Comparison of DEA and TEA performance for CO_2 capture from synthesis gas of ammonia under different operational conditions

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Abstract:

Aqueous solvent of di ethanolamine and tri ethanolamine has been the focus of research over the last decade because of the desire to obtain more efficient and economical chemical absorption solvent to eliminate carbon dioxide from synthesis gas of ammonia production. As well as being the promising technology which could be employed to control and reduce carbon dioxide emissions from fuel gas. However, the substantial disadvantage of this technology is high energy requirements. Though, the main objective facing this process is to select the most efficient and appropriate amine solvent between (DEA&TEA) with the least energy consumed while preserving the higher capture of CO_2 from synthesis gas. Therefore, this research aims to investigate the influence of solvent rate on the efficiency of CO_2 capture. Aspen hysys was employed to simulate an absorption plant and to investigate the influence of several variables on process efficiency. Increasing the amine loading rises the efficiency of absorption process, but till a particular limit. Similarly, increasing amine circulation rate rises the absorption process efficiency as long as below the equilibrium rate but the regeneration energy is directly affected by any change in the amine rates.

Keywords: *Carbon dioxide removal, Amine solvent, Regeneration energy, Synthesis Gas.*

I. INTRODUCTION

Carbon dioxide (CO_2) is one of the most significant greenhouse gases, which is produced by the use of fossil fuels. Jean-Baptiste Fourier recognized the role of gases in the environment in trapping heat close to the earth in 1827. Because of the abundance and availability of fossil fuel resources, it is expected that they will continue to play an important role in the global energy economy. Fossil fuels currently meet approximately 85 percent of the world's commercial energy needs, and anthropogenic greenhouse gas emissions to the atmosphere are expected to cause significant global climate change. [1],[2]

CO_2 is the most significant anthropogenic greenhouse gas, resulting primarily from the use of fossil fuels and many industries. As a result, the development of a good CO_2 capture technology is critical. Carbon capture and storage (CCS) [3] is currently regarded as technically feasible at the commercial scale using a variety of technologies. Actions to reduce costs (particularly for CO_2 capture) and to ensure the identification, performance, and monitoring of appropriate storage sites are included

The chemical absorbent process consists of an absorber and a stripper, and the solubility of carbon dioxide in aqueous alkanol amine solutions; and the heat of absorption are two of the most important data for the design of the CO_2 removal process. [3],[4]

The method of CO_2 recovery chosen is post-combustion capture. A final processing stage is used in this method to remove the majority of the CO_2 from the solvent products just before they are vented to the atmosphere. Wet scrubbing with aqueous amine solutions is used in the most commercially advanced methods. Mono ethanol amine (MEA), di ethanol amine (DEA), di-isopropanol amine (DIPA), and N Methyl di ethanol amine is industrially important alkano amines for this operation. Aqueous di-ethanol amine (DEA) is a chemical absorbent that is commonly used in refineries and petrochemical industries to remove H_2S and CO_2 from gases.

The selective removal of H_2S is accomplished using aqueous MDEA. Aside from MDEA, di-isopropanol amine (DIPA) has been shown to have a higher selectivity for H_2S over CO_2 than MEA or DEA. The process of removing H_2S and CO_2 from gas is known as sweetening [5].

The capital and operating costs of a CO_2 recovery plant are determined by a wide range of assumptions, the consequences of which have not been fully considered in most assessments of carbon capture technologies. An economical design can be useful in determining the best conditions at the lowest possible cost. [6] There are numerous technologies available for this purpose. However, the heat of absorption is proportional to the amount of steam required during the regeneration stage. The energy used to desorb carbon dioxide from the absorbent is critical because it accounts for at least half of the operating cost. The stripper's reaction with the absorbent and carbon dioxide is the opposite of the absorber's reaction. As a result, the amount of heat generated by CO_2 molecule absorption in the absorbent is the same as the amount of heat generated by CO_2 molecule desorption. The heat of absorption provides useful information for reboiler design. There are numerous influential parameters that affect total cost estimation, including percent CO_2 removal, solvent concentration, solvent loading, design pressure, and so on. [3]

Design conditions for the DEA solvent have been studied in some studies, and the effect of some parameter changes, such as operating pressure, lean amine temperature, and DEA weight percent, on total recovery and total cost has been analyzed. In addition, energy analysis and thermo economic performance evaluations for IGCC (integrated gasification combined cycle) and NGCC plants have been performed in some papers to reduce the energy penalty for CO_2 separation for DEA and K_2CO_3 solvents.

