Simultaneous Biogas Upgrade and Production of Precipitated Calcium Carbonate

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Abstract. Biogas upgrading is a necessary step to remove impurities and increase a calorific value of biogas before it can be used as a proper energy source. The most significant impurity in raw biogas is typically carbon dioxide, composing up to 50% of biogas volume. Carbon dioxide capture is therefore an important part of the upgrading process which in turn raises the question of the availability of final carbon storage. This problem can be addressed by using calcium hydroxide solution or other lime-based solvents as scrubber in carbon dioxide capture via carbonation where precipitated calcium carbonate (PCC) is formed as a by-product. This paper reviews the viability of packed column, bubble column, and spray column for simultaneous biogas purification by CO$_2$ capture and PCC synthesis, as well as examining various parameters that affect both carbon dioxide capture and the production of PCC. Among the three reviewed types of contactors, only packed column is deemed unsuitable for the simultaneous process. The optimal condition for both carbon dioxide scrubbing efficiency and PCC yield can be obtained by using a high liquid flow rate, low gas flow rate, and high solvent concentration. However, the desired characteristics of PCC should be considered in determining the operating parameters as the said characteristics such as crystal phase, morphology, and particle size are affected by several operating parameters, namely gas flow rate, solvent concentration, temperature, size of bubbles, and concentration of additives.

1. Introduction
Biogas is the gaseous product of organic matter degradation through anaerobic processes. The digestive process needed to produce biogas is typically composed of four steps: hydrolysis, acidification, acetogenesis, and methanogenesis. In order for bacteria to be able to degrade biomatter effectively, certain conditions need to be met which include: 1) anaerobic condition; 2) optimum temperature; 3) constant nutrient supply, and 4) optimum acidity or pH [1]. According to the German Solar Energy Society and IEA Bioenergy as cited by Akunna (2019) [2], the typical raw biogas is composed of 50-75% methane, 25-50% carbon dioxide, 0-10% nitrogen, 0-10% water vapor, 0.01-3% hydrogen sulfides, and other trace amounts of impurities. Removing these impurities, especially carbon dioxide, which is present in high quantities, is an important step in upgrading raw biogas to a viable fuel. The technologies available today are capable of removing most of these impurities and significantly increase the calorific value of biogas. One of the obstacles in using the current upgrading technologies is the availability of final storage for the scrubbed carbon in alignment with the carbon capture and storage (CCS) principle. Such is the case for the more commonly used chemical scrubbing using amine-based solutions. Amine
solution such as MEA and DEA has been used in solvent-based carbon dioxide capture for more than 90 years, commonly used in coal-fired power plants. It has the major advantages of achieving high efficiencies in removing carbon dioxide and its capability to be regenerated. However, finding a suitable place for the removed carbon dioxide has been a known challenge using amine-based solvent [3,4].

Other technologies have been developed to separate carbon dioxide directly into places for storage or sequestration. A method to achieve that using solvent-based CO₂ scrubber involves using calcium hydroxide as a solvent. In this process of carbonation/precipitation, Ca(OH)₂ is dissolved into Ca²⁺ and OH⁻ ions, while CO₂ is absorbed into water and form CO₃²⁻ carbonate ions. The Ca²⁺ and CO₃²⁻ would then bond and precipitate as CaCO₃ or precipitated calcium carbonate (PCC) which is a valuable by-product [5]. While the chemical composition of PCC is identical with ground calcium carbonate (GCC), its main difference with GCC lies in its production process and physical properties. GCC is typically produced by directly grounding earth minerals or limestones. The GCC end product would have the same purity as the feed limestone and with a much broader range of size distribution compared to PCC. Morphologically, GCC particles are typically irregular rhombohedral crystals whereas PCC has more regular and uniform crystalline forms [6].

