APPLICATION OF CONVENTIONAL AND IONIC LIQUID SUPPORTED POLYMERIC GAS SEPARATION MEMBRANES IN BIOHYDROGEN RECOVERY: THE ROLE OF OPERATIONAL CONDITIONS

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Biologically generated hydrogen – referring to the term of biohydrogen – research represents one of the hottest topics in the field of bioenergetics due to the inherent benefits of hydrogen over the other energy carriers, particularly its unique, environmental-friendly features and high energy content on gravimetric bases [Das & Veziroglu, 2001].

Though biohydrogen shows a high potential for future's sustainable development, there are still pending issues concerning two major obstacles in the technology, namely the consecutive production and purification. These steps need to be further improved to make biohydrogen a more reliable option.

As a result of the recent decades, it can be concluded that among the several ways to produce biohydrogen, dark fermentation would appear to be the most feasible from various points of views such as high stability, simple control requirements, high volumetric productivity, etc. This method enables one to achieve sufficient production rates by utilizing cheap and widely available organic wastes formed in large quantities globally. Although the dark fermentation is promising it usually suffers from low yields (mol H_2/mol substrate) [Hallenbeck, 2009]. Thus, an essential task is to achieve improved substrate conversion efficiencies [Hallenbeck, 2009, Nandi & Segupta, 1998]. In recent years, it has turned out that the accumulation of hydrogen in the bioreactor is a significant reason for low biohydrogen yields because hydrogen evolution is highly-sensitive to H_2 concentration and is subject to product inhibition [Nath & Das, 2004]. As hydrogen concentration increases in the bioreactor, H_2 synthesis decreases and metabolic pathways of the whole cell biocatalysts shift towards the formation of by-products such as lactate and other solvents (e.g. ethanol, acetone, butanol, etc.) [Nath & Das, 2004; Levin et al., 2004]. Consequently, systems should properly be designed and operated to reduce H_2 partial pressure – and thus the concentration of H_2 dissolved in the fermentation broth – before it leads to the repression of its generation [Hallenbeck, 2009; Nath & Das, 2004; Kim et al., 2006; Mandal et al., 2006].

For this purpose, various solutions such as nitrogen sparging, vigorous mixing have been proposed [Nath & Das, 2004; Kraemer & Bagley, 2007] but the development of novel methods is still needed e.g. by employing membrane separation. Membrane technology might aid to overcome the issue of low yields by allowing in-situ and continuous removal of biohydrogen from the reactor. However, this approach is poorly investigated in spite of its particular attractiveness.

In theory, a wide range of membrane applications are available to complete the task of hydrogen separation and can be classified into categories such as organic (usually made of artificial polymers) and inorganic membranes. These groups can be subdivided into porous and non-porous membranes.

Metallic (e.g. palladium) and metallic alloy membranes are well-known members of the inorganic, non-porous class [Yun & Oyama; 2011]. These are extremely selective to hydrogen but possess some drawbacks e.g. high cost, fragility and drastic operational circumstances (e.g. elevated temperature) that restrict its usefulness for biological systems.

The conventional porous, inorganic membranes separate gaseous compounds based on differences in molecular weight and diffusivity, representing an upper-limitation for the achievable process efficiency [Mulder, 1996]. The porous, organic (polymeric) membranes derive their selectivity based on the similar principle. Nevertheless, such membranes are often used to fabricate membrane contactors (MC) and liquid membranes (LM).

In LMs, various liquids fill the pores of the organic (polymeric) membranes serving as support/carrier matrixes. Nowadays, ionic liquids are preferentially applied instead of the traditional organic solvents and thus supported ionic liquid membranes (SILMs) can be prepared. Through this approach, the originally porous, polymeric membranes are transformed into non-porous ones and perform separation based on a mechanism called solution-diffusion. A similar separation principle characterizes the conventional non-porous, organic (polymeric) membranes (NPPM), as well.

In MCs, a porous, organic (polymeric) membrane stands for a physical barrier between the gas to be separated and the absorption liquid. The separation is dependent on the affinity of gases to the absorption liquid employed and therefore MCs can be described as devices combining membrane and absorption technology.

As a matter of fact, among the various alternatives introduced so far, SILMs, NPPMs and MCs appear as the most potential candidates for biohydrogen enrichment since their operational requirements are close to those required for molecular hydrogen fermentation (nearly ambient temperature and pressure), where they might able to express sufficient separation performance.

Although membrane contactors are interesting and suitable options for the purification of gaseous mixtures with biological origin [Teplyakov et al., 2002; Modigell et al., 2008; Beggel et al., 2010; Rongwong et al., 2012], their application receives somewhat less attention in comparison with NPPMs and SILMs. Therefore, MCs are now beyond the scope of this paper and only non-porous, polymeric and supported ionic liquid membranes are focused.

It is widely known that the feasibility of a membrane based gas purification system is dependent on three main factors:

- material selection for membrane fabrication
- design and configuration of membrane modules
- operation conditions

Membrane gas separation – especially the progress in material engineering – has recently been addressed in depth from various aspects [Abetz et al., 2006; Bernardo et al., 2009; Shao et al., 2009; Yampolskii, 2012]. However, none of the research and review articles was specifically dedicated to membrane operation in the important field of biohydrogen recovery. Therefore, such a comprehensive overview was aimed to give in this paper. The effects of the most crucial operational factors influencing the performance of the non-porous, polymeric and ionic liquid based membranes for biohydrogen concentration were discussed. Moreover the concept of the Gas Separation Membrane Bioreactor – integrating hydrogen production and purification into a single system – as a possible innovative way in biohydrogen technology was presented. The particular benefits of this special set-up as well as some technical challenges were reviewed.

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