The main goal is to design the capture plant by evaluating important parameters in a step-by-step manner. The most influential parameters that can affect total plant efficiency are inlet gas and solvent temperature (which, when reduced, increase the amount of absorption and rich amine loading and cooling water requirement), absorber pressure (which increases the physical absorption rate), and solvent flow-rate and concentration. It should be noted that the solvent circulation rate is the most important parameter in determining the plant's operating and capital costs. However, the solvent type is the most important parameter to consider when designing the plant. There are several amine solvents, each with its own set of advantages and disadvantages.

In this research, we compare and contrast the effects of two different amine types (DEA and TEA) on CO_2 capture from ammonia synthesis gas (hydrogen and nitrogen) and certain key operating parameters. The goal of these various investigations is to figure out which solvent is best for removing CO_2 from synthesis gas under various conditions and to construct a recovery plant with the best state. [2] Each analysis has been performed for different SOLVENT RATE for CO2 Capture in the synthesis
gas of AMMONIA production [1], [3]

II. PROCESS DESCRIPTION AND SOLVENT SELECTION

As shown in Figure 1, the system consists of two major components: an absorber that removes CO_2 and a regenerator (or stripper) that releases CO_2 (in concentrated form) while recovering the original solvent. At temperatures, the amine solvent removes CO_2 from the waste gas (order 80-120^{O}C). The energy provided by steam in the reboiler is used to reverse the chemical equilibrium and liberate the CO_2.The CO_2 extracted from the solvent during the regeneration process is dried, compressed, and transported to a safe geological storage areas.[3][4][5]

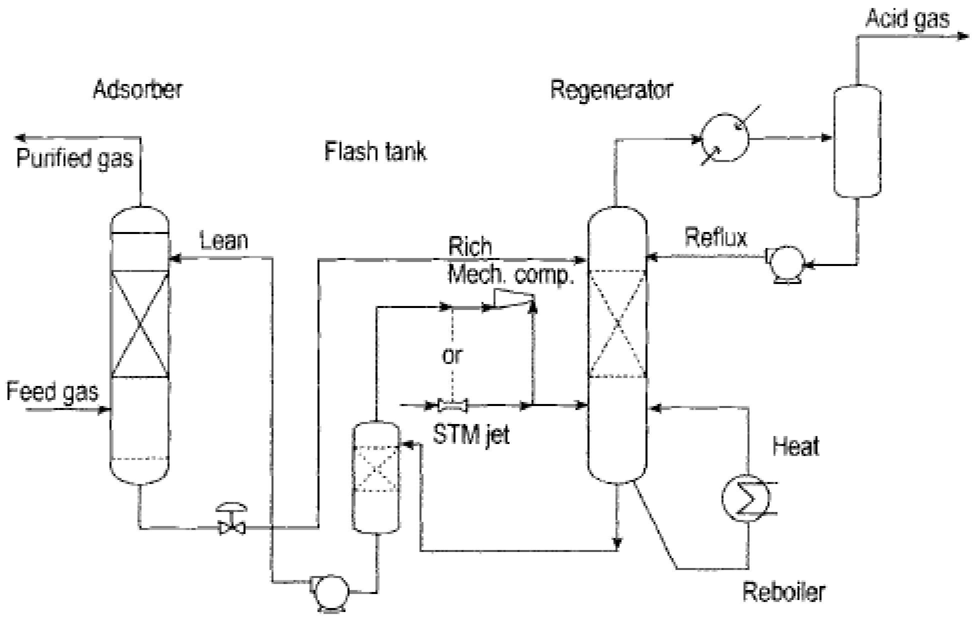

Figure 1 (PFD of a typical CO_2 capture from synthesis gas by amine-based system)[3]

