# FOAMING BEHAVIOUR OF AN AQUEOUS SOLUTION OF N-METHYLDIETHANOLAMINE (MDEA) AND AQUEOUS SOLUTION OF PIPERAZINE (Pz)-N-METHYLDIETHANOLAMINE (MDEA) FOR THE CARBON DIOXIDE REMOVAL

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# ABSTRACT

This work focuses on one of the severe problem arise by the usage of amine in the removal of acid gases namely carbon dioxide ($CO_2$) which is foaming. Foaming can cause reduction integrity of plant operation, excessive loss of absorption solvents, premature flooding, reduction in plant throughput, off-specification of products and high absorption solvent carryover to downstream plants. Foaming tendency can be experimentally evaluated by variation of parameters, such as temperature, concentrations and type of impurities (sodium chloride, acetic acid, iron sulphide). Prior to each experiment, aqueous solutions of MDEA of different concentration are prepared by volume (for concentration parameter), the prepared solutions are heated in a temperature bath to a set temperature (for temperature parameter) and different impurities are added into the solution (for impurities parameter). Effect of all this parameters will be evaluated based on height of foam in millilitre (ml) and collapse time of foaming in seconds (s). Nitrogen gas ($N_2$) will be use in this experiment as bubble gas. Results reveal that increase the pure MDEA concentration will decrease the foaminess. Similarly results also indicated that by increase the solution temperature will decrease the foam formation. For the investigation of foaming on temperature parameter, MDEA-Pz solution show greater to contribute on foaminess than pure MDEA solution at same amount of MDEA used. At the same amount of the impurities, iron sulphide appeared as the most influential contaminant to the foam formation, which promoted the highest foamability in any concentrations of piperazine-MDEA solution.

# ABSTRAK

Kerja ini memberi tumpuan kepada salah satu masalah yang teruk timbul oleh penggunaan amina dalam penyingkiran gas asid iaitu karbon dioksida ($CO_2$) yang berbuih. Berbuih boleh menyebabkan integriti pengurangan operasi kilang, kehilangan berlebihan pelarut penyerapan, banjir pramatang, pengurangan pemprosesan tumbuhan, di luar spesifikasi produk dan penyerapan yang tinggi terbawa bersama pelarut untuk tumbuhan hiliran. Berbuih kecenderungan boleh dinilai secara eksperimen oleh ubahan parameter, seperti suhu, kepekatan dan jenis kekotoran (natrium klorida, asid asetik, sulfida besi). Sebelum setiap eksperimen, penyelesaian akueus MDEA yang berbeza kepekatan disediakan oleh kelantangan (untuk parameter kepekatan), penyelesaian yang bersedia dipanaskan dalam mandi suhu ke suhu yang ditetapkan ( untuk parameter suhu) dan kekotoran yang berbeza ditambah ke dalam penyelesaian (untuk kekotoran parameter). Kesan semua parameter ini akan dinilai berdasarkan kepada ketinggian buih dalam mililiter (ml) dan runtuh masa berbuih di saat (s). Gas nitrogen ($N_2$) akan digunakan dalam eksperimen ini gas gelembung. Keputusan menunjukkan bahawa peningkatan MDEA kepekatan tulen akan berkurangan foaminess itu. Begitu juga keputusan juga menunjukkan bahawa dengan peningkatan suhu penyelesaian akan berkurangan pembentukan buih. Bagi menyiasat berbuih pada parameter suhu, penyelesaian MDEA - Pz menunjukkan yang lebih besar untuk contributited pada foaminess daripada penyelesaian MDEA tulen pada jumlah yang sama MDEA digunakan. Pada jumlah yang sama daripada kekotoran, sulfida besi muncul sebagai pencemar yang paling berpengaruh kepada pembentukan buih, yang dinaikkan pangkat foamability tertinggi dalam mana-mana kepekatan larutan piperazine - MDEA.

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| | |
|---|---|
| Pz | Piperazine |
| MDEA | Methyldiethanolamine |
| TEA | Triethanolamine |
| DEA | diethanolamine |
| MEA | monoethanolamine |
| DGA | diglycolamine |
| DIPA | diisopropanolamine |
| $CO_2$ | Carbon dioxide |
| $N_2$ | Nitrogen |
| $NH_3$ | Ammonia |
| RSH | mercaptans |
| COS | carbonyl sulfide |
| AGRU | Acid Gas Removal Unit |
| GPP | gas processing plant |
| DHU | Dehydration &Regeneration Unit |
| LTSU | Low Temperature Separation Unit |

*Subscripts*

| | |
|---|---|
| $b$ | bubble |
| $g$ | gravitational acceleration |
| $l$ | capillary perimeter |
| $\gamma$ | liquid solution |
| s | seconds |
| ml | millilitre |
| $\sum$ | Foaminess coefficient |
| $\mho_o$ | average steady foam volume |
| $h_o$ | reference height of the fritted glass plate |
| $h_1$ | height of the liquid system before feeding the gas |
| $h_f$ | height of the foam after a given time |
| $E_a$ | activation energy |

# 1 INTRODUCTION

## *1.1 Acid Gases in Natural Gas*

Natural, synthesis, and refinery of raw gases stream consists of acid gases such as hydrogen sulfide ($H_2S$), carbon dioxide ($CO_2$), ammonia ($NH_3$), hydrogen cyanide (HCN), carbonyl sulfide (COS), carbon disulfide ($CS_2$), mercaptans (RSH), nitrogen ($N_2$), water ($H_2O$), oxygen ($O_2$), elemental sulfur, mercury and arsenic. The listed acid gases can cause few problems including corrosion and fouling in pipelines, refinery gases treatment as well as in gas processing plants. $CO_2$ are the main acid gas which needs to be removed from natural gas.

