Mass Transfer Enhancement for CO₂
Absorption in Structured Packed Absorption Column

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Summary: The acidic gas, Carbon dioxide (CO_2) absorption in aqueous ammonia solvent was carried as an example for industrial gaseous treatment. The packed column was provided with a novel structured BX-DX packing material. The overall mass transfer coefficient was calculated from the absorption efficiency of the various runs. Due to the high solubility of CO_2, mass transfer was shown to be mainly controlled by gas side transfer rates. The effects of different operating parameters on K_Ga_v including CO_2 partial pressure, total gas flow rates, volume flow rate of aqueous ammonia solution, aqueous ammonia concentration, and reaction temperature were investigated. For a particular system and operating conditions structured packing provides higher mass transfer coefficient than that of commercial random packing.

Keywords: Mass Transfer rate, Efficiency, Structured packing, Mass Transfer Coefficient, Absorption.

Introduction

As a result of industrial revolution from the beginning of 18th century, many industries have grown and they are capable of polluting the earth which has resulted in climatic changes. Intergovernmental panel on climate change (IPCC) and National Oceanic and Atmospheric Administration(NOAA) shows that the world has been heating up since 1980s. Hence CO_2 capture and sequestration has gained importance in order to maintain clean environment [1]. Climatic change has been reported due to the emission of CO_2 rather than other greenhouse gases (methane, nitrous oxide, etc) [1].The presence of CO_2 along with moisture enhances the severity of the corrosion problems and also reduces the calorific value of the fuel. CO_2, associated with natural gas, if not removed will corrode pipelines and process equipment [2]. Many research works are being carried out to capture CO_2 and hence CO_2 sequestration has grown a widespread. In that context, plate column and packed column absorption has gained its importance. Packed column has gained vital importance due to several advantages like low liquid hold up, low pressure drop and less expensive.

There are various technologies to capture CO_2 including Solvent absorption, Chemical adsorption, biosorption, Membrane separation and Cryogenic separation [2]. Besides, solvent absorption is the reliable and most widely used method. Among the solvents, Monoethanolamine (MEA) is the most established for CO_2 capture but it has certain disadvantages like low CO_2 loading, high corrosion rate in equipments, amine degradation by SO_2, NO_2, HCl and O_2 in the flue gas. To overcome this difficulty, ammonia seems to have lower cost, higher capacity and efficiency. Aqueous ammonia overcomes the limitations of amine solutions with low energy requirement during solvent regeneration, which is not easily degraded; therefore the solution does not have corrosion problems [3, 4]. Moreover it has been used to capture the three acid gases (CO_2, SO_2 and NO_2) which reduce the cost of capture. Temperature (40^0C) plays a major role in the CO_2 capture. With increase in temperature, the mass transfer resistance increases in the liquid phase as the forward reactions proceeds at room temperature and vice versa [5]. Main carbon emitting source is the fossil fuel fired power plants which contributes about half of the total emissions [6]. Several researchers have carried out their work with random packing but structured packing shows superior performance. This superiority indicates that the use of structured packing can considerably improve the efficiency of CO_2 absorption. Structured packing is a flow device in which the available packing surface area promotes mass transfer area and provides lower pressure drop than dumped packing [7]. The present work highlights the enhanced absorption of CO_2 by structured packing with novel way of distribution of the solvents into the column. Removal efficiency and absorption capacity of CO_2 by employing NH_3, using structured packing was studied.
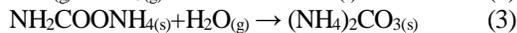
Aqueous Ammonia and Co₂ Reactions

The total reaction of aqueous ammonia with carbon dioxide can be described as the equation

$$CO_{2\,(g)} + NH_{3\,(aq)} + H_2O \rightarrow NH_4HCO_{3(aq)} \qquad (1)$$
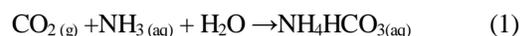
The actual process of the reaction is more complicated, that can be described as step-by-step reactions. First of all, the (5) equation occur,

$$CO_{2(g)}+2NH_{3(g)} \rightarrow NH_2COONH_{4(s)} \qquad (2)$$
$$NH_2COONH_{4(s)}+H_2O_{(g)} \rightarrow (NH_4)_2CO_{3(s)} \qquad (3)$$
$$CO_{2(g)}+2NH_{3(g)} \rightarrow CO(NH_2)_{2(s)}+H_2O \quad (4)$$
$$CO_{2(g)} +2NH_{3(aq)} \rightarrow NH_2COO^-_{(aq)}+NH_4^+_{(aq)} \qquad (5)$$

and CO_2, NH_3 react to generate NH_2COONH_4, then hydrolyzes in solution instantaneously as

$$CO_{2(g)}+2NH_{3(aq)} \rightarrow NH_2COO^-_{(aq)}+NH_4^+_{(aq)} \qquad (6)$$

Then, NH_4^+ and NH_2COO^- has an irreversible reaction in solution:
$$NH_2COO_{(aq)}+NH_4^+_{(aq)}+2H_2O \rightarrow$$
$$NH_4HCO_{3(aq)}+NH_3.H_2O_{(aq)} \quad (7)$$

