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Surface modification to produce superhydrophobic hollow fiber membrane contactor to avoid membrane wetting for biogas purification under pressurized conditions

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ABSTRACT

This article investigates CO_2 removal from biogas (containing 40% CO_2 and 60% CH_4) using a hollow fiber membrane contactor (HFMC) with K_2CO_3 aqueous solutions as absorbent at elevated pressures up to 10 bar. Superhydrophobic PTFE membrane fibers (with a water contact angle of 158.4° and sliding angle of 1.3°) were fabricated by spraying silica nanoparticles on membrane surface and then used in membrane module for absorption experiments. The modified membrane outperformed the original membrane at elevated absorption pressures, and the highest CO_2 removal efficiency and absorption flux reached 97.1% and 1.85×10^{-3} mol m^{-2} s^{-1}, respectively. A 2D axisymmetric non-wetted mathematic model was developed to determine the membrane wetness conditions during absorption experiments. The model validation results indicated that when using aqueous K_2CO_3 solutions as absorbent the modified superhydrophobic membrane used in this study was able to prevent membrane wetting even at pressurized conditions up to 10 bar. This work showed that the superhydrophobic membranes modified by spray-deposition technique have great potential for application in HFMC to avoid membrane wetting for biogas purification under pressurized conditions.

1. Introduction

Biogas is generally obtained by anaerobic digestion process of organic matter, and consists of CH_4 (53–70 vol%), CO_2 (30–50 vol%) [1], and other compounds such as H_2S, and NH_3. Due to its flammability and renewability, biogas production and utilization has increasingly been seen as an emerging alternative energy technology. However, raw biogas still needs several purification processes to achieve application standards, involving removal of CO_2 and other trace gas compounds.

Technologies such as pressurized water scrubbing, chemical/physical absorption, cryogenic distillation, pressure swing adsorption, and membrane separation [2] are readily available for biogas purification. Among these, the conventional liquid absorption process, mainly carried out in packed columns, is the most widely employed technologies for CO_2 removal in industry [3]. However, the conventional absorption process relies upon direct contact between gas and liquid, which leads to unavoidable operating drawbacks such as foaming, flooding, and entrainment [4]. To improve the absorption efficiency, hollow fiber membrane contactors (HFMC) have been intensively studied in recent decades as an alternative to conventional packed columns technology. In HFMCs, gas and liquid flow separately in the shell and tube side of membrane modules, the absorption occurs when CO_2 diffuses through the membrane pores and contacts the liquid phase in the opposite side of the membrane. In addition, HFMCs also have other advantages like high operational flexibility, low energy consumption, high surface-area-to-volume ratio, possibility of linear scale-up, as well as being a more predictable process [5].

The most frequently used chemical absorbents in HFMCs are alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) [6–9]. Although these solvents have been widely used and capture CO_2 efficiently on a commercial level, they still have several drawbacks. The obvious shortcomings include thermal and oxidative degradation, corrosion of equipment and pipes, high-energy consumption for regeneration, a toxic nature, and easily wetting the microporous membrane [10,11].

The aqueous solution of K_2CO_3 is thermally more stable than amines and has been recognized as a good alternative for CO_2 absorption. It has a low regeneration cost in general (especially for higher concentrations of CO_2 which in turn makes it a promising absorbent for biogas purification) and also has greater surface tension than amines with lower tendency for membrane wetting [12]. These features make aqueous K_2CO_3 solution a promising absorbent in HFMCs. However, the reaction

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Nomenclature

A	membrane contacting area, m^2
C_{i-j}	concentration of any component in model domains, $mol\,m^{-3}$
$C_{CO_2-tube,in}$	CO_2 concentration in the tube side at module inlet, $mol\,m^{-3}$
$C_{CO_2-tube,out}$	CO_2 concentration in the tube side at module outlet, $mol\,m^{-3}$
D_{i-j}	diffusion coefficient of any component in model domains, $m^2\,s^{-1}$
$D^w_{CO_2}$	diffusion coefficient of CO_2 in water, $m^2\,s^{-1}$
D_{ion}	diffusion coefficient of ions in the liquid phase, $m^2\,s^{-1}$
h_{CO_2}	specific gas constant of CO_2
K_1	equilibrium rate constant of reaction (1), $kmol\,m^{-3}$
K_2	equilibrium rate constant of reaction (2), $m^3\,kmol^{-1}$
K_3	equilibrium rate constant of reaction (3), $m^3\,kmol^{-1}$
K_4	equilibrium rate constant of reaction (4), $kmol^2\,m^{-6}$
k_1	forward reaction rate constant of reaction (1), s^{-1}
k_2	forward reaction rate constant of reaction (2), $m^3\,koml^{-1}\,s^{-1}$
L	effective membrane length, m
m_{CO_2}	solubility coefficient of CO_2 in liquid phase, $mol\,mol^{-1}$
$m^w_{CO_2}$	solubility coefficient of CO_2 in water, $mol\,mol^{-1}$
P	pressure, bar
$Q_{g,in}$	Gas stream flow rate at module inlet, $m^3\,s^{-1}$
$Q_{g,out}$	Gas stream flow rate at module outlet, $m^3\,s^{-1}$
R	gas constant, $m^3\,bar\,mol^{-1}\,k^{-1}$
R_{i-j}	reaction rate of any component in model domains, $mol\,m^{-3}\,s^{-1}$
R_{CO_2}	reaction rate of CO_2 in liquid phase, $mol\,m^{-3}\,s^{-1}$
$R_{CO_3^{2-}}$	reaction rate of CO_3^{2-} in liquid phase, $mol\,m^{-3}\,s^{-1}$
$R_{HCO_3^-}$	reaction rate of HCO_3^- in liquid phase, $mol\,m^{-3}\,s^{-1}$
r	radial coordinate, m
S	sum of volume parts of the molecules of gas component
T	temperature, K
V_j	velocity profiles in the tube or shell side, $m\,s^{-1}$
y_{i-j}	mole fraction of any component in model domains, $mol\,mol^{-1}$
z	axial coordinate, m

Greek letters

ε	membrane porosity,%
ϕ	module packing fraction,%
θ	gas compressibility factor

Subscripts

i	any component in the model domains
j	any compartment in the model domains

rate between K_2CO_3 and CO_2 is slow. The absorption efficiency can hardly reach the application standard at moderated operation conditions. Higher operating temperatures and pressures are needed to intensify the absorption process. The first experimental study of CO_2 absorption by K_2CO_3 aqueous solution was conducted by Nii and Takeuchi [13], Na_2SO_3, K_2CO_3, NaOH, and amine promoted K_2CO_3 were applied as absorbents in the fibers. Lee et al. [14] modeled the CO_2 absorption by K_2CO_3 in HFMC, and the operating parameters were optimized theoretically. Mehdipour et al. [12] developed a mathematical model to simulate the absorption of CO_2 with K_2CO_3 under both non-wetted and partially wetted conditions, and further investigated the effects of temperature and K_2CO_3 concentration. Faiz and Al-Marzouqi [15] modeled the simultaneous absorption of CO_2 and H_2S with K_2CO_3 using HFMC. The results showed a complete removal of CO_2 (5 vol%) and H_2S (5 vol%) was possible by using two stage membrane modules. To the best of our knowledge, the effects of operating pressure have not been experimentally studied in previous works. Elevating the operating pressure can significantly enhance the absorption performance in HFMC [16,17], thus the study of this important parameter is of interest. However, operating HFMC at high pressure may lead to membrane wetting [18,19], which in turn reduce the mass transfer rate and CO_2 absorption efficiency.

Generally, increasing the membrane hydrophobicity is a useful way to prevent liquid from penetrating the microporous membrane [20], thus, superhydrophobic membranes with a static water contact angle greater than 150° and a sliding angle less than 10° could be an ideal material in HFMCs to avoid membrane wetting. Spray-deposition is a simple and convenient process for industrial coating, and it has been used to fabricate superhydrophobic surfaces by controlling the precursor concentration and spraying conditions [21–23]. Zhang et al. fabricated superhydrophobic hollow fiber membranes by spray-deposition technology for membrane distillation, higher mass transfer flux was achieved by superhydrophobic membranes.

The aim of this study is to enhance CO_2 absorption with K_2CO_3 solution in pressurized membrane absorption conditions by using superhydrophobic membrane fibers. Spray-deposition technology was used to modify the polytetrafluoroethylene (PTFE) hollow fiber membranes surface. The original and modified membrane properties were analyzed by a variety of techniques such as contact angle measurement, scanning electron microscopy, atomic force microscopy, and gas permeation tests. The effects of original/modified membrane fibers on synthetic biogas (containing 40% CO_2 and 60% CH_4) purification by HFMC using K_2CO_3 solutions as absorbent were experimentally studied at different operating pressures. The operating pressure for the current technologies to upgrade biogas, such as water scrubbing, pressure swing adsorption, absorption using amine, and membrane permeation is commonly around 10 bar. Therefore, the pressure range applied in this study is from 1 to 10 bar. Since, the membrane wetting phenomenon cannot be detected directly, a comprehensive 2D axisymmetric mathematical model was developed to determine whether the membranes had been wetted under pressurized conditions.

2. Theory

2.1. Reaction mechanism of CO_2

The development of a complex reaction mechanism to describe the absorption of CO_2 in K_2CO_3 aqueous solution was presented by several researchers [24,25]. When the K_2CO_3 dissolved in water it ionized into K^+ and CO_3^{2-} ions. Various reactions that occur during CO_2 absorption in K_2CO_3 solution are presented below:

$$CO_2 + H_2O \overset{K_1}{\leftrightarrow} HCO_3^- + H^+ \quad (1)$$

$$CO_2 + OH^- \overset{K_2}{\leftrightarrow} HCO_3^- \quad (2)$$

$$HCO_3^- + OH^- \overset{K_3}{\leftrightarrow} CO_3^{2-} + H_2O \quad (3)$$

$$H_2O \overset{K_4}{\leftrightarrow} H^+ + OH^- \quad (4)$$

$$CO_2 + CO_3^{2-} + H_2O \Leftrightarrow 2HCO_3^- \quad (5)$$

Reaction (1) and (2) are considered as the rate controlling reactions. Reactions (3) and (4) are fast and can be assumed to be at equilibrium [26]. The overall reaction of CO_2 in K_2CO_3 solution can be written as