This is due to its properties which is very toxic and poisonous, extremely corrosive with the presence of water, and can cause catalyst poisoning in refinery vessels. In addition to that, if this gas is going to cryogenic plants, it may cause solidification. The presences of CO2 in natural gas also reduce the heating value of natural gas.

Therefore, removal of acid gases from natural gas is important to ensure the increasing of heating value of natural gas, reducing corrosion during the transport and distribution of natural gas, decreasing volume of natural gas transported in pipelines, and prevent atmospheric pollution by $SO_2$, which is arise from combustion of natural gas that have $H_2S$. The removal of acid gas in LPG plant is also required for reason of safety, gas and/or liquid product specification, to prevent freeze-out at low temperature, to decrease compression cost, to prevent poisoning of catalysts in downstream facilities and to meet environmental requirements.

### *1.1.1 Acid Gases Removal Process*

The process of removal of $CO_2$ from natural gas is usually referred to as gas conditioning or treating. It is a process that generally referred to the process of removing or reducing the amount of acid gases to an acceptable limit. In gas processing plant (GPP), the process of removing or reducing acid gases contaminants will be handled by Acid Gas Removal Unit (AGRU). In fact, activities on gas absorption processes for the selective removal of acid gases in industrial gas processing have been taken seriously since the contribution from the process have tremendous effects. Figure 1-1 shows the schematic diagram of the Acid Gas Removal Unit (AGRU), Dehydration &Regeneration Unit (DHU) and Low Temperature Separation Unit (LTSU).

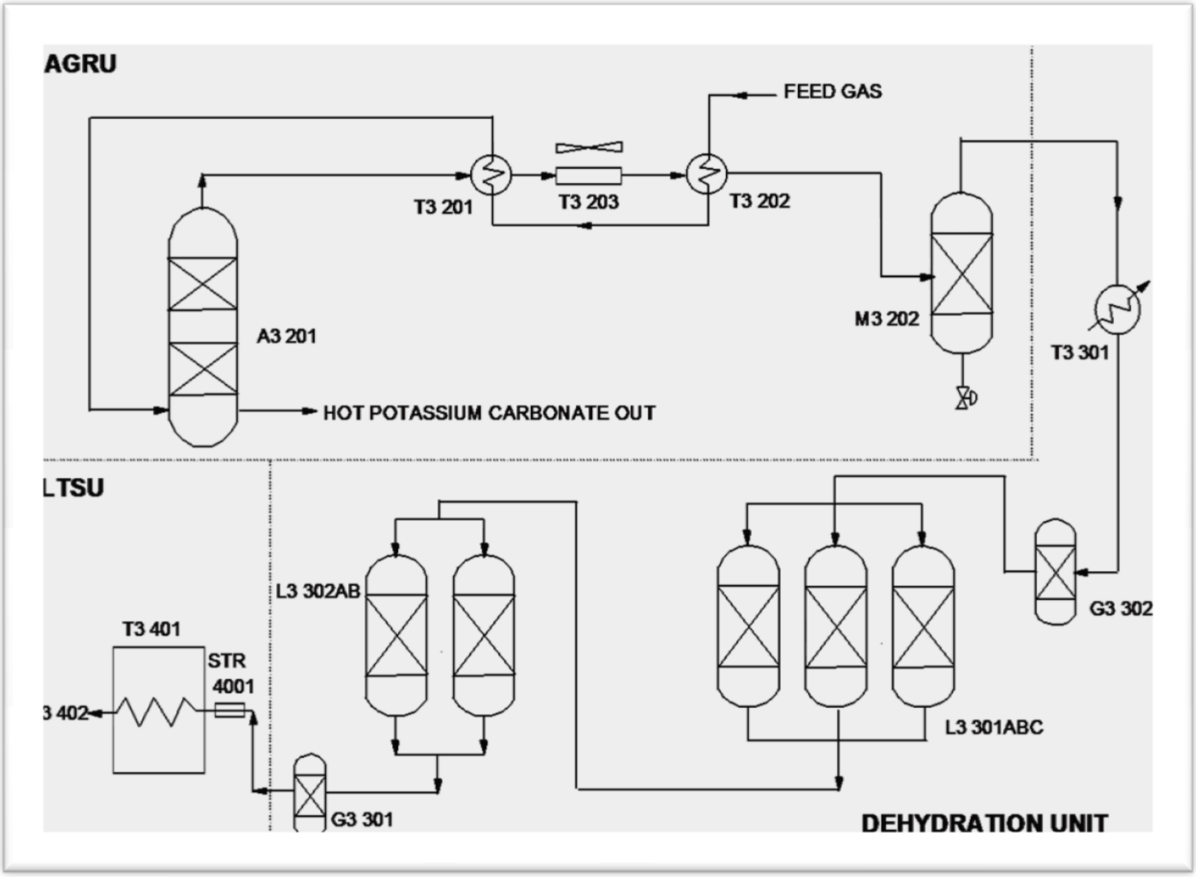

**Figure 1-1**: Sketch of the Acid Gas Removal Unit (AGRU), Dehydration & Regeneration Unit (DHU) and Low Temperature Separation Unit (LTSU).

There are many factors that must be consider in selecting an acid gas removal process including natural gas composition, acid gas content of the gas that needs to be processed, selectivity required for acid gas removal, final product specifications, gas throughput to be processed, temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered, $H_2S$ removal conditions with or without sulphur recovery, acid gas disposal method or environmental consideration and lastly relative economics which include capital cost, operating cost and royalty cost for process.

