BLENDING OF ALKANOLAMINES EFFECT TOWARDS ACID GAS REMOVAL IN A POST-COMBUSTION CARBON CAPTURE TECHNOLOGY

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by

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LIST OF ABBREVIATIONS

A-A Hex	Amine Amine Heat exchanger
CLEANGAS	Treated flue gas stream
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DEA	Diethanolamine
ELECNTRL	Electrolyte non-random-two-liquid
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen Sulphide
K_2CO_3	Pottassium Carbonate
LEAN-A	Lean amine entering the absorber
LEANOUT	Lean amine stream regenerated by stripper
L/G	Liquid amine to flue gas ratio
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MEACOO-	Monoethanolamine carbamate
MEA/MDEA	Blended amine
MV	Manipulated variable
N_2	Nitrogen
NO_X	Nitrogen Oxides
NTRL	Non-random-two-liquid
O_2	Oxygen
P	Pressure
PID	Proportional Integral Differential

PV	Process variable
RICHIN	Rich amine stream enter stripper as the feed
S	Sulphur
SHE	Safety, Health and Environmental
T	Temperature
TNB	Tenaga Nasional Berhad
SO_X	Sulphur Oxides

LIST OF SYMBOL

Symbol	Description	Unit
T	Temperature	^{o}C,K
P	Pressure	atm
%	Percentage	%
mol%	Mole percent	mol%
Molar flow rate	Molar flow rate	kmol/s,kmol/h,kmol/year
Mass flow rate	Mass flow rate	kg/hr,kg/s
QN	Reboiler heat duty	watt
wt%	Weight percent	wt%

KESAN CAMPURAN ALKANOLAMIN KEPADA PERBUANGAN GAS ASID DALAM TEKNOLOGI PENJERAPAN CARBON MELALUI PASCA-PEMBAKARAN.

ABSTRAK

Pembakaran arang batu telah mengeluarkan gas rumah hijau seperti CO_2 dan H_2S ke atmosfera. Oleh itu, isu utama ialah proses pembersihan kerana gasifikasi menghasilkan pelbagai bahan pencemar seperti zarah dan gas asid sebelum dibebaskan ke atmosfera. Pelepasan CO_2 dapat dikurangkan untuk penjanaan kuasa oleh tiga teknologi penangkapan yang merupakan pembakaran pasca pembakaran, pra-pembakaran dan pembakaran oxyfuel. Dalam kajian ini, tangkapan CO_2 pasca pembakaran melibatkan terutamanya pemisahan CO_2 daripada campuran CO_2 / N_2 yang digunakan. Teknologi penangkapan penyerapan digunakan untuk menangkap CO_2 dari loji kuasa dengan menggunakan alkanolamin campuran iaitu MEA dan MDEA. Kajian utama adalah untuk mengenal pasti nisbah terbaik campuran alkanolamines dan lain-lain keadaan optimum yang boleh meningkatkan kecekapan penyingkiran gas asid dan pemulihan amina. Data gas serombong TNBR digunakan sebagai kajian kes dan simulasi proses dengan menggunakan Aspen plus dapat mengoptimumkan proses ini. Simulasi yang keadaan mantap digunakan dan keadaan operasi yang optimum untuk penyerap dan pebuangan dikaji. Kondisi operasi untuk penyerap adalah 30^0C (1 atm), manakala penekan pada 117^0C (2 atm). Pengadunan terbaik nisbah alkanolamin pada 3: 7 dengan 40% berat amina dalam pelarut. Dengan membandingkan parameter yang dioptimumkan kepada keputusan TNBR, kecekapan pembuangan gas asid meningkat kepada 91.55% dengan kenaikan 5.81%. Duti panas terbaik dalam kes ini ialah 1000 watt yang diberi penalti tenaga yang rendah dan kos yang dikurangkan.

BLENDING OF ALKANOLAMINES EFFECT TOWARDS ACID GAS REMOVAL IN A POST-COMBUSTION CARBON CAPTURE TECHNOLOGY.

ABSTRACT

The combustion of coal has released greenhouse gases such as CO_2 and H_2S into the atmosphere. Therefore, one of the main issues is the clean-up process because gasification produces various pollutants such as particulates and acid gases before its release into the atmosphere. The CO_2 emissions can be reduced for power generation by three capture technologies which are post-combustion, pre-combustion and oxyfuel combustion. In this study, the post-combustion CO_2 capture involves mainly the separation of CO_2 from a CO_2/N_2 mixture is applied. The absorption capture technology is to apprehend CO_2 from power plant by using the blended alkanolamines which are MEA and MDEA. The primary study in this research is to identify the best ratio of blending alkanolamines and other optimum conditions that can affect the acid gas removal efficiency and amine recovery. The TNBR flue gas data are used as a case study and process simulation Aspen plus is utilized to optimize the process. In steady state simulation, the optimal operating conditions of absorber and stripper are found. The operating condition for absorber is 30^{o}C (1 atm), while stripper at 117^{o}C (2 atm). The best blending of alkanolamines ratio is at 3:7 with 40 wt % of amine in the solvent. By comparing the optimized parameters to TNBR's result, the efficiency of acid gas removal has an increment of 5.81% which is at 91.55% of efficiency. The best heat duty in this case is 10000 watts, which gives low energy penalty and reduced operating cost.

CHAPTER ONE: INTRODUCTION TO RESEARCH BACKGROUND

1.1 Introduction

The main fuel sources consumed is petroleum, natural gas, and coal whereas Malaysia is the third-largest consumer of energy in the Southeast. As Malaysia targets economic development and increased manufacturing, the country is focused on securing energy through cost-effective means and diversifying its fuel supply portfolio. Petroleum and other liquids and natural gas are the primary energy sources consumed in Malaysia, with an estimated share of 37% and 43%, respectively, in 2014. About 17% of the country's energy consumption is met by coal. Hydropower contributes 1%, and renewable energy contributes 2% of total consumption (Figure 1.1). The power sector's recent investment in more coal-fired power could raise the share of coal consumption in the next few years(Genel, 2017).

