; Yeh and Bai, 1999). High absorption capacity of CO_2 and reactivity lead high CO_2 removal efficiency. According to Zhang et al. (2008), the CO_2 absorption capacity of MEA solvent is higher than DEA and MDEA which can be ordered as follow: MEA > DEA > MDEA. Besides that, MEA and DEA as primary and secondary respectively are very reactive compared to tertiary amine which is MDEA, so MEA and DEA can perform high removal CO_2 in the absorber (Prachi Singh, 2011).

4.3.2 Lean solvent flow rate

In this section, the lean solvent flow rate is varied at constant inlet flue gas flow rate. These variation cause solvent flow rate to flue gas flow rate ratio, L/G is varied. The lean solvent flow rate is varied between 0.1 kg/s to 5 kg/s with 0.98 and 49 L/G ratio, respectively. Figure 4-4 shows the CO_2 removal efficiency at different lean solvent loading flow rate for MEA, DEA and MDEA.

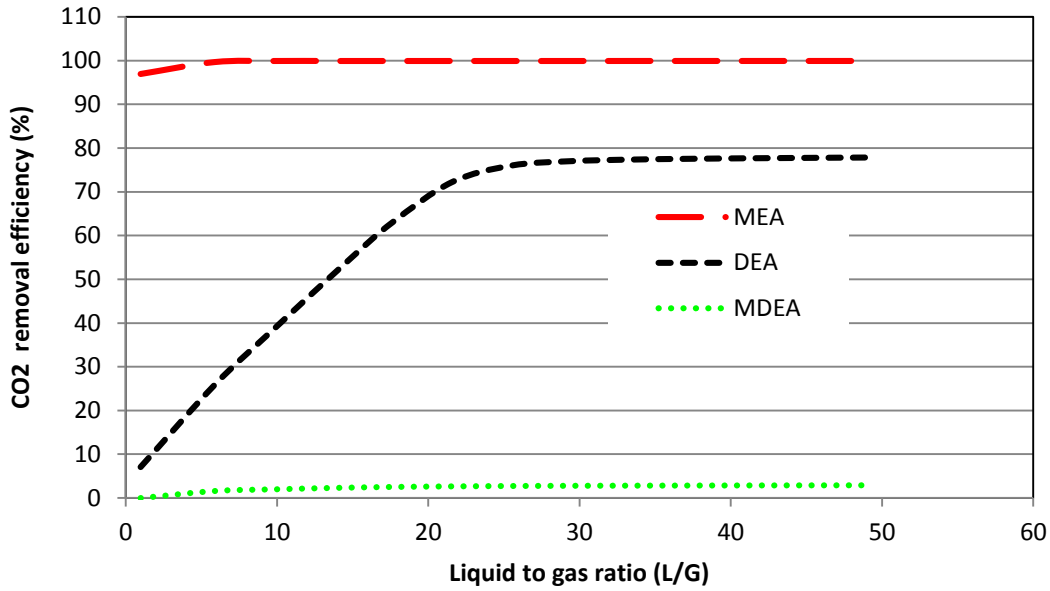


Figure 4-4: CO_2 removal efficiency of MEA, DEA and MDEA at varied L/G ratio

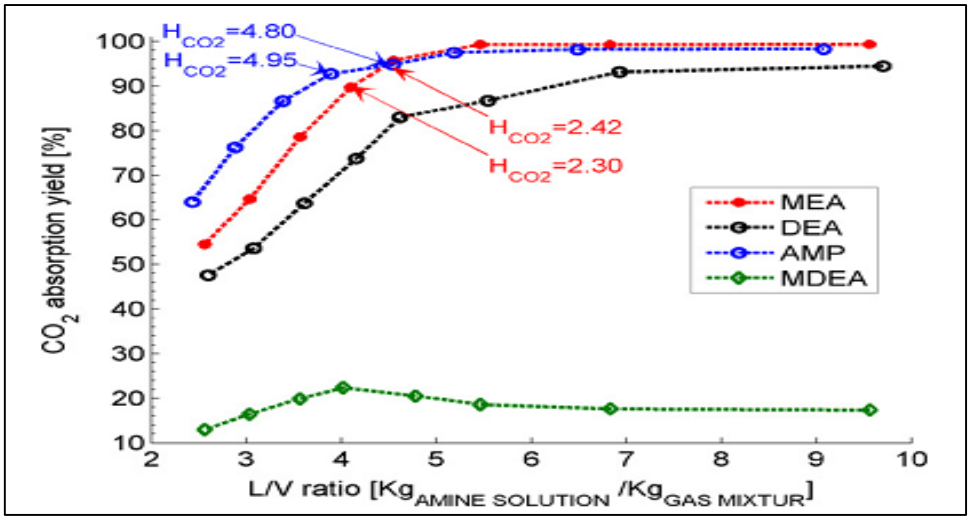


Figure 4-5: CO_2 removal efficiency of MEA, DEA, AMP and MDEA at various L/G ratio (Jozsef Gaspar, 2012)

