Upgrading Biogas with Absorption of CO_2 using Alkaline Solution - an Economic Experimental Study

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The focus of the present work is to study the effect of piperazine (PZ) solvent for the removal for CO_2 from biogas using carbon capture and utilization (CCU) technology. For rapid conversion of absorbed gaseous CO_2 into aqueous CO_2 a solution of monoethanolamine (MEA), diethanolamine (DEA) and piperazine (PZ) was undertaken. Barium Chloride ($BaCl_2$) was added as a precipitating agent to react with the aqueous CO_2 and thereby ultimately forming $BaCO_3$. The characteristics of the $BaCO_3$ precipitates using X-ray diffracometry (XRD), scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) and Fourier-transform infrared spectroscopy FT-IR analyses were analysed. The precipitates exhibited the witherite morphology AS confirmed by XRD results. FT-IR confirmed the formation of metal salt i.e. $BaCO_3$ and EDS confirmed that no impurities were present in it. It is found that the solvent piperazine enhanced CO_2 absorption with $BaCO_3$ purity remains unaffected. Further we also compared the properties of $BaCO_3$ produced in this work with the $BaCO_3$ directly used in other industries (such as earthenware, pottery, ceramics) and found that the properties matched well with marketed product. The method is economical due to simultaneous reactive absorption and precipitation in a single stage. Highly pure biogas (97%) was obtained along with the simultaneous production of industrial grade $BaCO_3$.

1. Introduction

Increase in carbon dioxide concentration in atmosphere from different sources like burning of fossil fuels, Industrial and vehicular emission are one of the major problems global warming. For eco-friendly reasons, many researchers have shown interest in the capture and utilization of CO_2 emitted by large stationary industrial combustion sources as well as vehicles (Herzog et al., 2003). One strategy is to use sorption desorption cycles with a suitable sorbent, such as Barium Chloride and Zinc Chloride (Gaur et al. 2009). During these cycles, CO_2 is separated from the combustion gases as $BaCO_3$ obtained by carbonation of $BaCl_2$ in the temperature range of 20–30°C. Increasing CO_2 concentrations in the atmosphere have been reported widely by the researchers and scientists. It is the main gas responsible for global warming (Park et al., 2014). It is therefore required to develop an economical way of capturing CO_2 and its utilization to control its emission. Various methods have been developed for capturing of CO_2 from biogas. Chemical absorption processes employ physical and chemical solvents such as selexol, rectisol, piperazine, metals salts and amines. Adsorption systems capture CO_2 on a bed of adsorbent materials such as activated carbon. CO_2 can also be separated from other gases by cryogenic methods like distillation method at low temperature. CO_2 can also be removed via hybrid process or cryogenic process which has shown much promise (Feng et al., 2010). Variety of Polymeric material is also employed in upgrading of biogas, metals catalysts and molecular sieves are also being assessed for membrane separation processes. Enhancement of CO_2 capturing is related with different aspects mainly like reaction rate, carbon dioxide loading, corrosion, solvent degradation and cost of solvent regeneration (Wang et al., 2017). Many researchers have proposed, new solvents such as blending of amines or ionic liquids, but the improvements were not much and some types of these solvents showed negative characteristics such as high viscosity, toxicity like monoethanolamine and piperazine (Rochelle et al., 2011) Many solvents also showed high degradation rate. Gaur et al., 2011 in their experiment have focused on improving the reactivity of amine sorbent as well as ammonia for its use in a reaction- based process for the separation of carbon dioxide (CO_2) from Landfill gas. Reaction-based separation processes can generate