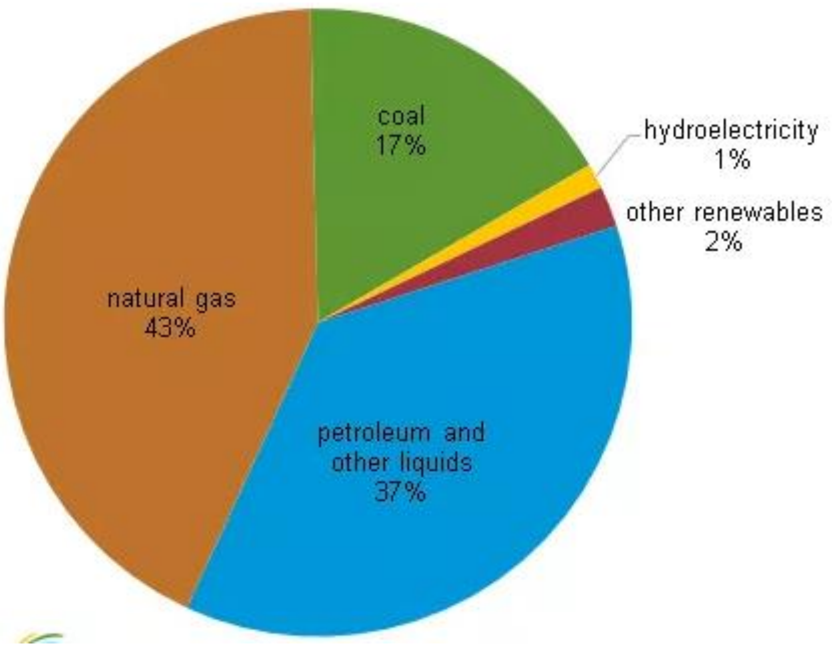


Figure 1.1: Malaysia energy consumption,2014 (Genel, 2017)

The flue gas is usually composed of carbon dioxide (CO_2), hydrogen sulphide (H_2S) and water vapor may also contain a small percentage of air pollutants such as particulate matter, carbon monoxide, nitrogen oxides, sulphur oxides and mercury. However, more than two-thirds of the flue gas is nitrogen. Usually, flue gas is produced in industrial furnace, a steam generator in a fossil fuel power plant or other combustion sources when natural gas, fuel oil, coal, wood or any other fuel is combusted (MiltBeychok, 2011). However, among all the H_2S and CO_2 major discussed due to consequences of this component. These two components are commonly higher corrosion rates, hazardous health impacts and deterioration to environment. It makes the environment become acidification and affects the human health. Furthermore, the presence of CO_2 and H_2S will cause the internal corrosion of carbon steel pipeline.(Choi *et al*,2011)

In addition, for carbon management for sequestration of CO_2 from our environment is done by Capturing CO_2 from flue gas. Thus, the important factors in selecting the capture system which is concentration of CO_2 in the gas stream, the pressure of the gas stream and the fuel type. There are three carbon capture technologies can be apply which is post-combustion, pre-combustion decarbonisation and oxyfuel combustion. The current status for 3 technologies is are summarized in Table 1.1. The technology for CO_2 separation are include absorption, adsorption, membrane and cryogenics (Figure 1.1). However, the suitable technology depends on the characteristics of the flue gas stream. Usually, the selection of a technology for a given capture application depends on many factors, i.e. partial pressure of CO_2 in the gas stream, extent of CO_2 recovery required, regeneration of the solvent, sensitivity to impurities, such as acid gases, particulates, purity of the desired CO_2 product, capital and operating costs of the process, the cost of additives necessary to overcome fouling and corrosion and where applicable, the environmental impacts.

In this research, the focus is on amine absorption technology which is commercialized technology used in natural gas industry. There are many type of amine solution eg Diethanolamine (DEA),Monoethanolamine (MEA), Methyldiethanolamine (MDEA), Diisopropanolamine (DIPA), Aminoethoxyethanol (Diglycolamine) (DGA) and mixed amine which is MDEA-MEA. The commonly used in industry single amine eg MEA which is CO_2 is removed from combustion flue gas stream but it give disadvantages for CO_2 separation from flue gases such low carbon dioxide loading capacity, high equipment corrosion rate, amine degradation by SO_2, NO_2, HCL and HF and oxygen in flue gas which induces a high absorbent makeup rate and high energy consumption during high temperature absorbent regeneration. However, the mixed amines is use to maximize the desirable qualities of the individual amines by reduction in energy requirements and modest reduction in circulation rates for amine blends relative to the corresponding single amine system of similar total amine concentration. In recent year, the use of sterically hindered amines in solution to remove carbon dioxide from acidic gases by scrubbing process has been the focus in chemical absorption (Olajire, 2010).

In Malaysia, TNB Janamanjung Sdn. Bhd. (TNBJ) is the coal-fired, in line with national strategy to reduce heavy dependence on natural gas as fuel source for power generation. The TNBJ has devoted considerable attention and resources to mitigate and minimize possible impacts that a coal-fired power station may have on the immediate and surrounding environment. These plants also have been designed based on the Environmental Quality (Clean Air) Regulations 1978 (TNBJ, 2018). In addition to its oil and gas sector, carbon capture and storage (CCS) could play a role as an emissions reduction technology for Malaysia’s power sector, given 95% of its electricity is generated by coal or gas This plant also apply the post-combustion carbon capture via amine absorption which is will capture the emissions from a power station’s flue gas

(Institute, 2015).

Optimization of amine absorption unit by considering all variables that affect the process performance such as reboiler heat duty, L/G parameter in the absorber, reboiler heat duty, stripper pressure ,flue gas flow rate, CO_2 concentration, solvent flow rate, solvent composition, absorber pressure and temperature, CO_2 recycle stream characteristics, stripper reboiler pressure, heat exchange between rich and lean solvent streams, stripper condenser temperature and other important process parameters. In addition, aspen plus is used to optimized the process.(Rodríguez *et al*,2011)

Table 1.1: The current status for 3 technologies

Post combustion capture	Amine scrubbing is well established for natural gas
Pre combustion capture	Integrated gasification combined cycle (IGCC), ammonia production and physical solvent separation is well established.
Oxyfuel combustion	Oxygen production is well established.

