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Renewable CO_2 absorbent for carbon capture and biogas upgrading by membrane contactor

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ABSTRACT

This study employs novel renewable absorbents derived from biogas slurry (BS) for biogas upgrading via membrane contactors. CO_2 absorption capacity of biogas slurry can be enhanced by adding alkali solutions, vacuum regeneration or vacuum membrane distillation (VMD). These methods are used to produce four types of renewable CO_2 solvents, including vacuum regenerated BS, recovered aqueous ammonia (RAA) from BS by VMD, calcium oxide treated BS and potassium hydroxide treated BS. These renewable absorbents for CO_2 capture from biogas by membrane contactors are investigated. CO_2 removal efficiency reduces but absorption rates increase with the rise in CO_2 volume fraction in the feed gas stream. Absorption temperature has a limited effect on CO_2 absorption rates of the renewable absorbents. RAA shows the best CO_2 absorption performance among the four types of renewable absorbents in the membrane contactor. RAA flowing on the tube side leads to a 50% higher CO_2 removal efficiency compared with RAA on the shell side. At low gas flow rates, partial absorbents and hollow fibers may not be utilized. Thus, selection of membrane module parameters, including the length of module, the number of hollow fibers, biogas flow rates and absorption performance, should be carefully considered when using membrane contactors for biogas upgrading.

1. Introduction

Climate change is driving global concerns due to its profound impacts on our environment. Carbon dioxide (CO_2) is considered as the primary greenhouse gas for climate change. Carbon capture and storage (CCS) embodies various technologies to capture CO_2 from power plants, followed by compression, transport and geological storage. Conventional CCS is mainly designed for reducing carbon emissions in fossil fuel combustion [1]. However, recent efforts in carbon reductions have also been made to explore renewable energy resources (e.g. biomass and solar energy) [2,3].

Particularly, biogas (product and upgrading) has attracted great interest since it can help meet future energy supply and reduce greenhouse gas emissions [4–6]. Biogas is produced by anaerobic digestion where anaerobic microorganisms convert waste organic matters into two main products: biogas and nutrient-rich digestate [7]. Biogas is a gas mixture of methane (CH_4 ~ 60 vol%), CO_2 (~40 vol%), and traces of hydrogen sulfide (H_2S), ammonia (NH_3), nitrogen (N_2), hydrogen (H_2), water vapor and other volatile compounds [4]. Compressed natural gas (CNG) and liquefied natural gas (LNG) can be acquired after biogas upgrading into bio-methane (CH_4 > 95 vol%) [3]. Minimization of CH_4 emissions, CO_2 removal efficiency, and CO_2 capture and utilization are of great interest in biogas upgrading [8].

Many technologies have been used for biogas upgrading, such as water scrubbing [2], pressure swing adsorption [9], chemical absorption [4,10,11] and membrane separation [12–14]. The main drawback for those commonly used methods (water scrubbing and pressure swing adsorption) is the high CH_4 loss (which may range from 2 to 20%) [2]. It is important to reduce CH_4 loss as the greenhouse effect of CH_4 is ~25-fold higher than that of CO_2 [12]. Thus, both economic feasibility and environmental risks should be considered when selecting methods for biogas upgrading [15]. Chemical absorption can achieve negligible CH_4 loss (< 0.1%), high CH_4 purity at atmospheric pressure and temperature, and simultaneous removal of H_2S in biogas upgrading [3,4,15]. However, chemical absorption has its drawbacks in carbon capture, such as huge energy inputs [16], severe equipment corrosion

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Nomenclature

A_T	the mass transfer area (m^2)
$C_{CO_2,F}$	CO_2 concentration in the feed stream (mol/L)
$C_{CO_2,R}$	CO_2 concentration in the retentate stream (mol/L)
C_l	concentration of the solution (mol/L)
d_e	equivalent diameter of the shell side (m)
D_g	gas diffusivity (m^2/s)
D_i	inner diameter of the module (m)
d_i	inner diameter of the hollow fiber (m)
d_{ln}	logarithmic mean diameter of the hollow fiber (m)
d_o	outer diameter of the hollow fiber (m)
E	enhancement factor
H	Henry's constant
J_{CO2}	CO_2 flux ($mol/m^2{\cdot}h$)
J_{chem}	chemical absorption flux ($mol/m^2{\cdot}h$)
J_{phy}	physical absorption flux ($mol/m^2{\cdot}h$)
k_g	gas phase mass transfer coefficient (m/s)
k_l	liquid phase mass transfer coefficient (m/s)
k_m	membrane mass transfer coefficient (m/s)
Ko	overall mass transfer coefficient (m/s)
L	length of the hollow fiber (m)
n	number of the hollow fibers (m)
Q_F	inlet gas flow rate (ml/min)
Q_R	outlet gas flow rate (ml/min)
T_g	gas temperature (°C)

Greek symbols

u_g	volumetric flow rate (m/s)
v_g	kinematic viscosity of the gas (m^2/s)
α	the fitting coefficient (dimensionless)
η	CO_2 removal efficiency (%)

[17,18], solvent degradation [19]. These disadvantages limit the application of chemical absorption for biogas upgrading.