The liquid circulation pumps and, more importantly, the lean solution pump are the major electrical energy sinks. Reboiler steam is used to add heat. Normally, more than 90% of the total process energy requirement is for regeneration of the loaded liquid in the desorber, which enters as reboiler steam[6]. These, along with solvent losses and financial costs, are the primary contributors to the overall gas cleaning process's operational
Costs the reboiler steam is required primarily for three purposes:

(1) To provide enough energy to reverse the exothermic amine-acid gas reaction;
(2) To dilute the CO2 gas throughout the desorber and thus act as a stripping gas;
(3) To provide enough sensible heat to warm the rich amine liquid feed.

The first two of the three energy sinks mentioned above are roughly equal in importance, whereas final heating of the incoming rich amine solution is usually less important. We can reduce costs, particularly for heating systems, by selecting good operational conditions and a suitable solvent. At the moment, there is a lot of interest in finding optimal solvents for CO_2 absorption as well as optimal process conditions for a given solvent. A number of Carbon Dioxide Capture projects are working to improve the CO_2 absorption process and lower the cost of CO_2 capture. The process solution chosen is determined by the pressure and temperature conditions under which the gas to be treated is available, as well as its composition in terms of major and minor constituents. as well as the purity requirements of the treated gas the reactive absorbent, DEA, is the most commonly used solvent in CO_2 capture plants. The most efficient amines are DEA and TEA.[7]

1. Solvent characteristics.

Amines are the preferred solvents for gas streams with a high concentration of CO_2. This is especially true when the gas is to be treated at high pressures and maximum CO_2 removal is required. This is why most CO_2 capture plants use DEA solvent because it has a hydrogen atom directly bonded to the nitrogen, has intermediate properties compared to primary amines, and is considered an alternative to MEA.[8]

DEA is more resistant to degradation and has lower corrosion strength than TEA, but it has a higher ability to remove CO_2 from sour gas than MEA and TEA.[9] Tertiary amines, such as tri ethanol amine (TEA), have a high equivalent weight, resulting in a lower absorption capacity than primary and secondary amines, as well as low reactivity and high stability.

2. Process chemistry

The amine process was considered as the most popular and effective acid gas removal method in the natural gas industry. However, it consists of several units, such as absorber, separator, heat exchanger, and stripper (amine regenerator). A regular process as shown in figure (1) will be utilized in this study. The principal reactions occurring when solutions of a DEA &TEA amine are used to absorb CO_2 from the synthesis gas are represented in the following reaction:[10]

$$H_2O \longleftrightarrow H^+ + OH^- \quad (1)$$

$$CO_2 + H_2O \longleftrightarrow HCO_3^- + H^+ \quad (2)$$

$$HCO_3^- \longrightarrow CO_3^{-2} + H^+ \quad (3)$$

$$DEACOO^- + H_2O \longrightarrow DEAH + HCO_3^- \quad (4)$$

$$DEAH + H^+ \longrightarrow DEAH_2^+ \quad (5)$$

$$TEA + CO_2 + H_2O \longrightarrow TEAH^+ + HCO_3^- \quad (6)$$

III. Feed gas properties and composition

The sample of feed gas was taken in Jan 2018 from Gasco site report to El Nasr company for Fertilizers, Suez, Egypt.so the natural gas feed passing by many steps before the acid gas removal process as shown in [3].The synthesis gas (gas after reforming and shift reaction) operation conditions and compositions are presented in table (1).

However, processed gas needs to satisfy the requirement of 100 ppm of CO_2 to meet the market's specifications of the product as well as environmental regulations and efficiency of ammonia production[11] as low percent of CO_2 with synthesis gas increasing the efficiency of ammonia production.[5]

Component	Mole %	Operation conditions	
Methane	10 %	Temp	$90^{O}C$
Hydrogen	40%	Pressure	31 bar
Nitrogen	30%	Mass flow	7 tonne/h
CO_2	20 %	Mass density	20.14 [kg/m^3]
H_2S	0	Molecular weight	19.62
Ar	0		

Table 1 (synthesis gas feed compositions and operation conditions)

IV. Process modeling and variable

The amine process was simulated by software program. DEA &TEA solvent was employed to absorb the acid Gases from the synthesis gas of ammonia .The Acid Gas model in the amine's property package was Utilized and proceeded using the operation conditions and compositions listed in table [1].

