審　査　の　結　果　の　要　旨

Development of perfluorocarbon-based supported liquid membranes for gas separation
（気体分離のためのパーフルオロカーボン液体膜の開発）

氏　　名　　カストロ　ドミングス　ベルナルド

This thesis deals with the development of supported liquid membranes for the separation of gaseous mixtures with special attention placed on the separation of H_2 and O_2 mixtures derived from photocatalytic processes. The membranes used perfluorocarbons as active liquids supported on porous alumina. The performance of the liquid membranes was tested under different conditions of pressure, humidity and support pore sizes.

Chapter 1 gives a review on gas separation technologies, followed by a thorough literature analysis on liquid membranes to provide background on these novel membranes.

Chapter 2 describes perfluorotributylamine (PFTBA) liquid membranes for H_2/O_2 separation. The membranes were formed by imbuing the liquid into porous alumina supports and were subject to single and mixed H_2/O_2 gas permeance tests at close to room temperature (30, 40 and 50 ^{o}C) and different flow rates. The membranes showed a solution-diffusion transport behavior with an average H_2/O_2 selectivity of 140 with a H_2 permeance of $1.0x10^{-9}$ mol $m^{-2}s^{-1}Pa^{-1}$. Small support pore sizes were used to reduce the vapor pressure of the liquid inside the porous support and increase membrane lifetimes. The diffusivity and solubility of the gases across the membrane were obtained by the time-lag technique. It was found that H_2 has higher solubility and diffusivity than O_2 giving rise to a higher permeance for the smaller sized gas.

Chapter 3 describes supported perfluorooctanol (PFO) liquid membrane for H_2/O_2 separation. The PFO membranes were prepared as the PFTBA membranes and were subject to single and mixed H_2/O_2 gas permeance tests at close to room temperature (30, 40 and 50 ^{o}C) and different flow rates. The membranes showed a sieving transport behavior with an average H_2/O_2 selectivity of 100 with a H_2 permeance of $2.9x10^{-10}$ mol $m^{-2}s^{-1}Pa^{-1}$. The diffusivity and solubility of H_2 and O_2 in the PFO membrane were measured by a time-lag technique. The membranes were found to have good water tolerance.

Chapter 4 describes supported perfluorotributylamine (PFTBA) liquid membrane for O_2/N_2 and H_2/N_2 separations. This chapter reports the implementation of the membranes to carry out the separation of O_2/N_2 and H_2/N_2. The PFTBA-supported membrane reached an average O_2/N_2 selectivity of 60 with an O_2 permeance of $8.0x10^{-10}$ mol $m^{-2}s^{-1}Pa^{-1}$. It is shown that the membrane's selectivity increased as the temperature increases but the stability of the membrane was reduced. Moreover, the separation of H_2 and N_2 was studied to provide insight on the functioning of the membrane and a H_2/N_2 selectivity of 100 was observed with a H_2 permeance of $1.0x10^{-9}$ mol $m^{-2}s^{-1}Pa^{-1}$. The permeance order was $H_2 > O_2 > N_2$, so the size of the permeating species was found to be an important contributor to the permeance. PFTBA presented an excellent separation performance when compared with conventional supported ionic liquid membranes (SILMs). The ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4] showed a maximum O_2/N_2 selectivity of 6 and permeance of $3.4x10^{-12}$ mol $m^{-2}s^{-1}Pa^{-1}$.

Chapter 5 describes a process simulation of perfluorocarbon-membranes for photocatalytic water splitting. The analysis uses a process flow scheme in Aspen Plus. The simulation showed that H_2 can be recovered with an efficiency of 90% and a purity of 99% and that the PFC membranes are competitive with pressure swing adsorption (PSA). The recovery of O_2 has a purity of 80% mainly mixed with hydrogen. The utilities required for this system such as cooling water and electricity for this set up were lower than those presented in PSA. An economic evaluation was performed using annualized payments as the economic indicator. The annualized payments of PSA and the membranes were set to match in order to estimate the capital costs of the membranes. The result of the economical evaluation showed that membranes can have higher capital costs and still be competitive with PSA. The main factor is the requirement of lower operating costs.

Chapter 6 contains the conclusions of the thesis and summarizes the findings of the PFTBA and PFO membranes. It also presents suggestions for future work which would lead to the commercialization of these membranes. These recommendations include testing several perfluorocarbons to understand the functionality of fluorine in these components. Examine the separation of other gas pairs such as CO_2/CH_4. Implement a continuous liquid feeding with the gas mixture to expand the lifetime of the membrane. Demonstrate the membrane in a photocatalytic water splitting system.

This thesis passes the requirements for the doctoral degree thesis in engineering and it can be judged to contribute to the development of chemical systems engineering.