CARBON DIOXIDE CAPTURE FROM REFORMING GASES USING ACETIC ACID MODIFIED CHEMICAL ABSORBENTS

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ABSTRACT

Carbon dioxide gas is a major problem in the production of natural gas. It may also contributes to operation problems such as foaming, corrosion, high solution viscosity and fouling, thereby decreasing the plant life. This study presents experimental results on the evaluation of modified amine solution (Diethanolamine, DEA) for CO_2 absorption. In this study, the absorption capacity of this solvent was compared with traditional DEA, ammonia and acetic acid ($C_2H_4O_2$). Experiments were carried out at 25C^o and 1 bar with DEA concentration between 0.5M and 2M, ammonia concentration varying 1M and 6M and the concentration of acetic acid between 1wt% and 15wt%. The results showed that carbon dioxide absorption by ammonia is better than that carried out by DEA and mixtures of NH_3, DEA and acetic acid. The most efficient absorbents (absorption capacity) were 6M NH_3, 2M DEA and a mixture of 6M NH_3 and 1wt% acetic acid at fixed gas flow rate of 80 ml/min and liquid flow rate of 22 l/h, where the CO_2 removal efficiency of 94.7%, 74% and 73% was obtained, respectively.

ABSTRAK

Gas karbon dioksida adalah masalah utama dalam pengeluaran gas asli. Ia juga boleh menyumbang kepada masalah operasi seperti bebuih, kakisan, kelikatan larutan yang tinggi dan kotoran, yang seterusnya mengurangkan jangka hayat loji. Kajian ini membentangkan keputusan eksperimen yang menilai larutan amin diubahsuai (Diethanolamin, DEA) untuk penyerapan CO_2. Dalam kajian ini, kapasiti penyerapan pelarut ini telah dibandingkan dengan ammonia (NH_3) dan asid asetik ($C_2H_4O_2$). Eksperimen telah dijalankan pada 25°C dan 1 bar dengan kepekatan DEA antara 0.5M dan 2M, kepekatan ammonia yang berlainan dari 1M ke 6M dan kepekatan asid asetik antara 1% berat dan 15% berat. Hasil kajian menunjukkan bahawa penyerapan karbon dioksida oleh ammonia adalah lebih baik berbanding DEA dan campuran NH_3, DEA dan asid asetik. Penyerap yang paling berkesan (kapasiti penyerapan) adalah 6M NH_3, 2M DEA dan campuran 6M NH_3 dan 1% berat asid asetik pada kadar aliran gas yang tetap 80 ml/min dan kadar aliran cecair 22 l/j, di mana kecekapan penyingkiran CO_2 masing-masingnya ialah 94.7%, 74% dan 73% telah diperolehi.

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LIST OF SYMBOLS

%	-	Percent
˚C	-	Degree Celsius
°	-	Degree
wt. %	-	Weight percent
g/mol	-	Gram per mole
ml/min	-	Mile liter per min
l/h	-	Liter per hour
ppm	-	Parts per million
M	-	Molar

LIST OF ABBREVIATIONS

AMP	-	2-amino-2-methyl-l-propanol
C_2H_4	-	Ethylene
$C_2H_4O_2$	-	Acetic acid
C_2H_6	-	Ethane
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
DEA	-	Diethanolamine
DGA	-	Diglycolamine
DIPA	-	Di-isopropanolamine
NH_3	-	Ammonia
Eq	-	Equation
ESA	-	Electric swing adsorption
FID	-	Flame ionization detector
GC	-	Gas chromatography
GPP	-	Gas processing plant
GHG	-	Green house gases
H_2S	-	Hydrogen sulfide
H_2	-	Hydrogen
MDEA	-	Methyldiethanolamine
MEA	-	Monoethanolamine
MS	-	Mass spectrometry
MW	-	Molecular weight
NTP	-	Normal temperature and pressure
PSA	-	Pressure swing adsorption
TEA	-	Triethanolamine
TSA	-	Temperature swing adsorption
TCD	-	Thermal conductivity detector

VSA	-	Vacuum swing adsorption
Wt.	-	Weight
EOR	-	Enhancing the oil recovery

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Removing of acid gas impurities, including Hydrogen Sulfide (H_2S) and carbon dioxide CO_2, from gas streams is a major operation in processing of gases. Natural and synthesis of the raw gases contain acid gases such as H_2S and CO_2. Removal of acid gas from gas mixtures is very important in natural gas processing (Bhide *et al*., 1998). Acid gases should be separated and removed from natural gas in order to: (a) decrease the volume of gas transported in pipelines, (b) increase the heating value and reduction of the corrosion through the transport of natural gas.