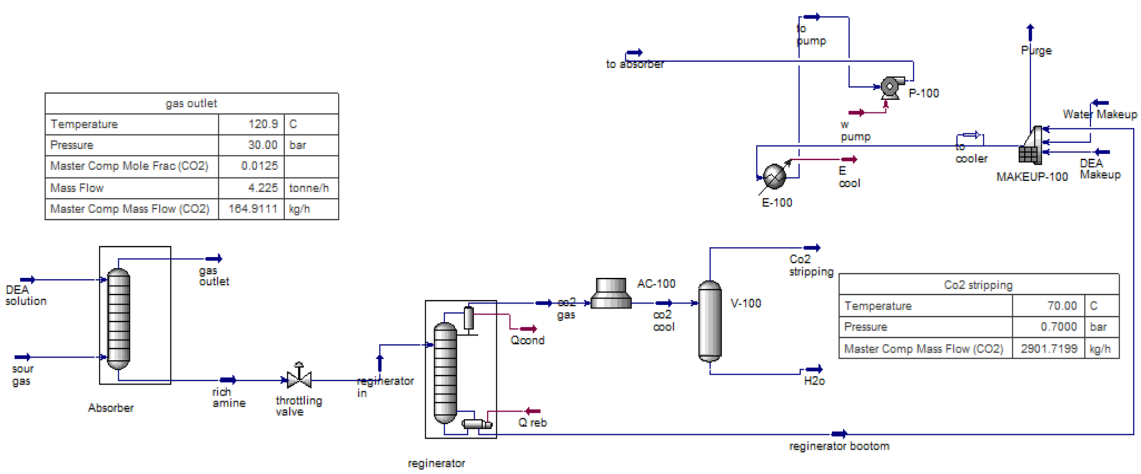

Figure 2. Schematic of CO_2 capture process using **DEA** solvent.

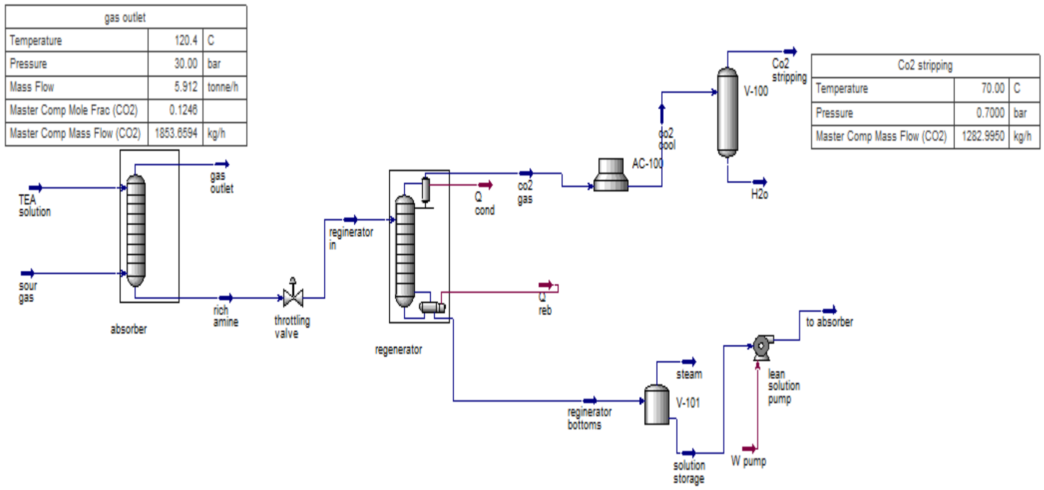

Figure 3. Schematic of co$_2$ capture process using **TEA** solvent

As shown in table [2], different solvent amines were used to improve the performance of the acid gas removal process while maintaining the same operating conditions. As a result, a few process parameters loading will be recorded and discussed, such as CO_2 in treated gas, CO_2 stripping to atmosphere, Amines and Energy requirements, and so on.