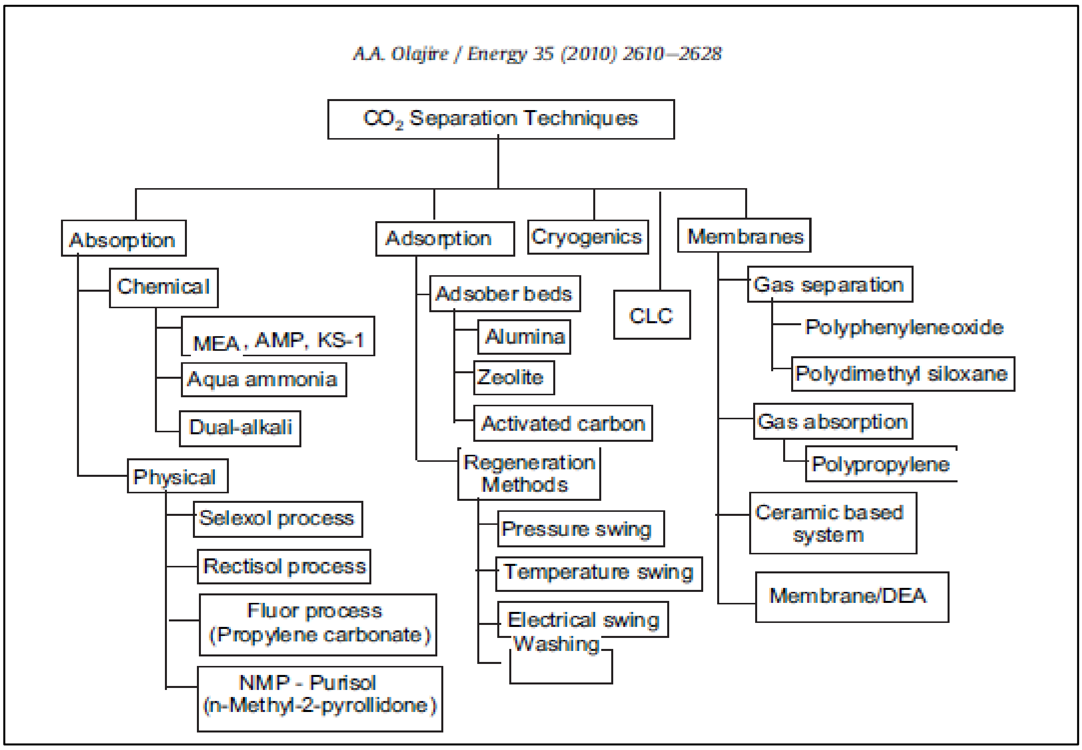


Figure 1.2 : The technology for CO_2 separation

1.2 Problem Statement

The fuel combustion and the other industrial activities and its emission into the atmosphere has increased have become a major target for reduction. The hydrogen sulphide (H_2S), carbon dioxide (CO_2) and particle contain in fuel gas must be processed and cleaned first before discharge. These gases will give harmful to the environment in their natural quantities. The several technique can be apply such as post-combustion CO_2 capture, adsorption process, adsorption process, cryogenics, membrane separation, pre-combustion CO_2 capture and oxy-fuel combustion. The U.S. Department of Energy (DOE) is considering three ways to capture CO_2 generated in coal-based power production which is post-combustion where CO_2 is capturing from power plant flue gas ,pre-combustion where CO_2 captures from gasifier coal synthesis gas, and oxy-combustion where oxygen is separate from air prior to combustion and produces a nearly sequestration-ready CO_2 effluent (Gibbins, J;Chalmers, 2008). The Post-combustion capture (PCC) of CO_2 from power plant flue gas has been the subject of many studies because is an effective technology to reduce greenhouse gases, consumes a less amount of energy in amine regeneration, low loading capacity.(Lee *et al.*, 2016)

In addition, chemical solvent is used for capturing CO_2 such as aqueous ammonia and alkanolamines. Currently, the technology of using alkanolamines or amines for removing hydrogen sulphide (H_2S) and carbon dioxide (CO_2) from the fuel gases. One of the processes which used in the industry to remove the acid gases from natural gas is alkanolamines process application. Many gas sweetening units, which are operating, may be optimized by simply changing their amines solution. The differences in the performance of absorption technology and amine solvent depend on amine reactivity. In this study, simulation software plays a key role in the process development to study process alternatives, assess feasibility and improve pollution control. The process simulator is used to predict the existing plant performance and potentially guide to selecting the optimum blend composition and other operating parameter such as pressure absorber, reboiler heat duty and else.

However, the common alkanolamines used in industry is single alkanolamines for example MEA which is primary alkanolamine. From the research, the primary alkanolamine is very stable and the reboiler heat duty is become higher thus the cost will increase for regeneration of MEA. Therefore, it is interesting to investigate post-combustion CO_2 capture with mixtures of amines. The key factor is to determine the operating conditions and the mixture composition that simultaneously maximize the advantages of both amines and minimize their disadvantages to improve the whole overall performance of the process.

The majority of these studies focused on the economics of CO_2 capture and the minimization of its energy consumption and initial investments for an amine sweetening unit was related to the solvent circulation rate, and another 10–20% depended on the regeneration energy requirement. Thus, one key challenge facing any CO_2 capture technology based on chemical absorption is the selection of an appropriate amine solvent and the reduction of energy consumption while maintaining the CO_2 emission target. (Svensson, Hulteberg and Karlsson, 2013)

1.3 Objectives

The acid gas absorption by using amine solution which is by blending MEA and MDEA has been studied to minimize the acid gas release to environmental and minimized the global warming. Usually, most industries used the third solution and single amine solution (eg MEA alone) in acid gas removal unit. In the research, the primary amine and tertiary amine is used to improve the performance of the absorption process and maximum the regeneration of amine by using Aspen plus. The combination of amine will give positive impact for future generation and will give low cost at the end of the process. Thus, to make the project is successful a few objectives has been set as follows:

I. To identify the optimum alkanolamine blending ratio and optimum operating condition to give the maximum yield of CO_2 absorption.

II. To investigate the effect of operating condition of acid gas removal unit using MDEA-MEA solvent to operate on high level of carbon dioxide (CO_2) absorption.

