A Novel Pressure Swing Steam Reforming Reactor

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This is a progress report for this new research direction project, in the area of Chemical Reaction Engineering (CRE), for the PI, who is an expert in Process System Engineering (PSE). The theoretical part of the project is carried out by the PI, and UCLA graduate students. The experimental part of the project is carried out by the co-PI, and a USC graduate student.

The grant has had several beneficial effects. Involved students were able to find permanent jobs. The Pi, co-PI collaboration is flourishing, resulting in a new experimental/theoretical research project in the area of CRE, funded by the United States Department of Energy. Furthermore, one of the UCLA students has secured a teaching assistant apprenticeship in the field of dynamic systems modeling, which is a direct consequence of the knowledge he acquired working on this project.

This PRF-supported project focuses on the development of a novel reactive separation process, that can be used to intensify steam reforming of methane (SRM) for the development of clean energy sources, such as hydrogen. The novel technology being investigated shows good promise to produce ultrapure hydrogen at much higher efficiencies than the conventional SRM processes.

On the experimental side, we focused on the preparation of hydrogen-permselective, high-temperature and steam-stable thin films with high fluxes and large separation factors; the fabrication of such films remains today a challenge. Silicon-based ceramic films are particularly promising in that regard due to their high temperature resistance and excellent chemical stability, and have been the focus of our research efforts at USC for the last couple of years [Nguyen et al., 2019]. In our study, we have used a new synthetic route for fabricating such nanoporous films via the pyrolysis of silicon-containing polymer films deposited by initiated chemical vapor deposition (iCVD) on macroporous silicon carbide supports. Specifically, we have systematically investigated the change in the chemical structure of poly(2,4,6,8-tetravinyl-2,4,6,8-tetramethyl cyclotetrasiloxane) films at different pyrolysis temperatures and found that the complete transition to a silica film occurred at ~1100 °C. Three different supports composed of silicon carbide powders of varying sizes were tested for film preparation. It was found that films formed with our process were microporous with separation factors several times above the corresponding Knudsen factors. Our synthetic route, therefore, offers a scalable and solventless method for producing silicon-based ceramic films for use in the high-temperature SMR and other reactive separation applications.

On the theoretical side, a first principle-based model, capturing the behavior of the novel storage reactor (SR) process, was developed, simulated and analyzed. The SR process combines reaction and separation in a transient three phase operation, and can deliver high purity products, and overcome equilibrium limitations. To
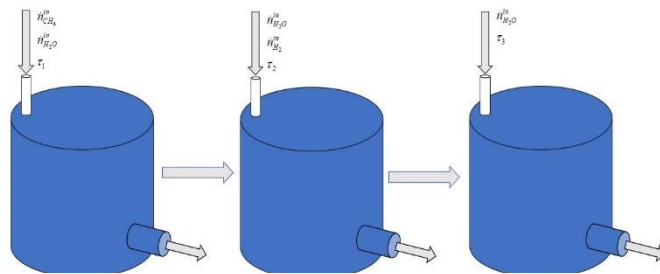

Figure 1: Three phase operation of SR showing varying inlet conditions during each phase.

assess SR behavior, a 0-dimensional dynamical model was developed, whose dimensionless form highlights that two dimensionless parameters, Da (Damkohler number) and $\Theta = 1/Pe_{mem}$ (inverse Peclet number), determine SR behavior. In order to quantify the extent to which the proposed SR outperforms a conventional stead-state reactor (SSR), a number of metrics were introduced accounting for the periodic nature of the process. A case study on hydrogen production through Steam Methane Reforming was carried out, and SR Conversion, Yield, and Hydrogen Recovery were all shown to be greater than their SSR counterparts. A parametric study was then carried out on the aforementioned dimensionless groups, and it was shown that maximizing both groups led to improved SR performance, highlighting the importance of considering both reaction and separation processes when determining reactor performance.

In analyzing the first dimensionless parameter, Θ, it was found that several process design and operational parameters can be adjusted to increase its value. First, the inlet flowrate can be reduced, thus increasing reactant residence time, and allowing for additional reactant conversion to occur within the gas domain. Second, the gas-storage domain interfacial area can be increased, allowing for increased transport between the two domains. Third, increased preferential hydrogen permeance through the storage medium's permselective layer can be pursued,

through appropriate selection of the layer's pore structure and material. Finally, high reactor operating pressure would also lead to higher Θ values.

An investigation into the effects of different stopping criteria for phase 1 of operation was also conducted. Two different criteria were selected, the first being the time at which the function $\omega_{CO_2,1} : \tau_1 \to \omega_{CO_2,1}(\tau_1)$ reaches its maximum value, i.e. $\tau_1^* \triangleq \underset{\tau_1 \in [0,\infty)}{\arg\max}\, \omega_{CO_2,1}(\tau_1)$, where $\omega_{CO_2,1}$ is a function describing the exit concentration of CO_2 from the reactor defined as the difference between the inlet and outlet time averaged molar flowrates of CO_2, divided by the summation of the time averaged inlet of CH_4 over all three phases. The second criterion was decided to be the time at which the hydrogen partial pressure inside the storage medium reaches 90% of the hydrogen partial pressure attained in the reactor for operating times approaching infinity (which is equal to the hydrogen partial pressure at the exit of the corresponding steady-state reactor). It was found that stopping criteria one was superior to that of the second across all metrics. The rationale for this is that for small values of τ_1, the value of the CO_2 related function is close to zero, while for large values of τ_1, the value approaches the corresponding product ratio of the steady-state, no storage, reactor. Using the first stopping criterion ensures that significant CO_2 product generation has occurred during the first phase, leading inevitably to significant H_2 hydrogen generation and storage, and also leaving the SR gas phase at the end of phase 1 in a CO_2 rich state, increasing the decarbonization efficiency during the second phase of operation. This work has been submitted for publication.

Publications

Nguyen, B., Dabir, S., Tsotsis, T., and Gupta, M. "Fabrication of Hydrogen-Selective Silica Membranes via Pyrolysis of Vapor Deposited Polymer Films," 10.1021/acs.iecr.9b02902, *Ind. Eng. Chem. Res.,* 2019.
Lowd, III, J., Tsotsis, T. T., Manousiouthakis, I. V. "On Process Intensification Through Storage Reactors: A Case on Methane Steam Reforming", submitted