The CO_2 removal efficiency increases with increasing lean solvent flow rate for each MEA, DEA and MDEA solvent as can be seen in Figure 4-4. The results also showed that increasing lean solvent flow rate caused the reduction in the CO_2 concentration in gas phase which indicate a higher CO_2 removal efficiency. According to Aroonwilas et al. (2002), increase lean solvent flow rate give higher degree of the wetted packing surface (hydrodynamics) which increase the mass transfer process of CO_2 absorption. The CO_2 removal efficiency for amines solvent can be arranged as the following order:

MEA > DEA > MDEA. This finding has similar pattern with the previous study by Jozsef Gaspar (2012) as shown in Figure 4-5. High CO_2 removal efficiency that achieved using MEA solvent is about 99 % at very low L/G ratio, 5.88. Meanwhile, DEA can achieve maximum 77% CO_2 removal efficiency at 25 L/G ratio and MDEA can only achieve very low CO_2 removal efficiency which is about 3%. Noted that the amine concentration (35 wt. %) was kept constant for all amine in this finding, so, increasing lean solvent flow rate only increasing the amount of amine molecule to react with CO_2 molecule with maintaining the amine absorption capacity. As mention is section 4.3.1, absorption capacity of MEA is higher than DEA and MDEA which give MEA to higher CO_2 removal in this finding.

4.3.3 Lean solvent temperature

In this simulation, the lean solvent temperature is varied while other parameters are kept constants. The lean solvent temperature is varied from 303.15 K to 323.15 K. Figure 4.6 shows CO_2 removal efficiency at different lean solvent temperature for MEA, DEA and MDEA.

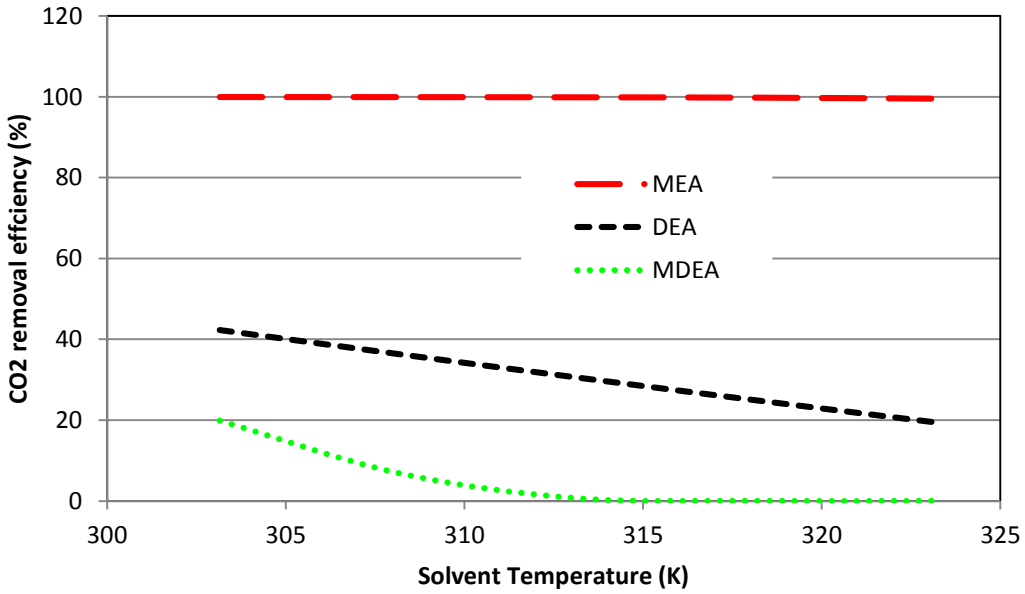


Figure 4-6: CO_2 removal efficiency of MEA, DEA and MDEA at lean solvent temperature.

