A Study of Upgrading Real Biogas via CO₂ Precipitation Route Under Indian Scenario

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Abstract – Our study focuses on upgrading real biogas obtained under Indian scenario using carbon capture and utilization (CCU) technology to remove carbon dioxide (CO₂) and utilize it by forming metal carbonate. Amines such as monoethanolamine (MEA), diethanolamine (DEA), and sodium hydroxide (NaOH) were used to rapidly convert gaseous CO₂ to aqueous CO₂ and BaCl₂ was used as an additive to react with the aqueous CO₂ and rapidly precipitating the aqueous CO₂. All experiments were conducted at 25 °C and 1 atm. We analyzed the characteristics of the BaCO₃ precipitates using X-ray diffractometry (XRD), scanning electron microscopy - Energy dispersive spectroscopy (SEM-EDS) and Fourier-transform infrared spectroscopy (FT-IR) analyses. The precipitates exhibited witherite morphology confirmed by the XRD results, and FT-IR confirmed that the metal salt formed was BaCO₃, and EDS showed that there were no traces of impurities present in it. The quantity of the BaCO₃ was larger when formed with DEA. Also, a comparison was done with a previous study of ours conducted in Korean conditions. Finally, we observed that the carbonate obtained using real biogas showed similar properties to carbonates available in the market. An economic analysis was done to show the cost effectiveness of the method employed by us.

Key words: Barium carbonate, Biogas, Precipitation, Methane, amines, Carbon dioxide

1. Introduction

Millions of dollars are invested in the generation of energy from the fossil fuels, and day by day fossil fuel supply is decreasing, so there is need for renewable sources of energy like biogas, wind, tidal and solar energy etc. Biogas production from waste biomass is one of the best mature renewable technologies present in the market [2-3] Biogas generation from the waste provides two simultaneous solutions to solid waste management and energy generation, which is favored by the current Swach Bharat policy of Indian Government. Biogas is mainly produced by the anaerobic digestion of biomass. Various designs of anaerobic digesters models like fixed and floating dome type digesters are used widely, but the floating type digester has gained much attention towards biogas generation due to ease of maintenance [4]. Biogas enhancement includes removal of CO₂ and other impurities like hydrogen sulfide, traces of ammonia and water vapor. Carbon dioxide capture and utilization (CCU) is one of the best ways to capture the CO₂ produced from biogas. Absorption process is one of the most common techniques for CO₂ removal. In the present scenario, one of the most effective methods for the uptake of CO₂ is the chemical absorption process, which usually employs aqueous solutions like amines, ammonia water and adsorption. The use of amines has certain disadvantage too, like corrosion and loss of amines due to volatile nature [20]. Ammonia water is also preferred over conventional amine absorbent due to high CO₂ loading [19]. Simultaneous removal of SO₂ and NOₓ along with CO₂ using amines makes the chemical absorption process more efficient [16]. DEA shows a higher CO₂ loading rate as compared to MEA [17]. A very high penalty cost is attached with the amine process for CO₂ capture from coal-fired plants [18]. Chemical absorption technique requires a huge amount of energy during the desorption step, which makes CO₂ capture uneconomical. To counter this problem, an effort was undertaken to convert CO₂ into solid carbonates [9]. In previous study, landfill gas was used in Korean conditions and CO₂ was successfully converted to carbonates [8-11]. This paper focuses on using a process similar to the earlier study, but the input gas is real biogas and pure CO₂. We have considered the Indian scenario instead of landfill gas. The data obtained during the present study is better than in the previous study [9]. The amount of carbonates formed is higher. Previous study [9] was just a technical note, so some technical and economic data are not mentioned. However, in the current study technical data such as biogas production rate, characterization of carbonates formed using techniques such as FTIR, XRD and SEM-EDS is covered. Also, economic analysis was done to show how converting CO₂ to carbonate makes the traditional CO₂ capture process profitable, which has not been discussed in literature till date. This technique really suits the Indian scenario and can make biogas plants a profitable venture.

2. Experimental

2-1. Materials

All the chemicals, such as MEA, DEA and NaOH, were pur-
chased from CDH (purity: >99%). Deionized water was used for solution preparation. All chemicals were of analytical grade and used as received without further purification. Fresh cow dung and water were obtained from the Narayani Ashram, Allahabad.

2-2. Absorption of CO$_2$

In the precipitation experiment we used 50 grams of BaCl$_2$ dissolved in water with additives like amines and NaOH. The first step involved saturation of the amine and BaCl$_2$ solution with biogas and pure CO$_2$ gas. Each amine was diluted to a different concentration with balance deionized water. The CO$_2$ absorption reactor was filled with 1 Liter solution of BaCl$_2$ and amines. We maintained the temperature at 25°C and 1 atm pressure. The biogas was passed into the absorption reactor and outlet/inlet gas was evaluated using CO$_2$ analyzer of different intervals after reacting with the amine solution. The entire process was conducted for 1 h. Then, we separated the liquid and solid by filtration through filter paper. In addition, we used gas chromatography to measure the initial and final biogas composition.