Depending on the operating condition of the reaction, PCC particles can be obtained in three different crystal polymorphs, namely are calcites, aragonites, and vaterites. Calcites are known to be the most thermodynamically stable, while aragonites are metastable and would gradually convert into calcites. Vaterites are by far the most unstable polymorph and are rarely seen in naturally occurring minerals. Calcite polymorphs typically have trigonal or rhombic crystalline structures such as rhombohedral, prismatic, and scalenohedrons. Vaterites are mostly spherical while aragonite polymorphs form needle-like structures [6,7]. By itself, PCC can be marketed in various grades according to the particle size, size distribution, and morphology, where its production is tailored according to each of their specific application. In paper industry, PCC is used to enhance the optical properties and print characteristics in paper as filler or coating pigment whereas in polymer industry, PCC is commonly used to manipulate various physical properties such as impact strength and viscosity of polymers including but not limited to PVC, urethane, silicone, and paint [8]. The crystal morphology of PCC is an important factor in determining specific properties of the particles such as light dispersion. Nanometer-sized rhombohedral PCC is particularly effective as coating in paper industries [9].

Several types of research have been done to simultaneously purify biogas and synthesize PCC. Baena-Moreno et al. (2018) conducted this with indirect aqueous carbonation method using NaOH aqueous solution. First, the carbon dioxide from biogas is absorbed into NaOH solution to form sodium carbonates, which will then be contacted with Ca(OH)₂ solution to regenerate the used NaOH and form calcium carbonates by precipitation [10]. In another study, Madhania et al. (2020) achieved the production of PCC from a biogas upgrading unit by direct carbonation method using Ca(OH)₂ solution with a bubble column contactor [11]. The experiment obtained PCC with the crystalline phase of calcite, as previously observed in the research conducted by Baena-Moreno et al. Based on these experiments, biogas purification and the synthesis of PCC can be conducted simultaneously. This paper is written with the goal of reviewing contactor types, specifically packed columns, bubble columns, and spray columns to determine the viability of each contactor types for simultaneous CO₂ absorption and PCC synthesis, as well as examining the effect of operating parameters specifically solvent concentration and reactant flow rates on CO₂ absorption and PCC synthesis based on previous studies. The effect of operating parameters on PCC production is examined from the apparent yield and particle characteristics of PCC, namely crystal phase, morphology, and particle size.

2. Review of contactor types on CO₂ capture by chemical absorption

Biogas scrubbing using solvents can be done using various types of contactors, the most common ones being packed column, bubble column, and spray column. While the type of contactors is definitely one of the performance factors, other factors in operating conditions can also significantly affect efficiency and performance, such as solvent concentration and the flowrates of gas and liquid.
2.1. Packed columns

Packings are often preferred for gas-liquid contactor due to the high surface area for mass transfer provided by the packing materials. Packing columns are widely used for absorption and separation due to their versatility for capacity increase and the wide range of options for packing materials, hence they are usually more economical than other types of contactors such as tray columns. The two types of typically used packing materials are structured and random packings which are packed into inside a vertical column where the gas and liquid would contact [12]. Packed columns do have some caveats, however. For instance, the efficiency of the column can significantly be reduced when the liquid feed is unevenly distributed, such as when the liquid flows down next to the column wall where the packings are less dense and bypasses a large section of the column, a condition known as channelling. Packed columns are also vulnerable to the flooding phenomenon, where if the gas velocity is too high it can cause the liquid to fill the column and increase the internal pressure, leading to higher pressure drop and an increased chance for the packings to be damaged. Moreover, for reactions that result in solid precipitates, depositions may form on the packing surfaces over time, leading to lower mass transfer coefficients and damages to the packing material [13]. The use of packed columns as CO$_2$ scrubber has been extensively studied in the past. In a past study, an experiment was conducted to observe the performance of a packed column in purifying biogas by absorbing CO$_2$ and comparing NaOH, Ca(OH)$_2$, and MEA as solvents. The study found that the different kinds of solvents vary in performance and CO$_2$ absorption capacity, but overall, the packed column has managed to remove over 90% of CO$_2$ from the raw biogas [14]. Other than the type of absorbent, other parameters that will affect CO$_2$ absorption in a typical packed column are the flowrates and concentrations of gas and liquid feed, operating temperature, CO$_2$ loading, and packing design [15]. Several studies have found that structured packings provide an overall better performance compared to random packings due to higher interfacial area and relatively lower pressure drop [16,17,18]. Unfortunately, no studies have been done on PCC synthesis using a packed column. As described previously, it is likely that using a packed column for PCC production would be problematic due to the likelihood of depositions forming on the packings’ surfaces.

