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Simulation of Carbon Dioxide Sequestration by Mono Ethylene Amine (MEA) and Methanol Solvents

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Carbon dioxide (CO_2) is emitted in a number of ways; it is spread naturally either through the carbon cycle or human activities like the burning of fossil fuels. One of most dominant pre-combustion methods for CO_2 sequestration is using solvent-based process in order to capture this gas from flue gas and then either store it in Earth layers or use in other industries. There has been a climb in carbon dioxide concentrations in the atmosphere of about 280 ppm in 1850 to 364 ppm in 1998. In recent study, sequestration methods of CO_2 and also its absorption by Amine and Methanol solvents is investigated and related process is simulated by Aspen HYSYS (ver.2006) simulator, both models are done in two 10 and 15 stages columns while sequestration by Methanol consumes more solvent compared with using MEA even though the former is more economical than the latter.

1. Introduction

As Lackner (2009) has reported, in October 2010 carbon dioxide in the Earth's atmosphere has been at a concentration of 388 ppm by volume. One mole of CO_2 emitted in the combustion of gasoline or diesel is associated with a heat release of 650 kJ to 700 kJ. This becomes a figure of merit for the energy impact of capturing CO_2 and also provides a scale for gauging the energy consumption in the capture process. By capturing a mole of CO_2 from the air, one enables the release of another mole of CO_2 which makes it possible to harness approximately 700 kJ of heat from fossil fuels in a carbon neural manner. When sunlight reaches the earth, some of it is converted to heat. *Greenhouse gases* absorb some of the heat and trap it near the earth's surface, so that the earth is warmed up by increasing their concentrations in the atmosphere, this process commonly known as the Greenhouse effect. As a result of increasing these gases, global average sea level have been rising, global average air and ocean temperatures have been increasing and wind pattern as well as snow, ice and frozen ground have been changing as Heydari et al. study has reported (2010).

As we know, life exists only because of this natural greenhouse effect, because this process regulates the earth's temperature. The planet's effective temperature is about −18 or −19 °C, about 33 °C below the actual surface temperature of about 14 °C or 15 °C, the mechanism that produces this difference between the actual surface temperature and the effective temperature is due to the atmosphere and is known as the greenhouse effect. The amount of heat in the troposphere depends on concentrations of atmospheric greenhouse gases and the remained amount of these gases in the atmosphere. Greenhouse gases exist naturally in the Earth’s atmosphere in addition to being emitted through human activities. This natural “carbon cycle” includes carbon dioxide used in plants during photosynthesis and the exchange of carbon dioxide between the atmosphere and the oceans. The primary natural processes that release CO_2 into the atmosphere (sources) and that remove CO_2 from the atmosphere (sinks) are:

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- Animal and plant respiration, by which oxygen and nutrients are converted into CO_2 and energy, and plant photosynthesis by which CO_2 is removed from the atmosphere and stored as carbon in plant biomass;
- Generated CO_2 is as a by-product of the combustion of fossil fuels or the burning of vegetable matter; among other chemical processes e.g. cement production and Utility units in refineries.
- Ocean-atmosphere exchange, in which the oceans absorb and release CO_2 at the sea surface;
- Volcanic eruptions, which release carbon from rocks deep in the Earth's crust (this source is very small).

Carbon capture and storage (CCS) has recently been gaining more and more attention as a climate change mitigation option. Absorbing Carbon dioxide is called *Sequestration*. The goal of carbon sequestration is to take CO_2 that would otherwise accumulate in the atmosphere and put it in safe and permanent storage. As Schach et al. (2010) have reported some methods would capture CO_2 from concentrated sources like power plants which is still using coal as one of most important resources. Indeed, on-site capture is the most sensible approach for large sources and initially offers the most cost-effective avenue to sequestration. For distributed, mobile sources like cars, on-board capture at affordable cost would not be feasible. CCS can be separated into three elements:

- Capture
- Compression and Transport
- Storage

2. The Methods of Carbon Dioxide Capture

In order to stabilize CO_2 levels, it is necessary not only to deal with CO_2 emissions from power plants, but from all sources in an industrial economy, while it is generally agreed that the reductions demanded by the Kyoto Treaty would be far less than what would ultimately be required to stabilize CO_2 levels in the atmosphere. A portion of the desired reductions will be achieved by improved energy efficiency and energy savings, and another part might be accomplished by transition to non-fossil, renewable energy resources. High CO_2 capture efficiency at low costs is essential requirement for carbon capture and storage technologies. Removal of Carbon dioxide from the gas mixture can be achieved by a number of separation techniques including absorption into a liquid solvent, adsorption onto a solid, cryogenic separation and permeation through membranes so that each of these methods put inside the defined divisions. However, these methods have the individual issues of high corrosion, large energy consumption, high cost, or low capacity and so forth based on Li et al. work (2010).