However, the DEA and TEA concentrations were held constant throughout the study at 30% wt. to investigate the impact of changing the solvent type on process efficiency in order to achieve the best possible optimal Processing conditions.

Parameters	DEA	TEA
Inlet gas flow rate [kgmole/m^3]	356.5	356.5
Inlet amine flow rate [kgmole/m^3]	4000	4000
Inlet gas Temperature	90	90
Inlet amine Temperature	120	12
Amine concentration [%]	30	30
Synthesis gas pressure [bar]	31	31
Amine pressure [bar]	35	35
Co2 inlet gas Composition mole %	20 %	20%

Table 2 (Typical data operation of Amines and synthesis gas Absorber)

V. RESULTS AND DISCUSSION

The simulation model of the acid gas removal process was successfully created, and the process flow diagram of the plant is presented in figure [2]&[3]. However, this study aimed to study the influence of using **DEA &TEA** amine on the efficiency of the acid gas removal process, by considering **several variables**.

1-Amine Solvent Type

The amine solvent type is one of the most important determinants of absorption efficiency. It is the primary focus of this paper. The simulation results of acid gas removal in software programme Figure [2][3] are shown in tables [3] &[4]. by employing two solvent types, di ethanolamine and tri ethanolamine The CO_2 capture in the case of DEA is greater than in the case of TEA, as shown in tables [3] and [4]. Where the CO_2 concentration in the synthesis gas was 100 ppm, which adequately met the study's objective.

Parameters	DEA	TEA
Outlet gas flow rate [kgmole/m^3]	299.8	338
Outlet Rich amine flow rate [kgmole/m^3]	4057	4019
Outlet gas Temp	120	120
Outlet Rich amine Temp	128	119
Co_2 outlet gas composition Mole % In treated gas	0.0125	0.1246
Co_2 outlet gas composition Mass flow In treated gas [kg/h]	165	1855

Table 3 (Simulation Results of Amine and acid gas Absorber) in hysys software.

Parameters	DEA	TEA
Rich amine flow rate [kgmole/m^3]	4057	4019
Co2 Stripping Composition Mass flow in [kg/h]	2901	1283
Reboiler duty	1.377e+007 kcal/h	1.568e+007 kcal/h
Condenser duty	6.999e+006 kcal/h	6.976e+006 kcal/h
No of stage	5	5

Table 4 (Simulation Results of Amine and acid gas Regenerator) in hysys software

2-Amine solvent loading

One of the most important determinants in the economic aspects of synthesis gas of ammonia production treatment with amine solvents is the amine solvent rate. It has a significant impact on the capital cost of the plant because it affects the size of the treatment plant's equipment such as absorber, heat exchangers, pumps, piping, and regenerator. It also influences the amount of energy required for amine regeneration due to the direct influence of the liquid rate on reboiler heat duty.[12][13]

In general, increasing the amine circulation rate increases the amount of acid gas that can be removed, as shown in figure [4], which increases the amount of regeneration energy required to recover the carbon dioxide from the amine. However, if an adequate amount of lean amine (load) is added to allow the processed gas to leave the absorption tower in equilibrium with the amount of lean amine, increasing the circulation rate will not reduce the amount of carbon dioxide in the processed gas. This obvious fact was looked into and clarified.

As illustrated in figure [4], increasing the flow rates of amine solvent rate increases co_2 capture from synthesis gas at constant concentration, temperature, and solvent.

