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Continuous process of biogas purification and co-production of nano calcium carbonate in multistage membrane reactors

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HIGHLIGHTS

- Capture CO_2 and synthesis nano $CaCO_3$ at the same time.
- Two-stage cross flow membrane reactors with continuous operation mode were made.
- Produce gas with CO_2 content lower than 3% and $CaCO_3$ with 72.8 nm average particle size.
- The apparatus could run smoothly for at least 5 h.

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ABSTRACT

CO_2 capture is one of the key technologies in biogas production. Using lime slurry to purify biogas and co-production of nano calcium carbonate is an economical approach. In this work, multistage cross flow membrane reactors with continuous process were designed. Factors that influence CO_2 absorption efficiency such as $Ca(OH)_2$ slurry concentration, flow rate, additives, gas flow rate, membrane length and the connecting pipe length were studied to select the proper parameters. Results show that high slurry flow rate, low gas flow rate, long membrane and connecting pipe and the dosage of additives may enhance CO_2 absorption, while $Ca(OH)_2$ concentration has little impact on it. The hydrophobicity modification on the ceramic membrane using a silane coupling agent was also carried out. The change from hydrophilicity to hydrophobicity gave the reactor a higher mass transfer efficiency. Using the parameters carefully chosen based on the work above, the two-stage membrane reactors assembled successfully purified the gas (with end gas CO_2 content lower than 3%) and produced nano calcium carbonate with 72.8 nm average particle size. Extension of the experiment showed that this apparatus could run smoothly for at least 5 h. This work may provide a new method in biogas purification and nano calcium carbonate synthesis.

1. Introduction

Biogas is a promising renewable resource [1] which can help alleviate environment pollution and relieve the energy crisis. Its market demand is rising globally. The purification of biogas is one of the key technologies in its application because its purity weighs heavily against its quality [2]. The removal of CO_2 in biogas can raise its caloric value to compressed natural gas (CNG) standard [3], which is crucial in biogas promotion.

Recent technologies used for CO_2 capture are primarily water scrubbing [4], chemical absorption [5], pressure swing adsorption [6], and membrane separation [7]. Each has its merit, but researchers are still looking for new methods with a more economical approach and which can utilize CO_2 properly.

As a high performance filler and coating, nano calcium carbonate has been widely used in many industrial fields [8]. The main production method is precipitation, using the chemical reaction

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in which CO_2 reacts with $Ca(OH)_2$, forming $CaCO_3$ and H_2O. Thus CO_2 could be utilized [9]

Some researchers have attempted to produce nano calcium carbonate with membrane reactors. Wang et al. [10] used a micro-dispersion minireactor, which has a microfiltration membrane as dispersion media, to synthesize calcium carbonate nanoparticles with sizes ranging from 34.3 to 110 nm. The mass transfer efficiency was significantly enhanced compared with the membrane-free reactor. This technique had been applied to industry [11], Jia et al. [12–16] published a series of works in the field of synthesizing nano calcium carbonate via a hollow fiber membrane reactor, and described the mass transfer mechanics at length. However these works do not focus on the capture efficiency of CO_2.

Our previous work [17] developed a membrane reactor that could capture CO_2 and synthesis nano calcium carbonate at the same time. However, the operational mode of this apparatus is batch operation. The $Ca(OH)_2$ slurry circulates in the reactor until reacted completely. The method is labor intensive and unfit for large scale production. This work aims to switch the apparatus to a continuously operating one by redesigning the process and enhancing the performance.

2. Material and methods

2.1. Apparatus and reagents

The membrane reactor (Fig. 1) is made up of a membrane tube, shell, gas and liquid inlet, outlet and connective devices. The membrane tube (Jiangsu Jiuwu Hi-tech Co., Ltd.) is made of α-alumina/zirconia with a 1.16 m length (in some experiments a 0.58 m membrane is used) and 30 mm diameter. It has 19 lumens with 4 mm diameter and the average pore size of the membrane is 500 nm. In the experiments, $Ca(OH)_2$ slurry flowed through the lumens of the membrane and contacted with the gas permeated through the micro pores of the membrane. Slurry and gas then flowed out together from the outlet, and separated in the gas–liquid separator. The schematic diagram of the two-phase flow is showed in Fig. 2.