2.2. Bubble columns

One of the extensively used contactors in multiphase processes are bubble columns which consist of a cylinder column and a bubble generator at the bottom to disperse the gas feed. The main advantages of a bubble column contactor are its simple design and construction, high removal efficiency, and the high mass and heat transfer coefficients it provides, leading to higher mass and heat transfer rates [19]. A previous research, the absorption of CO$_2$ using a bubble column contactor and BaCl$_2$ solution as solvent was studied. The column’s performance is evaluated from the parameters of pH by adding a controlled concentration of NaOH, gas superficial velocity, liquid flow rate, and the feed concentrations. Of the other factors, pH and gas superficial velocity seemed to be the parameters that affect the performance the most. In the study, the contactor’s performance was evaluated based on the amount of CO$_2$ absorbed per amount of absorbent and unit volume of the scrubber, then compared the scrubbing factor of the bubble column in their experiment with packed column contactors from other studies. They have found that compared to packed columns, bubble columns have higher scrubbing factor, indicating that bubble columns are more effective in scrubbing CO$_2$ [20]. It should be noted, however, that these other studies using packed column contactors used a different kind of solvent and different operating conditions. Bubble columns has also been proven effective as biogas scrubber as well as for synthesizing PCC, as has been done in a previous study [11].
2.3. Spray columns

Spray columns are one of the more popular alternatives to packed columns as wet scrubbers. While spray columns have typically lower efficiency than packed column for scrubbing gaseous contaminants, the drawbacks of packed column such as high pressure drop and operational cost have made spray columns more attractive as alternative for gas scrubbers. Comparatively, spray columns have a simpler design and construction, lower pressure drop, and lower operating costs. Furthermore, spray columns are effective to use in gas-liquid transfer cases where precipitates form [21]. According to one study, the removal efficiency of spray columns can be increased by adjusting operating conditions such as pressure, nozzle type, and number of stages [22]. One study found that using a larger nozzle may significantly increase the mass transfer coefficient, although using a nozzle with smaller orifice size is more favourable for low liquid flow rates since the droplets are not fully developed if larger nozzles are used, leading to lower interfacial area and mass transfer coefficient. The same study compared the mass transfer performance in a spray column and a packed column and found that the spray column gives a much higher mass transfer coefficient due to the higher interfacial area the nozzle provides [23]. As the efficiency can seemingly rival that of a packed column and having none of a packed column’s drawbacks, the application of spray columns as CO$_2$ scrubber is promising. The main disadvantages of using a spray column is the high pumping cost for forcing the solvent through the nozzles and the relatively lower mass transfer rates caused by droplet coalescence and the wetting of internal column walls [24].

| Contactor      | Advantages                                         | Disadvantages                                         | Ref.       |
|----------------|----------------------------------------------------|-------------------------------------------------------|------------|
| Packed column  | - High availability of mass transfer area          | - Higher operational cost                              | [13],[16]  |
|                | - High absorption efficiency                       | - Higher pressure drop                                 |            |
|                | - High absorption rate                             | - Chance of channeling and/or flooding                 |            |
|                |                                                    | - Deposition of precipitates on packing surfaces       |            |
| Bubble column  | - High absorption efficiency                       | - Limited research regarding the use of bubble columns as CO$_2$ scrubber | [19][20]   |
|                | - Simple design and construction                   |                                                      |            |
|                | - High absorption rate                             |                                                      |            |
| Spray column   | - Simple design and construction                   | - High pumping cost                                    | [21],[22], |
|                | - Low pressure drop                                | - Low mass transfer rates due to formation of liquid film | [23],[24]  |
|                | - Relatively cheaper operational cost              |                                                      |            |

3. The effects of operating conditions on CO$_2$ capture and PCC production

3.1. CO$_2$ capture by chemical absorption

3.1.1. Solvent concentration. One of the parameters that significantly affect a scrubber’s removal efficiency is the concentration of the liquid-phase solvent used, no matter what type of contactor or what kind of solvent is used. Several studies found that whether an amine-based solution such as MEA or DEA, the most widely used solvent for CO$_2$ chemical absorption, or Ca(OH)$_2$ aqueous solution is used,
increasing the solvent concentration tend to increase the removal efficiency. This is because the higher the solvent concentration, more active absorbents are available and therefore will lower the CO\textsubscript{2} loading [25,26,27]. However, increasing absorbent concentration will also lead to higher costs, so more consideration should be taken whether the increase of absorption efficiency will be worth the additional cost.