pure streams of CO_2. Upon regeneration, it is desirable that the only gas coming off the sorbent/solvent is CO_2. If other gases such as SO_2 or moisture also evolve in the regeneration, then the separation process would not be effective, as it would merely concentrate the CO_2 but fail to yield pure CO_2. The conversion of ZnO to $ZnCO_3$ at 8-13 °C when ZnO powder was exposed to CO_2 and H_2O for over 100 days and they observed a comparable pickup of water and CO_2 by ZnO and it converted to $ZnCO_3$(Sawada et al., 1996). Sterically hindered amines are one of the best solvent used so far for in separation of CO_2 .Mostly MEA, DEA and MDEA are widely used in industries. Certain recent studies have been designed to evaluate absorption columns using chemical solvents with affinity towards CO_2, such as monoethanolamine (MEA), Methyldiethanolamine (MDEA) and aqueous ammonia (NH3 (ac)) (Wang et al, 2017). Among these solvents, MEA is easily available and has wide range of industrial application, but it has low absorption capacity along with a high corrosion rate and high energy consumption in desorption and low absorption. Absorption rate of tertiary amines like MDEA was lower than MEA, while MDEA offered greater thermal stability in absorption, low volatility and low energy consumption (Aron et al., 2005). The absorption of CO_2 with NH3(ac) in post-combustion gases has been evaluated under a wide range of operation conditions, presenting satisfactory results for CO_2 capture compared to amines and highlighting its high absorption capacity and forming stable compound like $BaCO_3$ at the same temperature and pressure conditions (Arenas et al., 2014). The literature to date (Gaur et al., 2014, Park et al., 2017) indicates that carbonation method has been used so far, but no literature is found regarding the use of piperazine along with MEA/DEA and $BaCL_2$ for biogas purification. Therefore our objective is to study the effect of piperazine on $BaCO_3$ precipitates.

To demonstrate the effect of piperazine on biogas upgrading and minimizing the overall absorption process along with manufacturing of industrial grade barium carbonate an alkaline aqueous solution of 4% MEA and 4% DEA along with 1-3% piperazine and 50 gram barium chloride solution for CO_2 absorption in a 1 L volume reactor is used. Present work also shows cost effective possibility of CO_2 capture and utilization as compared to the commonly used method absorption at industrial scale.

2. Experimental

2.1 Reagents

Barium Chloride Dihydrate ($BaCl_2.2H_2O$, CDH purity 99%), Monoethanolamine (MEA, CDH purity 99%), Diethanolamine (DEA, CDH purity 99%) and Piperazine (PZ, CDH purity 99%) were used in this present study for synthesis of Barium Carbonate precipitate. All the solutions were prepared using deionized water. All chemicals were of analytical grade and used as received without further purification. Biogas was collected from floating type anaerobic digester present in Belvedere Printing Press, Allahabad.
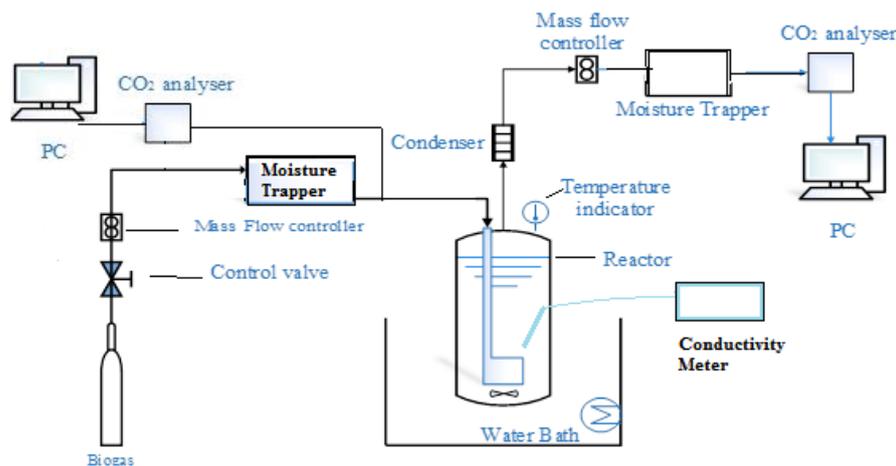