The $Ca(OH)_2$ slurry was transported by peristaltic pump (BT300-2 J, Baoding Longer pump Co. Ltd.). Its volume flow rate increased proportionally with the rotating speed, thus calculate the flow rate by the rotating speed is possible. The CO_2 content in the gas was determined by an infrared gas analyzer (HP-FX02, Nanjing Hope instrument Co., Ltd). The XRD pattern of the calcium carbonate was analyzed by Riguka Smartlab TM 9KW using Cu $K_\alpha$radiation (40 kV, 100 mA). The particle morphology was observed by transmission electron microscope (JOEL JEM-2100). The experiments used mixed gas containing approximately 50% CO_2 and 50% N_2 (volume fraction). The reagents used, including $Ca(OH)_2$, EDTA, $ZnSO_4$ and $(NaPO_3)_6$, were analytical grade.

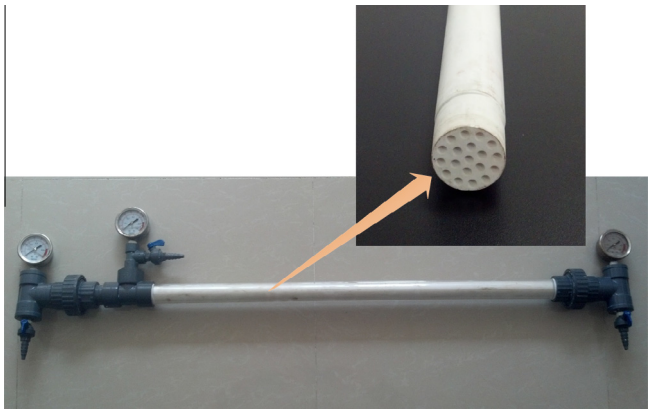

Fig. 1. Membrane reactor.

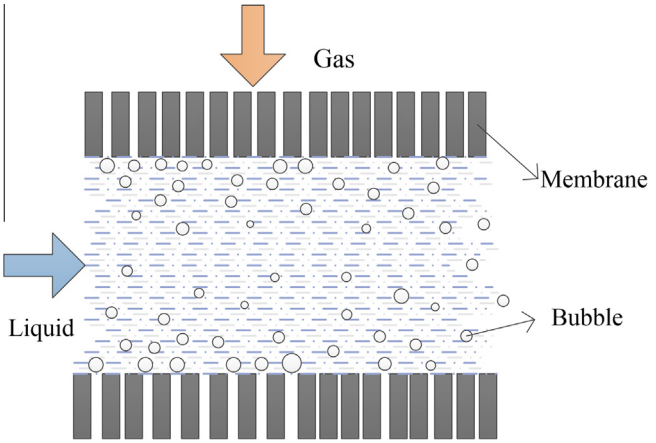

Fig. 2. Schematic diagram of the two-phase flow.

2.2. Process design

The studies focusing on CO_2 capture usually consume excessive absorbent, while those focusing on calcium carbonate synthesis usually consume excessive CO_2. From the carbonation equation:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \quad (1)$$

we can see clearly that to capture CO_2 and synthesize calcium carbonate at the same time, the molar ratio of CO_2 and $Ca(OH)_2$ must be 1:1. In other words, neither of the two reactants should be excessive. This calls for a reactor with high mass transfer efficiency as well as rational design.

To meet the demand above, multistage cross flow membrane reactors were developed and the schematic diagram of the process is showed in Fig. 3.

In the first stage reactor, $Ca(OH)_2$ slurry flows in the membrane lumens and reacts with the gas flowing out from the second stage; slurry and gas are then separated in the gas–liquid separator. The purified gas flows out as a product, and the incompletely reacted $Ca(OH)_2$ slurry flows into the second stage. There, it reacts with the new, high CO_2 content gas and separates. The slurry then flows out as a product. The incompletely reacted gas flows into the first stage for once more purification. In our conception, the first stage reactor should capture CO_2 higher than 95%, and the second reactor should consume $Ca(OH)_2$ completely.

Our consideration for the two stage cross-flow process is that both CO_2 content and $Ca(OH)_2$ dosage are driving force of the reaction. To capture CO_2 thoroughly, excessive $Ca(OH)_2$ is needed; to consume $Ca(OH)_2$ completely, it calls for ample CO_2. This contradiction could be resolved by separating one reactor into two. In the first stage reactor, $Ca(OH)_2$ slurry with high concentration contacts with the gas with relatively low CO_2 content, the CO_2 could be completely captured; in the second stage reactor, the raw gas containing relatively high CO_2 content could consume the $Ca(OH)_2$ slurry flowed from the first stage completely.

If two stages are not sufficient to achieve the goals, reactors with three or more stages are advisable. The flow pattern in these extra stages would also be cross flow.

2.3. Surface modification of the membrane

To achieve higher mass transfer efficiency, surface modification of the membrane was carried out to transform the hydrophilic