III. To identify the optimum operating condition to give maximum amine recovery on stripper for regeneration of amine.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

The anthropogenic greenhouse effect represents one of the mostly discussed problems of the day and cause of growing climate change. In order to reduce the greenhouse gases with effective technology the post combustion carbon capture (PCC) is used to capture more than 70% of the CO_2 emissions. Thus, the more-efficient and improved process of acid-gas removal from large point sources of CO_2 and H_2S has been research. The acid-gas removal unit is used in acid gas removal process by several separation techniques from the fuel gas which is membrane, physical absorption, chemical absorption and cryogenics. The commonly used techniques is chemical absorption into liquid solvent because the absorption is highly effective against various acid-gas concentration and relatively inexpensive (Sarntharm Mudhasakul,2013). The suitable solvent affects the efficiency of acid-gas removal because different solvent have differ significantly toward capacity, degradation, cost and regeneration. The commonly used solvent is aqueous solution of alkanolamines such as MEA, DEA and MDEA. The used of blend amine is also reduces the operating costs and improves products quality. The simulation software is used to study the process alternative, assess feasibility and improve pollution control. One of the challenges in this process is the changes in flue gas flow rate and reboiler heat duty will affect the lean loading, liquid to gas ratio and percentage of CO_2 removal. (Harun, Nittaya et al. 2012).

2.2 Flue Gas

In a global context, among all the industries emitting CO_2, fossil-fuelled power plants generate the largest amount of CO_2 emission and that accounts for about 33–40 percent of the total. (Brunetti *et al.*, 2010) .The CO_2 concentration in the atmosphere is increasing. The change of atmospheric CO_2 level over the years between 1000 and 1997 and actual CO_2 level during 1958–2004 as shown in figure 2.1 (Song, 2006). Thus, CO_2 needs to be separated and captured from the flue gases of such point sources before direct sequestration. (Yang *et al.*, 2008) .Typically, about 75-90% of the CO_2 is captured using this technology, producing a nearly pure (>99%) CO_2 product stream.

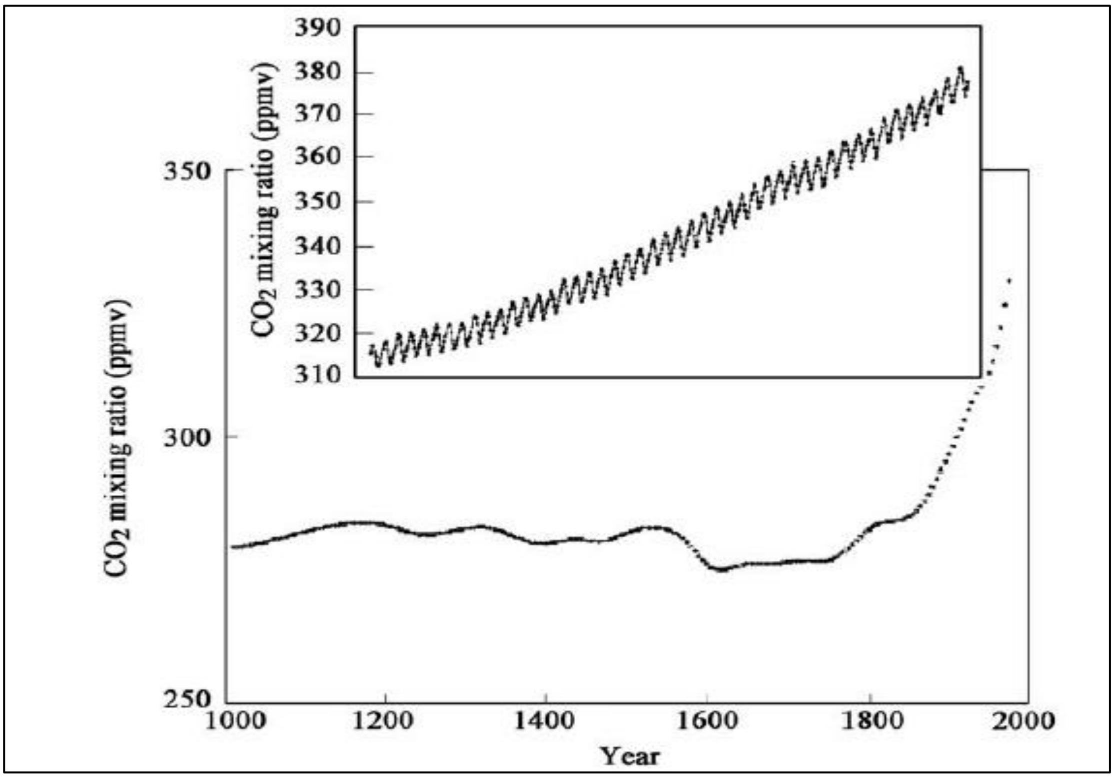


Figure 2.1 : Atmospheric CO_2 concentrations during 1000–2004 based on the analysis of ice cores and logged atmospheric CO_2 concentrations during 1958–2004(Song, 2006)

2.3 Acid Gas Separation Technologies

The CO_2 emissions can be reduced for power generation by three capture technologies which is post-combustion, pre-combustion and oxyfuel combustion. The concentration of CO_2 in the gas stream, the pressure of the gas stream and the fuel type are important factors in selecting the capture system.(Olajire, 2010). Based on (Mondal *et al*, 2012) there are several existing capture technologies are available to capture CO_2 from power plant such as physical and chemical absorption, adsorption, cryogenic and membrane processes. However, Brunetti highlight that the conventional separation processes for CO_2 separation are absorption with ammines, adsorption with porous solids with high adsorbing properties such as zeolite or active carbon and cryogenic separation. Amine-based absorption with an aqueous monoethanolamine (MEA) solution is the most common technology for post-combustion capture, since it is capable to achieve high level of CO_2 capture about 90% from flue gas due to fast kinetics and strong chemical reaction. However, its use is by far the best available technology owing to the fact that the ammines are corrosive and susceptible to degradation by trace flue gas constituents.