As shown in Figure 4.6, the CO_2 removal efficiency was decreased as lean solvent temperature increased for all amines. This is because more amine are vaporise to gas

which reduce the amount of liquid amine to react with CO_2 from the flue gas. According to Anusha (2005), decreasing the temperature of the absorber can increase its performance. It is impractical to lower the absorber temperatures by cooling the flue gas feed, so only option is to lower the temperature of the lean solvent as much as possible (Addington and Ness, 1999). Besides that, amine solvent losses highly happen at overhead of absorber because of amine takes up the heat of absorption from high amount of reaction between CO_2 in gas phase with amine solvent when the lean liquid enters (Stewart and Lanning, 1994). Amine solvent losses from vaporization can contribute to negative economic impact which increases the amount of amine solvent make-up. MEA showed the highest CO_2 removal efficiency even though the trend is decrease as temperature of solvent increase compared to DEA and MDEA which can be ranked in order as follow: MEA > DEA > MDEA. As temperature of lean solvent increasing, the CO_2 removal efficiency of MDEA decreasing until no CO_2 absorption occurs in the scrubbing process.

4.3.4 Lean solvent flow rate and amine concentration

As mention in previous sections, MEA show the highest CO_2 removal efficiency compared to DEA and MDEA. This is because the simulation was modelled using the best suited operating conditions that led to the better CO_2 removal efficiency for MEA analysis which might not suitable for DEA and MDEA solvents. Figure 4.7, 4.8 and 4.9 show the CO_2 removal efficiency at various amine solvent flow rate and concentration of MEA, DEA and MDEA respectively.

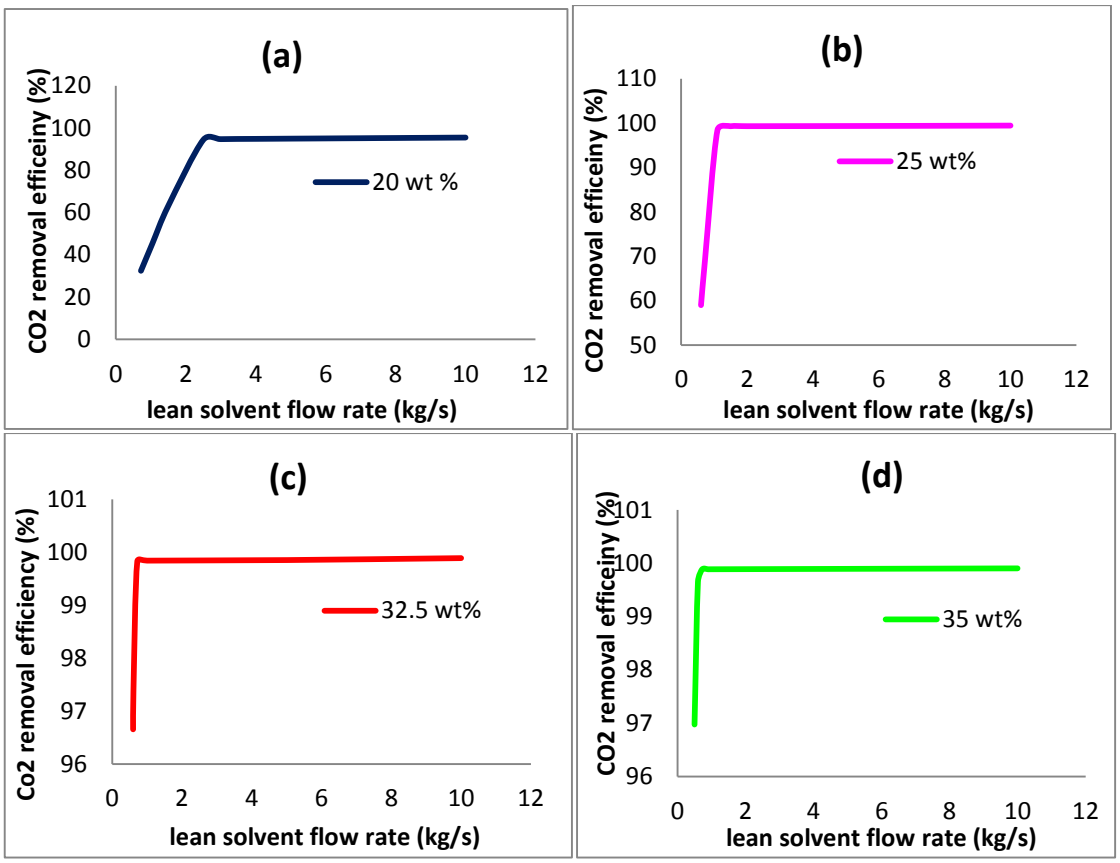


Figure 4-7: CO_2 removal efficiency of MEA varies lean solvent flow rate for 20 wt. %, 25 wt. %, 32.5 wt. % and 35 wt. %.

