CO₂ Capture using Sodium Silicate Solution in a Packed Bed Column

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Abstract. The use of solid adsorbents such as amine-modified silica aerogels to capture CO₂ has been commonly used but poses several obstacles, including expensive raw materials, production complexity, and considerations for adsorbent regeneration. This research develops sodium silicate solution as a carbon scrubber in a packed column. Besides being able to capture CO₂, the amorphous silica which has economic value can also be produced. The packing size and CO₂ flow rate were studied to prevent the deposition of silica inside of the packed column. The precipitated product analysis using XRF, XRD, FTIR, and SEM Image observed that CO₂ was well absorbed by sodium silicate solution. The amorphous silica precipitated concentration reaches 98.6%.

Keywords: Sodium Silicate Solution, CO₂ Capture, Solid Adsorbents

1 Introduction

Wang and Song [1] reported that CO₂ concentrations in the air will exceed 550 ppm by 2050 if no action is taken to curb CO₂ emissions, it could lead to catastrophic impacts on global climate and human nutrition. In general, amine-modified silica aerogels are promising materials for carbon capture for the post-combustion processes with their superior properties. Silica gel functionalized with amines uses two different methods, namely wet impregnation and grafting via silane chemistry [4]. Modification of silica aerogel-amine by various methods has been carried out, with a complicated process and requires expensive auxiliary materials [5-8]. The CO₂ absorption using various solid adsorbents has also been developed. Girimonte et al (2020) investigate the adsorption of CO₂ using impregnated mesoporous silica in a confined-fluidized bed [9]. On the other hand, the CO₂ adsorption process using solid silica media requires an absorbent regeneration process [10]. The use of liquid absorbent developed in this study provides a solution to this problem. Apart from the un-required regeneration of the adsorbent, amorphous silica is also obtained as a product that has economic value. This research develops the capture of CO₂ using sodium silicate (Na₂SiO₃) solution. In addition to TEOS sodium silicate is commonly used as an ingredient for the production of mesoporous silica and silica aerogels [11,12]. The packed columns with cylindrical packing for silica precipitation have been studied previously [13]. This experiment uses spherical packing with a focus on the absorption of CO₂ into

sodium silicate solution by controlling the gas flow rate. The packed column is generally used to scrub the unwanted material from the gas stream with the aid of a liquid solvent. The industrial separation process uses packed columns for the adsorption, distillation, and stripping processes. The absorption process can be effective if the contact area between the two fluids is large and the movement of the two phases is strong enough. The working principle of the packed column is based on increasing the solubility of the liquid, increasing gas absorption, alkalinity, and decreasing vapor pressure. The equilibrium established can be reached at adequate times. Hydrodynamics of packed tower is noted by observing the pressure differential as a function of air flow rate against each water flow rate. Gas and liquid contact are expected to occur properly in the packed column and ensure the dissolution of CO₂ in sodium silicate as much as possible. Na₂SiO₃ has ionic bonds formed with the tendency of atoms to gain or lose electrons to be stable. In addition to good gas-liquid contact, sodium silicate concentration and acidity (pH) can also affect the growth of silica precipitated. The amount of CO₂ gas affects the pH of the solution and will most likely affect the type of salt formed, whether NaHCO₃ or Na₂CO₃. Na₂CO₃ salt was formed at an alkaline pH of about 10 while NaHCO₃ was formed at pH 8. The reaction that may occur between sodium silicate and CO₂ undergoes several mechanisms as follows.

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However, it is necessary to adjust the flow rate or residence time in the column so that the precipitation of particles unformed inside the packed column. In addition, uncontrolled gas flow rate may also cause turbulence in the porous of the packing which can cause instability in the growth of silica particles. If the packing size is different, the void volume ratio is also different. Hydrodynamic properties such as pressure drop will be strongly influenced by the mean voidage of the packed bed. For this reason, various spherical particle sizes are interesting to study regarding the effect of their void fraction in the packed bed on the growth of precipitated particles. The aim of this research is to study the effect of gas flow rate and packing size on the carbon capture and the morphology of the precipitated particles. It was reported that the shaped-growth stability was affected by stirring. The instability caused by stirring may allow the salt to crystallize from the emulsion droplets resulting in long needles with rods sticking out sideways [14]. This phenomenon is also possible to occur in the growth of silica and the formation of salt crystals due to the movement of the two phases is strong enough in the fixed bed column.