2.3.1 Post Combustion

Post-combustion CO_2 capture, which is at the end of the wet exhaust flue gas of power plants with fossil fuels burned completely with air, involves mainly the separation of CO_2 from a CO_2/N_2 mixture.

2.3.2 Pre Combustion

Process with fossil fuels decarbonized prior to combustion, primarily captures CO_2 from a CO_2/H_2 mixture. It is usually operated at a high pressure and a slightly elevated temperature

2.3.3 Oxy Combustion

Combustion process of fossil fuel without N_2 (i.e. using O_2 separated from air), with the combustion of fossil fuels in a nearly pure O_2 environment. As a consequence, the product of combustion is almost entirely CO_2

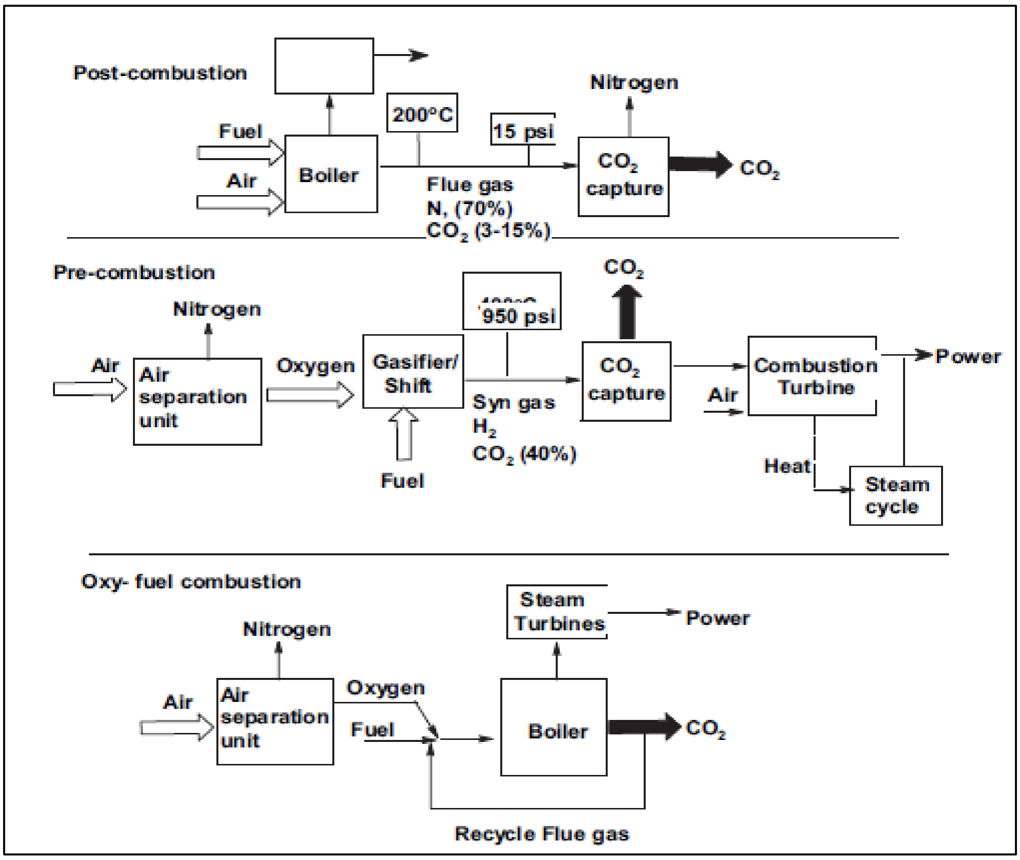


Figure 2.2 : Three capture technologies

Table 2.1 : Function of acid gas cleaning technologies

Acid gas cleaning technologies	Function
Physical absorption (Keskes *et al.*, 2006)	➢ Physical absorption processes are thus particularly appropriate for the treatment of CO_2-rich gas streams. ➢ Process : • Solexol • Purisol
Chemical absorption (Mondal, Balsora and Varshney, 2012)	➢ Holds good result in terms of removal efficiency and can be used for low concentration flue gases. ➢ Chemical absorbents such as MEA, DEA, MDEA, and DIPA are commonly used.
Adsorption (Meisen and Shuai, 1997)	➢ Process for removal of one or more components of a mixture with the help of a solid surface. ➢ Based on significant intermolecular forces between gases and the surfaces of certain solid materials. ➢ Depending on the temperature, partial pressure, surface force and adsorbent pore sizes, single or multiple layers of gases can be adsorbed
Cryogenic (Gupta *et al*, 2003)	➢ Widely used commercially for separation of CO_2 from streams having high CO_2 concentrations (typically more than 50%). ➢ It is not normally used for dilute CO_2 streams such as flue gas from coal/natural gas fired boilers as the amount of

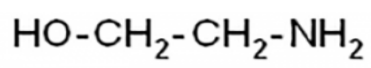
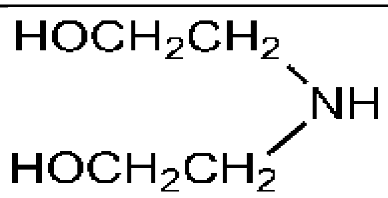
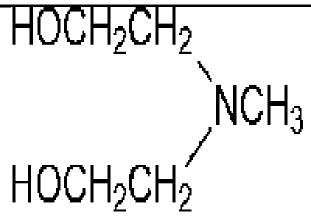
	energy required for refrigeration is uneconomical for the plant.
Membrane	➢ To separate certain components from a gas stream, which can be CO_2 from flue gas (post-combustion system), CO_2 from natural gas (natural gas processing), and CO_2 from hydrogen (pre-combustion systems) or oxygen from nitrogen (oxyfuel combustion system). ➢ Membranes are semi-permeable barriers able to separate substances by various ➢ With regards to CO_2 capture, the membrane processes are classified into two types: • Gas separation membrane • Gas absorption membrane

According to Hasan *et al.* among the available PCC technologies, the absorption process using aqueous amine is most commonly used for treating flue gases from power plants. However, PCC using aqueous amine consumes a considerable amount of energy to regenerate amine solvent. Thus, low loading capacity and degradation have been pointed out as obstacles of commercialization of this technology.