Membrane absorption is an emerging and promising process for CO_2 absorption since it integrates the advantages of absorption (high selectivity) and membrane separation (modularity and compactness) [20]. Compared with conventional chemical absorption, membrane absorption has several superior characteristics, such as a much smaller footprint, higher operational flexibility and predictability, lower risks of flooding, foaming and channeling, and lower operational costs [20]. As a result, membrane contactors combining chemical absorbents have been employed for biogas upgrading (CO_2 absorption) [21,22]. Membrane contactors do not provide selectivity but act as barriers to separate two phases and increase the interfacial contact area for mass transfer. Wetting is the most critical challenge in membrane contactors with chemical absorbents [20,23,24]. Thus, absorbent selection is of great significance in membrane contactors for biogas upgrading. However, there are few studies on membrane contactors with renewable absorbents for biogas upgrading.

In this study, we select low cost renewable CO_2 absorbents from anaerobic digestion combining membrane contactor technology for biogas upgrading. As a once-through CO_2 absorption method, this new approach can not only reduce carbon capture costs due to no need for regeneration, but also produce valuable products [25–27]. CO_2 absorption performance of the renewable absorbent in terms of absorption capacity, rate and efficiency is investigated. Effects of gas and liquid flow rates, absorption temperatures, flow orientation, and membrane module parameters on biogas upgrading performance are also explored. This study paves a new way to use renewable absorbents for simultaneous carbon minimization and biogas upgrading.

2. Materials and methods

2.1. Materials

Raw biogas slurry (BS) was collected from a pilot thermophilic anaerobic biogas digestion plant (digestion substrate: pig manure; digestion temperature: ~55 °C), Huazhong Agricultural University, Wuhan, Hubei Province, PR China. The collected raw biogas slurry was stored aerobically at ambient temperature prior to experiments until no biogas was produced. Undissolved solids and partial suspended solids were separated by centrifuging (4000 rpm) for 20 min. The supernatant liquid (i.e. BS) was used for further measurements and experiments. Characteristics of the BS measured at 15 ± 2 °C are shown in Table 1. Chemical oxygen demand (COD) and pH value of the BS were measured with a CM-03 COD meter (Beijing Shuanghui Jingcheng Electronics Co., Ltd.) and a pH meter (Metler Toledo, FE20K), respectively. Total ammonia nitrogen (TAN), was determined in a Smartchem 200 Discrete Auto Analyzer (Italy AMS-Westco) [28]. Total solids (TS) concentration was measured by the standard methods [29]. Volatile fatty acid (VFA) concentration was determined using GC-FID (SP-2100A) [30]. The turbidity was determined by a photoelectric turbidity meter (WZT-1, Shanghai Jingjia Scientific Instrument Co., Ltd.). Electric conductivity (EC) of the BS was determined with a conductivity meter (DDS-307A, Shanghai INESA Scientific Instrument Co., Ltd.). Each liquid sample was measured at least three times to determine the average values and standard deviations. The effects of uncertainties from the readings and device accuracies were also considered.

Chemical reagents: potassium hydroxide (KOH, purity ≥ 99.9%), calcium oxide (CaO, purity ≥ 99.9%) and aqueous ammonia ($NH_3{\cdot}H_2O$, mass fraction is about 25%–28%) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. $CO_{2.}$ absorption in the membrane contactor

Before different types of CO_2 absorbents used in the membrane contactor, pure CO_2-water system was operated to test the mass transfer resistance from the membrane and the mass transfer resistance variation with water flow rates. Pure water was used as the CO_2 physical absorbent flowing on the tube side of the hollow fiber membrane, while pure CO_2 with a constant flow rate of 2 L/min flowed on the shell side. The absorption temperature was maintained at 35 °C.

CO_2 absorption capacity of BS was enhanced by vacuum regeneration [27], alkaline addition [26] and vacuum membrane distillation (VMD) [31]. Four types of enhanced BS with the same TAN concentration of 0.3 mol/L were used in hollow fiber membrane contactors to absorb CO_2 from simulated biogas, including vacuum regenerated BS (RBS, a CO_2 loading of 0.09 mol/L), recovered aqueous ammonia (RAA) from BS by VMD, calcium oxide (CaO, 0.27 mol/L) treated BS (CBS) and potassium hydroxide (KOH, 0.27 mol/L) treated BS (KBS). The experimental setup for CO_2 removal from biogas in hollow fiber membrane

Table 1
Properties of the biogas slurry.

Parameters	Values	Units
pH	8.03 ± 0.21	–
Electric conductivity (EC)	25.39 ± 0.32	mS/cm
Turbidity	1125.6 ± 10.6	NTU
Chemical oxygen demand (COD)	3390.5 ± 18.7	mg/L
Total ammonia nitrogen (TAN)	0.3 ± 0.1	mol/L
Total solid (TS)	5589 ± 57	mg/L
Volatile fatty acid (VFA)	0.05 ± 0.02	mg/L