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An Overview of CO_2 Capture Technologies

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Abstract - *Carbon capture and storage (CCS) is the most indicated technology to decrease CO2 emission from fossil fuels sources to atmosphere. Also, CO2 separated from flue gases can be used in enhanced oil recovery (EOR) operations where CO2 is injected into oil reservoirs to increase mobility of oil and reservoir recovery. Pure CO2 has many applications in food/beverage and different chemical industries such as urea and fertilizer production. CCS consists of three basic stages: (a) separation of CO2, (b) transportation, and (c) storage. CO2 separation is a major stage in CCS. There are three major approaches for CCS: pre-combustion capture, oxy-fuel process, and post-combustion capture. Because of the importance in selecting suitable process for CO2 separation, in this paper various technologies for this purpose have been focused.*

Key Words: CO2 capture, Absorption, Desorption, Absorbent, Amines

1.INTRODUCTION

Out of the ten primary Green House Gases(GHGs), water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are naturally occurring and other gases like Perfluorocarbons (CF_4, C_2F_6), hydrofluorocarbons (CHF_3, CF_3CH_2F, and CH_3CHF_2), and sulfur hexafluoride (SF_6), are present in the atmosphere due to industrial processes. Water vapor is the most important, abundant and dominant greenhouse gas, and CO2 is the second-most important one.

CO2 is the primary anthropogenic greenhouse gas, accounting for 77% of the human contribution to the greenhouse effect. Combustion of fossil fuels is the main contributor of anthropogenic emissions of CO2. CO2 concentration in flue gases depends on the fuel such as coal (12–15 mol- % CO2) and natural gas (3-4 mol-% CO2). In petroleum and other industrial plants, CO2 concentration in exhaust stream depends on the process such as oil refining (8-9 mol% CO2) and production of cement (14–33 mol-% CO2) and iron and steel (20–44 mol-%). Cement and petrochemical plants are two major industries for CO2 emission, such that cement industry contributes about 5% to global anthropogenic CO2 emissions.

The first international agreement on emissions of GHGs is the Kyoto Protocol. In this protocol, industrialized countries agreed to stabilize or reduce the GHGs emissions in the commitment period 2008–2012 by 5.2% on average. But the result of global CO2 emissions was not encouraging; therefore, in 2011 Durban COP meeting, this protocol was extended until 2017. Several countries with high GHGs emission like China, India, Brazil, and even Iran have added to this Protocol. Given that the earth's average temperature continues to rise, Intergovernmental Panel on Climate Change (IPCC) stated, global GHG emissions must be reduced by 50 to 80 percent by 2050 to avoid dramatic consequences of global warming [1–3].

There are several gas separation technologies being investigated for post-combustion capture, namely, (a) absorption, (b) adsorption, (c) cryogenic distillation, and (d) membrane separation.

2. CO2 SEPARATION TECHNOLOGIES

2.1 Amines

The most commercially available technology is using amines as absorbent. Amines undergo a chemical reaction with CO2 forming water soluble salts. In this an aqueous solution containing 25-30 wt% amine is contacted with flue gas or other CO2 -containing stream. CO2 in the vapor phase dissolves in solution and reacts with the amine to form a salt Fig.1. The salt is then dissociated from the "rich" solution from the contactor by heating. To pull CO2 from solution and recover it as a gas, stripping steam is used [4]. The advantage for amine process is that the amine/ CO2 reaction is fast and enables aqueous amines to effectively scrub CO2 from post combustion flue gas where CO2 is diluted and at low pressure. The main challenges are: Because amine sorption involves a chemical reaction, a significant amount of heat must be applied to recover the absorbed CO2 -Amine solution that is too concentrated, rich, or lean is corrosive to carbon steel. This effect is exacerbated by oxygen in flue gas which degrades corrosion inhibitors. This causes amine attrition & fouls heat transfer equipment.

