Techno-economic feasibility analysis on carbon membranes for hydrogen purification

Xuezhong He

Department of Chemical Engineering, Norwegian University of Science and Technology, NO-7491, Trondheim, Norway

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ABSTRACT

H_2 production from a biomass fermentation process provides a great opportunity for green and sustainability economy compared to use fossil fuels (e.g., steam methane reforming process), but the process usually produces a humidified gas containing 35–65 (vol.%) H_2 and 40–50 (vol.%) CO_2. A novel, energy efficient two-stage carbon membrane system for H_2 purification based on the combination of H_2 selective carbon molecular sieve membranes in the first stage and CO_2 selective carbon membranes in the second stage was proposed. The concept is the first unique technology providing a low H_2 purification cost <1 \$/kg H_2 produced at a feed pressure of 20 bara based on process simulation and cost estimation. The produced high purity CO_2 (>95 vol.%) and H_2 (>99.5 vol.%) can be integrated into a gasification reformer and Fischer-Tropsch reactors to improve the biodiesel productivity from biomass.

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1. Introduction

Hydrogen production from biomass is the most promising scenario due to the waste minimization issue and the demands for the sustainable development. The hemoheterotrophic ("dark") fermentation deserves particular interests due to the advantages of high bacterial growth rate, hydrogen production rate, low energy demands, minimal pollution generation, no oxygen limitation problems and low capital costs for at least small-scale production facilities [1]. Dark fermentation H_2 production (instead of using fossil fuel-like steam methane reforming) provides a great opportunity for H_2 generation, but the process usually produces a humidified gas containing H_2 and CO_2 where hydrogen content normally ranges between 35 and 65 (vol.)%, and may also contain volatile organic compounds (VOC), H_2S and NH_3 [1]. H_2 purification from this gas stream requires novel separation technologies. The existing technologies for H_2 purification are pressure swing adsorption (PSA), cryogenics, palladium (Pd) membranes [2–4]. Conventional PSA or cryogenics will not be suitable for small scale H_2 productions from fermentation processes due to the expected high costs. Even though the palladium membranes have already been commercialized for H_2 purification such as H_2 Pure™ and HYSEP, the membrane production cost is still high and the lifetime is relatively short due to the H_2 embrittlement, which leads to a high capital expenditure (CAPEX). Moreover, the low processing temperature in a fermentation process will cause membrane

cracking due to the Pd-H two phases in this regime (typically <200 °C) that differ considerably in their lattice constant [5] when no pre-heating employed. Some literature has already reviewed the status of different polymeric membranes for hydrogen purification [6–9]. The issues and challenges with gas separation membranes to be applied for the concentration of fermentatively produced H_2 gas has been reviewed recently by Bakonyi et al. [6]. Li et al. compared the H_2-selective and CO_2-selective membrane materials and processes, and pointed out the future direction on the development of energy-efficient membranes [7]. With respect to the non-porous polymeric and mixed matrix membranes, it is quite challenging to achieve a high H_2 purity (>99%) requirement with low selectivity (<10) [6,10–13]. Moreover, the composition of the biohydrogen gas mixture, in particular its impurity (e.g., H_2S) content was found to significantly influence the polymeric PDMS membrane performance reported by Bakonyi et al. [14]. They also pointed out that polymeric membranes were mostly tested under ideal laboratory conditions in the literature though in reality, the hydrogen generated by fermentation process is a part of a complex biogas stream, leading to the potential differences in the modules behavior. A hybrid polymeric membrane/absorber system might be a solution to achieve the separation requirement for biohydrogen purification reported by Bakonyi et al. [15], but the process complexity and economic feasibility should be further investigated. The above described challenges direct to the development of an alternative membrane material with high H_2/CO_2 selectivity and good chemical stability exposed to the impurities (e.g., H_2S) which are usually existed in the raw

biohydrogen gas mixture, and can bring down the H_2 purification cost, and potentially expand the H_2 production from new fermentation processes.

Carbon membranes have great advantages on their mechanical and chemical stabilities when exposed to a high pressure and/or a high temperature process, and the performance can exceed the Robeson upper bound (2008) based on the molecular sieving transport mechanism, and reach the industrial attractive region [16]. Carbon membranes possess ultramicroporous structure, which are mainly prepared by the carbonization from polymeric precursors such as cellulose derivatives [17–20], polyimide [21–25], and polyacrylonitrile (PAN) [26]. By carefully controlling the pyrolysis conditions, the pore size of the produced carbon materials can be well tailored at nanoscale, and to separate the gas molecules which are much alike in the size (molecular sieving). Moreover, the surface properties of carbon membranes can also be modified to present a selective surface flow (SSF) mechanism where more condensable gas like CO_2 has a high permeance compared to the less/no condensable gas of H_2. Both molecular sieve and selective surface flow carbon membranes provided great potentials for selected gas separations (e.g., CO_2/CH_4 [27,28], hydrocarbon separation [24,29]). In addition, carbon membranes are also expected to tolerate the impurities (e.g., H_2S) when exposed to a fermentation gas stream. This statement is based on experience achieved with a carbon membrane pilot tested at a biogas plant in Southern Norway [30]. Thus, the feasibility of carbon membranes for purification of H_2 produced from new fermentation processes was studied in this work. An energy efficient two-stage carbon membrane system was designed to achieve the separation requirement for hydrogen purification from a fermentation process without combining with other separation technique.