3.1.2. Gas and liquid flow rates. Many studies involving CO\textsubscript{2} absorption have reach the conclusion that increasing gas flow rates will decrease CO\textsubscript{2} removal percentage, due to shorter contact time between the gas and liquid phases [16,27]. Conversely, it is well agreed in various experimental studies that higher solvent flow rates will result in better removal efficiencies. The reason for this is because higher liquid flow rates will lead to the increase of active absorbents available and the increase of wetted packing surface for packed column, hence increasing mass transfer rates [13,15,16].

3.2. PCC synthesis by carbonation
Precipitated calcium carbonates can be synthesized as a valuable by-product of CO\textsubscript{2} absorption by means of carbonating aqueous solution of Ca(OH)\textsubscript{2}. Quality of PCC can be graded according to its physical and chemical properties, such as particle size and size distribution, purity, and morphological features, which are affected by various operating conditions. One of the parameters also affected by the differing operating conditions which could be of great interest for PCC production is the yield of PCC.

3.2.1. Purity and yield. PCC has the typical purity of over 99% where it can be directly used for industrial applications. The carbonation method for synthesizing PCC has the advantage of low operating cost and producing PCC with higher yield and purity. If done without the usage of additives, the carbonation method is considered as an environmentally friendly approach to produce calcium carbonates due to the consumption of carbon dioxide [28]. In one study, the formation of PCC with average purity of 98.6\% by carbonating milk-of-lime suspension was observed. The same study showed that decreasing gas flow rate from 379.5 to 224 ml/min and increasing solvent concentration from 0.2 to 1 M has decreased the purity of the final product from 99\% to 98\%, indicating that CO\textsubscript{2} flow rate and/or solvent concentration may affect the purity of PCC, albeit insignificantly [29]. A different study showed that the yield of PCC can be increased by increasing solvent concentration and operating temperature. A low pH has also been observed to reduce PCC yield. According to the researcher, this was caused by PCC’s instability in acidic conditions. The same study showed that using higher concentrations of polyethylene glycol additive increases the yield of PCC [30]. In a prior research, the increase of PCC yield was observed from increasing reactant concentration using Ca(OH)\textsubscript{2} direct carbonation. Furthermore, the experiment showed that the addition of sucrose to the solvent solution can increase the yield of PCC by increasing the solubility of Ca components in the solution [11].

3.2.2. Crystal phase and morphology. The typical phase of PCC synthesized in near-room temperature is observed to be calcite [10,11,29,30,31,32]. While the crystalline phase of the PCC does not seem to be affected by the reactant concentration [30,31], one study shows that the morphological features of calcite phase PCC differed by using different concentrations of solvent. In the study, low concentration of 0.2 M resulted in rhombohedral calcites, and increasing the MOL concentration to 0.56 and 2 M resulted in prismatic and scalenohedron calcites respectively [29]. Operating temperature has been observed to be the most significant factor to the phase of the final PCC product. Heating the solution to 50°C led to vaterites being formed alongside calcites, and further increase of temperature up to 80°C has been observed to promote the formation of aragonite phase crystals. Heating to 100°C and above showed dominantly calcite phase crystals forming [33,34]. Other than temperature, one study has reported that gas flow rate seemed to influence the crystal phase of PCC. Higher flow rates in constant temperature led to faster precipitation and supersaturation, limiting vaterite transformation to calcite phase and hence resulting in a larger percentage of spherical vaterite polymorphs [35]. His findings were different from those observed by Jimoh et al. (2017), where the latter’s experiment showed the increase of gas flow
rate affected the morphology and size of the particles while the crystalline phase remain unaffected [29]. It may be attributed to the lower flow rate variables used in the study (224 mL/min and 379.5 mL/min). Han et al. observed the appearance of vaterite polymorphs in significant numbers (vaterite fraction > 0.3) when the gas flow rate is nearing 1 L/min. It has also observed that higher initial concentration of solution promotes the formation of PCC. These findings are in agreement with the results of an experiment conducted by another study in which the increase of vaterites were observed as the gas flow rate was increased from 1 to 3.3 L/min [33]. Below is a table summarizing how various operating conditions influence the polymorph and structure of PCC particles.