The reactions of primary and secondary amines with CO$_2$

\[
\text{CO}_2 + R_1R_2\text{NH} \leftrightarrow R_1R_2\text{NH}^+ \text{CO}_2^-
\]

(1)

\[
R_1R_2\text{NH}^+ \text{CO}_2^- + R_3R_4\text{NH} \leftrightarrow R_1R_2R_3R_4\text{NH}^+ + R_3R_4\text{NCO}_2^-
\]

(2)

\[
R_1R_2\text{NH}^+ \text{CO}_2^- + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + R_1R_2\text{NCO}_2^-
\]

(3)

\[
2\text{RNH}_2 + \text{CO}_2 \leftrightarrow \text{RNH}_3\text{CO}_2^- \text{RNH}_3^+
\]

(4)

\[
\text{RNH}_2\text{HCO}_3^- \leftrightarrow \text{RNH}_2\text{HCO}_3^- + \text{RNH}_2
\]

(5)

\[
\text{RNH}_3\text{HCO}_3^- + \text{RNH}_2 \leftrightarrow 2\text{RNH}_3\text{CO}_2^-\text{RNH}_2
\]

(6)

\[
2\text{RNH}_3\text{CO}_2^- + \text{BaCl}_2 \leftrightarrow 2\text{RNH}_32\text{Cl}^- + \text{BaCO}_3
\]

(7)

Fig. 1. A. Anaerobic digester setup used during this study B. Exact dimensions of anaerobic digester.

Fig. 2. Schematic diagram of carbonation experimental apparatus.
2-3. Physical Characterization
The X-ray diffraction (XRD) patterns of the BaCO_3 were recorded with Rigaku D/MAX-2400 X-ray diffractometer system using a Cu Ka radiation (λ 1.5406 Å) in the 2θ range from 5º to 65º, operated at 40 mA and 40 kV, and a scanning speed of 10º Min⁻¹. The FT-IR spectra were measured on an ATR FTIR spectrophotometer into the sample cell with a thickness of 0.005 mm between two KBr plates in the range of 4000 - 400 cm⁻¹. Surface morphology of the BaCO_3 was analyzed using CARL ZEISS EVO 50 with resolution - 2.0 nm at 30 kV, acceleration Voltage-0.2 to 30 kV, magnification-5x to 1,000,000x, field of view-8.5 mm at the analytical working distance (AWD), X-ray analysis 8.5 mm AWD and 35º take-off angle; detectors used were SE in HV - Everhart-Thornley and BSD in all modes - quadrant semiconductor diode.

3. Results and Discussion
3-1. Biogas Production
The biogas was obtained from a real biogas plant situated in Narayani Ashram near our University. The photograph and dimensions of the real biogas plant are in Fig. 1. The gas holder volume was 0.75 m³; brick insulation of around 10 cm was done around anaerobic digester to maintain the temperature. The feed rate was around 5 kg per day. Biogas was produced from cow dung over a period of 29 days and it increased gradually as mentioned in Fig. 3. Biogas production increased progressively after the 16th day. The biogas was analyzed using GC and it was mainly composed of CO_2, CH_4, H_2S, water vapor and ammonia. The components of biogas are mentioned in Table 1. Methane was present in the range 55-65 volume %, CO_2 was present in the range 35-40%, and rest of the components were less than 5%. Our analysis matched the references [5-7] as discussed in Table 2. We used high quality silica gel before the biogas entered the reactor. Silica gel effectively removed all the minor components present in the biogas. The biogas entering into the reactor mainly consisted of methane CH_4 and CO_2. The Indian subcontinent provides the ideal temperature for high quality methane production.

It was observed that the digester temperature fluctuated between 28 ºC and 35 ºC while the pH of the medium was between 6.5-7.2. In the anaerobic digestion the pH initially decreased to 6.6, and after the thirteenth day pH was around 7, as displayed in Fig. 4. In biogas generation, pH plays a vital role; if pH is decreased beyond 6 then no biogas is generated. The range of temperature and pH matched the reference data [5-7], as mentioned in Table 2.

Methanogens produce methane as a metabolic by-product in anaerobic conditions. They uniquely belong to the archaea kingdom, which are very pH sensitive, so it is mandatory to maintain the pH around 7 and temperature above 25 ºC.

Volatile fatty acid (VFA) also plays a vital role in gas production; as we can observe from Fig. 5 that cow-dung in 1:1 ratio mixtures with water gives a high VFA as compared to cow dung 1:2 ratio mixture. The VFA value obtained by us matched the VFA in references which used cow dung as a feed as mentioned in Table 2.