The process of removing or reducing acid gases contents can be classified into four types of process which are the absorption based on Chemical Solvents, absorption based on Physical Solvents, adsorption and by gas permeation. In Malaysia, only GPP B (GPP 5 and GPP 6) is operated using Amine absorption process while GPP A (GPP 1, 2, 3 and 4) is based on UOP's Benfield process. Both GPP used the chemical absorption process to remove $CO_2$.

Acid gases removal processes based on chemical solvents involved chemical reaction in removing the $CO_2$ gas from the gas stream. This process is so called "reactive separation", where acid gases are separated or removed (absorbed) by chemically reacting them with special solvents. The reaction may be reversible or irreversible. In reversible reactions, the reactive material (solvent) removes $CO_2$ in the contactor (absorber column) at high pressure and low temperature. The reaction is reversed by high temperature and low pressure in the regenerator (stripper column).

In irreversible processes, the chemical reaction is not reversed and removal of the acid gases requires continuous make up of the solvent. In general, there have two types of chemicals used as the solvents in these chemical absorption processes, which whether by using aqueous alkanolamine or simply "amine" or by using potassium carbonate. In this work, we will be focus on absorption processes by using aqueous alkanolamine (amine) due to the problem arise from the usage of amine in order to remove acid gases content in natural gases which is forming. This forming occurrence will be further discuss and be the aim for this work.

### *1.1.2 Amine scrubbing*

The absorption of $CO_2$ using aqueous solution of amine is also known as amine scrubbing process. Currently, in the acid gas removal unit (AGRU), gas processing plant B (GPP B) is the only GPP that use amine solvent in their operation. Figure 1-2 shows the process flow diagram (PFD) for the amine scrubbing process. It is originally applied to gas treating back in 1930, and then has become the most widely used solvents for the removal of acid gases from natural gas streams. Amine processes are particularly applicable where acid gas partial pressure or low levels of acid gas are desired in the treated gas.

Because of the water content of the solution minimizes heavy hydrocarbon absorption; these processes are well suited for gases rich in heavier hydrocarbons. Originally, Triethanolamine (TEA) was the first used commercially for gas treating. It has been displaced for convention applications by other amines such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), diglycolamine (DGA) and methyldiethanolamine (MDEA).

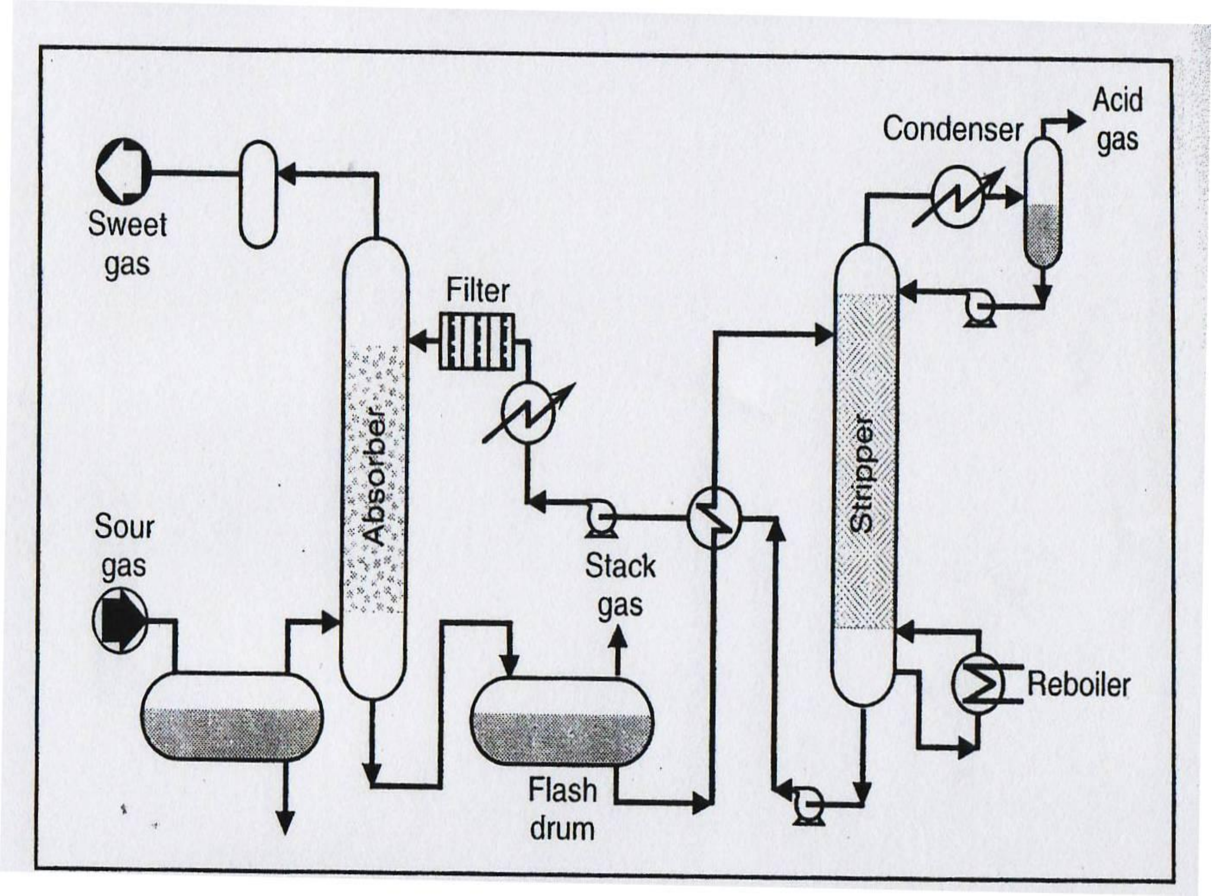

**Figure 1-2:** Typical PFD for Acid Gases Removal by Amine Scrubbing

Amines can be categorized into three classes namely, primary amine ($RNH_3$) such as MEA and DGA, secondary amine ($R_2NH$) such as DEA and DIPA, and tertiary amine ($R_3N$) such as TEA and MDEA. Again for this work, absorption process by using amine will be focus on methyldiethanolamine (MDEA) due to the fact that this type of amine is arousing growing interest.