For operational industries the application of redevelopment is limited, thus less reconstruction actions are needed. There are three basic technologies being developed recently:

- Post-combustion capture,
- Pre-combustion capture,
- Oxy-fuel combustion capture

Carbon dioxide capture is just half the job, it needs to have somewhere to stash securely. Carbon dioxide sequestration in deep geological formations is considered a promising mitigation solution for reducing greenhouse gas emissions to the atmosphere. According to Vilarrasa et al. (2010) report, the injection of supercritical CO_2 in deep saline aquifers leads to the formation of a CO_2 plume that tends to float above the formation brine, as pressure builds up, CO_2 properties i.e. density and viscosity can vary significantly. The risks of CO_2 storage in a geological reservoir can be divided into (i) CO_2 leakage (ii) CH_4 leakage (iii) Seismicity (iv) Ground Movement (v) Displacement of Brine based on Damen et al. researches (2006).

3. Process Description

The process of solvent-based CO_2 capture can be briefly described as follows: Prior to CO_2 removal, the flue gas is cooled down so that water vapour and other condensable gases are removed in a separator while absorption capacity is increased by temperature drop as Zhou et al. (2008) have reported. The flue gas contacts lean solvent in an absorber so CO_2 absorbs in solvent and off gas is sent to the atmosphere. Rich solvent stream is transported to stripping column to separate CO_2 from solvent then solvent returns to absorber and extracted CO_2 utilizes within industries or store in earth layers. For the absorption and stripping process, the first step is to find a solvent whose properties meet the requirements of the process such as low energy for regeneration and a high CO_2-loading capability. An aqueous amine solution, an aqueous ammonia solution, nearly pure methanol solvent or 2-amino-2-methyl-1-propanol (AMP) aqueous solution are often used for absorption of carbon dioxide based on Kim et al. (2010) report. Oxidizing environment e.g. reaction with NO_x or SO_x can cause solvent degradation and equipment corrosion but use of inhibitors can reduce these negative effects. Figure 1 illustrates the schematic of CO_2 capturing process by absorption.

Kim et al. (2010) performed a study on capability of CO_2 capture by using mono-ethanol amine solution (MEA) and Methanol solution and compared duty value for condenser and reboiler and also amount of consuming solvent in the same condition by PRO/II simulator for both systems. In recent study, CO_2 absorption by MEA and methanol solvents is investigated and related process simulated by Aspen HYSYS (ver.2006) simulator. One of most significant resources of carbon dioxide is steam methane reforming which is the method for producing 48 % Hydrogen globally and produced by following equilibrium reactions (Equations 1-3):

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad \Delta H^{\circ}_{298} = +206\ kJ\ /\ mol \tag{1}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41\ kJ\ /\ mol \tag{2}$$

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \qquad \Delta H^{\circ}_{298} = +165\ kJ\ /\ mol \tag{3}$$

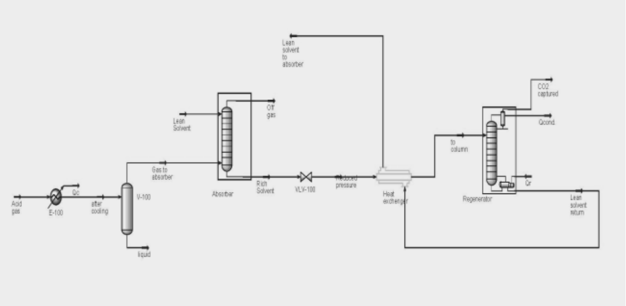

Figure 1: Absorption of carbon dioxide from reaction effluent by Methanol and MEA