3-2. Carbonate formation
There are nine different types of prepared solutions which are marked as A, B, C, D, E, F, G, H and I. Solutions A, B and C consist of 1, 2 and 3 wt% NaOH, respectively; solutions D, E and F consist of 1, 2 and 3 wt% MEA, respectively; solutions G, H and I consist of 1, 2 and 3 wt% DEA, respectively. The pH of the final solution set-

<table>
<thead>
<tr>
<th>Table 1. Concentration of main components present in biogas</th>
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<tbody>
<tr>
<td>Main Components</td>
</tr>
<tr>
<td>Methane (CH_4)</td>
</tr>
<tr>
<td>Carbon Dioxide (CO_2)</td>
</tr>
<tr>
<td>Hydrogen Sulfide (H_2S)/water vapor/Ammonia</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Comparison of parameters measured in anaerobic digester</th>
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</thead>
<tbody>
<tr>
<td>Parameters</td>
</tr>
<tr>
<td>VFA</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
</tbody>
</table>
settled between 7~8 as mentioned in Table 3. Taking a cue from our previous work [9], we decided to take 50 g of Barium salt. The amount of carbonates obtained from the alkaline solution is also displayed in increasing order D<G<A<E<H<F<B<I<C. In Table 4 the amount of carbonate formed is displayed. Most of the solutions were neutralized after the precipitation reaction was over. We can also observe in Table 5 that quantity of carbonates obtained during the current study is higher than in the previous study.

3-3. FTIR

FTIR characterization of the precipitated BaCO₃ obtained by the absorption of CO₂ was done. The result of the FTIR graph is shown in Fig. 6. The spectra are similar to the spectrum of pure BaCO₃ which presents peaks primarily at k = 1428, 878 and 736 cm⁻¹. The BaCO₃ salt obtained from pure CO₂ and biogas showed increased absorbance at higher concentration, which was similar to characteristics of pure BaCO₃. Similar peak was observed in [13]. Both the FTIR results showed that there is not much difference in property of barium carbonate obtained from different gas input.

3-4. XRD

The barium carbonate obtained using amines and BaCl₂ was char-

Table 3. Change in pH of different solutions before and after passing biogas

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Initial pH</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% NaOH + 50g BaCl₂·2H₂O (A)</td>
<td>12.89</td>
<td>7.93</td>
</tr>
<tr>
<td>2 wt% NaOH + 50g BaCl₂·2H₂O (B)</td>
<td>12.50</td>
<td>7.86</td>
</tr>
<tr>
<td>3 wt% NaOH + 50g BaCl₂·2H₂O (C)</td>
<td>12.10</td>
<td>7.62</td>
</tr>
<tr>
<td>1 wt% MEA + 50g BaCl₂·2H₂O (D)</td>
<td>12.82</td>
<td>7.52</td>
</tr>
<tr>
<td>2 wt% MEA + 50g BaCl₂·2H₂O (E)</td>
<td>12.03</td>
<td>7.13</td>
</tr>
<tr>
<td>3 wt% MEA + 50g BaCl₂·2H₂O (F)</td>
<td>11.16</td>
<td>7.16</td>
</tr>
<tr>
<td>1 wt% DEA + 50g BaCl₂·2H₂O (G)</td>
<td>13.20</td>
<td>7.80</td>
</tr>
<tr>
<td>2 wt% DEA + 50g BaCl₂·2H₂O (H)</td>
<td>12.72</td>
<td>7.60</td>
</tr>
<tr>
<td>3 wt% DEA + 50g BaCl₂·2H₂O (I)</td>
<td>12.03</td>
<td>7.03</td>
</tr>
</tbody>
</table>

Table 4. Amount of carbonates formed using biogas and pure CO₂

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Amount of carbonates formed (g[sorbent L⁻¹]) (biogas)</th>
<th>Amount of carbonates formed (g[sorbent L⁻¹]) (pure CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% NaOH + 50g BaCl₂·2H₂O (A)</td>
<td>22.3</td>
<td>30</td>
</tr>
<tr>
<td>2 wt% NaOH + 50g BaCl₂·2H₂O (B)</td>
<td>36.6</td>
<td>40</td>
</tr>
<tr>
<td>3 wt% NaOH + 50g BaCl₂·2H₂O (C)</td>
<td>48.8</td>
<td>54.8</td>
</tr>
<tr>
<td>1 wt% MEA + 50g BaCl₂·2H₂O (D)</td>
<td>12.7</td>
<td>24.1</td>
</tr>
<tr>
<td>2 wt% MEA + 50g BaCl₂·2H₂O (E)</td>
<td>26.2</td>
<td>34.2</td>
</tr>
<tr>
<td>3 wt% MEA + 50g BaCl₂·2H₂O (F)</td>
<td>36.3</td>
<td>43.2</td>
</tr>
<tr>
<td>1 wt% DEA + 50g BaCl₂·2H₂O (G)</td>
<td>16.6</td>
<td>24.7</td>
</tr>
<tr>
<td>2 wt% DEA + 50g BaCl₂·2H₂O (H)</td>
<td>28</td>
<td>36.1</td>
</tr>
<tr>
<td>3 wt% DEA + 50g BaCl₂·2H₂O (I)</td>
<td>39</td>
<td>45.6</td>
</tr>
</tbody>
</table>

