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A Novel Pressure Swing Steam Reforming Reactor

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This project represents a new research direction, in the area of Chemical Reaction Engineering (CRE), for the PI, who is an expert in Process System Engineering (PSE). The project is both experimental and theoretical in nature and is carried out by the PI, co-PI, students at UCLA (Jack Lowd (Ph.D.), Flavio Cruz (Ph.D.), Omar Sheikh (Ph.D.), and Chaunjun Jiao (M.S.)), and a Ph.D. student at USC (Bryan Nguyen). The experimental component of the research project is being carried out at the well-equipped CRE experimental laboratory of the co-PI at USC by all project participants. The theoretical component of the research project is being carried primarily at the computational laboratory of the PI at UCLA. The geographic proximity of UCLA and USC (14 miles) is enabling this project execution mode.

Incorporating experimental expertise into the PI's skillset has furthered his career by enabling him to secure (jointly with the co-PI) experimental/theoretical research projects in the area of CRE, funded by the United States Department of Energy. Furthermore, the UCLA students are being trained in a variety of theoretical and experimental techniques, providing him with a unique set of skills rarely found in US academic circles. In addition, the students have gained a practical understanding of the research being carried out, and potential applications in a variety of relevant industrial fields.

The focus of this project is the development of a novel reaction-separation device that can overcome equilibrium limitations typically encountered in the Steam Methane Reforming (SMR) of natural gas (and of other light hydrocarbons), which is used extensively in petroleum refineries. In addition, the project advances the state of the art in the process intensification of other petroleum refining operations.

In carrying out the research project, our first accomplishment has been to identify a three vessel/phase configuration of the proposed novel, SMR reaction-separation device, that is simpler than the four vessel/phase configuration originally outlined in our research proposal. The associated operating mode of this configuration is as follows: in the first phase, the reactor operates in REACTION-LOADING mode at constant pressure; it is fed a mixture of steam and methane, which *reacts* to form hydrogen, which in turn selectively permeates into the storage media *loading* them up with pure hydrogen. In the second phase, the reactor operates in DECARBONIZATION-STORAGE mode again at constant pressure; it is fed a mixture of steam and hydrogen, so that the hydrogen partial pressure in the reactor is above the hydrogen partial pressure in the storage vessels, thus *decarbonizing* the reactor contents, and maintaining the hydrogen within the *storage* media. In the third and final phase, the reactor operates in FLUSH-UNLOADING mode again at constant pressure; it is fed pure steam, thus *flushing* the reactor contents, and *unloading* the hydrogen contained in the storage media. Figure 1 shows the three vessel/phase configuration, complete with recycle and splitting streams. The inlet feeds consist of a stream of pure methane fed directly to the reactor operating in phase one, and a stream of pure steam fed to the reactor operating in phase three. A portion of the exit stream from the phase three reactor is used as the feed for the reactor operating in phase two, while the second phase reactor effluent containing unreacted material is recycled and mixed with the stream of pure methane going into the reactor operating in phase one.

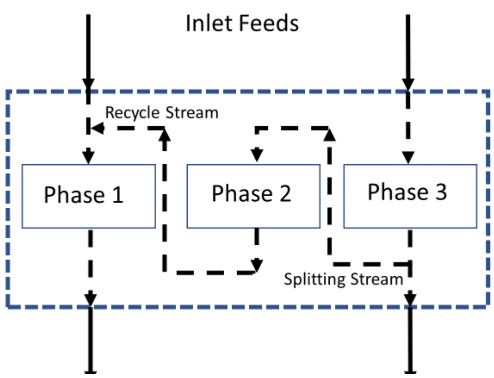

Figure 1: Three phase configuration of reaction-separation vessel.

A first principle-based, dynamic model of the described novel SMR reaction separation process has been developed. The model considers this process as a composite system comprised of two subsystems: the reactor gas domain (denoted by g) and the storage media domain (denoted by s), which are spatially exclusive, but communicate by allowing selective species transport between them. Accumulation, reaction, and permeation terms for all participating species are incorporated into species conservation laws which give rise to a set of non-linear ordinary differential equations, that is brought into dimensionless form in order to facilitate process design and optimization and to elucidate the influence of various parameters on process dynamic behavior. The end result of this effort has been to identify only three dimensionless parameters D1, D2, and D3 which characterize process operation. This reduction has enabled a comprehensive and systematic parametric study, whose focus is the identification of optimal process operating conditions. These parametric studies are carried out in the MATLAB and COMSOL software platforms, where the process model has been programmed. We are in the process of submitting to an archival journal a manuscript describing the aforementioned dimensionless process model and the associated parametric studies.

On the experimental component of the project we have been carrying out the following efforts. First, we focused on creating short, cylindrical, ceramic membrane-based, storage media, to be coated with a layer that would be perm selective to hydrogen. This storage medium shape was chosen so as to facilitate the characterization of the transport properties and effectiveness of the various coating layers of the storage medium. To this end, the membrane is capped on one end, while its the other end is left open so as to allow the measurement of the amount of gas permeating into the storage medium with a bubble-flow meter. The pressure on the permeate-side was measured by a pressure gauge.

The membrane is comprised of three layers. The first layer consists of a SiC support structure which provides mechanical integrity and is thermally stable. This support structure is characterized by large pore sizes which allow for high gas fluxes. Experimental studies on support fabrication resulted in the identification of optimal particle sizes for the starting powder of 0.5μm, which yielded membrane supports with excellent mechanical integrity and with large enough pore sizes to allow for high permeances, as shown through permeance testing. In order to create the cylindrical tubes, the support powder is compressed at high pressure and then placed in a furnace. It was also determined that an applied pressure of 12000 PSI for two minutes yielded the best results. Figure 2 shows the experimental setup for the support fabrication and permeance testing.

Figure 2: Experimental set up. (L) Tubular support mold in press. (R) Permeance testing reactor.

The second layer is a mesoporous scaffold layer that is pyrolyzed to condition the surface for further deposition of heat treated layers. The mesoporous layer is added to the support through the use first of dip coating, in a hexane solution in which SiC particles, and a long chain polymer are suspended, and then pyrolysis at 750^{o}C. This method of deposition was found to be superior to that of chemical vapor deposition (CVD), because a more uniform coating was achieved, as seen by a reduction in variability when conducting permeance testing. We have been experimenting with the addition of polystyrene in the mesoporous scaffold layer and have found that while there is a noticeable increase in the separation factor the overall permeance is reduced. We plan to investigate this phenomenon further in order to isolate the mechanism that allows for greater separation, while reducing factors that negatively impact permeance.

The third layer is the nano-porous membrane layer, which utilizes a polystyrene sacrificial interlayer. The membrane support tube with the scaffold mesoporous layer is first dip coated in a mixture of polystyrene and toluene and is allowed to dry for an hour. A mixture of hexane and preceramic polymer is then dip coated on top of the sacrificial layer and then pyrolyzed. The combination of a sacrificial layer and a top nano-porous membrane layer is called a dual layer. Experiments have been run on membranes with one, two, and three dual layers placed and results indicate that significant increase in separation factor is achieved with the addition of two dual layers. However, this is marked by a significant decrease in the permeance of the membrane. Future studies will include investigations into various preceramic polymers in order to maximize desirable properties.