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Potentialities of a dense skin hollow fiber membrane contactor for biogas purification by pressurized water absorption

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ABSTRACT

Gas purification technologies are a key step in the technological chain using energy sources such as natural gas, coal gas or biogas, and represent a significant part of production costs. Numerous separation technologies exist to achieve required purity specifications depending on the particular application (absorption, adsorption, cryogenic, membranes). The objective of this work is to present an evaluation of the potentialities of using a membrane contactor based on a dense skin Poly (Phenylene Oxide) (PPO) hollow fiber module for CO_2 absorption from biogas by pressurized water through simulations and experiments. In this system, the liquid flowing on the shell-side is in direct contact with the dense skin, thus enabling pressurization and avoiding membrane wetting in order to maintain stable absorption performances.

The overall mass transfer coefficient K_{ov}, CO_2 removal efficiency, and CH_4 loss are evaluated for a range of liquid and gas flow rates. A one-dimensional (1D) model based on resistance in series provides very good predictions of the experimental results when the Graetz approach is used for shell-side mass transfer calculations.

Membrane mass transfer resistance is shown to be negligible compared to the liquid resistance. Consequently, the overall mass transfer performances of the dense skin contactor are close to typical values of packed columns (10^{-5}–10^{-4} m/s). Thanks to the increased gas-liquid interfacial area offered by the membrane contactor, a significant volume reduction of the absorption unit (up to 15 process intensification factor) is potentially achievable. Moreover, a selective dense skin could minimize methane losses.

1. Introduction

Biogas generation from biomass anaerobic digestion (agricultural wastes, landfill) has in recent years attracted much attention for offering a wide range of applications within a sustainable framework. Apart from being a renewable energy carrier, biogas can be burned in a combined heat and power unit (for heat and electricity generation), upgraded for natural gas pipeline injection or used as feedstock for the chemical industry [1–4].

Nevertheless, several purification steps are required to achieve specifications for each application and have a significant impact on the overall cost, which presents a major challenge [2–4]. The biogas purification process generally aims to:

i) remove carbon dioxide (a major biogas component together with methane), typically down to 2% vol,
ii) achieve drying,
iii) eliminate impurities such as N_2, O_2, H_2S or NH_3 and vapors that can cause corrosion, toxicity and reduce the heat value.

Table 1 shows typical biogas compositions and purification requirements.

Several processes have been proposed in order to achieve biogas purification which include absorption (in a physical or a chemical solvent), adsorption, cryogeny or membrane separation [4–6]. Gas-liquid absorption by Pressurized Water Absorption (PWA) is currently used at industrial scale and is considered to be one of the most efficient technologies [5].

The use of water as absorbent in the purification process to remove gas impurities (such as carbon dioxide, sulfur dioxide, ammonia) through absorption effectively offers a combination of major

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Table 1
Typical biogas composition and purification requirements [2–5].

Component	Composition unit	Raw biogas		Purification requirements	
		Anaerobic digestion	Landfill biogas	Heat and electricity generation	Pipeline injection and transportation
CH_4	%	53–70	30–65	96–98	> 96
CO_2	%	30–55	25–47	< 2–4	< 2–4
H_2O	%	3%	–	32 mg/m^3	< 0.01 (US)
H_2S	ppm	0–2000	30–500	< 16	< 4
O_2	%	0–5	0–3	< 1	< 0.5–3
H_2	%	–	0–3	–	–
N_2	%	0.01–6	< 1–17	< 1	–
NH_3	ppm	< 100	0–5	–	–

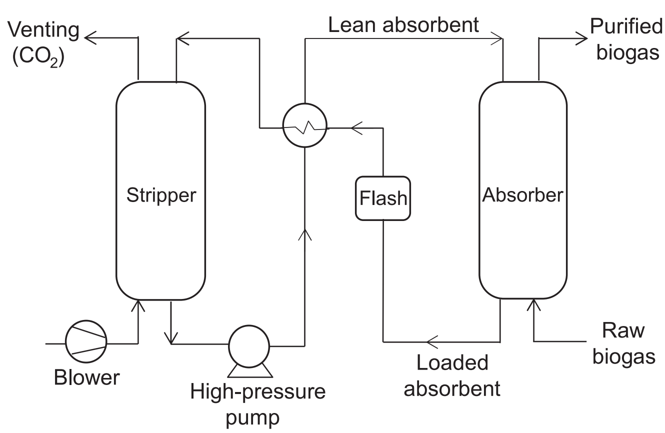

Fig. 1. Diagram of a gas absorption/regeneration unit with a physical solvent, packed column configuration: solvent regeneration is achieved by liquid depressurization.