Table 5. Comparison of current work with [9]

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Amount of carbonates formed (g[sorbent L⁻¹]) (Biogas)</th>
<th>Amount of carbonates formed (g[sorbent L⁻¹]) (pure CO₂)</th>
<th>[9] (g[sorbent L⁻¹]) (Landfill Gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt% NaOH + 50g BaCl₂·2H₂O (J)</td>
<td>49</td>
<td>56</td>
<td>NA</td>
</tr>
<tr>
<td>5 wt% MEA + 50g BaCl₂·2H₂O (K)</td>
<td>40</td>
<td>48</td>
<td>34</td>
</tr>
<tr>
<td>5 wt% DEA + 50g BaCl₂·2H₂O (L)</td>
<td>42</td>
<td>49.2</td>
<td>35.90</td>
</tr>
</tbody>
</table>

Fig. 5. Variation in between VFA and Time (days) for different ratio of cow dung and water.

Fig. 6. FTIR of BaCO₃ obtained from pure CO₂ and biogas.
A study of upgrading real biogas via CO$_2$ precipitation route under Indian scenario

Fig. 7. XRD graph of BaCO$_3$ obtained from (A) pure CO$_2$ and (B) Biogas.

Fig. 8. A and C- SEM of Barium carbonate obtained from pure CO$_2$. B and D EDS of Barium carbonate obtained from biogas.
more stable BaCO₃ as compared to the other amines due to more absorbance of CO₂ ions and precipitation of aqueous CO₂ in carbonate. Obtained BaCO₃ was also compared to the other studies done by other researchers, and we found that similar peaks were obtained [8-10]. The h,k,l value can be readily indexed as (110), (111), (002), (112), (220), (221), (132) and (113).

3-5. SEM-EDS of BaCO₃

Fig. 8 shows the SEM micrograph of carbonate samples. BaCO₃ obtained from BaCl₂ had nanorod-like structure. As we can see, the graph obtained from the biogas provided more stable structure as compared to the pure CO₂. When pure CO₂ was used for the reaction, it provided less nanorod-type shape structure of BaCO₃ [8]. In Fig. 8B the nanorods are of inferior quality as compared to Fig. 8A due to the presence of some impurities present in biogas, whereas pure CO₂ provides sharper rods. Our barium carbonate SEM was compared to other studies, and we found similar data when conventional method was used for barium carbonate production. Similar images were obtained by other researchers [8]. For elemental analysis of the material, further EDS was performed. No traces of impurity were present. Our micrograph and EDS confirmed that it was similar to the pure BaCO₃ obtained from other conventional methods. The main mineral was Ba. EDS of all samples is shown in Fig. 8. The entire spectrum shows similar elements present in the barium carbonate: barium, carbon and oxygen. It was observed that BaCO₃ formed by the biogas had more Barium as compared to the pure CO₂. The main target of this research was to produce high quality barium carbonate which can be directly sold in the market. Nanorod BaCO₃ has wide range of application even in fuel cells as an alkali-earth metal-carbonate-based catalyst [14].

### 3-6. Economics

For calculating the economic feasibility of the process we considered a biogas plant which can be fed with 1000 kg cow dung every day. Most of the dairy farms in India have around 100 cows, which can generate around 1000 kg cow dung, which produces around 20 kg of CH₄ and 27 kg of CO₂. The detailed economy comparison of MEA-based process and BaCO₃ process is displayed in Table 6.

As we can observe from Table 6, using just amines for CO₂ removal is not economical as we end up paying a penalty of 27.4 USD per kg of methane produced. Using BaCO₃ route we are able to make a profit of 14 USD per kg of methane produced, which makes the carbonate route an effective CO₂ removal technology. Detailed economic analysis will be done in future studies.

According to the Indian standard, when using methane for automotive purposes the methane content should be minimum 90%, which we can easily obtain via the BaCO₃ route for CO₂ capture.

### 4. Conclusion

Carbonation method was used in purification of real biogas using amines and BaCl₂. Barium carbonate formed by the carbonation method has wide use in the glass, ceramic and paint industries. From economical point of view, this process is very reliable and cost-effective as compared to other methods. The process is extremely economical and simple to scale up. The quality of methane obtained from this process is exceedingly high quality and it can be used in numerous processes.

### References

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A study of upgrading real biogas via CO$_2$ precipitation route under Indian scenario


