INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Programme of Study	:	Ph.D.

Thesis Title:
Performance Optimization of Pd-Ag Based Catalytic Membrane Reformer for 'On-Site' Hydrogen Production via Methanol Steam Reforming

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Thesis Submitted to the Academic Division	:	Chemical Engineering
Date of completion of Thesis Viva-Voce Exam	:	10/06/2025
Key words for description of Thesis Work	:	Hydrogen Production, Hydrogen Separation, Pd-Ag Membrane, Methanol Steam Reforming, Multi-pass Membrane Separator, Double Stage Membrane Reformer, Concentration Polarization, Feed Distribution, Scale-up, Cu-Fe/AZZ Catalyst, SiC Foam

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Hydrogen being the most abundant element on the earth has not been exploited to its full capacity till now. Despite having the highest energy-to-weight ratio (141.9 kJ g^{-1}) among other parallel competitors like gasoline (47.5 kJ g^{-1}) and diesel (44.5 kJ g^{-1}), the potential of hydrogen is still underutilized. The commercial exploitation of hydrogen as a renewable energy carrier has been the subject of significant effort over the past two decades. Safe storage and transportation are the primary impediments to commercialization. In order to overcome these challenges, producing and utilizing H_2 at the application site (on-site) is deemed to be advantageous. However, hydrogen is perpetually present in its compounded forms, including alcohols, water, coal, biomass, and other hydrocarbons. In order to extract hydrogen from these sources, a variety of methods are employed, including steam reforming (SR), autothermal reforming (ATR), partial oxidation (POX), pyrolysis, gasification, and fermentation. Steam reforming of hydrocarbons is the most prevalent commercial method owing to its high efficiency (70-85%). Hydrogen produced using these methods is always accompanied by gases (CO_2, CO, CH_4, N_2, and O_2). Membrane technology plays a crucial role due to its operational flexibility, ability to produce ultra-pure hydrogen, and compatibility with simultaneous reaction-separation processes, hence enhancing overall efficiency. Furthermore, they are quite practical for small-scale and portable applications and produce high-purity hydrogen at the cost of minimal energy and space. Pd-based dense composite membranes have always been the favorite for efficient hydrogen separation. From a practical standpoint, a Pd-based membrane

offers high hydrogen permeability with ideally infinite selectivity. Additionally, it can operate at high temperatures and pressure for extended periods while consuming little energy and requiring little maintenance. Among different sources of H_2 generation, methanol is the simplest alcohol and has the potential to revolutionize the process of producing hydrogen onboard/onsite because of its abundance of availability, low cost, high hydrogen density, environmental friendliness, and ease of transport and storage under ambient conditions. Moreover, its energy density is 80% higher than that of liquid hydrogen, with a gravimetric and volumetric hydrogen storage capacity of 12.5 (wt%) and 99 kg m^{-3}, respectively. There is more hydrogen in a cubic meter of methanol (99 kg m^{-3}, atm) than there is in a cubic meter of liquid hydrogen (70 kg m^{-3}, 20 K), formic acid (53 kg m^{-3}, atm), H_2 compressed cylinder (39.9 kg m^{-3}, 70000 kPa), and even AlH_3 based metal-organic framework (85 kg m^{-3}, achieved in practice). Its low reforming temperature (523-623 K) due to the absence of a C-C bond also lowers the possibility of coke production at high temperatures. The presence of the –OH functional group is also a good attribute, as it reduces the amount of water consumed in the steam reforming reaction to produce hydrogen, hence reducing the steam reforming process temperature. To fully utilize hydrogen's potential, it must be separated from methanol due to its lower heating value (119.9 MJ kg^{-1}) which is roughly 6.5 times higher than methanol's (18.1 MJ kg^{-1}). Consequently, methanol can serve as a future 'Hydrogen Carrier' that can be readily accommodated by the existing infrastructure. Hence, to integrate the simultaneous methanol steam reforming (MSR) and H_2 separation in a compact device, novel membrane reformers (MR) devices are currently being conceptualized that integrate hydrogen production and separation into a single reactor unit. The fundamentals of MR are derived from Le Chatelier's principle, which states that the continuous removal of the H_2 through the membrane shifts the thermodynamic equilibrium towards the desired product resulting in enhanced conversion.

While the basic idea behind an MR may seem straightforward, the task of combining a high-temperature, low-pressure steam reforming reaction with a low-temperature, high-pressure membrane separation process presents a significant obstacle. The heat and mass transfer limitation of the packed bed reactor limits its large-scale application, especially for endothermic reactions like MSR. Concentration polarization and the reactive nature of other gases negatively affect the membrane performance. A tradeoff between selectivity and flux needs to be tuned to attain the best possible membrane performance as well as catalytic activity. The reactor geometry, such as the membrane configuration, reactor dimensions, and reactor shape, can influence the mass transfer of reactants and products, heat transfer, and fluid dynamics within the reactor.

The main aim of the present study is to perform a comprehensive investigation of the design of membrane reformers and the production of fuel cell grade high-purity hydrogen through methanol steam reforming using Pd-Ag membrane. In order to achieve the objectives outlined earlier in Chapeter-1, a composite Pd-Ag membrane is prepared using the ELP technique over the alumina support. Multiple cycles of deposition are performed to obtain a dense Pd-Ag membrane till 400 kPaG. After the preliminary leak test, the membrane performance is examined by subjecting it to pure H_2 and N_2 under varying temperatures (573-773 K) and pressure (100-300 kPaG) conditions. The investigation also encompasses the examination of the effect of mixture gases, such as H_2/N_2,

H_2/CO_2, H_2/CH_4, H_2/CO, and feed load on the performance of the membrane. In addition to this, the long-term thermal heat cycle stability of the membrane is performed to assess its potential for commercial exploitation. However, the effect of concentration polarization significantly reduces the H_2 permeation capacity of the membrane. Therefore, a multi-pass membrane separator (MPMS) is designed to have four passes and multiple feed injection facilities to enhance the H_2 recovery from the mixture gas. This configuration not only improved the regulation of the H_2 partial pressure across the separator but also optimized the interaction between the feed gas and the membrane. MPMS performance is tuned for various locations inside the separator, baffle proximity, feed load, and membrane-to-pass ratio. The study demonstrated that multi-pass membrane separators minimize concentration polarization. Additionally, multiple membranes with baffles improved the separator performance to a higher degree compared to the same case without baffles. At last the effect of feed distribution in different pass over the separator performance was studied. It was observed that proper feed distribution is crucial to maintain the hydrogen partial pressure inside each pass. This significantly improved the overall hydrogen recovery while minimizing the effect of concentration polarization. After optimizing the MPMS, the same system is integrated with an additional membrane reformer unit to recover more hydrogen from the retentate side. The MR was packed with the SiC-foam-supported Cu-Fe/AZZ catalyst prepared via a wash-coating technique. The use of a SiC-based foam significantly reduced the heat and mass transfer issue in endothermic MSR, owing to its exceptional thermal conductivity. Initially, the performance of the MR is evaluated with varying operational parameters such as weight hourly spase velocity (WHSV), temperature (523-673 K), pressure (100-400 kPaG), and number of membranes. At last, the effect of adding MPMS is examined at the same operating parameters, and the entire system is termed a Double Stage Membrane Reformer (DSMR). A comparative study of the traditional reformer (TR), MR and DSMR is done based on the various parameters including conversion, hydrogen recovery, hydrogen yield, H_2 production rate, and overall permeate H_2 purity.