2 Experimental

The experimental apparatus (Fig.1) consisted of a packed column with a column inside diameter of 4.6 cm, an outside diameter of 5 cm, a packing bed height of 30 cm, a spherical packing diameter in the range of 1.0, 1.5, and 2.5 cm, the distance from the top packing to a liquid discharge of 13.5 cm. Flow rates of inlet liquid 10 mL/min and flow rate of carbon dioxide inlet in the range of 1, 2, 3, 4 and 5 L/min. Flow rates of inlet/outlet liquid and pH of solution were measured.

Fig. 1. Experimental apparatus

The packed column operates as a fixed bed so that the bed was kept from being fluidized for all packing size. Spherical packings were marbles made of glass were obtained from a toys shop in Surabaya. Sodium silicate solution flowed from the bottom of the packing column until it reaches a little below the outlet hole. The liquid inflow was temporarily stopped. CO₂ gas flowed through a diffuser under the packing column

so as to encourage the liquid to flow out through the outlet hole at the top of the column. After the liquid flows out of the top of the column., the valve of liquid entering the column was opened at a rate of 10mL/min until a steady-state was reached. The liquid flowing out of the column was accommodated in the reservoir vessel until it reaches an operating time of 20 min by closing the outlet valve at the same time as the gas and liquid inlet valve closing. The process of precipitation takes place in a reservoir vessel. The precipitation time was set at 24 h. The solid precipitated was separated by filtration using Whatman paper. The solid precipitated was washed using demineralized water. The washing operation was carried out twice in a 500ml glass beaker using 300 ml of demineralized water. The precipitated particles was dried in an oven at 100°C for 24 h. The dried particles then reduce in size to obtained 100 mesh powders for the analysis required.

Characterization

The precipitated powders were characterized by X-ray diffraction (XRD), XPert-PRO with PANalytical measurement, and by FTIR (Shimadzu 8400S) wavenumbers range of 400-4000 cm⁻¹ at room temperature. The morphology was characterized using SEM images (SU3500) with image resolution at 3 kV, 10 nm BSE image resolution at 5kV

3 Results and Discussion

In the synthesis of silica by precipitation method using an acid solution, the silica monomer grows into a polymer along with the formation of salt. The salts formed combine in the precipitated silica but are easily removed by washing operations and leave pure spherical silica particles. Meanwhile, the silica precipitated resulting from the CO₂ adsorption process in the packed bed column were in the form of flocs where the salts in the form of rods were distributed in silica flocs. The salt crystals (NaHCO₃) appear to separate from the flocculated silica.

3.1 The Effect of gas flow rate

The observation of precipitation in the variety of gas flow rates showed that particle deposition occurred inside the column for a CO₂ flow rate of 1 L/min using packing diameters of 1 and 1.5 cm. At a rate greater than 1 L/min the silica was precipitated in a reservoir vessel outside the column. Fig. 2 showed the XRD pattern of precipitated silica prepared by various flow rate in the range of 1 - 5 L/min using 1.5 cm of diameter spherical packing. The XRD patterns showed the amorphous silica structure of the precipitated products for all preparations of gas flow rate. Sodium silicate has a pH of about 12.7, when the rate of CO₂ gas has increased the pH will decrease, this will also affect the formation of sodium hydrogen carbonate (NaHCO₃) or sodium carbonate (Na₂CO₃) salts. The concentration of sodium silicate used in the experiment was relatively high (1,031mg/L). So the possible reaction that occurs when

CO₂ comes into contact with sodium silicate solution (Na₂SiO₃) follows the mechanism :

In the presence of Na⁺ can be precipitated into NaHCO₃ (low solubility) as follows :

In the presence of H⁺, the pH decreased which caused SiO₂ to precipitate.