| Operating conditions | Crystalline phase | Particle shape | Ref |
|----------------------|------------------|----------------|-----|
| Gas flow rate (L/min) | Temperature (°C) | Solvent concentration (mol/L) | Solvent | Crystalline phase | Particle shape |
| 0.22-0.38 | 25 | 0.2-1 | MOL | Calcite | Rhombohedral [29] |
| 0.38 | 25 | 2 | MOL | Calcite | Prismatic [20] |
| 0.38 | 25 | 2.2 | MOL | Calcite | Scalenohedron [29] |
| 0.5 | 250 | 0.41 | Ca(OH)₂ | Calcite | Rhombohedral [34] |
| 0.9 | 25 | 0.3-0.5 | Ca(OH)₂ | Calcite | Rhombohedral [35] |
| 0.9 | 25 | 0.001-0.1 | Ca(OH)₂ | Vaterite | Spherical [35] |
| 1.8 | 25 | 0.1 | MOL | Vaterite | Spherical [29] |
| 0.5 | 25-100 | 0.41 | Ca(OH)₂ | Vaterite | Spherical [34] |
| 0.9 | 60 | 0.001 | Ca(OH)₂ | Aragonite | Needle-like [35] |
| 0.5-3.3 | 50-250 | 0.41 | Ca(OH)₂ | Aragonite | Needle-like [33],[34] |

3.2.3. Particle size. Various studies have reported that in using carbonation method, the particle size of PCC can be reduced by lowering gas flow rate, typically averaging between 1-3 microns from carbonation in ambient temperature [29,36]. Using microbubble generator or MBG to produce PCC seemed to result in a significantly finer particle size compared to conventional bubble column and air diffuser, and therefore bubble diameter seemingly affects the size of CaCO₃ particles produced. While using MBG, the flow rate of CO₂ does not significantly affect particle size of PCC [31,37]. According to one study, coarser particles of PCC possess better optical properties than finer particles, due to larger percentage of impurities in the finer particles [38]. It is therefore important to consider the desired characteristics of the PCC product when deciding for an operating parameter.

4. Conclusions
Out of the three reviewed types of contactors (packed columns, bubble columns, and spray columns) bubble and spray column have been determined to be preferable for simultaneous biogas upgrade and PCC production. Microbubble generators have been reported to be effective for absorbing CO₂ and producing PCC with finer particle size compared to conventional bubble columns. The effects of operating conditions, specifically solvent concentration, solvent flow rate, and gas flow rate have been examined. Using a low CO₂ flow rate, high solvent flow rate, and high solvent concentration leads to typically favorable conditions, with higher CO₂ removal percentage and higher yield of PCC. However, the desired characteristics of PCC product should be considered when deciding on operating parameters as the characteristics of PCC are significantly affected by operating conditions such as temperature, solvent concentration, and feed flow rate. Additionally, the presence of additives such as sucrose and polyethylene glycol have been reported to increase the yield of PCC as well as drastically influence particle size, although the effect of additives on CO₂ removal efficiency has not been thoroughly researched. This shows that there is promising opportunity for further development of technology and research in simultaneous biogas purification and PCC production.
References

[1] Gomez C D C 2013 Biogas as an Energy Option – A Review Wellinger A et al (Cambridge: Woodhead Publishing) 1–16

[2] Akunna J C 2019 Anaerobic Waste-Wastewater Treatments and Biogas Plants (Boca Raton: CRC Press) 4

[3] Rochelle G T 2009 Science 325 1652–4

[4] Wu Y, Carroll J J and Du Z 2011 Carbon Dioxide Sequestration and Related Technologies (John Wiley) 128–131

[5] Huijgen W J J 2007 Carbon dioxide sequestration by mineral carbonation PhD Dissertation Energy Research Centre of the Netherlands, Petten, Netherlands

[6] Xiao J, Wang Z, Tang Y and Yang S 2010 Langmuir 26 4877–83

[7] Erdogan N 2017 Physicochem. Probl. Miner. Process 53 57–68

[8] Ciullo P A 1966 Industrial Minerals and Their Uses (Westwood: Noyes Publications) 25–8