2.4 Alkanolamine

An amine with only one organic group directly bonded to nitrogen is a primary amine, with two organic groups it is a secondary amine and with three it is a tertiary amine. Thus, alkanolamine is where the organic group contains an OH group. A general amine has the formula NR1R2R3 where R1, R2 and R3 are organic groups or hydrogen directly bonded to the central nitrogen atom. MEA is a primary alkanolamine often used for CO_2 removal. DEA is a simple secondary amine and N-methyldiethanolamine (MDEA), with R1 and R2 as C2H4OH-groups and R3 as a CH3-group, is probably the most used tertiary amine for CO_2 removal. When used as solvents, the amines are typically 20–40 wt. % solutions in water (Øi, 2017). Recently, the differences in the performance of absorption technology and amine solvent depend on amine reactivity as shown in Table 2.4.

Table 2.2 : Characteristics of alkanolamine.

Monoethanolamine(MEA)	**Diethanolamine (DEA)**	**Methyldiethanolamine (MDEA)**
		
Primary	Secondary	Tertiary
Boiling is 170.5˚C	Boiling point is 269˚C	Boiling point at 247.3˚C
Molecular weight is 61.08	Molecular weight is 105.14	Molecular weight is 119.1
Flash point TCC is 95˚C	Flash point TCC is 154	Flash point TCC is 101˚C
Vapour pressure 20˚C is 4mmgh	Vapour pressure 20˚C is <0.01	Vapour pressure 20˚C is <0.01
Very reactive	Very reactive	Less reactive
Fast rate	Fast rate	Low rate

Higher stripping energy Requirement	Higher stripping energy requirement	Lower stripping energy requirement
High volume acid gas removal	High volume acid gas removal	Low volume acid gas removal
MDEA<MEA<DEA		

According to Sadegh (2013) chemical absorption of acid gases by amine-based absorbents is the most preferred chemical solvent technology for acid gas removal. In addition, alkanolamines are the most commonly used category of amine chemical solvents used for acid gas removal and been used in a large variety of industries over years. In addition, the development of amine-based mixture solvents, whose application may save ~20% regeneration energy, compared to MEA. (Svensson *et al*, 2013). Mostly, aqueous solutions of MEA and MDEA are used as solvents for gas sweetening. However, the use of blend amines is also increasing, since it reduces the operating costs and improves products quality. These solvents are claimed to consume less energy during solvent regeneration compared to single alkanolamines and yet provide satisfactory capture efficiency.

The performance of aqueous MEA, DEA, tri-ethanolamine (TEA) and AMP solutions is analysis by (Kim *et al.*, 2013).According to their work, primary (MEA) and secondary amines(DEA) showed lower CO_2 loadings and thus lower absorption capacities due to chemical equilibrium limitations, but also higher regeneration heat requirements compared to tertiary (TEA) and sterically hindered (AMP) amines. Among these solvents, MEA is the most widely used because it has a faster rate of reaction with CO2, which allows absorption to take place in a shorter column. However, the operating cost of the absorption process using MEA is prohibitively high mainly because of the significant amount of energy required for solvent regeneration and severe operational problems such as corrosion and solvent degradation. At the present time, AMP and MDEA are receiving a great deal of attention because they require relatively low energy consumption for solvent regeneration, leading to significant savings in process costs.(Aroonwilas and Veawab, 2004)

2.5 Simulation

Design, operation, simulation and optimization of acid gas removal from natural gas process and CO_2 capture from combustion gas plants, require accurate prediction of phase and chemical equilibrium, as well as thermal properties of the system. (Zhang and Chen, 2011).The sensitivity analyses and the optimization of the process were accomplished using the Sensitivity and the Optimization sections of Model Analysis Tool of Aspen Plus.(Giwa and Giwa, 2013). Simulation-based also used to analysis comparing the performance of various blends of MEA, DEA, methyl-diethanolamine (MDEA) and AMP.

According to result from the simulation based improvement techniques for acid gases sweetening by chemical absorption done by Muhammad and GadelHak, (2015) that the sweetening units still require improvements in future demands of natural gas sweetening technology. Several improvements are required, which is enhancing the capacity of the absorber, reducing the energy requirements of the stripper, optimizing the operating conditions for the steady state operation, coping up with operating disturbances and decreasing the running and the capital costs.

However, simulation of CO_2 capture using MEA scrubbing is analyse to evaluation of the process alternatives in order to minimizing the cost of implementation.(Alie *et al.*, 2005). However, the optimization is done to determine the best operating condition to the amine process. The several optimization parameter which are studied such as column type and design ,solvent selection, solvent concentration ,temperature, pressure, solvent circulation rate and rich amine loading.(Justin C. Slagle, 2013)

2.6 Chemical Reaction and Kinetic

All the equilibrium expressions and their respective parameters are taken from Austgen *et al,(*1989). The power law expressions are used for the rate-controlled reactions as shown below:

$$r = kT^{n} \exp\left(-\frac{E}{RT}\right) \prod_{i=1}^{N} C_i^{a_i} \tag{2.1}$$

Where:

r = Rate of reaction;

k = Pre-exponential factor;

T = Absolute temperature;

n = Temperature exponent;

E = Activation energy;

R = Universal gas constant;

N = Number of components in the reaction;

Ci = Concentration of component i;

ai = The stoichiometric coefficient of component i in the reaction equation.