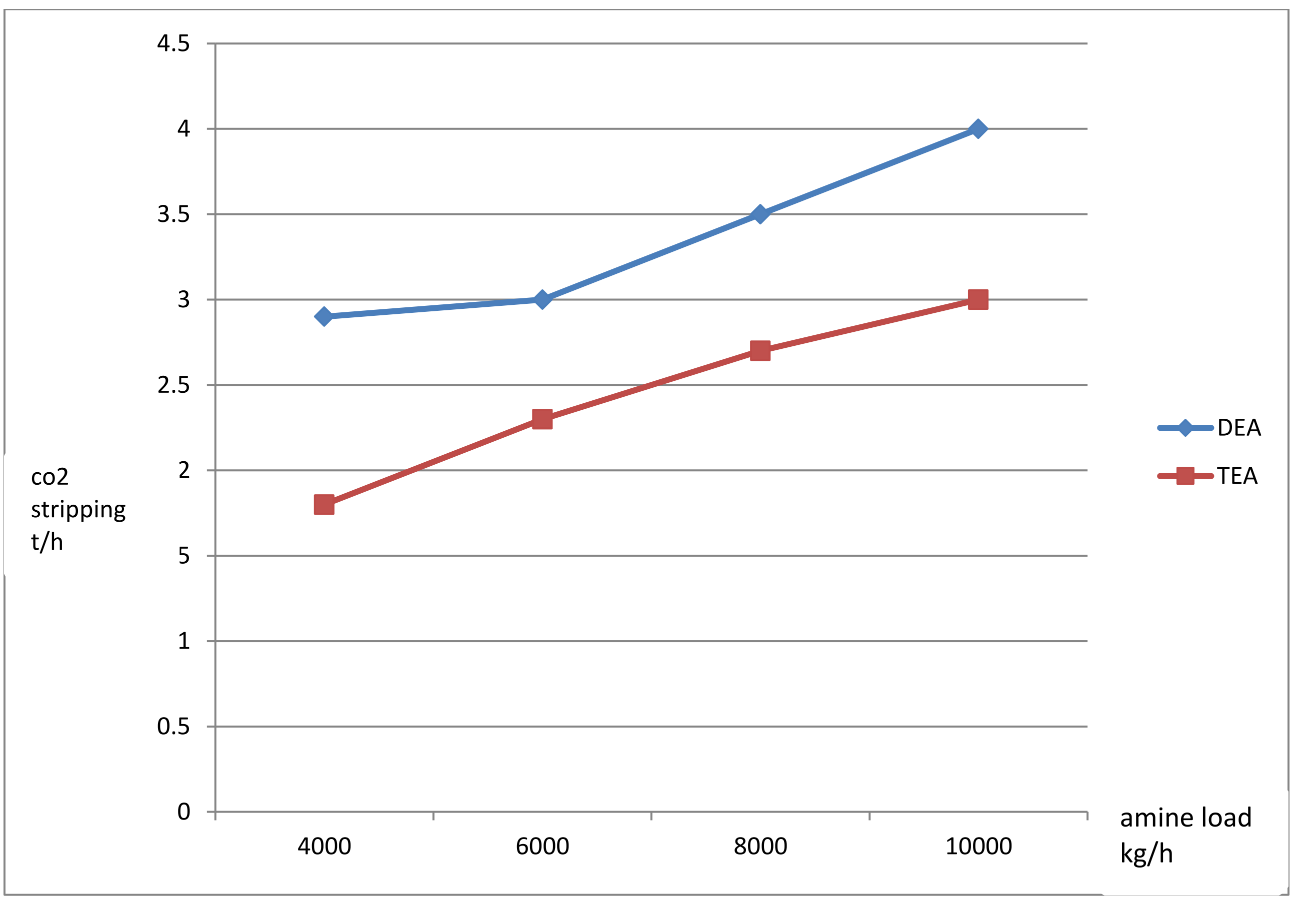

Figure [4]: Effect of lean amine rate on CO_2 stripping rate.

3-Energy Requirements

The energy required for a regeneration process is one of the most important factors to consider when designing a synthesis gas sweetening plant. Increasing energy requirements, on the other hand, will result in higher operating costs. According to the results of the preceding study, increasing the flow rates of the amine solution results in an increase in the required reboiler energy for the recovery of the lean amine. Similarly, increasing the circulation rate increases the size of the regeneration unit, which increases the required reboiler energy[1][13]. As a result, the required energy for the two solvent types DEA&TEA was simulated using the optimal investigated operation conditions at a temperature of 120 ^{0}C and a circulation rate ranging from 4000 Kg/hr to 10000 Kg/hr., as shown in table[5].