The formation of ammonium (NH_4^+) and carbamate(NH_2COO^-) ions is very fast, reaction equation (5) is irreversible, and the reaction equations (2)-(4) are reversible. The explosive limit for NH_3 gas is 15-28%. Therefore, in order to be safe and simple, the wet method is used in this study. Reaction equations (4) and (5) are the most probable in this study for CO_2 removal by aqueous ammonia scrubbing. Acid gas absorption process is described by the mathematical model based on a two-film theory of gas-liquid absorption. Whitman (1923) designed the simplest two film-theory for mass transfer analysis. The two film theory is expressed by considering the following assumptions:

Mass transfer rate depends on the rate of migration of a molecule in each gas or liquid phase.

1. An assumption that the gas and liquid phases are in unstable contact with each other and separated by an interface area.
2. This model proposes that a mass-transfer zone (film) takes place in the gas and liquid phases on either side of the interface.
3. Complete mixing takes place in gas and liquid phases and the interface is at equilibrium with respect to gas molecules transferring in or out of the interface.

From the above assumptions, the two film theory is derived as,

$$N_A = k_G(P_{AG} - P_{Ai}) \qquad (8)$$
$$N_A = k_L(C_{Ai} - C_{AL}) \qquad (9)$$

where N_A= rate of transfer of component A, k_G = mass transfer coefficient for gas film, k_L = mass transfer coefficient for liquid film, P_{AG} = partial pressure of solute A in the gas phase, P_{Ai} = partial pressure of solute A at the interface, C_{Ai}& C_{AL} = concentration of solute A at the interface and liquid phase and K_{Ga_v} is volumetric overall mass transfer coefficient. Absorption rate is given by
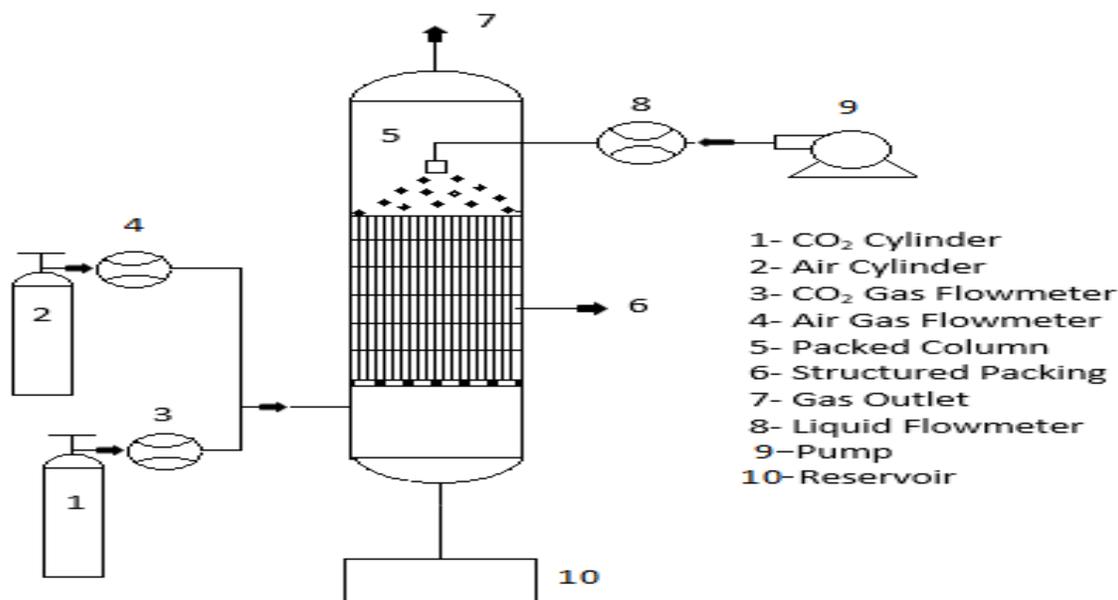
$$\varphi = K_G a_v P_{CO2} \qquad (10)$$

1- CO₂ Cylinder
2- Air Cylinder
3- CO₂ Gas Flowmeter
4- Air Gas Flowmeter
5- Packed Column
6- Structured Packing
7- Gas Outlet
8- Liquid Flowmeter
9- Pump
10- Reservoir

Fig. 1:   Experimental setup of Packed Absorption Column.

Experimental

The schematic diagram of the experimental setup is shown in the Fig. 1. It is a glass column of 5.5 cm ID and 60 cm height that is packed with a novel BX DX structured packing material. The liquid (ammonia) and gas flows in counter current direction as the liquid is pumped to the top and the gas is allowed to flow through the bottom. Both phases are assumed to be laminar and ideally mixed at regular interval. The inner surface is wetted by the liquid channels. CO_2 gas is stored in cylinder and feed solution is stored in feed tank. Then mass transfer characteristics for various flow rates can be determined by titration method. Thus, mass transfer process of CO_2 absorption into aqueous ammonia solution is mainly controlled by the resistance of the liquid phase. The reduction in the K_{Ga_v} results from an increase in the viscosity of the liquid solution which causes the reduction in the rate of molecular diffusion. The increasing viscosity also tends to cause a reduction in the effective interfacial area between gas and liquid in the packed column. Temperature is an important parameter influencing reaction kinetics. The reaction of CO_2 absorption into aqueous ammonia solution is reversible, the forward reactions are dominant at room temperature, the backward reactions occur at temperatures of around 38°-60°C.

Results and Discussion

Effect of solvent flow rate on percentage CO_2 removal efficiency

The effect of the solvent flow rate on % CO_2 removal efficiency was investigated and shown in Fig. 2. As the solvent flow rate increases the removal efficiency also increases. The mole ratio of aqueous ammonia to carbon dioxide increases with the solvent flow rate, which adversely increases the removal efficiency. According to the equation(10), the CO_2 absorption in aqueous ammonia was enhanced by increasing the solvent flow rate. With the increase in liquid flow rate, more liquid would spread on the structured packing which results in higher interfacial area and this leads to an increase in the absorption rate of CO_2. The increasing trend was mainly due to increased wettability of the packing material of the gas liquid contactor by increasing the solvent flow rate. Previous studies reported that beyond increasing the concentration above 15 % the aqueous ammonia will be volatilized and hence the removal efficiency would decrease [3]. But here, while increasing the solvent concentration to 12% the removal efficiency decreases. On the other hand, high flow rates leads to lesser contact time for the mass transfer to take place, while a very low flow rate means improper and

incomplete wetting of the packing material takes place leading to dry pockets that would hinder the mass transfer process. Hence, an optimum flow rate can be determined for the CO_2 removal process. From this graph, as the solvent flow rate increases the CO_2 removal efficiency also increases. The removal efficiency of NH_3 has been compared with MEA (in the Table-1) and found that NH_3 has higher removal efficiency than MEA.

Table-1: Comparing the absorption efficiency of NH_3 and MEA.

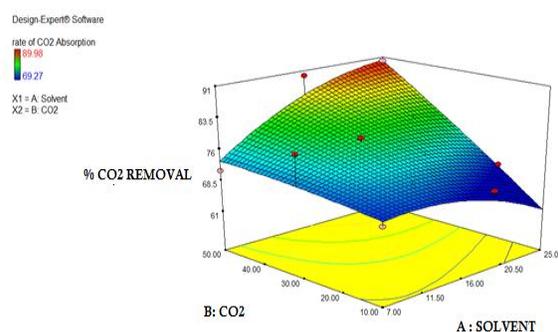| Solvent Flow rate, LPH	7	9	10	11	15	17
CO_2 removal efficiency by NH_3	66	71	75	79	81	91
CO_2 removal efficiency by MEA	34	41	44	67	77	84

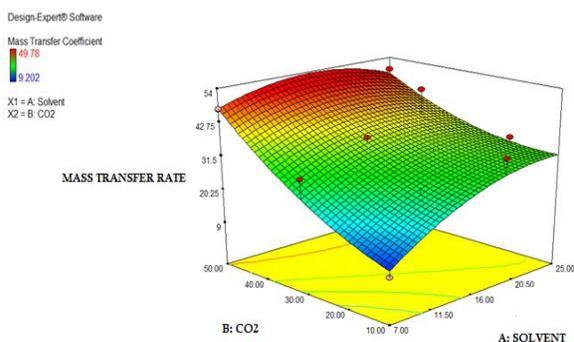Fig. 2: Liquid flow rate on % removal efficiency.

Fig. 3: CO_2 absorption rate on liquid flow rate.

Effect of rate of CO_2 absorption on solvent flow rate

The effect of the rate of CO_2 absorption on solvent flow rate was shown in Fig. 3. The absorption rate increases with increasing solvent flow rate. This is due to the increase in solubility of CO_2 in solvent which is attributed to the fact that the increase in ammonia concentration yields higher amount of the active ammonia molecules diffuse toward the gas liquid interface and react with CO_2 resulting in higher enhancement factor. As a result of increase in

enhancement factor, the liquid side mass transfer coefficient and absorption rate increases with decreasing the mass transfer resistance in the liquid phase. As the solvent flow rate increases the overall mass transfer coefficient also increases, which results in easier removal of CO_2.

Effect of overall mass transfer coefficient on gas flow rate

This graph shows the effect of volumetric overall mass transfer coefficient on CO_2 flow rate in Fig. 4. Increasing gas flow rate results in increasing trend of mass transfer coefficient. As a result of increase in gas flow rate results in speed up of the gas absorption operation. Absorption rate is enhanced with the increase in gas flow rate and it is also proportional to gas phase partial pressure. With increase in gas flow rate and constant liquid flow rate there will be decrease in removal efficiency of the gas.
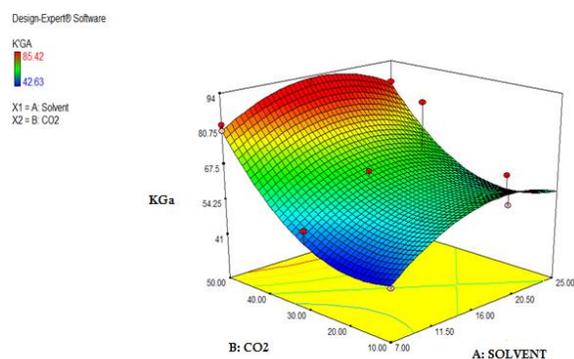

Fig. 4:   Overall mass transfer coefficient on CO_2 flow rate.

Effect of flow rate on number of transfer units (NTU)

The effect of gas and liquid flow rate on NTU was studied and shown in Fig. 5. The number of transfer unit required is a measure of difficulty of the separation. The NTU is similar to the number of theoretical plate required. Hence, a larger number of transfer units will be required for a very high purity product.

Effect of flow rate on height of transfer units (HTU)

The effect of gas and liquid flow rate on HTU was investigated and shown in Fig. 6.The height of transfer unit is the separation effectiveness of the packing for the particular separation process. More efficient the mass transfer, lesser the value of

HTU. The liquid flow rate is found to be inducing the HTU and NTU of the packed tower among other parameters. Increasing the flow rate of the liquid increases the overall mass transfer coefficient, meaning easy removal of CO_2 and hence an increase in NTU and reduction in HTU. Nevertheless, too high flow rate would lead to lesser contact time for the mass transfer to take place, whereas a very low flow rate would lead to improper and incomplete wetting of the packing material, leading to dry pockets that would hinder the mass transfer process. Hence, an optimum flow rate can be determined for which the CO_2 removal process is most feasible.
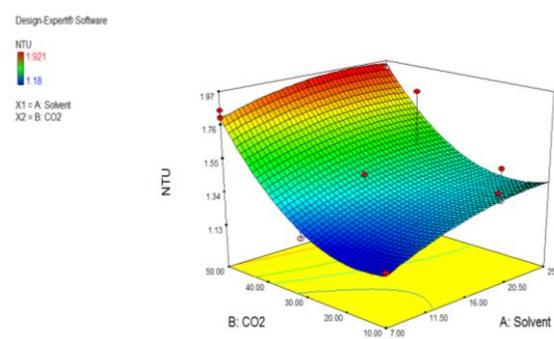

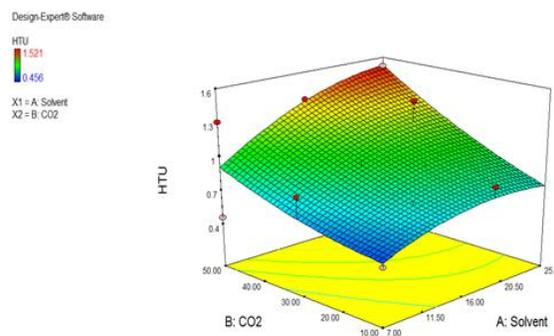Fig. 5:   Solvent flow rate and CO_2 flow rate on NTU.

Fig. 6:   Solvent flow rate and CO_2 flow rate on HTU.

Conclusion

From the experimental study of absorption of CO_2 in structured packed column using aqueous ammonia solvent the following conclusion are made. It is found that overall mass transfer coefficient increases with increase in solvent flow rate due to the fact that the increase in liquid flow rate leads to increase in liquid side mass transfer coefficient. It is also found that the increase in solvent concentration leads to increase in overall mass transfer coefficient. Because increase in solvent concentration yields a higher amount of active

solvent molecules towards diffusion in gas- liquid interface and react with CO_2, resulting in higher chemical reaction enhancement factor and decrease in mass transfer resistance in liquid phase.

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