2.6.1 Equation Equilibrium

Dissociation of water

$$2H_2O \leftrightarrow H_30^{+} + OH^{-} \tag{2.2}$$

Dissociation og hydrogen sulphide

$$H_2O + H_2S \leftrightarrow H_3O^{+} + HS^{-} \tag{2.3}$$

Dissociation of bisulfide

(2.4)

$$H_2O + HS^- \leftrightarrow H_3O^+ + S^{2-}$$

Dissociation of carbon dioxide

$$2H_2O + CO_2 \leftrightarrow H_3O^+ + HCO_3^- \tag{2.5}$$

Dissociation of bicarbonate

$$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-} \tag{2.6}$$

Dissociation of protonated alkanolamine

$$MEAH^+ + H_2O \leftrightarrow MEA + H_3O^+ \tag{2.7}$$

$$MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+ \tag{2.8}$$

2.6.2 Reaction Kinetic

Bicarbonate formation

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{2.9}$$

$$HCO_3^- \leftrightarrow CO_2 + OH^- \tag{2.10}$$

Carbamate formation reaction

$$MEA + CO_2 + H_2O \leftrightarrow MEACOO^- + H_3O^+ \tag{2.11}$$

$$MEACOO^- + H_3O^+ \leftrightarrow MEA + H_2O + CO_2 \tag{2.12}$$

Hydrolysis of CO2 to bicarbonate

$$MDEA + CO_2 + H_2O \leftrightarrow MDEAH^+ + HCO_3^- \tag{2.13}$$

$$MDEAH^+ + HCO_3^- \leftrightarrow MDEA + CO_2 + H_2O \tag{2.14}$$

CHAPTER THREE: METHODOLOGY

3.1 Introduction

The amine unit operation is the acid gas (H_2S, CO_2) - alkanolamine-water system that involve two unit which is absorber and stripper column. Typically two type of absorber which is trap and packed column. In the absorber column, typically reaction is absorption of acid gas by amine solvent to produce rich amine. In order to increase the efficiency to remove the acid gas the suitable type of column, height of absorber and ratio of blending amine need to consider. Then, the solvent circulation rate is play important role in order to determine the efficiency of sour gas removal and also can affect the plant cost. When the circulation rate is lower the heat duty will be lower and the plants cost will reduce. Before enter the stripper the rich amine is heated by heat exchanger. On a global basis, energy consumption of coal and natural gas is 24% and 21% respectively in 2004 and expected will be 38% and 30% respectively electricity demand in 2030(Steeneveldt et al ,2006).Thus some strategies need to be done for reduce the reboiler heat duty and heat exchanger. However, the acid gas removal by the stripper is used to optimize capture process operating condition and to propose new design that minimize energy consumption and reduce plant cost. (Harun *et al.*, 2012) . Thus, the project is carrying out by a few step as shown in Figure 3.1. The purpose of simulation is to model and predict the performance of a process. It involves the decomposition of the process into its constituent elements (e.g. units) for individual study of performance. The process characteristics (e.g. flowrates, compositions, temperatures, pressures, properties, equipment sizes, etc.) are predicted using analysis techniques such as computer-aided process simulation tools which is Aspen Plus. In process simulation, the process inputs and flowsheet and are required to predict process outputs. It is a computer-aided software which uses the underlying physical relationships (e.g., material and energy balances, thermodynamic equilibrium, rate equations) to predict process performance (e.g., stream properties, operating conditions, and equipment sizes.

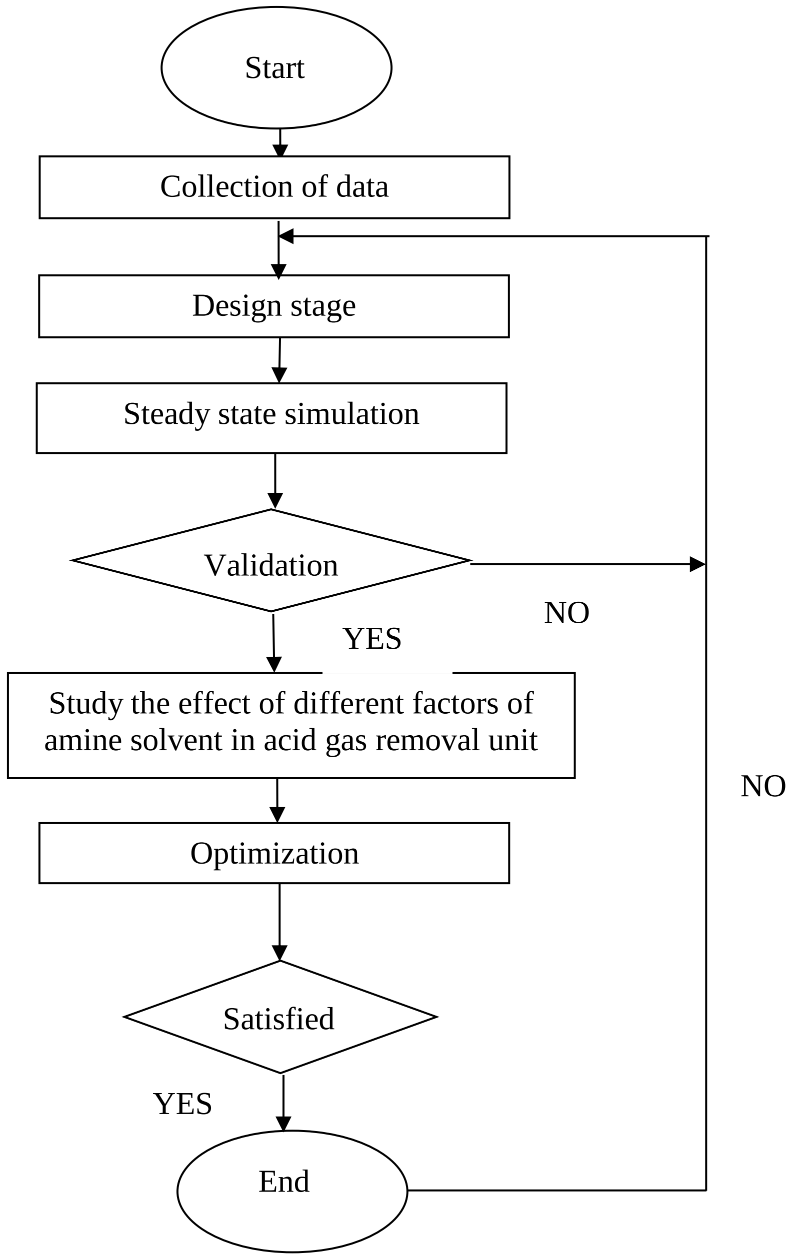


Figure 3.1: Step is carrying out of this project

3.2 Software Tool

The aspen plus is used in this process to achieve the e three objectives. The common application used aspen plus is aspen properties and aspen simulation. Each of the part has their own function that we need to play around to get the valid result as shows in table below.