As the concentration of MEA solvent and lean solvent flow rate increasing, the CO_2 removal efficiency in amine scrubbing process also increasing as showed in Figure 4.7. The lean solvent flow rate in order to achieved 99% CO_2 removal efficiency of MEA solvent as follow: 2.5 kg/s for 20 wt. %; 1.1 kg/s for 25 wt. %;0.72 kg/s for 32.5 wt. %;0.6 kg/s for 35 wt. %. This result showed that low concentration of MEA need high lean solvent flow rate to achieve high CO_2 removal by increasing the amount of amine available for reaction.

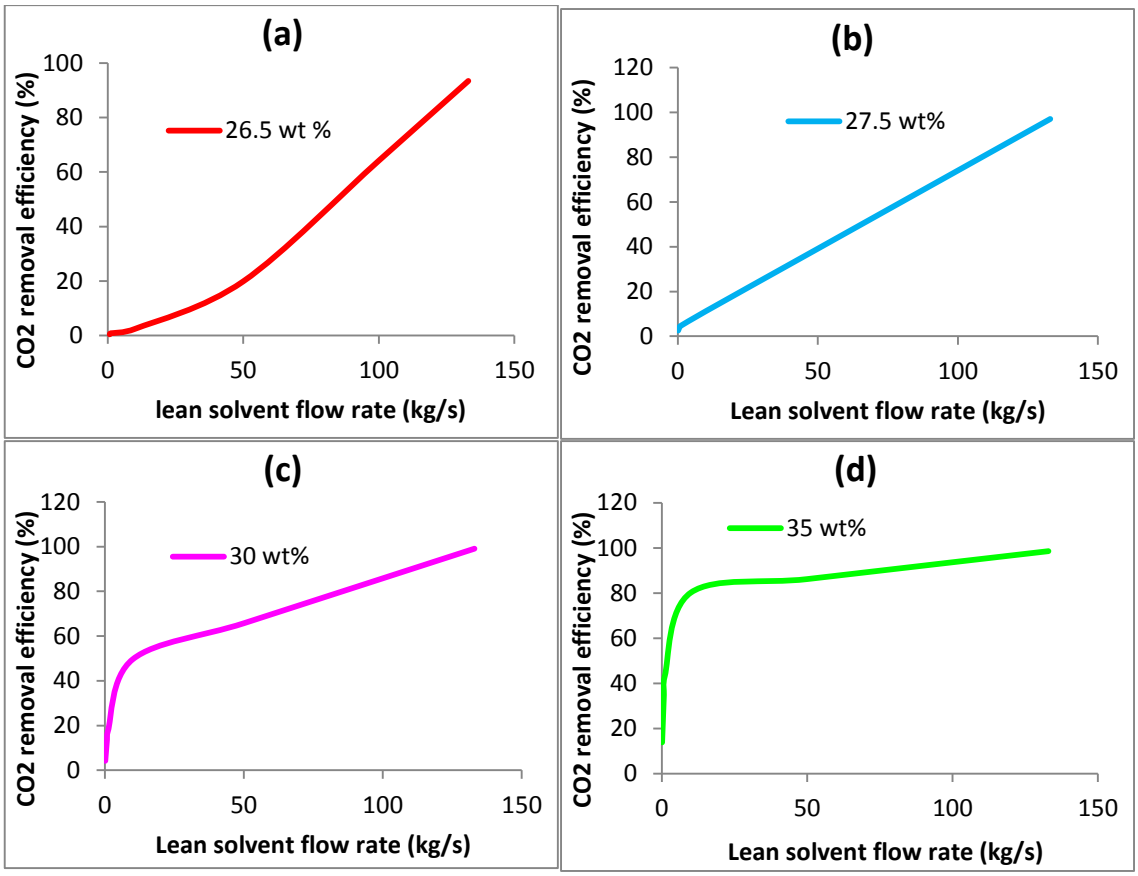


Figure 4-8: CO_2 removal efficiency of DEA varies lean solvent flow rate for 26.5 wt. %, 27.5 wt. %, 30 wt. % and 35 wt. %.

Figure 4.8 shows the CO_2 removal efficiency of DEA solvent is increased as the lean solvent flow rate and DEA concentration increased. The CO_2 removal efficiency for 26.5 wt. % and 27.5 wt. % of DEA concentration has linear correlation with lean solvent flow rate. Meanwhile, the CO_2 removal efficiency at 30 wt. % of DEA concentration increasing quickly to 50 % at 10 kg/s of solvent flow rate, and then increasing gradually to about 99 % at 133 kg/s. Lastly, CO_2 removal efficiency 35 wt. % jumped to 80 % at 10 kg/s, and then continued to increase gradually to about 99 % at 133 kg/s.