Figure 1: Experimental Setup

2.2 Absorption of CO_2

Figure 1 shows the experimental setup. In the precipitation experiment we have used a 50 gram of $BaCl_2.2H_2O$ dissolved in water with additives like MEA and DEA. Biogas with 80ml/min flow rate was firstly passed through activated carbon (filled in moisture trapper for removal) of small traces of Hydrogen sulphide,

water vapour and ammonia. The first step involves saturation of the amine, piperazine and barium chloride solution with CO_2 gas. Piperazine was diluted to a different concentration with balanced deionised water along with MEA and DEA. The CO_2 absorption reactor was filled with 1 Litre solution of $BaCl_2.2H_2O$, amines and piprazine. We maintained the temperature at 25º C, the pressure was 1 atm. The CO_2 was passed into the absorption reactor and outlet/inlet gas was evaluated using CO_2 analyser of different intervals after reacting with the alkaline solutions. Whole process was conducted for 1 h. Then, we separated the liquid and solid by filtration through filter paper. In addition, the system uses a Gas Chromatography to measure the initial and final gas composition. The aqueous solution used was collected for subsequent treatment.

3. Results and discussion

3.1 Carbonate Formation

The apparatus design is shgown in Figure 1 . In our experiment six different solution were taken solutions A-C consist of 1, 2 and 3 wt. % Piprazine respectively with 4% MEA, solutions D-F consist of 1, 2 and 3 wt. % piperazine respectively with 4% DEA . From the literature review we have decided to take 50 g of Barium salt instead of using molar equality due to economical consideration for future study at pilot plant scale. The amount of carbonates obtained from the alkaline solution is also displayed in increasing order A<D<B<E<C<F. In Table 1 amount of carbonate formed is shown. Most of the solutions were neutralized after the precipitation reaction was over. The pH of the final solution settled between 7-8 as mentioned in table 1. Initial and Final composition of biogas is also shown. 4% DEA and 3 % Piprazine shows higher capacity of barium carbonate formation along with 97% pure Methane.

Table 1: Amount Carbonates obtained, Initial and final pH of Solution , Initial and Final Composition of Biogas

Solution	Initial pH	Final pH	Amount of carbonates formed(g[sorbent L]$^{-1}$) (Biogas)	Biogas Composition Before (%)		Biogas Composition After(%)	
				CH_4	CO_2	CH_4	CO_2
1% PZ + 4 wt % MEA+ $BaCl_2$ (A)	12.32	7.82	34.1	65	35	90	10
2% PZ + 4 wt % MEA+ $BaCl_2$ (B)	12.73	7.63	41.2	65	35	92	8
3%PZ + 4wt % MEA + $BaCl_2$ (C)	12.96	7.16	47.2	65	35	94	6
1%PZ + 4 wt % DEA+ $BaCl_2$ (D)	12.40	7.90	37.7	65	35	93	7
2% PZ + 4 wt % DEA+ $BaCl_2$ (E)	12.72	7.70	46.1	65	35	95	5
3%PZ + 4 wt % DEA+ $BaCl_2$ (F)	13.03	7.03	49.6	65	35	97	3