2. Carbon membranes for H_2/CO_2 separation

2.1. Carbon molecular sieve membranes

Lie et al. reported that H_2/CO_2 separation used cellulosic-based carbon molecular sieving membranes [31]. The metal added carbon membrane, especially MgO-carbon membrane showed a high H_2/CO_2 selectivity of 81 with a H_2 permeance of 0.05 m^3(STP)/ (m^2 h bar). It was worth noting that results were reported at 30 °C, and the membrane performance of both H_2 permeance and H_2/CO_2 selectivity are expected to increase at higher operating temperature (e.g., 100–150 °C). For the smaller gas molecules (e.g., H_2), the influence of temperature on permeation (diffusion, activated transport) is more significant compared to the CO_2 molecules due to a reduction of CO_2 solubility coefficient at higher temperature. Thus, H_2/CO_2 selectivity are expected to increase with temperature. However, due to the challenges on module sealing at higher operation temperature, the carbon membrane system is usually recommended to be operated at <200 °C.

2.2. SSF carbon membranes

The concept behinds the selective surface flow (SSF) carbon membranes is that when operated at a lower temperature (<20 °C), the larger and more condensable gas molecules (e.g., CO_2) will adsorb on the pore walls, and "flow" through the membranes, which will result in a reduced pore size and eventually hinder the smaller and more inert molecules (e.g., H_2) to transport through the membranes. The separation will thus depend on the critical temperature (T_{crit}, high T_{crit} means more condensable) of gas component [32], which is specially suitable for the 2nd stage membrane unit. This separation method was first patented by Air

Products & Chemicals Inc. in early 90'ies, while later Carbon Membranes Ltd. in Israel also documented the excellent separation performance of their self-supported hollow fibers for various gas mixtures. They used (chemical vapor deposition (CVD) for pore adjusting (tailoring with oxidation) after the pyrolysis. The company had to close down for reasons not discussed here. The importance of process conditions such as pressure and temperature for a SSF separating membrane was reported by K. Vennes [33] – their focus was separation of propane (T_{crit} = 96.7 °C) from propene or H_2. Thus, low temperature and higher pressure will favour the permeation. Moreover, Trinh et al. reported the CO_2 permeation through a carbon membrane by molecular modelling at various temperatures [34] – they documented that an adsorbed layer of CO_2 on the pore wall was formed. The experimental data of the SSF carbon membranes reported by Paranjape et al. [35] was used as simulation basis in this work.

3. Process concept design

3.1. Process description and simulation basis

The combination of biomass gasification with Fischer-Tropsch (FT) synthesis is designated as biomass-to-liquids (BTL). Nowadays, the main objective of the research and development projects on BTL is to produce the second generation bio-fuels by biomass gasification combined with FT synthesis [36]. In this work, the FT synthesis process integrated with carbon membrane unit for H_2/CO_2 separation was designed to provide an alternative route for the production of transportation fuels (biodiesel) from biomass as illustrated in Fig. 1. The humidified gas stream produced from a biomass dark fermentation process mainly contains H_2 and CO_2 where hydrogen content usually ranges from 35 to 65 (vol.)%. The H_2 gas stream was then fed into a carbon membrane unit for H_2/CO_2 separation. Moreover, biomass was also fed into a gasification reformer to produce syngas. Part of the captured high purity CO_2 (>95 vol.%) from the retentate stream in the membrane unit was sent to the gasification reformer to shift reaction to left side and improve the CO productivity. While the permeate high purity (>99.5 vol.%) H_2 stream from the carbon membrane system was added to the syngas, which can adjust the H_2/CO ratio to the optimal value of 1.9 in the first FT reactor. The additional H_2 was used as H_2 makeup in the subsequent (i.e., 2nd and 3rd) FT reactors to maintain the H_2/CO ratio at 1.9 [37]. Developing an energy efficient H_2/CO_2 separation carbon membrane system is crucial to achieve an economic process for biodiesel production from biomass.

In order to document the technology and economic feasibility of a carbon membrane system for H_2 purification from a fermentation process, process simulation was conducted in a gas stream with the characteristics listed in Table 1. The membrane performance reported in the literature [31,35] was used as the simulation basis listed in Table 2. The following assumptions were made in the process simulation:

- No feed and permeate pressure drop employed.
- Compressor efficiency was set 75%.
- A counter-current configuration was used in the membrane transport model.

3.2. Membrane process design

A novel, energy efficient two stage carbon membrane system for H_2 purification was designed (see Fig. 2) based on the combination of H_2 selective hollow fiber carbon membranes (Carbon molecular sieve membranes (CMSMs)) in the first stage and CO_2 selective carbon membranes (Selective surface flow (SSF) carbon