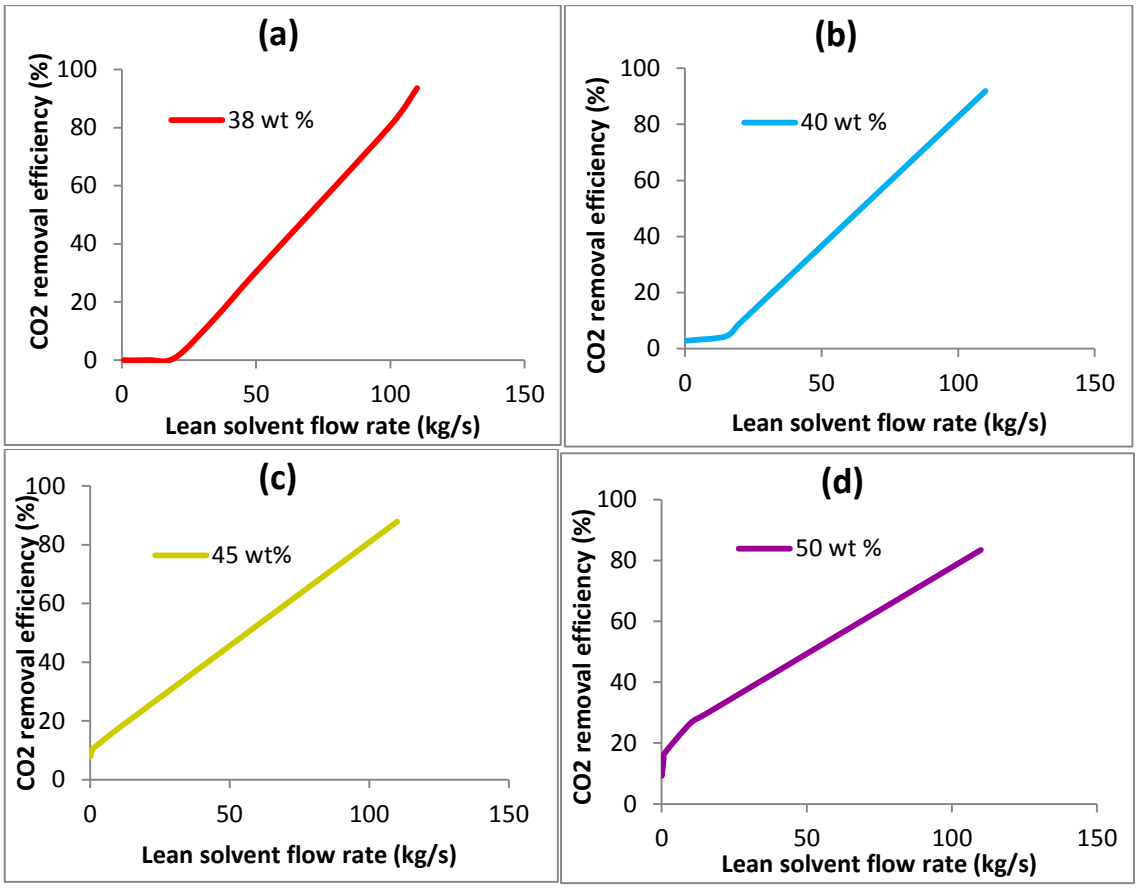


Figure 4-9: CO_2 removal efficiency of MDEA varies lean solvent flow rate for 38 wt. %, 40 wt. %, 45 wt. % and 50 wt. %.

As can be seen in Figure 4.9, the CO_2 removal efficiency of MDEA is increased as the lean solvent flow rate and MDEA concentration increased. The CO_2 removal efficiency at 38 wt. % increases dramatically start from 0% at 20 kg/s to 93% at 110 kg/s and CO_2 removal efficiency 40 wt. % increases dramatically start from 15% at 4.4 kg/s to 91% at 110 kg/s. Meanwhile, CO_2 removal efficiency 45 wt. % increases dramatically start from 7.8% at 0.1 kg/s to 87.9% at 110 kg/s and CO_2 removal efficiency 50 wt. % increases dramatically start from 9.3% at 0.72 kg/s to 83.5% at 110 kg/s. This finding showed that the increasing MDEA concentration give higher CO_2 removal efficiency at low lean solvent flow rate. However, the increases MDEA concentration gives lower CO_2 removal efficiency at high lean solvent flow rate. Higher amine concentration in lean solvent, increasing the density and viscosity of solution which affect the reaction kinetic which reduce the CO_2 absorption rate (Jozsef Gaspar, 2012)

As the lean solvent flow rate and amine concentration increase, the CO_2 removal efficiency also increasing as shows in Figure 4.7, 4.8 and 4.9. Figure 4.7 show that constant CO_2 removal efficiency 99% at lean solvent flow rate greater than 1 kg/s for 20 wt. %, 25 wt. %, 32.5 wt. % and 35 wt. % MEA solvent. While, DEA and MDEA can reaches high CO_2 removal efficiency approximately 99% at 133 kg/s and 110 kg/s respectively. This finding showed that MEA can achieve high CO_2 removal efficiency at low concentration and solvent flow rate which can be reduce the cost of amine.