3.2 Scanning Electron Microscopy (SEM)

Surface Morphology of the $BaCO_3$ was analysed using CARL ZEISS EVO 50 with Resolution - 2.0nm at 30kV, Acceleration Voltage-0.2 to 30 kV, Magnification-5x to 1,000,000x ,
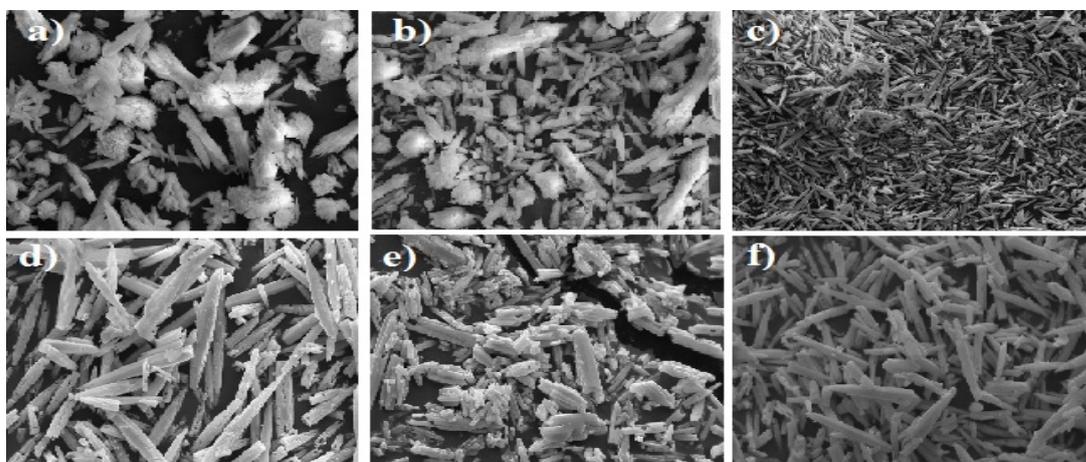

Figure 2: SEM micrograph of Barium Carbonate

Field of View-8.5 mm at the Analytical Working Distance (AWD), X-ray Analysis 8.5 mm AWD and 35° take-off angle, Detectors used were SE in HV - Everhart-Thornley and BSD in all modes - quadrant semiconductor diode. SEM technique is used to study the morphology of the precipitated Barium Carbonate. Fig. 2 shows the SEM pictures of carbonate samples. BaCO3 obtained from BaCl2 had rod like structure. Amines provided more stable structure as compared to the MEA. Amines provided needle shape structure of BaCO3 while NaoH showed less sized shaped rod. Our SEM micrograph was similar to the Gaur et al. 2010 and Park et al. 2013.
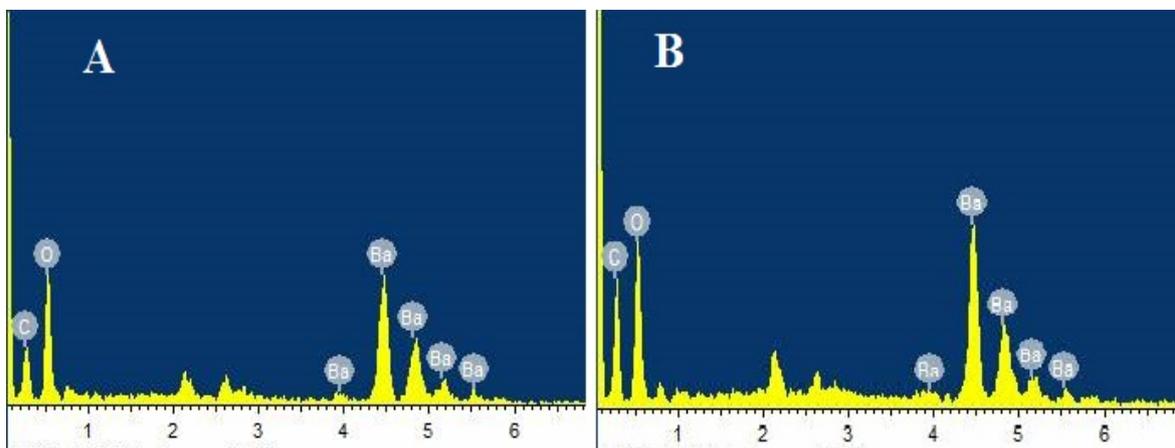