Table 3.1: Aspen engineering suite and its function

Aspen engineering suite	**function**
Aspen plus	Process simulator for steady state and equipped with property database via aspen properties.
Aspen properties	Provide physical property method and model(Electrolyte-NRTL) and component physical
Aspen simulation	Useful in process optimization

3.3 Process Description

An amine unit operates by 2 units which is the first unit is absorption process and second unit is regeneration process. At first unit operation involve absorber column typically is packed and tray column. Then, the absorber typically operates at 40^0C and 1atm (for flue gas). The flue gas that contain acid-gas which is commonly H_2S and CO_2 with typically concentration in natural gas are between 0 to 50%(molar basis) enter the absorber column at the bottom where the lean amine solution which is solvent enter the column at the top. The lean amine solution play important role to remove the acid-gas from the system. Hence, in order to increase the efficiency of acid-gas removal the suitable blending ratio of alkanoamine is important. Typical amine concentration is depending on amine type and acid gases. In this case, typically concentration of MEA is between 20 to 30% and for MDEA concentration is between 30 to 50%. In the absorber, the lean amine solution with flue gas contacted counter-currently where the amine solution flow down the column and contacted with flue gas then the acid gases react with the lean amine solution to form rich amine which is loaded with acid-gases and exit at the bottom of absorber and the sweetened gas exit the top of the column and goes for further processing.

The rich amine exits the bottom of absorber and enters to the second unit operation which is regeneration process that involve stripper to remove the acid gases and circulated the lean amine solution to the top of the absorber. The typical operating temperature of the stripper is around 120^{0}C and pressure is around 1, 2 bar. In this process, higher use of energy to produce heat in order to break the chemical bounds between acid gases and solvent. Thus, it will cause the plant cost increase. Usually it depends on the solution circulation rate where circulation rate decrease the plant costs also reduces. In stripper column, the rich amine flow down the column to reboiler by heat to strip acid gases from the solution and the solution is regenerated.

3.4 Design

3.4.1 Flow Sheet

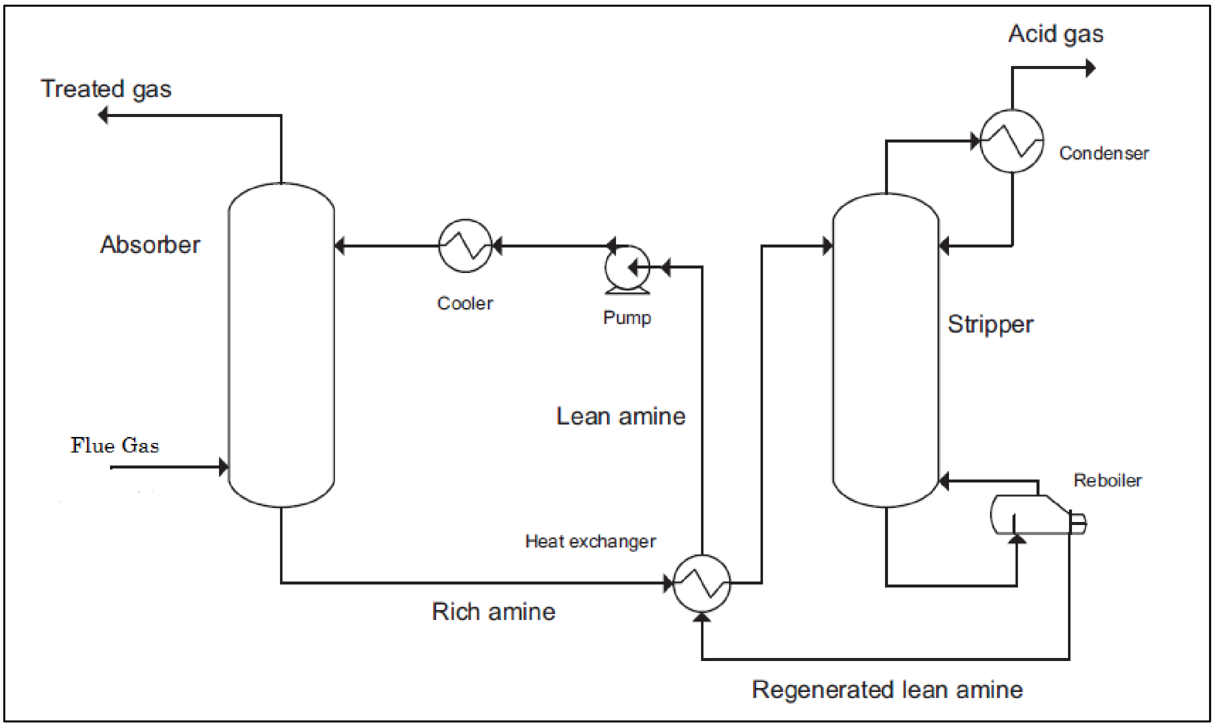


Figure 3.2: Design of Amine process

The flue gas from the plant is entering to absorber. In addition, to get the complete removal of acid gas there are some other equipment need to used such as stripper, rich amine heat exchanger, reboiler, and lean amine cooler as shown in figure 3.2. For simulation purpose this design is used as the reference in designing the Aspen layout for the flue gas simulation.

3.4.2 Material Balance

The TNBR pilot plant produces 24.753 kg/hr flue gas. Thus, a simple calculation is done to obtained lean amine flow rate. Then, the initial value is inserting into aspen simulation to get the optimum parameter. However, a few assumptions need to be considered:

Assumptions:

- The heat loss is negligible.
- No reaction between MEA and CO,SO_2 and NO_2.
- Insignificant at T<100^{0}C for carbamate polymerization.
- Pressure of absorber and stripper is 1 atm
- 100%of CO_2 is stripped.
- Evaporation loss of amine and water is negligible

3.4.3 Unit Operation Sizing

The design for column sizing is based on the mole flow rate produce by TNBR. The data for designing the column is obtained in table 3.2. In addition, to achieve our target to get maximum stripped CO_2 the packed and trap column need to be compared by using the data from Table 3.2.

Table 3. 2: Design for column sizing. (Law *et al* , 2017)

Criteria	Design information
Flue gas density	0.039
Molar flow rate	1-25
Space velocity	14400