4.4 Summary

This chapter presents the result and discussion of parameter that affect the CO_2 removal efficiency by using different amine solvent. The lean solvent flow rate was changed from 0.13 kg/s to 0.102 kg/s to validate the temperature profile from the simulation in this study with the pilot plant data from Dugas (2006). Each of amine used in this study has different CO_2 absorption capacity which leads to different CO_2 removal efficiency. Increases the solvent flow rate will increase the mass transfer which gives better CO_2 absorption rate. Increases the lean solvent temperature reduce CO_2 removal efficiency due to vaporization of amine before react with CO_2 in gas. The CO_2 removal efficiency for all parameter for amine used in this study can be ranked as follows: MEA > DEA > MDEA.

5 CONCLUSION

5.1 Conclusion

In this study, a comparison the performance of different amines for CO_2 removal from power plant using amine scrubbing process is performed using pilot plant data from Dugas (2006). Aspen Plus v12.1 is used as simulator programme in this study and eNRTL method is selected to determine thermodynamic properties in modelling a stand-alone absorber column. The flue gas flow rate in simulation is adjusted from 0.13 kg/s to 0.102 kg/s so that the simulation is respond satisfactorily with pilot plant temperature profile. MEA has the highest CO_2 removal efficiency compared to DEA and MDEA as the amine concentration increasing. This is due to the high CO_2 absorption capacity and high reactivity of MEA solvent since it is primary amine. Additionally, by comparing the solvent flow rate of each amine, MEA also show the highest CO_2 removal efficiency compared with DEA and MDEA which can be arranged in following order: MEA > DEA > MDEA. Increases lean solvent flow rate at constant amine concentration only increase the amount of amine to react with CO_2 and increase the mass transfer process of CO_2 absorption. Besides that, increasing lean solvent temperature reduce the CO_2 removal efficiency by reduction amount of amine molecule in solvent due to amine vaporization. Lastly, MEA can achieve 99% CO_2 removal efficiency at as low as 1 kg/s lean solvent flow rate compared to DEA and MDEA which need 133 kg/s and 110 kg/s, respectively. Thus, MEA shows the better performance in CO_2 removal efficiency compared to DEA and MDEA at low lean solvent flow rate and concentration.

5.2 Recommendation

To investigating the comparison between amine solvent in amine scrubbing process, stripper column model can be add to find another variable that can be observed. Also, it is known that the activities in absorber affect the activities in stripper column. The energy consumption require for amine regeneration can be influenced by heat of reaction of amine solvent and stripper pressure. The lower the heat of reaction of amine, the lower the energy consumption for amine regeneration which gives the lower capital cost investment for the plant. The difference amine concentration can give difference

reboiler heat duty which affects the energy consumption for amine regeneration. Besides that, equipment operating condition can be added in absorber column such as column height, number of stages and type of packing to determining the best conditions for each amine that give better CO_2 efficiency removal. Other than that, find more correlation between parameters involve to determine the best process design and operating conditions for each amine.

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APPENDICES

A1. Temperature profile of pilot plant and simulation of stand-alone absorber

Pilot plant		**Simulation**	**0.13kg/s**	**0.102kg/s**
height of column (m)	**Temperature (K)**	**height of column (m)**	**Temperature (K)**	**Temperature (K)**
0	330	0	330.00	330.00
2.19	335.661	1.22	328.67	333.98
3.11	326.161	2.44	335.42	334.66
4.48	322.161	3.66	338.67	324.28
5.55	323.422	4.88	339.39	316.98
6.77	318.694	6.1	332.47	314.54

A2. CO_2 removal efficiency versus concentration of MEA

	MEA concentration				
	20 wt. %	**26.6 wt. %**	**31.5 wt. %**	**32.5 wt. %**	**35 wt. %**
Flow rate CO_2 in flue gas (lbmol/h)	4.6354	4.6354	4.6354	4.6354	4.6354
Flow rate CO_2 in vent gas (lbmol/h)	3.1331	0.1580	0.0118	0.0081	0.0054
CO_2 removal efficiency (%)	32.41	96.59	99.74	99.83	99.88