Besides MDEA, DIPA also shows great interest in chemical absorption as it allows high selective absorption of $H_2S$ over $CO_2$. As it is highly selective for $H_2S$ and easier to regenerate than MEA and DEA, it has become the industry’s standard for selective treating application. Due to that, DIPA has been used in the commercial Adip process and as constituents in mixtures with physical solvents, such as sulfolane and water in the Sulfinol process (Maddox, 1974; Maddox and Morgan, 1998; Ratman, 2002). In advantages, amine solutions are basic and hence non-corrosive. They are in fact used as corrosion inhibitors.

However, in the presence of sour gases (gas that containing undesirable quantities of hydrogen sulfide, mercaptans and /or carbon dioxide), significant corrosion is liable to occur at points where the temperature and concentration of the sour gases are high. The primary amine has been proved to be the most corrosive amine.

In industrial gas processing for the removal of acid gases from the raw natural gas streams in gas absorption processes, alkanolamine is widely accepted as common chemical absorbent used to remove/reduce acid gases content (Kohl and Riesenfeld, 1985) in refineries. The use of aqueous solutions of N-metyldiethanolamine (MDEA) to accomplish selective removal of acid gases was first proposed by Frazier and Kohl (1950).

However there is a frequent problem in these amine processes which is foaming. This is due to many causes such as suspended solids, condensed hydrocarbons, amine-degradation products and foreign matter from corrosion inhibitors (e.g. contaminants in the water).

## *1.2 Foam theory*

### *1.2.1 Foam characteristics*

Generally, foam is existed as a colloidal system with convergence of gas bubbles accumulation which being dispersed in a liquid. Gap between each bubble is separated by a firm narrow liquid film, termed as lamella. In fact, foams that generated can be categorized into two classes that is Kugelschaum and Polyederschaum, by depend on gas and liquid fraction. Kugelschaum is defining as sphere-shaped foam with lamella thickness diameter between the gas bubbles similar to the gas bubbles diameter. This type of foams can be seen next to the liquid surface and possess greater liquid fraction. Meanwhile, Polyederschaum is a variation of Kugelschaum as it transform into polyhedral-shaped. This occurs when amount of liquid in the lamella is decreased due to drainage. It then located between Kugelschaum and gas phase and subjected to foam coalescence. Figure 1-3 shows the foam characteristics based on gas and liquid fraction criteria.

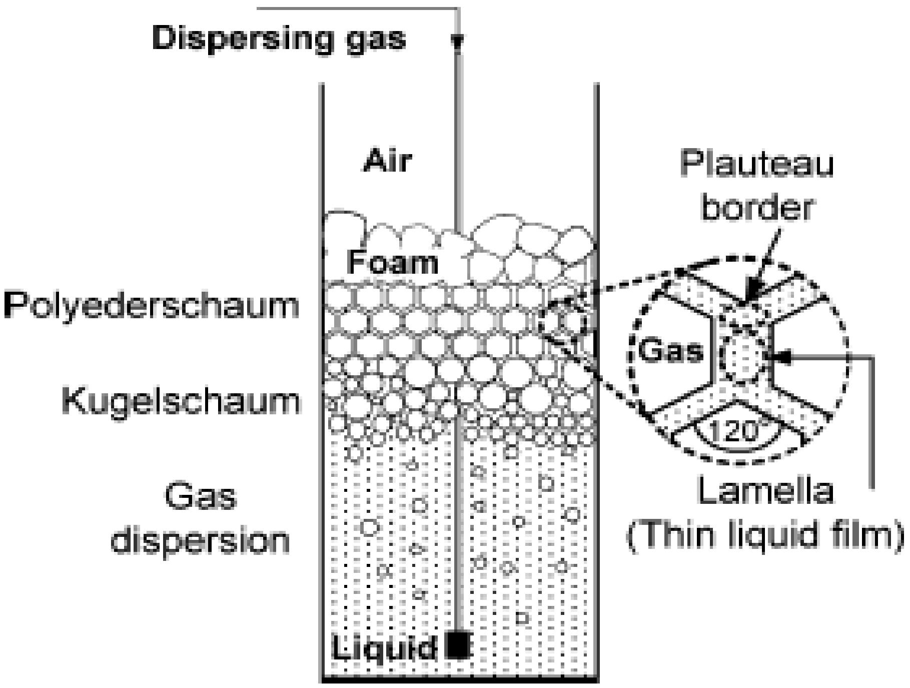

**Figure 1-3**: Foam characterization based on gas and liquid fraction criteria

### *1.2.2 Foam mechanism*

In order to form foam, gas is forced into liquid through a diffuser. Figure 1-4 shows the three principal forces influencing bubble formation. From figure, it shows that buoyancy, surface and hydrostatic forces are the most important criteria in the foam formation. It is begins when a bubble from the diffuser is raised up by bulk liquid as a result from the buoyancy force ($F_{buoy}$) generated. It can be represent as a function of density difference between liquid and gas ($\rho$), bubble volume ($V_{bub}$) and gravitational acceleration (g) as equation below.