Silica preparations at the rates of 2L/min and 4L/min showed the presence of NaHCO₃ observed by the peaks at 20, 27.7°, 29.0°, 30.2°, 34.6°, and 44.7° respectively. This is consistent with XRF analysis. The concentrations of SiO₂ in the precipitation products prepared by 1.5 cm packing diameter at the rate of 1-5 L/min were 97.9, 85.6, 98.2, 98.0, and 97%, respectively. The silica concentration in the precipitated product prepared at the rate of 3L/min using 1 cm and 2.5 cm packing was obtained 98.6% and 97.3%, respectively. The purity level of the precipitated silica depends also on the washing operation using demineralized water. Some of the silica precipitated products were observed to still contain carbonate salts based on XRD patterns, SEM images, and IR spectra. In other words, CO₂ has been successfully captured by a sodium silicate solution which produced carbonate salts and amorphous silica.

Fig. 2. XRD pattern of precipitated silica prepared by CO₂ flow rate of (a) 1L/min (b) 2 L/min (c) 3L/min (d) 4 L/min, and (e) 5 L/min

Silica floc was in the form of irregular lumps while the salt crystals were needles shaped. The formation of this salt comes from a reaction in the emulsion that produced long needles with rods sticking out to the sides. The silica floc formed in all treatments in this study was on average irregular with varying floc diameters. Fig.3. showed the SEM Image of precipitated silica prepared by CO₂ flow rate of 1- 5 L/min using 1 cm of diameter spherical packing.

Fig.3. SEM Image of precipitated silica prepared by CO₂ flow rate of (a) 1L/min (b) 2 L/min (c) 3L/min (d) 4 L/min, and (e) 5 L/min

Fig.4 showed IR-spectra of precipitated silica prepared by CO₂ flow rate of 1 - 5 L/min. It was observed that the spectra of silica particles prepared with variations in the CO₂ flow rate tended to have the same pattern. The absorbed CO₂ was identified at wavenumbers of 1665 - 1700 cm⁻¹, and about 1472 - 1473 cm⁻¹. The intensity of the vibrations of the asymmetric covalent bonds of Si-O and Si-O-Si was in the wavenumber range of 1000 -1100 cm⁻¹.

Fig. 4. IR-spectra of precipitated silica prepared by CO₂ flow rate of (a) 1L/min (b) 2 L/min (c) 3L/min (d) 4 L/min, and (e) 5 L/min

The gas flow rate and packing size also affect the precipitation time in the reservoir vessel set for 24 h. It was observed that the greater the gas flow rate and packing size, the faster the silica was deposited (less than 2 h). Precipitation time was considered complete when the amounts of solids no longer increased in the reservoir vessel. Prolonged precipitation (about 6 h) occurred in the preparation at a flow rate gas of 2 L/min and a packing diameter of 1.5 cm.

3.2 The Effect of Packing Size

It has been previously described that the operation of the packing column is carried out so that deposits unformed inside the packing column. However, at a gas rate of 1L/min, a precipitate formed inside the packing column

and covered the packing for 1 and 1.5 cm packing diameter. At a CO₂ rate of 1L/min, packing diameter of 2.5 cm it was observed that a precipitate formed in the reservoir outside the column. In addition to its effect on the deposition process, the size of the packing also affects the amount of precipitated product. Columns containing packings with the smallest diameter (1 cm) produced more precipitated products than those with larger packing diameters (1.5 and 2.5 cm). Fig.5 Showed the SEM Image of precipitated silica prepared with packing diameter of (a) 1 (b) 1.5 and (c) 2.5 cm

Fig.5. SEM Image of precipitated silica prepared at gas flow rate of (A) 1 L/min and (B) 3 L/min with packing diameter of (a) 1 (b) 1.5 and (c) 2.5 cm

4 Conclusions

Sodium silicate solution can be used to capture CO₂ gas very well in packed columns. The gas rate must be controlled to prevent the precipitation of silica inside the packed column. The relatively high concentration of sodium silicate in this study was most likely the cause of the formation of silica aggregates (floc silica). The spherical silica growth is still possible in lower concentration of sodium silicate. However, the process of carbon absorption and silica precipitation in packed columns is interesting to be developed further, apart from being an adsorbent, it is necessary to study the growth of silica and its surface functionalization.

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