A3. CO_2 removal efficiency versus concentration of DEA

	DEA concentration				
	26.5 wt. %	**30 wt. %**	**32.5 wt. %**	**35 wt. %**	**40 wt. %**
Flow rate CO_2 in flue gas (lbmol/h)	4.6354	4.6354	4.6354	4.6354	4.6354
Flow rate CO_2 in vent gas (lbmol/h)	4.6172	3.9969	3.6069	3.2566	2.6797
CO_2 removal efficiency (%)	0.39	13.77	22.19	29.75	42.19

A4. CO_2 removal efficiency versus concentration of MDEA

	MDEA concentration					
	38wt. %	**40 wt. %**	**42 wt. %**	**46 wt. %**	**50 wt. %**	**55 wt. %**
Flow rate CO_2 in flue gas (lbmol/h)	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354
Flow rate CO_2 in vent gas (lbmol/h)	4.6353	4.5049	4.3524	4.1098	3.9442	3.8414
CO_2 removal efficiency (%)	0.001	2.82	6.11	11.34	14.91	17.13

A5. CO_2 removal efficiency versus L/G ratio of MEA

	L/G ratio								
	0.980	**5.882**	**9.804**	**17.647**	**21.569**	**25.490**	**33.333**	**41.176**	**49.020**
Flow rate CO_2 in flue gas (lbmol/h)	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354
Flow rate CO_2 in vent gas (lbmol/h)	0.1403	0.0163	0.0052	0.0052	0.0051	0.0051	0.0050	0.0050	0.0050
CO_2 removal efficiency (%)	96.97	99.65	99.89	99.89	99.89	99.89	99.89	99.89	99.89

A6. CO_2 removal efficiency versus L/G ratio of DEA

	L/G ratio								
	0.980	**5.882**	**9.804**	**17.647**	**21.569**	**25.490**	**33.333**	**41.176**	**49.020**
Flow rate CO_2 in flue gas (lbmol/h)	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354
Flow rate CO_2 in vent gas (lbmol/h)	4.3067	3.4351	2.8432	1.7124	1.2879	1.1128	1.0494	1.0355	1.0274
CO_2 removal efficiency (%)	7.09	25.89	38.66	63.06	72.22	75.99	77.36	77.66	77.84

A7. CO_2 removal efficiency versus L/G ratio of MDEA

	L/G ratio								
	0.980	**5.882**	**9.804**	**17.647**	**21.569**	**25.490**	**33.333**	**41.176**	**49.020**
Flow rate CO_2 in flue gas (lbmol/h)	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354	4.6354
Flow rate CO_2 in vent gas (kmol/h)	4.63519	4.56206	4.54470	4.51993	4.51403	4.51025	4.50666	4.50447	4.50272
CO_2 removal efficiency (%)	0.005	1.58	1.96	2.49	2.62	2.70	2.78	2.82	2.86

A8. CO_2 removal efficiency versus lean solvent temperature of MEA

	Temperature				
	303.15 K	**308.15 K**	**313.15 K**	**318.15 K**	**323.15 K**
Flow rate CO_2 in flue gas (lbmol/h)	4.6354	4.6354	4.6354	4.6354	4.6354
Flow rate CO_2 in vent gas (lbmol/h)	0.0015	0.0027	0.0050	0.0096	0.0229
CO_2 removal efficiency (%)	99.97	99.94	99.89	99.79	99.51

A9. CO_2 removal efficiency versus lean solvent temperature of DEA

	Temperature				
	303.15 K	**308.15 K**	**313.15 K**	**318.15 K**	**323.15 K**
Flow rate CO_2 in flue gas (lbmol/h)	4.6354	4.6354	4.6354	4.6354	4.6354
Flow rate CO_2 in vent gas (lbmol/h)	2.6736	2.9498	3.2190	3.4807	3.7334
CO_2 removal efficiency (%)	42.32	36.36	30.56	24.91	19.46

A10. CO_2 removal efficiency versus lean solvent temperature of MDEA

	Temperature				
	303.15 K	**308.15 K**	**313.15 K**	**318.15 K**	**323.15 K**
Flow rate CO_2 in flue gas (lbmol/h)	4.63541	4.63541	4.63541	4.63541	4.63541
Flow rate CO_2 in vent gas (lbmol/h)	3.71305	4.31489	4.60515	4.63532	4.63540
CO_2 removal efficiency (%)	19.90	6.91	0.65	0.0019	0.0002