[9] Price G J, Mahon M F, Shannon J and Cooper C 2011 Crystal Growth & Design 11 39–44

[10] Baena-Moreno P M, Rodriguez-Galan M, Vega F, Reina T R, Vilches L F and Navarrete B 2018 Processes 6 1–12

[11] Madhania S, Ikhansa Y, Rizaldy M Z, Afdiwibowo A, Kusdianto and Winardi S 2020 AIP Conference Proceedings 2219 03004–1–6

[12] Gruenewald M and Radnjanski A 2016 Absorption-Based Post-Combustion Capture Feron P H M (Woodhead Publishing) 341–63

[13] Qing Z, Yincheng G and Zhenqi N 2011 Energy Procedia 4 519–24

[14] Tippayawong and Thanompongchart 2010 Energy 35 4531–5

[15] Aroonwilas A, Tontiwachwuthikul P and Chakma A 2001 Separation and Purification Technology 24 403–11

[16] Aboudheir A, deMontigny D, Tontiwachwutikul P and Chakma A 1998 1998 SPE Gas Technology Symposium (Calgary: Society of Petroleum Engineers) 1–4

[17] Arachcige U and Melaen M C 2012 European Journal of Scientific Research 87 117–26

[18] Lassauce A, Alix P, Raynal L, Royon-Lebeaud A and Haroun Y 2014 Oil & Gas Science and Technology – Rev. IFP Energies nouvelles 69 1021–34

[19] Chen P-C, Luo Y X and Cai P W 2014 Chemical Engineering & Technology 38 274–82

[20] Chen P C, Shi W, Du R and Chen V 2008 Ind. Eng. Chem. Res 47 6336–43

[21] Seyboth O, Zimmerman S, Heidel B and Scheiffknecht G 2014 Energy Procedia 63 1667–77

[22] Jafari M J, Matin A H, Rahmati A, Azari M R, Omidi L, Hosseini S S and Panahi D 2018 Atmospheric Pollution Research 9 783–90

[23] Kuntz J and Aroonwilas A 2009 Energy Procedia 1 205–9

[24] Javed K H Mahmud T and Purba E 2010 Chemical Engineering Journal 162 448–56

[25] Setameteeukul A, Aroonwilas A and Veawab A 2008 Separation and Purification Technology 64 16–25

[26] Yu H, Qi G, Xiang Q, Wang S, Fang M, Yang Q, Wardaugh L and Feron P 2013 Energy Procedia 37 6256–64

[27] Srichat P-C, Suntivarakorn R and Kamwilaisak K 2017 Energy Procedia 138 441–5

[28] Barhoum A, Van Assche G, Makhlof A S H, Terryn H, Baert K, Delplancke M P, El-Sheikh S M and Rahier H 2015 Crystal Growth & Design 15 573–80

[29] Jimoh O A, Otitoju T A, Hussin H, Ariffin K S and Baharun N 2017 S. Afr. J. Chem 70 1–7

[30] Somarathna Y R, Mantilaka M M M G P G, Karunaratne D G G P, Rajapakse R M G, Pitawala H M T G A and Wijayantha K G U 2016 Cryst. Res. Technol. 51 207–14

[31] Bang J-H, Jang Y N, Kim W, Song K S, Jeon C W, Chae S C, Lee S-W, Park S J, Lee M G 2011 Chemical Engineering Journal 174 413–20

[32] Nadliriyyah N and Triwikantoro 2014 Jurnal Sains dan Seni ITS 3 B107–11

[33] Lailiyah Q, Baqiya M and Darminto D 2012 Jurnal Sains dan Seni ITS 1 B6–10

[34] Wardhani S, Prasetia F, Khunur M M, Purwonugroho D and Prananto Y P 2018 Indones. J. Chem
18 573–9
[35] Han Y S, Hadiko G, Fuji M and Takahashi M 2006 *Journal of the European Ceramic Society* **26** 843–7
[36] Feng B, Yong A K and An H 2007 *Materials Science and Engineering* **445-6** 170-9
[37] Bang J-H, Song K, Park S, Jeon C, Lee S-W and Kim W 2015 *Energies* **8** 12304–13
[38] Kemperl J and Maček J 2009 *Int. J. Miner. Process* **93** 84–8