advantages: interesting thermodynamic properties (solubility, selectivity towards CH_4), wide availability, low cost, and an absence of solvent losses and methane contamination issues (green solvents compared to organic liquids). Moreover, PWA has been proven to be more energy efficient when compared, for example, to amine scrubbing [5] and requires a simple process design given that absorbent regeneration is achieved through simple solvent depressurization (without the need for heat exchangers or reboilers). The standard PWA process, shown in Fig. 1, makes use of two packed columns (absorption and regeneration units) with a pressurized water recycling loop. Because carbon dioxide, hydrogen sulfide and ammonia show low absorption rates, relatively tall countercurrent packed columns are required combined to high solvent (water) flow rates [3]. Consequently, to achieve significant unit volume reduction, priority is given to developing intensified gas-liquid absorption units for this application.

Membrane contactors are one of the most effective strategies for intensified gas-liquid absorption processes [7]. Large intensification factors, compared to those for packed columns, have been reported for applications such as oxygen degassing and post-combustion carbon dioxide capture by absorption in chemical solvents [8]. Similarly, carbon dioxide absorption in water by membrane contactors has been investigated by several authors (see Table A.1 in Appendix A). The various studies listed in Table A.1 are almost systematically based on microporous hydrophobic membranes. Surprisingly, no estimation of the intensification potential of membrane contactors, compared to the baseline technology (packed column) has been reported. Moreover, the use of microporous membrane addresses issues in terms of pore wetting; in that event, a large decrease of the mass transfer performances can result, leading to a significant decrease of the intensification factor, even for a slight wetting ratio of the membrane material [9]. The risk of wetting is likely to be high for biogas purification by PWA; the absorption process indeed requires high liquid pressure and a slight overpressure on the liquid side can induce massive pore wetting effects. Trace contaminants in the gas phase can also decrease the liquid surface tension, leading to increased risks of wetting. Additionally, bacteria growth in the aqueous phase can generate surface fouling and pore blocking effects [5]. One potential solution to prevent the above problems consists in using a dense, permeable membrane material in place of a microporous material. For carbon dioxide absorption in chemical solvents, this possibility has been shown to offer a remarkable wetting protection effect [10] with a negligible penalty on mass transfer performances [11]. This possibility, however, remains largely unexplored for Pressurized Water Absorption application, with the exception of two recent studies which use thick selfstanding silicone rubber membranes, of 165 and 35 μm respectively [12,13]. In that case, the membrane mass transfer resistance is likely to be significant, thus limiting the intensification potential. It can be shown that, even with super-permeable polymers, the dense layer thickness should be limited to 5–10 μm in order to generate a limited mass transfer resistance for physical absorption processes [14]. This matter supports making use of dense skin composite membrane contactors for PWA application to ensure both wetting protection and a maximal intensification potential (Fig. 2). Additionally, the mechanical resistance offered by the dense skin composite membrane opens up unique possibilities for increased energy efficiency due to the fact that the liquid solvent can be maintained under pressure during the regeneration step by gas depressurization [14]. Finally, for biogas purification purposes, the possibility with a dense polymeric layer to generate a selective mass transfer (CO_2/CH_4 permeability ratio) could be of interest for limiting CH_4 losses by dissolution in the liquid solvent. This process performance variable is, in fact, important for both economical and environmental reasons [15], but is still only rarely considered in biogas purification by PWA process. To our knowledge, no study to date has reported on the use of dense skin composite hollow fiber membrane contactors for biogas purification.

Based on the state of the art summary presented above, this study intends to achieve the following objectives:

i) Perform a series of measurements of CO_2 removal efficiency and methane losses from a CH_4/CO_2 mixture by a dense skin hollow fiber module under a set of operating conditions.
ii) Evaluate the mass transfer performances of dense skin composite membranes and compare them to the existing literature