$$F_{buoy} = \rho V_{bub} g \qquad (1.1)$$

To ensure the bubble to escape from the diffuser, it is compulsory for the buoyancy force to overcome the hydrostatic force and the surface force ($F_{surf}$), which is formed between the surface tension of liquid solution ($\gamma$) and capillary perimeter ($l$).

$$F_{surf} = \gamma l \qquad (1.2)$$

After foams are produced within the system, they eventually exhibit a thinning process which is caused by drainage, foam coalescence and foam rupture. Once these three bubbles attach together from one another, a plateau border (PB) is produced by concaving three lamella to bubbles with an angle of 120°, the decreased to 109°. This occurs when four bubbles joined at the PB. At meantime, a polyhedral or honeycomb system of bubbles is produced and enables the liquid to flow through PB structure. Once modified of smaller bubbles into the bigger ones, disproportionate or Ostwald ripening can be seen clearly. Existence of surface tension from lamella rearrangement resulting a pressure gradient of the pressure within the concaved and convex side. This pressure gradient that formed is called as capillary pressure ($\Delta P_{\text{cap}}$).

Due to the increase in capillary force, liquid then flow from lamella into the PBs (capillary flow or Laplace flow). Thus forced the liquid to a very thin lamella thickness and foam rupture. Foam drainage drastically generated resulting increases in capillary force due to the fluctuate in radii of curvature. This marks that the generated force as an external stress, that essential for the bigger bubble to breaking up into the smaller ones. In addition, drainage can also be caused by gravitational and hydro equilibrium force.

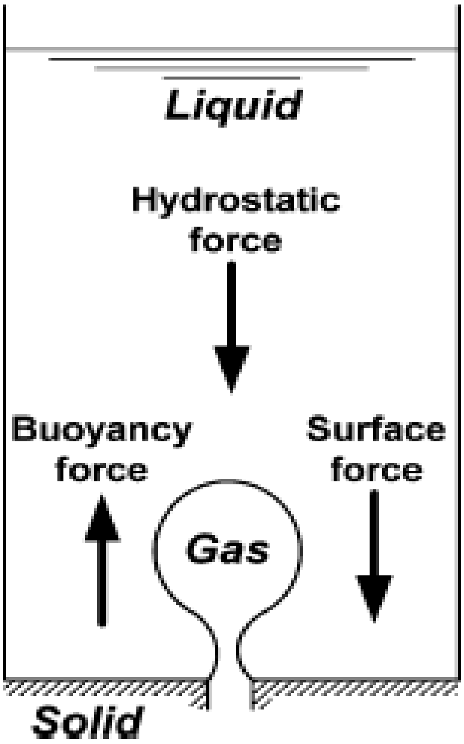

**Figure 1-4**: Three principal forces influencing bubble formation

### 1.2.3 Foam stability

Naturally, there are three measurements for the foam instabilities which are thinning, coalescence and rupture. All these instabilities enhance to the decrease in surface area and surface free energy, which indicated as a negative characteristic to foam stability. They are affected by surface elasticity, Marangoni effect, surface and bulk viscosity, repulsive Coulombic force and gravitational force. In general, surface elasticity ($E$) is a parameter that indicated of ability for the surface to sustain a thinning process as a result of surface tension gradient. It can be expressed as a change in surface tension with respect to a change in surface area ($A$).

$$E = 2A\ (d\gamma/dA) \qquad (1.3)$$

Due to the gas dispersion, a surface tension gradient is created between stretched and no stretched surface area and it are exposed to extreme expansion and shrinkage. During this activity, surface elasticity needs to balance this gradient by applied viscous forces in order to induce the covered liquid to flow from stretched to outstretched area due to the self-contraction of the surfaces. As a result, stretched area becomes thicker, and foam stability is improved. This mechanism is referred to as Marangoni effect.

In addition, bulk viscosity and surface viscosity also play a role in the foam stability. In fact, bulk viscosity is defined as liquid viscosity at the interface between gas bubbles and liquid in the Lamella. However, surface viscosity is stated often to be higher than bulk viscosity and seen to be increase directly with an increasing of bulk viscosity. Higher bulk viscosity is more favourable as it always decreases the generated drainage due to gravitational force.

But too high in bulk viscosity enable to cause destruction of surface elasticity as a result to a very high surface tension. This is due to fact that a surface medium has a difficult to move easily with a small amount of external stress. This in turn, causes a solid –like to form at a high surface viscosity and the decreases the foam stability. Other external stress can also gives an impact on the foam stability. This can be seen when the Coulombic forces can slow down the gravity drainage and also in the opposite ways.

## *1.3 Problem statement*

One of the severe problems in the $CO_2$ absorption process using the amine solution is the foam formation. Acid gases or the impurities in a gas stream are desirable to be remove to prevent corrosion problems and other operational problems, as well as to increase heating value of the gas. Despite having relatively high solubility of $CO_2$, amine solutions can have many drawbacks such as foaming. In order to reduce foaming, the elements such as concentration, temperature and impurities must be controlled by continuous research. Therefore, research must be done in order to investigate the effect of foaming behaviour on operation condition used in industry involving $CO_2$ absorption. Previous research has proved that MDEA aqueous solution can remove $CO_2$ better than any other alkanolamine such MEA, DEA and TEA. Hence, in this study, it is proposed to investigate the foam behaviour of an aqueous solution of (MDEA) as a function of different type of impurities, concentrations and temperature.