Many possible combinations of processes and separation methods can be conceived for CO_2 removal such as absorption, adsorption, membranes and cryogenic separation (Geankoplis, 2003a). More than seventy years the absorption method utilizing alkanolamines has been known and considered the best way in eliminating H_2S and CO_2 for purification and separation (Chew *et al*., 2010). It works regarding to the reaction of weak base and weak acid to from a water soluble salt.

1.2 Problem Statement

From 1960s and 1970s on, a number of alkanolamine have come into general use, but there is not much information available on which amine is the best to do a particular service. Many incompetent amine gas sweetening units can be optimized simply by varying the amines. 50 to 70% of the initial investment for an amine sweetening unit is directly associated with the magnitude of the solvent circulation rate and another 10–20% of the initial investment depend on the regeneration energy requirement.

Approximately 70% of gas sweetening plants operating costs, excluding labour expenses, is due to the amount of energy required for solvent regeneration (Loo and versteeg, 2006). Amines are different in properties and each one of them has a unique set of properties this makes them either desirable or undesirable under certain condition. The kind of alkanolamine choice will affect the required circulation rate of amine solution, the energy consumption for regeneration and the ability to selectively remove either H_2S alone or CO_2 alone if desired. The overall cost of a sweetening unit can be dependent on choosing the best amine for the conditions of process. Therefore, it is important to know the performance of MEA, DEA and MDEA as chemical solvents in acid gas for removing acid gas impurities including hydrogen sulfide and carbon dioxide from refinery, synthesis and natural gas streams in major operation of gas processing (Lepaumier *et al*., 2009c).

The CO_2 gas separation is important in many industrial processes such as gas processing plant (GPP). CO_2 is highly acidic and corrosive when combines with water. Chemical solvents scrubbing technology has been effectively applied for CO_2 capture. Therefore, absorption technology has been utilized for removing toxic gases such as carbonyl sulfide, hydrogen sulfide, carbon dioxide, and so on. Alkanolamines was recently used to enhance the CO_2 separation by means of absorption. Therefore search for amines mixture with suitable modification to accommodate CO_2 removal has become a subject of considerable interest (Franco *et al*., 2009; Bedella, 2009).

In process of replacing alkanolamines with acidic oxides absorption degradation and Corrosion are the phenomenons which are not desirable. In plant opration, degradation products are considered to be a big problem (Thitakamol *et al*., 2009, Thitakamol and Veawab, 2008).

Today MDEA among all of the alkanolamines is widely used as an absorption solvent of acid gases because MDEA has characteristics such as higher absorption capacity, high H_2S selectivity, lower heat degradation, lower regeneration energy and low corrosion (Closmann *et al*., 2009; Klare *et al*., 2000). MDEA is commonly used in the 20 to 50 mass percent ranges (Aroonwilas and Veawab, 2004).
It has been shown by Sakwattanapong which for MEA systems the replacement cost of amine would be 4% of the total cost of CO_2 (Sakwattanapong *et al*., 2009).

1.3 Objective of the Study

The objective of this work is to investigate the effects of different mixtures of amine, ammonia and modified amine solution with ammonia and acetic acid on CO_2 capture from reforming gas.

1.4 Scope of the Study

The following scopes are necessary to establish the desired objectives of this work.

i. The fixed parameters for this work are column diameter and height, and operation temperature, and pressure.

ii. Mixtures of different mass percent of diethanolamine (DEA) and ammonia (NH3) ranging from 0% DEA - 100% NH_3, and 100%DEA - 0%NH3 are employed to determine the best mixture for CO_2 removal.

iii. Acetic acid between 1 to 15% of total mass is mixed with the best mixture of DEA and NH_3 to study its effect towards CO_2 removal.

iv. The CO_2 removal will be characterized using gas chromatography (GC) and gas analyzer.

1.5 Significant of Study

The study is essential, to model and improve the process of acid gas removal based on diethanolamine (DEA) and ammonia (NH_3) by using modified amine solution with acetic acid. Additionally, this study also significant, to identify the best chemical solvent for process by comparing DEA, NH_3 and mixtures of different mass percent of diethanolamine (DEA) and ammonia (NH_3) ranging from 0% DEA - 100% NH_3, and

100%DEA - 0%NH_3 are employed to determine the best mixture and Acetic acid between 1 to 15% of total mass is mixed with the best amine mixture to study its effect towards CO_2 removal. This study presents measurements of CO_2 absorption in NH_3, DEA, mixture NH_3 to acetic acid and Mixture NH_3, DEA to acetic acid. Previous researchers have studied CO_2 absorption into aqueous solution of DEA (Glasscock, 1990; Little, 1991; Phillips *et al*., 2007) and NH_3 (Resnik *et al*., 2004; Yeh *et al*., 2005), but not in mixture of these reactive solvents.

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