Figure 3: EDS micrograph of Barium Carbonate A) using 1% PZ B) using 3% PZ

For elemental analysis of the material further EDX was done to check the purity of Barium carbonate powder obtained after the experiment and there was no traces of impurity were present and DEA provides the more pure form of Barium Carbonate. Carbonate increased with the concentration of amines in the reactor, possibly due to the greater formation of BaCO3 during the precipitation reaction. The percentages of BaCO3 crystallinity were 78.9%, and 87.7% with MEA, and DEA respectively. The amount of absorbed CO2 in 1 wt% MEA remained in solution after forming the solid. First three images of MEA (A-C) and DEA (D-F) with increasing concentration 1-3% piperazine respectively. To determine the presence of other types of impurities, the salts were analyzed by EDS (figure no. 3).The entire spectra show same elements present in the barium carbonate that is Barium, Carbon and Oxygen. It was observed that BaCO3 formed by the MEA solution has more barium followed by the DEA. Solution with 3 wt. % PZ has higher % of barium and 1 wt % PZ has less Barium.

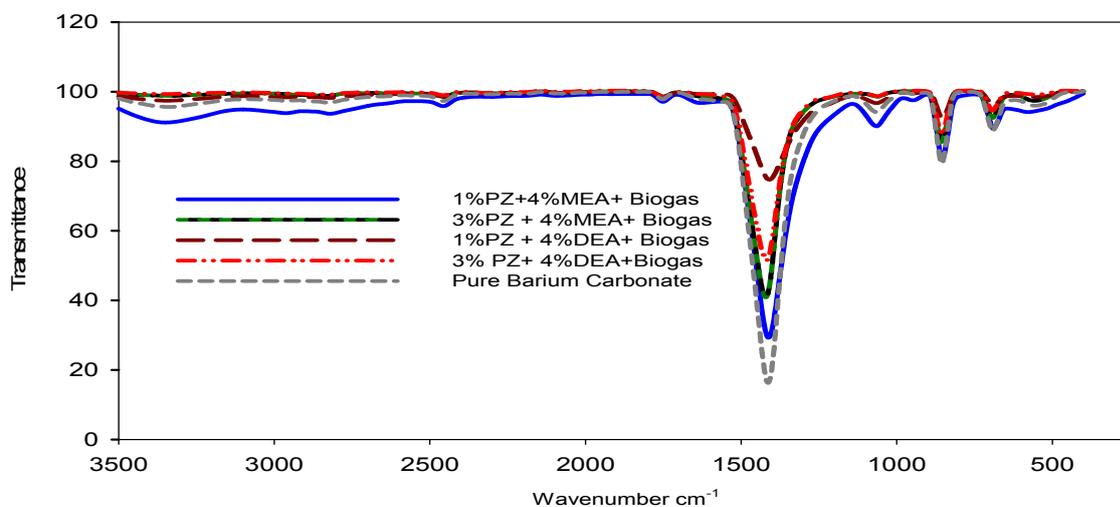**3.3 Fourier-transform infrared spectroscopy (FTIR)**

Figure 4: FT-IR graph of obtained Barium Carbonate.

The FT-IR spectra were measured on a ATR FTIR Spectrophotometer into the sample cell with a thickness of 0.005 mm between two KBr plates in the range of 3500- 400 cm-1. The uncertainty in the experimental results was found to be within ± 3% error. FTIR characterization of the Solid material obtained by the absorption of CO_2 for each concentration of 1-3(A-C respectively) wt % piperazine with 4% MEA and 1-3 (D-F respectively) wt % piperazine with 4% DEA was done(figure no. 4) . The spectra are similar to the spectrum of pure $BaCO_3$ which presents peaks primarily at k = 1428, 878 and 736 cm. The $BaCO_3$ salt obtained with DEA showed increased transmittance at higher concentration of piperazine, it was observed that 1% piperazine presents less intense peaks, 4% DEA with 3% piperazine shows that a greater concentration of the $BaCO_3$ salt was generated. The $BaCO_3$ salts obtained by varying the aqueous solution concentration showed that when increasing the piperazine concentration, the amount of $BaCO_3$ increases due to the greater availability of dissolved CO_2 ions.