## *1.4 Objective*

Regarding to the issue arise, the objectives of this study are:

1) To study the effect of concentration of MDEA on foaming behaviour of different temperature.
2) To study the effect on foaming behaviour with the addition of Piperazine (Pz).
3) To study the effect on foaming behaviour with the presence of different types of impurities.

## *1.5 Scope*

In these experiments, chemical use is aqueous MDEA solution with concentrations varies from 20%to 100% on volume basis. The solution with the best result on based on its foam height and collapse time will be chose to be added with piperazine (Pz) and be tested for its foaming behaviour at temperature 40 $^{o}$C, 50 $^{o}$C, 60 $^{o}$C, and 70 $^{o}$C. Foam behaviour on the solution will also be tested with the presence of three different types of impurities that is iron sulphide, acetic acid and sodium chloride. All of the sample solution will be introduced to $CO_2$ with $CO_2$ loading of 0.4 mol / mol.

# 2 LITERATURE REVIEW

## *2.1 Overview*

This paper presents the experimental studies regarding foaming behaviour of an aqueous solution of N-Methyldiethanolamine (MDEA) and aqueous solution of Methyldiethanolamine (MDEA) mixed with Piperazine (Pz) for the carbon dioxide removal. Foaming experiment has been conducted by testing 3 parameters, which is effect of solution temperature, effect of solution concentration and effect of impurities.

## *2.2 Introduction*

Foaming is one of the famous problems that widely encountered in gas treating plants and gas absorption process as a result from process using aqueous alkanolamine solutions. Foaming has be seen negatively since its presence will leads to serious impact to industrial plant such as loss of absorption capacity, reduced mass transfer area and efficiency also carryover of amine solution to the downstream plant.

Based on plant an experience, foaming usually occurs during plant start-up and operation in both absorber and regenerator. From previous study regarding research of foaming in amine solution which have been published, Pauley found that the effect of hydrocarbon and organic acids on the foaming tendency of monoethanolamine (MEA), methyldiethanolamine (MDEA), diethanolamine (DEA) and formulated MDEA (Pauley *et al.*, 1989a, 1989b).

In general, foaming is caused by various chemical contaminants such as suspended solids, condensed hydrocarbons, amine-degradation products, foreign matter from corrosion inhibitors, from grease or from contaminants in the water, fine particulates like iron sulfide and additives containing surface active chemicals (Abdi and Meisen, 2000; Al-Dhafeeri, 2007; Pauley, 1991; Pauley *et al.*, 1989b; Spooner *et al.*, 2006; Stewart and Lanning, 1994; von Phul, 2001).

Such a way to prevent or reduce the foaminess problem many measures has been applied including mechanical filtration, carbon adsorption, solution reclamation (distillation) and antifoam addition.

## *2.3 Foaming*

The foaming tendency in DEA solution that have been studied by McCarthy and Trebble found that the foaming is influenced by the presence of various contaminants such as carboxylic acid (McCarthy and Trebble, 1996). They reveal that only carboxylic acid with minimum six carbons could provoke the foaminess compared to the clean DEA solution.

In 1989, Pauley and his colleagues have been successfully studied on foaming factors. They count on the effects of alkanolamine types, liquid hydrocarbon and degradation products on foaming tendency and foam stability by using air as a dispersing gas under atmospheric pressure. Alkanolamines that have been tested included MEA, MDEA, DEA and two formulated MDEA (with no specified additives).

It has been found that MEA, DEA and MDEA produce weak and unstable foam and the two formulated MDEAs had higher foaming tendency and stability. Addition of liquid hydrocarbon to MEA, MDEA, and two formulated MDEA solution enhanced on foam stabilities on MDEA and formulated MDEA due to the formation of a gelatinous layer except for MEA.

Examination on the effect of the degradation product accomplish with adding of organic acids like formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid, n-hexanoic acid, octanoic acid, decanoic acid and dodecanoic acid. MEA is the only that was tested with all organic acids while DEA, MDEA and one-formulated MDEA were tested with the last four of the organic acids. From this, it was found that the degradation products caused an increase in both foaming tendency and foaming stability in pure alkanolamine solutions.

Experimental investigation on DEA was been further handled by Mccarthy and Trebble in 1996. The purpose of their work is to evaluate the impacts of methanol, corrosion inhibitor, antifoam agent, lubrication oil, organic acids, degradation products and suspended solids at temperatures starts from 20 $^oC$ to 85 $^oC$ under pressures 0.1-3 Mpa. In this work, McCarthy and Trebble attempt to force the solutions into a Jerguson high – pressure sight glass container. This was achieved by purged with air, nitrogen ($N_2$), $CO_2$ and ethane ($C_2H_6$). At first, results show that the most investigated additives and impurities did not propagated the foaming in the clean aqueous DEA solution but instead role as foam promoters, the foams already existed within the system. Once the temperature and pressure were increased, foams were increase drastically due to the reduced surface tension.

Generally, in the presence of surface tension on a bubble circumstances cause the spreading of surfactant molecules from area of low surface tension to area of high surface tension. Due to this surface spreading process results in movement of the covering bulk of liquid in the direction opposite to the liquid drainage, causing in retardation of the liquid drainage and provision of transient stability to the foam (Bikerman, 1973).

Previously, few results have been indicated on the foaming enhancing of aqueous solutions of one alkanolamine: for 30 mass % of DEA (McCarthy and Trebble, 1996) and 50 mass % of MDEA (Yanicki and Trebble, 2006) with variation impurities in contact with nitrogen, methane and ethane, at selected temperatures. In which for MDEA and DEA in the range of 0.2-4M in contact with nitrogen (Hesselink and van Huuksloot, 1985).