In summary, it has been demonstrated that the TEA solvent required more energy than the DEA solvent for carbon dioxide recovery.

Amine flow rates [kgmole/h]	Reboiler duty [kj/h]	
	DEA	TEA
4000 kgmole/h	5.760e+007 kj/h	6.5e+007 kj/h
6000 kgmole/h	5.8e+007 kj/h	6.8e+007 kj/h
8000 kgmole/h	5.85e+007 kj/h	6.95e+007 kj/h
10000 kgmole/h	5.9e+007 kj/h	7.1e+007 kj/h

Table 5 (results of increasing the amines flow rates on the reboiler duty)[12]

VI.Conclusion

In this work, modeling study of carbon dioxide removal is studied, and systematic approach is compared between different absorption process techniques based on different amine solvent. This study was performed to determine best amine solvent type between (DEA&TEA) has an adequate ability to reduce the existence of carbon dioxide to less than 100 ppm with synthesis gas (hydrogen, nitrogen) of ammonia production. Simulation and analysis of each case have been performed using Aspen Hysys software. However, results showed that DEA solvent has more CO_2 capture and less energy required than TEA at the same condition.

VII .References

[1] Ave. E van Nieuwenhuyse 4 B-1160, “Production of ammonia 2000,” *EFMA*, no. 1, p. 40, 2000.

[2] N. S. Darani, R. M. Behbahani, Y. Shahebrahimi, and A. Asadi, “Simulation and Optimization of the Acid Gas Absorption Process by an Aqueous Diethanolamine Solution in a Natural Gas Sweetening Unit,” 2021, doi: 10.1021/acsomega.1c00744.

[3] Max Appl., *Ammonia Principles and Industrial Practice*. WILEY-VCH, 1999.

[4] N. P. Lieberman and E. T. Lieberman, *A Working Guide to Process Equipment*, no. 1. 2008.

[5] E. Cooper and R. Weiland, “Reducing CO2 Slip from the Syngas Unit of an Ammonia Plant,” *Nitrogen + Syngas 2016*, vol. 2, pp. S165–S170, 2016, [Online]. Available: https://www.protreat.com/files/publications/171/Manuscript - Reducing CO2 Slip.pdf.

[6] T. Study, “ENVIRONMENTAL ASSESSMENT FOR CO 2 CAPTURE AND,” no. March, 2007.

[7] A. Valera-medina, H. Xiao, M. Owen-jones, W. I. F. David, and P. J. Bowen, “Ammonia for power,” *Prog. Energy Combust. Sci.*, vol. 69, pp. 63–102, 2018, doi: 10.1016/j.pecs.2018.07.001.

[8] F. Vega, M. Cano, S. Camino, L. M. G. Fernández, E. Portillo, and B. Navarrete, “Solvents for Carbon Dioxide Capture,” in *Carbon Dioxide Chemistry, Capture and Oil Recovery*, 2018.

[9] Y. K. Salkuyeh and M. Mofarahi, “Comparison of MEA and DGA performance for CO 2 capture under different operational conditions,” no. January 2011, pp. 259–268, 2012, doi: 10.1002/er.

[10] F. R. & L. FELICIA WUISAN, “COMPARISON OF MEA, DEA AND TEA AS CO2 ABSORBENTS FOR MEASUREMENT OF CARBON-14 ACTIVITY IN CORAL REEF SAMPLE FROM SPERMONDE ISLANDS Waode ,” *Angew. Chemie Int. Ed. 6(11), 951–952.*, vol. 16, no. 2, pp. 119–141, 1967.

[11] “Inorganic Chemical Industry 8.1-1,” vol. 93, pp. 1–6, 1991.

[12] A. Solusions and Z. Aliabad, “Removal of CO2 and H2S using Aqueous,” no. October, 2018.

[13] C. Prof. Egenhofer and L. Dr. Schrefler, “Composition and Drivers of Energy Prices and Costs in Energy Intensive Industries.,” no. January, pp. 2–6, 2014.