

# Optimization of Heat Recuperating Reactor Strategies for Autothermal Fuel Reforming to Hydrogen

Niket S. Kaisare<sup>1</sup> and Dionisios G. Vlachos<sup>1\*</sup>

<sup>1</sup>Department of Chemical Engineering and Center for Catalytic Science and Technology,  
University of Delaware, Newark, DE 19716 (USA)

\*vlachos@udel.edu

## Introduction

An important component of a stationary or mobile power generation system, based on the Polymer Electrolyte Membrane (PEM) fuel cells, is the integrated unit that converts hydrocarbon-based fuels into hydrogen. The last decade has witnessed rapid development in various technologies, such as the millisecond contact time reactor [1] and microreactor fabrication and design [2], which could make decentralized generation of hydrogen possible.

Autothermal hydrogen generation in a catalytic microreactor or monolith requires coupling of endothermic reforming reactions with exothermic oxidation or partial oxidation reactions. The oxidation and reforming reactions can be carried out in separate reactors, as is the current industrial practice, or combined in a multifunctional device. Combustion of fuel represents loss of hydrocarbons in heat generation instead of hydrogen generation. Heat integration is required to recover some of the heat of combustion and improve the overall device efficiency [3] and is expected to be one of the most critical factors in commercialization of small-scale devices. Such heat recuperation can be obtained by carrying the catalytic reactions in a counter-current heat exchanger or by temporal thermal coupling using a reverse-flow reactor. While partial oxidation scales down much better than steam reforming, its slight exothermicity makes it inadequate for very small scales due to heat losses. Thus, best heat recuperation strategies and suitable chemistries for small scales are currently unclear. In this work, we model various heat recuperation strategies and chemistries to provide designs for small-scale hydrogen production.

## Hierarchical Model Development

We model a single reactor (parallel plate geometry) channel using a transient pseudo two-dimensional model developed in [4]. The model explicitly accounts for longitudinal transport, and for transverse heat and mass transfer through Nusselt and Sherwood number correlations. It is benchmarked against 2D computational fluid dynamics results.

Catalytic reactions play a key role not only in conversion and hydrogen selectivity, but also in the thermal response of the reactor. It is therefore necessary to use appropriate reaction kinetics that are valid over a wide range of operating conditions. Microkinetic models for C1 chemistry on Platinum (Pt) and Rhodium (Rh) were developed in our group that are applicable over a wide range of operating conditions and processes, e.g., steam and dry reforming, combustion, and partial oxidation of methane [5]. While such detailed models are accurate, they are computationally demanding for reactor design and optimization. Hence, we perform a computer-aided, *a posteriori* model reduction to obtain low complexity, high fidelity kinetic models that are then used for optimization of dynamically operated reactors. In conjunction with the aforementioned pseudo 2D reactor models, our approach delivers reliable, yet

computationally efficient reactor-chemistry models. This hierarchical model development was demonstrated for optimization of catalytic combustion and water-gas-shift reactions [6,7].

## Results and Discussion

The aim of this paper is to determine optimal heat recuperating designs and chemistries for microreactors, including the choice of catalyst, heat recuperation reactor geometry and various operating parameters that affect hydrogen generation. We found that methane partial oxidation/reforming follows different mechanisms on Pt and Rh catalysts. On both catalysts, two spatial zones were observed: an oxidation zone near the entrance, followed by a reforming zone. In the oxidation zone, complete oxidation reaction ( $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ ) dominates on Pt, whereas a combination of partial and complete oxidation reactions ( $\text{CH}_4 + 1.5 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$ ) dominate on Rh. Steam and dry reforming take place at different extents on the two catalysts in the reforming zone. Such spatial chemistry distribution provides opportunities for novel heat recuperation strategies.

We compare a traditional straight-channel steady state reactor design with various heat recuperating reactor strategies, such as reverse-flow and counter-current catalytic reactors. We target optimal designs of the heat-recuperating reactor that maximize hydrogen yield and minimize energy loss. Specifically, implications of the indirect partial oxidation route on optimal reactor design are presented. This is motivated by earlier work, where spatial separation of oxidation and reforming zones was found to reduce the amount of hydrogen generated in a reverse-flow reactor [8]. The effects of materials properties and the geometry of the catalytic reactor on stability, thermal efficiency and hydrogen yield, are studied. Finally, different chemistries (steam reforming, partial oxidation, and ammonia cracking) are compared.

## Significance

The outcome of this work provides a systematic methodology for design and optimization of novel heat-recuperating reactors for more energy efficient decentralized or portable hydrogen generation. However, the impact of this work goes beyond hydrogen generation, as the quest for improving process efficiencies and reduced waste products is increasingly leading towards use of integrated multifunctional reactors. This work provides a valuable step in optimization of “heat integrated systems” [3], i.e., reactors that combine reactions and heat exchange in a single device.

## References

1. Schmidt, L.D., *Stud. Catal. Surf. Sci.* 130A, 61 (2000).
2. Jensen, K., *Chem. Eng. Sci.* 56, 293 (2001).
3. Kolios, G., Glockler, B., Gritsch, A., Morillo, A., and Eigenberger, G., *Fuel Cells* 5, 52 (2005).
4. Kaisare, N.S., and Vlachos, D.G., *Proc. Combust. Inst.* 31, in press (2007).
5. Mhadeshwar, A.B., *PhD Thesis*, University of Delaware (2005)
6. Kaisare, N.S., Deshmukh, S.D., and Vlachos D.G., in *IMRET*, Potsdam, Germany (2006).
7. Vlachos, D.G., Mhadeshwar, A. and Kaisare, N.S., *Comput. Chem. Eng.* 30, 1712 (2006).
8. Kaisare, N.S., Lee, J.H., and Fedorov, A.G., *Ind. Eng. Chem. Res.* 44, 8323 (2005).