Usually, contaminants or impurities in alkanolamine solutions are originated from diverse sources and able to exist in different states. Even though single impurities may initiate a typical plan of activity, gas conditioning solutions seldom contain only one or two contaminants. Indeed, there are plenty type of impurities that are exist in different concentrations, where most of them able to contribute adverse impacts on the process.

In general, the contaminants in natural gas stream are hydrocarbon liquids, iron sulfide, sodium chloride, acetic acid, methanol and glycol. Normally, at the conditions of high pressure and low temperature of the absorption tower, heavy hydrocarbons together with several lower boiling contents of the feed gas are dissolved completely or partially in alkanolamine solutions (Jou *et al.*, 1996).

During this circumstance, hydrocarbons with lower boiling point are flashed off in the flash drum or are discharge in the stripping tower at the bottom. Meanwhile, heavy hydrocarbons tend to flow at the opposite direction and stay in the process and enhance another type of impurities in alkanolamine solutions. During this process, formation of foams are continue in the system even able to generate a more stable foam on the regenerator which allocate at the top of the absorber as shown in Figure 2-1. Table 2-1 shows the effect of degradation products on foaminess coefficient.

**Table 2-1**: Effect of Degradation Products on Foaminess Coefficient.

| Degradation product | av foaminess coefficient (min) |
|---|---|
| None | 0.79 |
| Amomonium thiosulfate | 0.97 |
| Glycol acid | 0.94 |
| Sodium sulfite | 0.92 |
| Malonic acid | 0.92 |
| Oxalic acid | 0.90 |
| Sodium thiocyanate | 0.90 |
| Sodium chloride | 0.90 |
| Sodium thiosulfate | 0.85 |
| Bicine | 0.85 |
| Hydrochloric acid | 0.83 |
| Formic acid | 0.83 |
| Acetic acid | 0.82 |
| Sulfuric acid | 0.77 |

For the non-volatile impurities, most of them are emerge from many types of sources for instance gas wells and make up water. Particulates also one of the non-volatile impurities, which carried out by raw feed gas into the alkanolamine solutions. In fact, contaminant that is very common in its presence and categorized as undesirable substance is iron sulfide. It is seen to be unwanted because of its characteristic that is able to stabilize the generating foams and enhance foaming tendencies.

In this case, iron sulfide also could be originated with the presence of sulfur component in the carbon steel circumstance. For the long term operations, iron (Fe) from the involved equipment material that acted as cover from any possible damages will react with sulfur to produce iron sulfide waste or fine particulates. In addition, within the close loop of amine system, these iron sulfides will increase the foam formation activity in the solvent extremely.