A11. CO_2 removal efficiency versus lean solvent flow rate at varies MEA concentration

	MEA concentration					
	20 wt. %			**25 wt. %**		
Flow rate (kg/s)	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**
0.6	4.6354	3.2520	29.84	4.6354	1.9012	58.98
0.72	4.6354	3.1331	32.41	4.6354	1.4349	69.04
1.1	4.6354	2.5289	45.44	4.6354	0.0710	98.47
1.5	4.6354	1.7092	63.13	4.6354	0.0313	99.32
2	4.6354	0.2605	94.38	4.6354	0.0310	99.33
3	4.6354	0.2428	94.76	4.6354	0.0304	99.34
5	4.6354	0.2317	95.00	4.6354	0.0293	99.37
10	4.6354	0.2081	95.51	4.6354	0.0249	99.46

	MEA concentration					
	32.5 wt. %			35 wt. %		
Flow rate (kg/s)	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**
0.6	4.6354	0.1550	96.66	4.6354	0.0163	99.65
0.72	4.6354	0.0081	99.83	4.6354	0.0054	99.88
1	4.6354	0.0073	99.84	4.6354	0.0052	99.89
2	4.6354	0.0071	99.85	4.6354	0.0050	99.89
3	4.6354	0.0070	99.85	4.6354	0.0049	99.89
5	4.6354	0.0068	99.85	4.6354	0.0048	99.90
10	4.6354	0.0051	99.89	4.6354	0.0045	99.90

A12. CO_2 removal efficiency versus lean solvent flow rate at varies DEA concentration

	DEA concentration					
	26.5 wt. %			**27.5 wt. %**		
Flow rate (kg/s)	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**
0.1	4.6354	4.6274	0.17	4.6354	4.5175	2.54
0.72	4.6354	4.6172	0.39	4.6354	4.4312	4.41
1	4.6354	4.5987	0.79	4.6354	4.4207	4.63
10	4.6354	4.5245	2.39	4.6354	4.1159	11.21
50	4.6354	3.7147	19.86	4.6354	2.8210	39.14
100	4.6354	1.6600	64.19	4.6354	1.2029	74.05
133	4.6354	0.3038	93.45	4.6354	0.1347	97.09

	DEA concentration					
	30 wt. %			35 wt. %		
Flow rate (kg/s)	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**
0.1	4.6354	4.4411	4.19	4.6354	4.3067	13.85
0.72	4.6354	3.9967	13.78	4.6354	3.2567	34.85
1	4.6354	3.8334	17.30	4.6354	2.8432	43.13
10	4.6354	2.3342	49.64	4.6354	0.9889	80.22
50	4.6354	1.5875	65.75	4.6354	0.6908	86.18
100	4.6354	0.6562	85.84	4.6354	0.3183	93.63
133	4.6354	0.0415	99.10	4.6354	0.0724	98.55

A13. CO_2 removal efficiency versus lean solvent flow rate at varies MDEA concentration

	MDEA concentration					
	38 wt. %			**40 wt. %**		
Flow rate (kg/s)	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**
0.72	4.63541	4.63535	0.001	4.63541	4.50468	2.820
1	4.63541	4.63497	0.010	4.63541	4.47538	3.452
10	4.63541	4.63440	0.022	4.63541	4.43253	4.377
20	4.63541	4.59134	0.951	4.63541	4.21900	8.983
35	4.63541	3.95254	14.732	4.63541	3.57840	22.803
50	4.63541	3.22517	30.423	4.63541	2.93792	36.620
100	4.63541	0.89590	80.673	4.63541	0.80216	82.695
110	4.63541	0.29455	93.646	4.63541	0.37508	91.908

	MDEA concentration					
	45 wt. %			50 wt. %		
Flow rate (kg/s)	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**	**Flow rate CO_2 in flue gas (lbmol/h)**	**Flow rate CO_2 in vent gas (lbmol/h)**	**CO_2 removal efficiency (%)**
0.72	4.6354	4.27205	7.839	4.6354	4.20587	9.266
1	4.6354	4.16379	10.174	4.6354	3.94574	14.878
10	4.6354	4.14575	10.563	4.6354	3.86406	16.640
20	4.6354	3.83037	17.367	4.6354	3.40213	26.606
35	4.6354	3.66706	20.890	4.6354	3.27035	29.449
50	4.6354	3.01367	34.986	4.6354	2.74319	40.821
100	4.6354	2.52360	45.558	4.6354	2.34782	49.350
110	4.6354	0.89010	80.798	4.6354	1.02997	77.780