3.4 X-ray Diffraction (XRD)

The $BaCO_3$ samples were filtered using filtration method and the separated solid was dried at 102º C for 2 hours before analysis. For morpholgy The X-ray diffraction (XRD) patterns of the $BaCO_3$ were recorded with Rigaku D/MAX-2400X-ray diffractometer system using a Cu Ka radiation (l ¼ 1.5406 Å) in the 2q range from 5º to 65º, operated at 40 mA and 40 kV, and a scanning speed of 10º Min-1. The solution (50 g $BaCl_2.2H_2O$+ MEA + water) was used in the experiment. A white precipitate was observed at bottom of the reactor at ambient temperature and pressure. The mixture was well mixed with magnetic stirrer.The solution was then filtered using a filter paper and the residue was dried in a vacuum oven at 102◦ C. The barium carbonate obtained using amines and $BaCO_3$ was characterized by XRD to determine its crystalline phase.
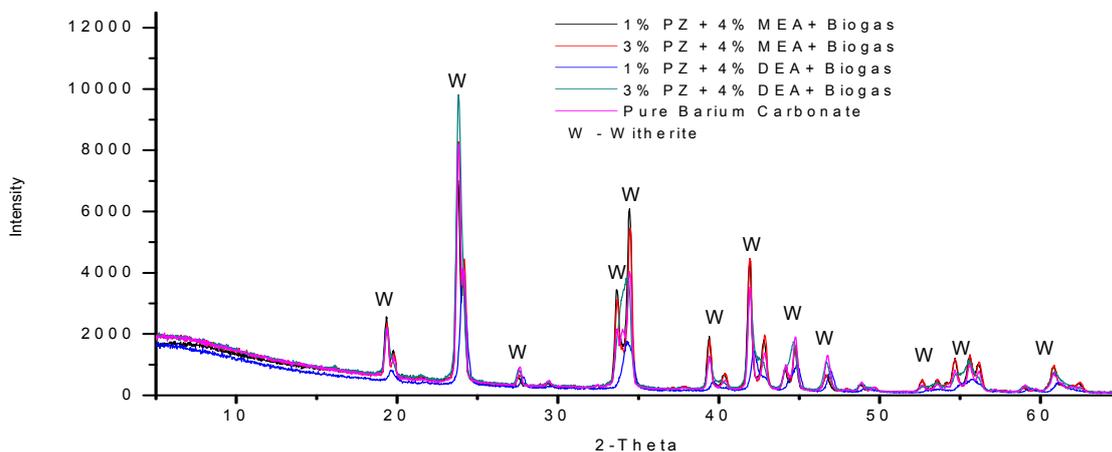

Figure 5: XRD of obtained Barium Carbonate

The results of the XRD analysis are shown in Fig. 5, As far as morphology is concerned X-ray diffraction pattern were obtained in this study as shown in Fig. 5 which matched the one numbered 41-0373 in JCPDS for orthorhombic $BaCO_3$ and We found that the different carbonate structure are derived from the amine structures. According to Fig 5, the peaks were characteristic of witherite. There is also no effect of Piperazine on the structure of $BaCO_3$. All the patterns are well matched with the pure $BaCO_3$.

4. Conclusion

Carbonation of CO_2 using amines, piperazine and Barium Chloride has shown much more advantage over other process. Using piperazine with MEA/DEA highly stable compound ($BaCO_3$.) of industrial grade is obtained simultaneously with 97% pure methane (acceptable in Indian subcontinent). Barium Carbonate obtained here by the carbonation method has wide range of Industrial application. From our results we can say that piperazine increases the absorption of CO_2 without affecting the properties of Barium Carbonate.From economic point view this process is very reliable and cost effective. The quality of methane obtained from this process is exceedingly high quality and it can be used in numerous processes like natural gas or in fuel cells. The process can be easily scaled up to industry level. India is developing country and this process can help obtain extremely pure methane and low-priced metal carbonates of industrial grade.

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