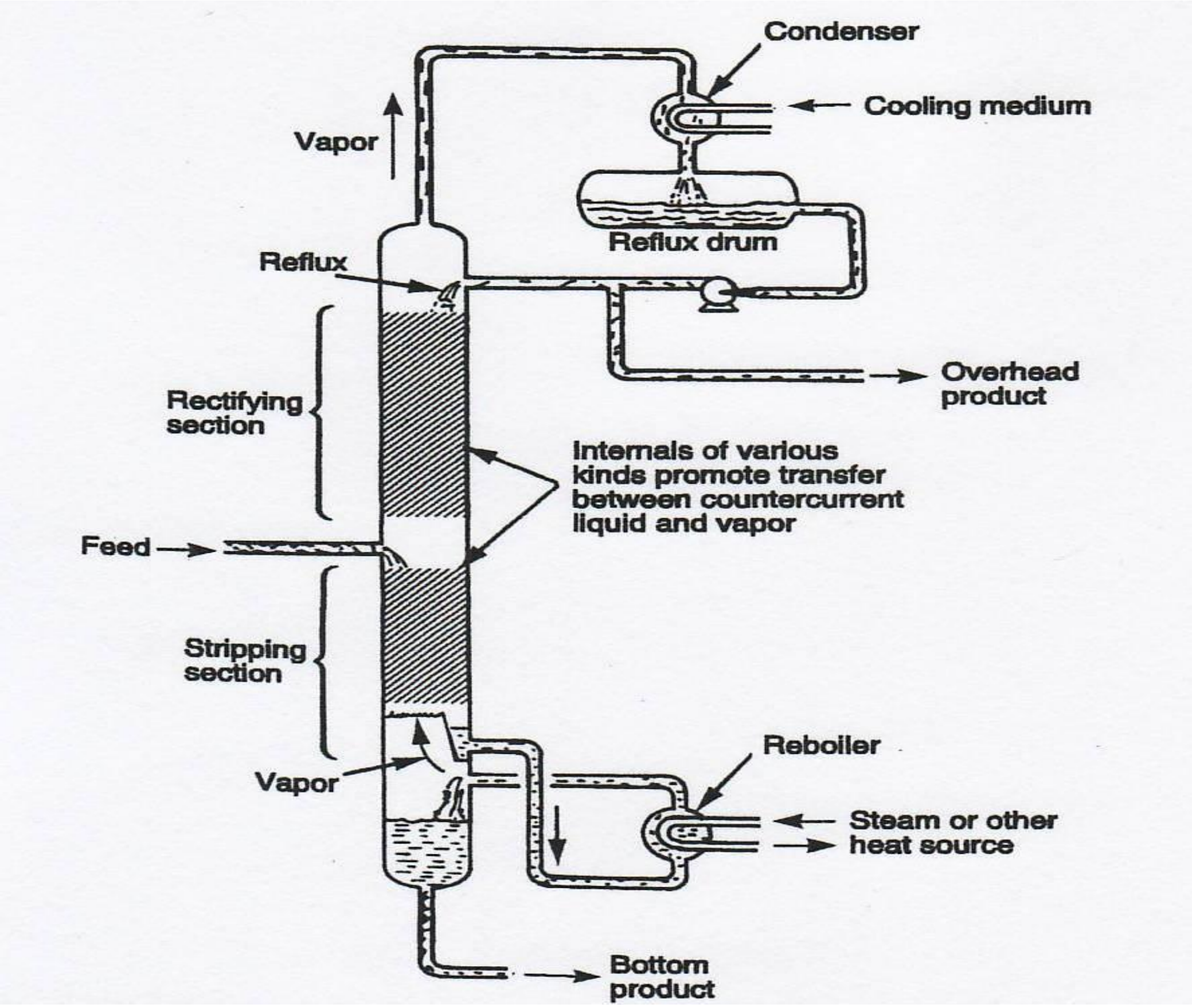

**Figure 2-1:** Fractionation schematic diagram.

Meanwhile in 1998, rather than employing investigation on foaming with the available experimental setup, Harruff successfully invented a new edition a foam testing apparatus. Through his achievement of modified on the tools involved, Harruff try to assess foaming tendency of diglycolamine (DGA) at operating conditions of gas treating plants at which approximately 93 $^{o}$C and up to 6.9 MPa. This is done by applying $N_2$ gas as a dispersed phase. The results indicated that foaming cause by DGA solution is form at a high temperature and slightly dependent at variation of pressure.

In reality, impurities that exist in a solid state of any type tend to lower the efficiency of the absorber (overhead) and stripper (bottom) by cause a plugging at contactor trays, contactor packing’s and piping system. Often, when seawater is utilities as a cooling medium in the natural gas treating or conditioning process, sodium chloride will be formed in the equipment.

The reason of the presence of sodium chloride is because of the leaking on some tube in the sea cooling water exchangers.

In other cases, in the placed at the low pressure circumstances, leaks on the lean amine cooler can be found. Technically, this leak happen due to the unsustainable carbon steel against corrosion during the operations. In the exchangers, introduction of cooling of seawater occur with a higher pressure. At the moment, a small leak could be found in the exchanger as the cooling accomplish throughout into the solvent circulation loops. Because of this, there is a possibility accumulation resulting in the system and enhance corrosion on the stainless steel material. Due to this also, an increasing on the total dissolved solid in the amine solvent, which result further severe was foaming.

Introduction of acetic acid into amine system along with delivery raw gas starting from the upstream side due to the corrosion inhibitor injection. Sometime, the corrosion inhibitor agent containing unacceptable amount of acetic acid and delivers into amine solutions which trigger a foaming activity. Apart from that, acetic acid also can be present from the wells where impurities are coming out and more badly it will be too late to be treated in the top gas treating units.

Ultimately, accumulations of acetic acid in the liquid slugs along the pipeline and in the equipment were collected in the slug catcher’s area. Once a failure of the system occurs in this area, selected amount of the liquids would be discharge into inlet facilities of the acid gas removal unit (AGRU). Meantime, as the excessively accumulation within amine system, it would create severe foaming problem during the long period operations.

Besides, methanol also has been identified as one of the chemical that present as it is injected into the inlet facilities or in the gas treating process in order to avoid hydrate formation. At the time the separation of liquid is under operation which intended to drop the liquid mist from this injection, very small quantity of methanol can be transferred over into the amine system to create severe foaming activity.

In general, the greater hydrate formation is identified, the higher frequent methanol is injected and the massive possibility of foaming. Meanwhile, other types of amine solvent impurities that also present in the gas treating or gas conditioning unit, for instance glycol is often acted as gas dehydration in the top stream operations. The purpose of this is to prevent any possible hydrate formation along the pipeline and the equipment. In addition, once the glycol located in the amine system, again it will create foaming within the operations.

## *2.4 Piperazine activated MDEA*

Nowadays, the addition of a primary or secondary (alkanol) amine to an aqueous MDEA solution has found widespread application in the removal and absorption of carbon dioxide. The principle of such an aqueous blend of a so-called 'activator' with a tertiary amine is based on the relatively high rate of reaction of $CO_2$ with the primary or secondary alkanolamine combined with the low heat of reaction of $CO_2$ with the tertiary alkanolamine, which leads to higher rates of absorption in the absorber column and lower heats of regeneration in the stripper section. One of the activators presently used in industry is the cyclic diamine piperazine:

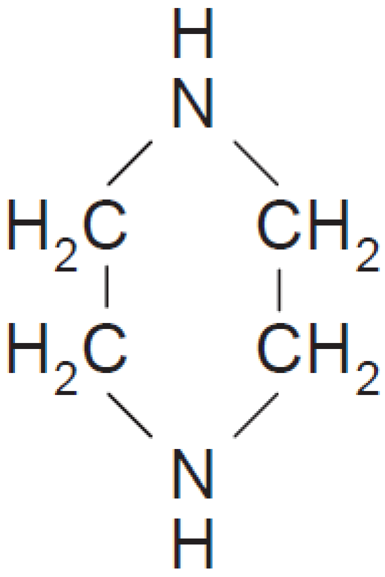

**Figure 2-2:** Piperazine (Pz)

The piperazine (PZ) activated MDEA process was patented by BASF in the early 80s [Appl et al., 1982], and has been subject of several studies over the past decade as it has proven to be a successfully solvent in the bulk removal of carbon dioxide. Crucial for an optimal design and operation of both an absorber and a desorbed column is information concerning mass transfer related issues (including e.g. hydrodynamics and kinetics) on one hand and thermodynamic equilibrium on the other hand. However, the information available in the literature on $CO_2$ absorption in piperazine activated MDEA is still rather limited: