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Permeation properties of polymeric membranes for biohydrogen purification

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ABSTRACT

Palm Oil Mill Effluent (POME), generated from the oil extraction process, possesses high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). POME can be treated in an efficient bioreactor under controlled conditions to produce high value biohydrogen mixture containing CO_2. The H_2 existence in the valuable gas mixture (in a reasonable quantity) could be used as a clean energy source for renewable energy i.e., in hydrogen fuel cell. CO_2 presence in fuel cell causes CO_2 poisoning and affects its performance. Therefore, the purification of H_2 from CO_2 produced from POME fermentation is desirable to ensure that an appropriate purity of H_2 is achieved. This work focused on the performance of gas membrane separation technology; by specifically using two different polymeric membranes, namely polysulfone (PSF) and polydimethylsiloxane (PDMS). Based on the results obtained, the selectivity for H_2/CO_2 was achieved using PSF membranes; with the values obtained of 1.54–3.32 at a pressure of 1–8 bar. This result shows that PSF membranes have better performance for H_2 purification than PDMS membranes. This is supported by the analysis of the membranes after the test, which includes Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) analyses. PSF membranes showed no changes on their FTIR spectra after permeation, while PDMS membranes, of 75 and 200 μm thicknesses, recorded higher transmittance of their spectra after permeation. The flexibility of the PDMS membranes is evidence of more permeance of the hydrogen mixture that leads to less selectivity of H_2/CO_2. Meanwhile, SEM and AFM analyses proved the morphology effects; which include changes of pore size distribution cross-section, membrane thickness and surface roughness, after permeation of the applied pressure from 1 to 8 bar, which was possibly due to the compaction effect.

Abbreviations: AFM, Atomic Force Microscopy; EHC, Electrochemical Hydrogen Compression; FTIR, Fourier Transform Infrared; GC, Gas Chromatography; GPU, Gas Permeation Unit; HID, Helium Ionization Detector; IGCC, Integrated Gasification Combined Cycle; MC, Membrane Contactor; MMMs, Mixed Matrix Membranes; MOF, Metal Organic Framework; PA, Polyamine; PC, Polycarbonate; PDMS, Polydimethylsilixone; PEI, Polyetherimide; PES, Polyethersulfone; POME, Palm Oil Mill Effluent; PSA, Pressure Swing Adsorption; PSF, Polysulfone; SEM, Scanning Electron Microscopy; VSA, Vacuum Swing Adsorption.

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Nomenclatures

Z	Average Thickness
ID	Internal Diameter
(P/l)	Pressure-normalized flux
i	Gas *i*
Q_i	Volumetric flow rate of gas *i*,
P	Pressure difference across the membrane
A	Membrane effective surface area
l	Membrane skin thickness
α	Selectivity

Introduction

Biohydrogen (H_2), produced from the fermentation of Palm Oil Mill Effluent (POME) in the oil palm industry, is a recently identified potential alternative energy [1]. Basically, POME fermentation using a mixed culture at a temperature of 55 °C with a pH value of 5.5, mainly produces an H_2 and CO_2 gas mixture [2]. The upgrading (separation and purification) of the H_2 has become a key issue; since only purified H_2 is specifically used for power generation in efficient hydrogen fuel cell applications [3]. This is a way of increasing the market value of the gas for specific applications, such as electricity generation and fuel car consumption, which is currently applied in countries like Sweden, Denmark, Switzerland and France [4].

Membrane gas separation has been investigated for over 150 years, and since 1980, the technology has been used commercially [5]. This technology is used in a number of industrial processes that include the production of oxygen enriched air, the separation of CO_2 and H_2O from natural gas, the purification of H_2, and the recovery of vapours from vent gases [6]. To date, gas membrane technology is an appealing and prosperous technique used to upgrade biohydrogen from fermented gas mixtures; as it is environmentally safe and has relatively easy scalability and portability etc. [3,7]. Membrane separation is based on transmembrane pressure and the differences in permeation rates of the gaseous components. Gaseous species with high permeation rates are rapidly separated from the mixture by the driving force of the transmembrane pressure [8]. Polymeric membranes, such as polysulfone (PSF), polyamide (PA) and polycarbonate (PC), are attractive choices for such separation, because of their inherent advantages, such as low cost, high energy efficiency, ease of operation and they possess a smaller ecological footprint than conventional separation processes, such as Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA) [9].

The performance of the gas membrane separation process depends strongly on membrane permeance and selectivity. Membranes with a high permeance lead to higher productivity and lower capital costs, whereas membranes with a high selectivity lead to more efficient separations, higher recovery and lower power costs. Indeed, membranes that possess high values of selectivity and permeance simultaneously lead to the most economical gas separation processes [10], which are normally aimed at gas separation and purification. The determination of membrane material permeance and selectivity is essential for the design of gaseous mixtures membrane separation processes and to identify the most appropriate range of conditions. It is also used to understand the fundamental mechanisms governing the transport process [11]. The permeance and selectivity characteristics for H_2 and CO_2 separation using membrane technology at different conditions by several authors is summarized and presented in Table 1.

Different membrane materials were used for H_2 and CO_2 separation using membrane technology in the reported studies (refer Table 1). Modigel et al. (2008) conducted a study on CO_2 removal from H_2 using a membrane contactor (MC) with Methyl ethanol amine as the liquid carrier and the selectivity of CO_2/H_2 recorded was at 5.03. Kumbharkar et al. (2011) on the other hand performed mix gas separation of H_2 and CO_2 using polybenzimidazole based asymmetric hollow fiber membrane at 400 °C with H_2/CO_2 selectivity found at 27.28. Next Ramírez-morales et al. (2013) performed a fermentative hydrogen separation using Polydimethylsilixone (PDMS) gas membrane module and showed CO_2 permeance is more favourable than H_2 with the selectivity of CO_2/H_2 at 5.77, slightly better than the work reported by Modigel et al. (2008) [12]. The current work by Wang et al. (2015) on H_2/CO_2 separation using Amine-modified Mg-MOF-74/CPO-27-Mg membrane possessed selectivity of 28 at 1 bar and 25 °C comparable to the one reported by Kubharkar et al. (2011) [13]. Meanwhile Bakonyi et al. have reported on fair selectivity values for H_2/CO_2 upon using different type of polymer membrane from polyimide [14] and PDMS [15]. Based on this summary, it can be concluded that different type of membrane used for the membrane system will result in different permeance and selectivity trend also supported by otherwork [16,17]. Hence, this work focused on the performance of different membranes, from Polysulfone (PSF) and Polydimethylsilixone (PDMS) based polymers, in the separation of POME fermented gases containing CO_2 and H_2 mixtures. The membrane performance in term of its permeance and selectivity was investigated using a specially fabricated gas permeation unit. The best membrane will be used in the gas permeation unit for the separation and purification of biohydrogen/CO_2 mixture directly produced from the fermentation of POME in a bioreactor, which the purified H_2 will be further utilised in a fuel cell system.

Experimental

Materials

Polysulfone (PSF) Udel-P1700 asymmetric membranes with a thickness of 250 μm, supplied by the Advanced Membrane Research Centre (AMTEC), University of Technology Malaysia, were synthesized in a mixture of *N,N* dimethylacetamide, tetrahydrofuran and ethanol at an appropriate composition. The PSF membrane used in this study however belongs to the group of glassy materials and hence is H_2-selective polymeric membranes as stated by Ismail and Yaacob (2006) [18]. The T_g values of the membrane reported is 193.6 °C [10]. The density of the membrane was ranging from 0.0585 to 0.0712 g/cm^3. This means that permeance of H_2 is theoretically higher than

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