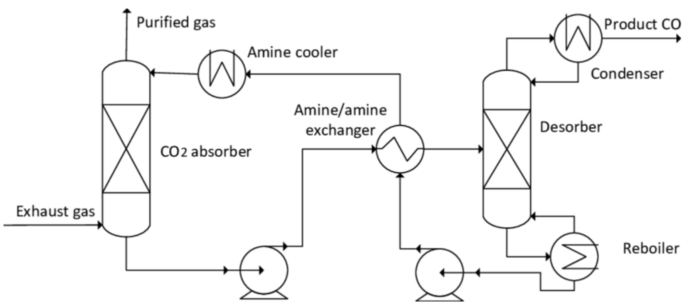

Fig -1: Principle for a standard CO2 removal process based on absorption followed by desorption in amine solution

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2.2 Aqueous Ammonia

In this technology, Ammonia reacts with CO2 to form ammonium carbonate which on disassociation releases a pure stream of CO2. The advantage of this process is reduced heat of reaction compared to amines and potential for SOx and NOx capture with fertilizer by-product (ammonium sulfate and ammonium nitrate) Fig.2. Main disadvantages are that (1) Need to cool down flue gas to 80°F for ammonia carbonate to be stable, (2) Reaction cycles involving ammonia reacting with CO2 do not offer energy savings compared to amines. , (3) Degradation of carbonate in the CO2 absorber causes ammonia slip in the flue gas exhaust.[5] The process can be improved by (1) process optimization to increase CO2 loading, (2) additives to raise process temperature above 70°F, (3) increase percent conversion of SOx and NOx to fertilizer by-products.

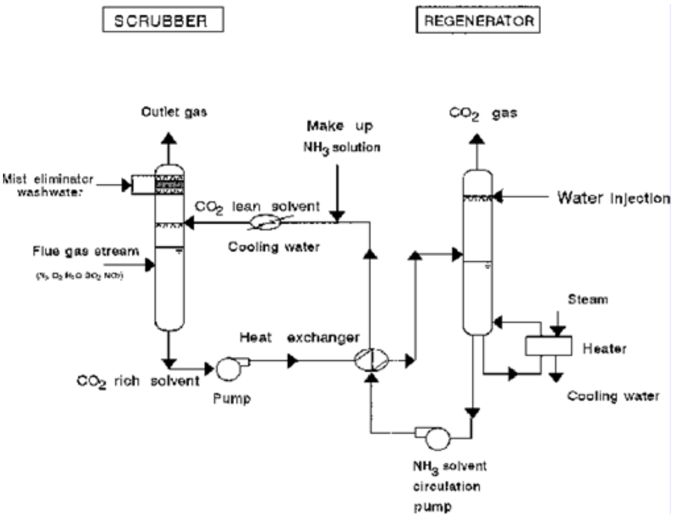

Fig -2: CO2 scrubber and ammonia regeneration system

2.3 Membrane/Liquid Sorbent Hybrids

In this method, flue gas is contacted with a membrane, and a sorbent solution on the permeate side absorbs CO2 and creates a partial pressure differential to draw CO2 across the membrane[6]. The advantage of this technology is that the membrane shields the amine from the contaminants in flue gas, reducing attrition and allowing higher loading differentials between lean and rich amine. The main two drawbacks associated with this technology are (1) High Capital cost associated with the membrane, (2) The fact that membranes may not keep out all unwanted contaminants

2.4 Ionic Liquids

Ionic liquids are a broad category of organic chemical compounds consisting of anionic and cationic components. They can dissolve gaseous CO2 and are stable at temperatures up to several hundred degree C. Ionic liquids can avoid cooling down syngas and heating it back up in a gasification application. Ionic liquids require little heat for CO2 recovery. The disadvantage is high cost and high viscosity.

2.5 Amine-enriched adsorbents

A carbon material with amine compounds fixed upon it exposed to a CO2 rich process stream. The amine sites absorb the CO2. The temperature of the material is raised to release the CO2. The advantage is high storage capacity and use of tertiary amines allows potential for lower energy required per CO2 captured. However, it is difficult to lower and raise the temperature of a solid material. Also, small diameter particles can cause high pressure drop across absorber.

2.6 Enzymatic CO2 sorbents

Enzyme-based system achieves CO2 capture and release by mimicking mammalian respiratory mechanism. The features include fast kinetic, resistance to SOx and NOx, and pH swing based operation offers potential to produce CO2 above atmospheric pressure. The disadvantage includes 100o F operating limit and exothermic CO2 sorption reaction requiring cooling of flue gas, entrained solids in flue gas from coal boilers may block membrane channels, and possible sensitivity to acid gases.

2.7 Chilled ammonia CO2 capture

ALSTOM's unique system, based on chilled ammonia, captures CO2 by isolating the gas from the power plant's other flue gases and can significantly increase the efficiency of the CO2 capture process. The system uses a CO2 absorber similar to SO2 absorbers and is designed to operate with slurry Fig.3. The cooled flue gas flows upwards in counter current to the slurrycontaining a mix of dissolved and suspended ammonium carbonate and ammonium bicarbonate. More than 90% of the CO2 from the flue gas is captured in the absorber. The remaining low concentration of ammonia in the clean flue gas is captured by cold-water wash and returned to the absorber. The clean flue gas, which now contains mainly nitrogen, excess oxygen and low concentration of CO2, flows to the stack. The process has the potential to be applied to capture CO2 from flue gases exhausted from coal-fired boilers and natural gas combined cycle (NGCC) systems, as well as a wide variety of industrial applications.

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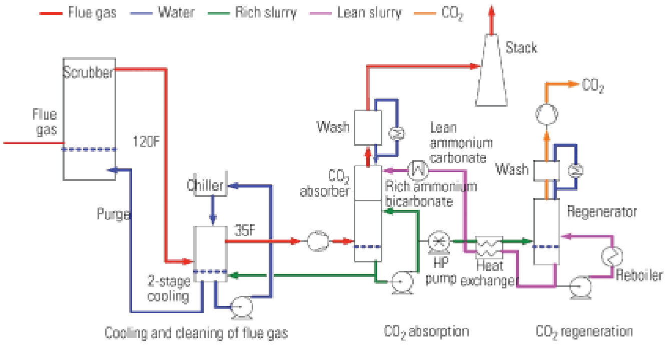

Fig -3: Chilled ammonia CO2 capture

2.8 Phase Transitional Absorption

Phase Transitional Absorption is a two or multi phase absorption system, CO2 rich phase and CO2 lean phase. During Absorption, CO2 is accumulated in CO2 rich phase. After separating the two phases, CO2 rich phase is forward to regeneration. After regeneration, the regenerated CO2 rich phase combines CO2 lean phase to form absorbent again to complete the cycle[7]. The advantage for Phase Transitional Absorption is obvious, significantly saving on regeneration energy. Because CO2 lean phase was separated before regeneration, only CO2 rich phase was forward to regeneration. This absorption system has the features of high absorption rate, high loading and working capacity, low corrosion, low regeneration heat, no toxic to environment, etc. The process evaluation shows that this process is able to save 80 % energy cost by comparing with MEA process.
Regeneration study showed that the desorption rate increases sharply with the increase of the regeneration temperature. Absorbent can be regenerated at 95o C. At 125o C, the CO2 was released from the absorbent vigorously. The regeneration energy requirement for the Phase Transitional Absorption process is about 15 percent of that of the benchmark MEA-based process. The capital costs of this case are 80% less than the conventional case. The absorbent of Phase Transitional Absorption has very little corrosion to carbon steel by comparing with MEA Process at the absorption temperature range.

3. CONCLUSIONS

Among the methods used to separate and purify gases, the gas-liquid absorption method is one of the most powerful and efficient techniques. A conventional system designed to separate and purify gas consists of a gas phase (mixture of gas including the one to be isolated) and a liquid phase (solution that maximizes absorption). Amine—CO2reaction is fast but higher amount of energy is required to recover CO2. Chilled ammonia technique removes more than 90% of the CO2 from the flue gas in the absorber. Phase transitional absorption has the capability to overcome the shortcomings of conventional MEA absorption. The phase transitional absorbent is stable in the flue gas environment. Its other advantages include high absorption rate, high CO2 loading and working capacity, low regeneration temperature and heat requirement..

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