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# BIOHYDROGEN RECOVERY AND CONCENTRATION BY MEMBRANE GAS SEPARATION

Ph.D. THESES

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# Introduction

Biohydrogen may be considered as breakthrough in the production of hydrogen – what is called the energy carrier of the future – since it is an environmental friendly process with low energy demand where hydrogen can be produced from organic wastes. One drawback is that other gases (like $CO_2$) could be generated through metabolism and inert gas (mainly nitrogen) is present to provide anaerobic conditions. These gases dilute hydrogen which must be concentrated before use. The other aspect is that the process is strongly product inhibited so the produced gases must be recovered from the head space of the fermenter by a convenient and safe method.

Membrane gas separation seems the most promising method in the comparison of other separation techniques because it doesn’t need chemicals as absorption methods, works on ambient temperature and needs less energy than cryogenic technology. Additional benefit is the possibility of flexible connection to other (ie. microbiological) methods.

The volume of the produced gaseous mixture from the biohydrogen fermentation is generally between few ml to 10 litres. This volume is much less than the classical gas separation equipments can handle so they are unsuitable to recover biohydrogen. Moreover in membrane research so far separation of hydrogen was mainly used in catalytic (de)hydrogenation reactions with high temperature (200-800 °C) hence the majority of applied membranes had very good heat resistance and were made from very expensive, inorganic material. However, there is no need for elevated temperature in biohydrogen separation therefore much cheaper polymeric membranes with less heat resistance but adequate hydrogen flux can be also suitable for this object. Hence the purpose was to design and build a gas transporting, compressing and collecting system radically different from conventional ones where the gas separating module(s) can be integrated into the system.

In this PhD work recovery and concentration of hydrogen produced by various microbes in fermenter under anaerobic conditions were studied in lab-scale membrane gas separating equipments.

## Experimental methods

A non-porous, hollow fibre polyethersulphone-polyimide membrane with 12 $cm^2$ surface area and 0.1 μm active thickness was tested to separate the hydrogen/nitrogen gaseous mixtures in an equipment built in the doctoral work. To separate hydrogen/$CO_2$ gaseous mixtures three hollow fibre membranes with different pore sizes were tested in another equipment built for this purpose. Three-component gaseous mixtures were separated with the connection of the two modules. The fluxes of the membranes were measured each time with liquid seal system. The compositions of two- and three-component mixtures were determined by gas pipette and gas chromatograph, respectively.

Three different hydrogen producing strains were studied in this work. *Thiocapsa roseopersicina* is a Gram-negative, purple, sulphur bacteria which consumes reduced sulphur compounds (sulphide, thiosulphate, elemental sulphur) as electron donor but organic substrates (glucose, acetate) can also provide this function. *Escherichia coli* and *Thermococcus litoralis* produce hydrogen through dark fermentation under anaerobic conditions by decomposition of organic substrates. The composition of substrates and the operation of the fermenter were optimal in all cases. The latter was determined by pre-experiments in case of *Escherichia coli*. The substrate of *Thermococcus litoralis* was extract of the waste feather. An increase of the pressure indicated the gas formation in the fermenter which was measured by a manometer while the composition was determined by gas chromatograph.

# Novel scientific results

1. Lab-scale device was designed and built for membrane purification of biohydrogen where different membranes were tested to separate $H_2/N_2$ and $H_2/CO_2$ model mixtures. It was found that

    a. porous HDPE membrane is suitable to separate hydrogen/carbon dioxide mixture. The basis of the separation is the Knudsen-mechanism and selectivity coefficient of 3.44 can be achieved that is close to the theoretical maximum.

    b. dense, hollow fiber, composite polyether-sulfone/polyimide membrane is suitable to separate hydrogen/nitrogen mixture with separation coefficient of 26 [1,8].

2. Integrated system was developed by connection of photobioreactor containing the hydrogen producing strain *Thiocapsa roseopersicina* working under nitrogen atmosphere and the equipment described in theses 1. In the course of operation the built-in polyether-sulfone/polyimide membrane increased the initial 8-10% hydrogen containing $H_2/N_2$ mixture above 40% [4].

3. Fermentation experiments were carried out with capable strains for hydrogen production of *Escherichia coli* and it was concluded that the xl1-blue species under 27 hours fermentation time, at 2.5/1 substrate/gas volume ratio and with periodical gas removal can be operated properly. Two-stage membrane separation equipment described in theses 1. was attached to fermenter containing three component ($H_2/N_2/CO_2$) mixture. At the first stage high density polyethylene membrane, at the second stage polyether-sulfone/polyimide membrane was applied and the hydrogen content of the mixture raised by three times while the $CO_2$ concentration remained on the same level in the permeate [12].

4. The two-stage lab-scale membrane separation system was attached to fermenter containing anaerobic, hypertermophilic (operating at 85 °C) *Thermococcus litoralis* strain. Based on the experimental results it was found that one step gas recovery from fermenter contains more hydrogen than the fractional recovery with nitrogen washing. In concordance with the result of model experiments the final permeate of the two-

stage membrane system contained 70.3% hydrogen that is high enough to utilize in fuel cells [2].

## Conclusion

The aim of the PhD work was to design and build a membrane gas separation equipment which can recover and concentrate the biohydrogen containing mixture generated in fermenter. Hydrogen concentration must reach 70% for fuel cell applications.

Depending on metabolic pathway of hydrogen production the head space of the fermenter can contain two (hydrogen, nitrogen) or three (hydrogen, nitrogen, carbon dioxide) component mixtures. Their concentration depends on the fermenting strain and operational conditions. The selection of membranes with appropriate properties to separate effectively the mixtures with different amount and quality was part of the work. To test the modules and for further measures lab-scale, one- and two-step equipments were built where the two- and three-component gaseous mixtures from fermenter were recovered, transported and separated in energy saving manner. Permeability and selectivity parameters of the membranes were measured with pure single gases and model mixtures. The theoretical basis of the optimal operational conditions was set by selection and solution of the model which suited well the given module configuration and confirmed the measured results.

In the second part of the experimental work lab-scale integrated hydrogen producing and separating system was built by coupling the gas separation equipments and the fermenter. The flexible separation process with various microbes fermenting under optimal conditions reached the maximum hydrogen concentration value from the membranes selectivity point of view.

No reports on other system combining biohydrogen production and membrane gas separation processes has been found in literature, so far. Therefore this process – developed by using the results of theoretical background, as well – can form the basis of a pilot plant where gases are produced through biological way by decomposition of agricultural wastes and the end-product is purified hydrogen. This system can solve the supply of fuel cells and help the development of hydrogen economy.

## List of related publications


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