The steam reforming of methane consists of three reversible reactions: the strongly endothermic reforming reactions (1) and (3), and the moderately exothermic water-gas shift reaction (2). It should be emphasized that CO_2 is not only produced via the shift reaction (2), but also directly via the steam reforming reaction (3). This implies that reaction (3) is not just the 'overall reaction', despite the fact that in literatures steam-methane reforming is often considered to be a combination of reactions (1) and (2) only. In the first absorption system by 98.5 %wt methanol solution, inlet gas stream from reactor effluent stream with 2,491 kg/h and molar composition which is followed as: Methane 0.15 %, water 14.8 %, Carbon monoxide 29.6 %, carbon dioxide 23.4 % and Hydrogen 31.9 % is entered to a heat exchanger to cool down up to 45 °C and then introduced to a separator to separate gas and liquid phases and condensable components that are 302 kg/h accompanied with 99.5 % mol water, then main stream is entered to absorber with the pressure 59 barg. Methanol solution in 35 °C contacts with acid gas in the tower with 10 stages to absorb 95 % by mol carbon dioxide. Off gas at top of absorber is included 1.9 % mol CO_2 and 1.5 % mol methanol which is wasted and should replace by make-up solvent. Rich solvent after pressure drop by control valve up to 29 barg and preheating to 113 °C by a exchanger for reducing utility and energy saving is introduced to top of regenerator which is included 12 stages with a condenser and re-boiler for removal of acid gases. Regeneration is completed when CO_2 content is less than 1,000 ppm and most amount of solvent is regenerated while condenser temperature would be set on 45 °C for cooling by water also lean solvent temperature would be 109 °C after crossing mentioned heat exchanger. For the simulation of CO_2 capture by methanol as a solvent, NRTL activity model (Equations 4) is used for calculation of liquid phase non-idealities so Peng-Robinson Equation of state (Equation 5) is utilized for the estimation of vapour phase non-idealities.

$$\ln\gamma_i = \frac{\sum_{j=1}^{n}\tau_{ji}x_jG_{ji}}{\sum_{k=1}^{n}x_kG_{ki}} + \sum_{j=1}^{n}\frac{x_jG_{ij}}{\sum_{k=1}^{n}x_kG_{kj}}\left(\tau_{ij} - \frac{\sum_{m=1}^{n}\tau_{mj}x_mG_{mj}}{\sum_{k=1}^{n}x_kG_{kj}}\right) \tag{4}$$

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)-v(v-b)} \tag{5}$$

In other case, 30 %wt MEA aqueous solution contacts with acid gas main stream to extract at least 95 % mol carbon dioxide, the process operation condition for absorber is same as the methanol absorber so that remain CO_2 content in off gas is about 1.1 % mol and amount of waste MEA is negligible, but for regeneration the rich solvent is preheated up to 105 °C and column pressure is decreased up to 1.5 barg in the column with 12 theoretical stages which is included a condenser and reboiler so that its specifications are to reach CO_2 content to less than 1,000 ppm and solvent purity about 30 %wt. in bottom of column while lean solvent is cooled by heat exchanger up to 107 °C. For this simulation, Amine Package thermodynamic model in Aspen Hysys is used for modelling of CO_2 capture by MEA solution. Generally, it is observed that most noticeable parameters in CO_2 production rate for both absorption systems are operating pressure of absorber, CO_2 loading concentration, solvent concentration, solvent temperature and flow rate, theoretical stages of absorber.

4. Results and Discussion

Our simulations are focused on capturing by methanol and MEA solution that are done in both 10 and 15 stages absorber and regeneration columns to investigate effect of theoretical stages on condenser and re-boiler duties and solvent flow rate. The results show CO_2 capturing by methanol consumes more solvent than absorption by MEA although by increasing number of stages solvent flow rate is fallen for both. Also for 10 stages column, solvent to feed mass ratio in methanol absorber is 4.64 while it's 4.04 for MEA column so that mole percent of absorbed CO_2 in MEA is more, beside utility cost (condenser and re-boiler energy consumption) and CO_2 content in lean solvent in MEA system is much more than the methanol system. Therefore, by comparison of these results is concluded because of being two columns in both systems and less CO_2 content in lean solvent and duty values in Methanol system than MEA system, the former is more economic although it has more solvent waste than the MEA system in off gas stream and consumes more solvent flow rate, also decreasing lean solvent temperature in methanol causes to rise molar flow of captured CO_2 in rich solvent in comparison with the MEA, Figure 2 and Figure 3 show absorption of whole CO_2 in acid gas stream for 98.5 %wt methanol solution in 10 °C when CO_2 captured flow rate is almost 26.4 kgmol/h while it's 26.1 kgmol/h for 30 %wt MEA aqueous solvent.

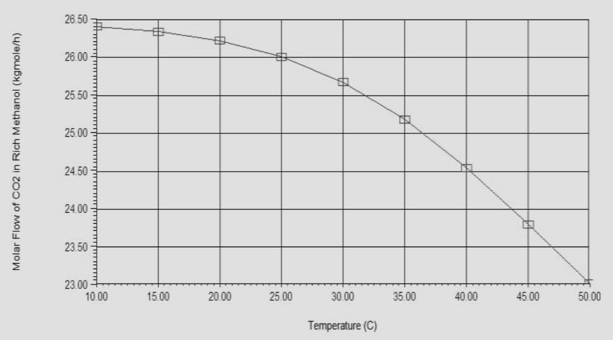

Figure 2: Change of molar flow CO_2 in rich Methanol vs. lean solvent temperature

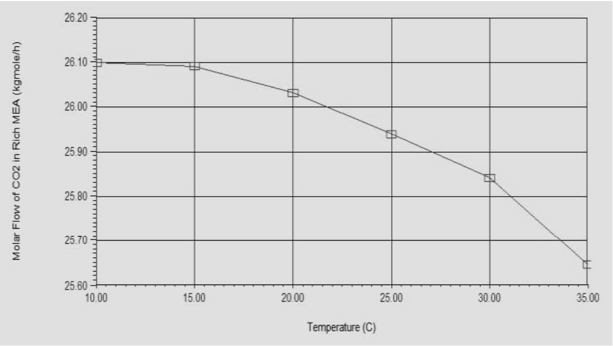

Figure 3: Change of molar flow CO_2 in rich MEA vs. lean solvent temperature

Figure 4 and Figure 5 indicate captured CO_2 molar flow and solvent-feed mass ratio versus solvent molar flow changes for methanol and MEA systems. For the methanol system, solvent molar flow to absorb whole CO_2 is about 475 kg mol/h and ratio would be 6.9 while for the MEA, flow rate is 520 kg mol/h with a ratio 5.44. Table 1 compares operating condition such as solvent flow rate and regenerated solvent weight percent for both systems. By increasing number of stages in the absorbers, solvent flow rate is just reduced 4 % and 2 % for methanol and MEA respectively but due to rising initial investment to add five more stages, using the 10 stages columns for both absorber and regenerator would be more economical.

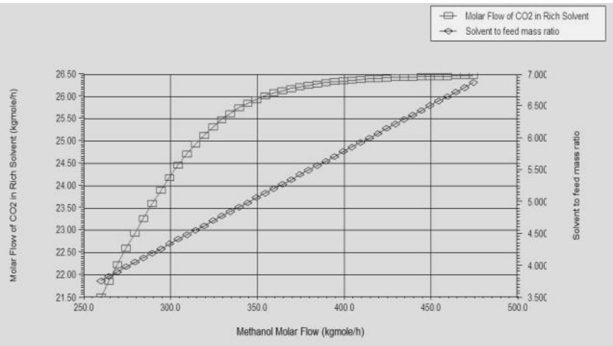

Figure 4: Captured CO_2 molar flow and methanol-feed ratio vs. methanol molar flow

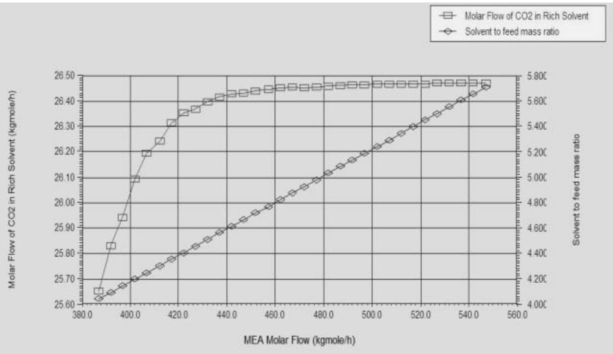

Figure 5: Captured CO_2 molar flow and MEA-feed ratio vs. MEA molar flow

Table 1: Comparison between Methanol and MEA Absorption in two Different Cases

Solvent Parameters	CO_2 absorption by MeoH		CO_2 absorption by MEA	
Theoretical Stages	10	15	10	15
% Mole of absorbed CO_2	95	95	96.8	98.8
Solvent Mass flow (kg/h)	10170	9755	8841	8659
Solvent to feed mass ratio	4.64	4.45	4.04	3.95
Condenser Temperature (°C)	45		45	
Condenser Duty (kj/h)	-5.7×10^5	-5.58×10^5	-7.53×10^7	-7.0×10^7
Reboiler Temperature (°C)	175		137	
Reboiler Duty (kj/h)	3.5×10^6	3.38×10^6	7.78×10^7	7.23×10^7
CO_2 content in Lean Solvent (ppm)	346	328	789	980
% weight of regenerated Solvent	98.4	98.4	29.98	29.98

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