Process Intensification Principles for Competitive Solar Fuels

Lucas Freiberg[1], Matt Coblyn[1], Goran Jovanovic[1], Nick AuYeung[1]
1. Department of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, OR, USA

Introduction

A diverse portfolio of clean energy solutions is needed to break humanity's dependence on fossil fuels. However, intermittency often complicates direct use of renewable energy sources like wind and solar. To store solar energy for thermal requirements (i.e. transportation fuels, industrial processes, residential heating), solar radiation can be concentrated and stored indefinitely in the form of chemical bonds, accomplished by driving an endothermic reaction.

Applying *process intensification* principles to this problem, several ideas were developed to make solar fuel production more efficient, compact and practical. Ultimately, a reduced capacity cost (i.e. $/kg$_{fuel}$/day) will make solar fuels more competitive.

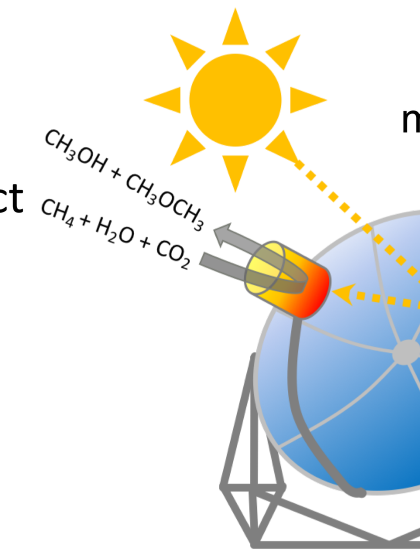


Figure 1 (left). Illustration of modular, solar-thermochemical fuel production.

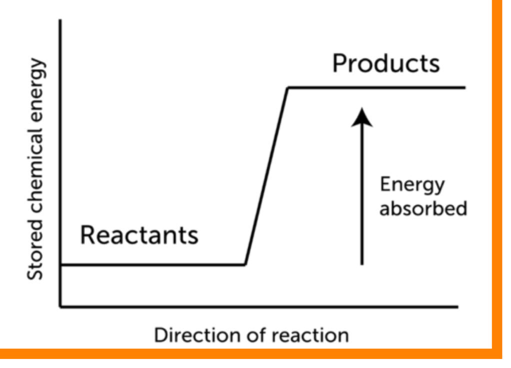


Figure 2 (right). Reaction coordinate diagram of an endothermic reaction.

Bi-/Tri- Reforming Modal Switching for Continuous Syngas Production

Economy of scale and continuous operation are what make conventional chemical processing profitable. However, the future will see safer, decentralized chemical processes in the form of modules. Solar energy systems benefit from modularity; large scale power towers with heliostat arrays, for instance, present large initial capital investment and financial risk. Modules can be "numbered up" over time to meet capacity goals, delivering solar fuels at or near point of use (i.e. Hydrogen Fuel Station), no costly pipelines needed.

The solar concentrator dish is a major cost driver in such a system. Micro- and milli-scale reactor channel dimensions are utilized to greatly increase efficiency of a module, wasting as little concentrated solar heat input as possible to reduce capacity cost. Solar intermittence is another roadblock to competitive solar fuels, restricting operation only to times when the dish sees the sun. Bi-/Tri-reforming modal switching is presented here as an option to maintain high temperatures required for reforming during times of solar intermittency or diurnal cycles.

In this scheme, Bi-reforming of methane ($3CH_4 + 2H_2O + CO_2 \rightarrow 8H_2 + 4CO$) is performed over a nickel catalyst. Oxygen is then predictively throttled into the stream and reacted over the same catalyst when clouds pass over. Partial oxidation of methane provides exothermic heat of reaction that is used by the endothermic steam and CO_2 methane reforming reactions. This autothermal operational mode is called Tri-reforming of methane ($5CH_4 + 2H_2O + CO_2 + O_2 \rightarrow 12H_2 + 6CO$) .

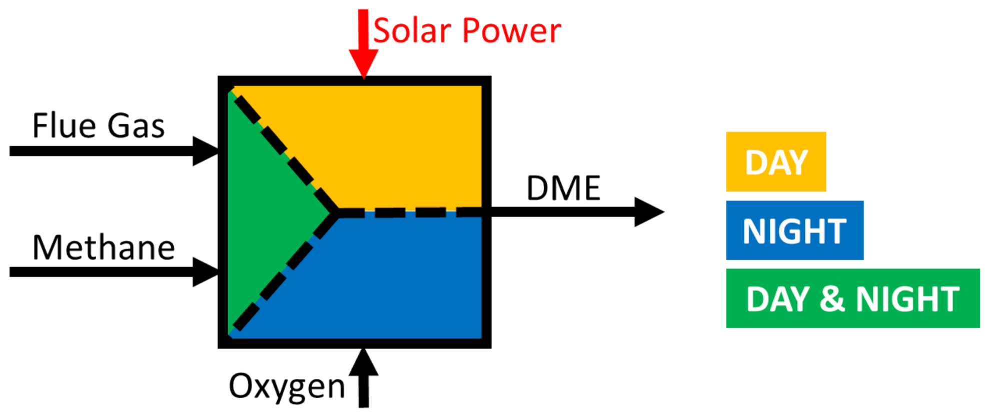


Figure 3. Block diagram illustrating bi-modal switching. Oxygen is throttled into the feed to maintain reforming temperatures during solar intermittence.

Solar Simulator

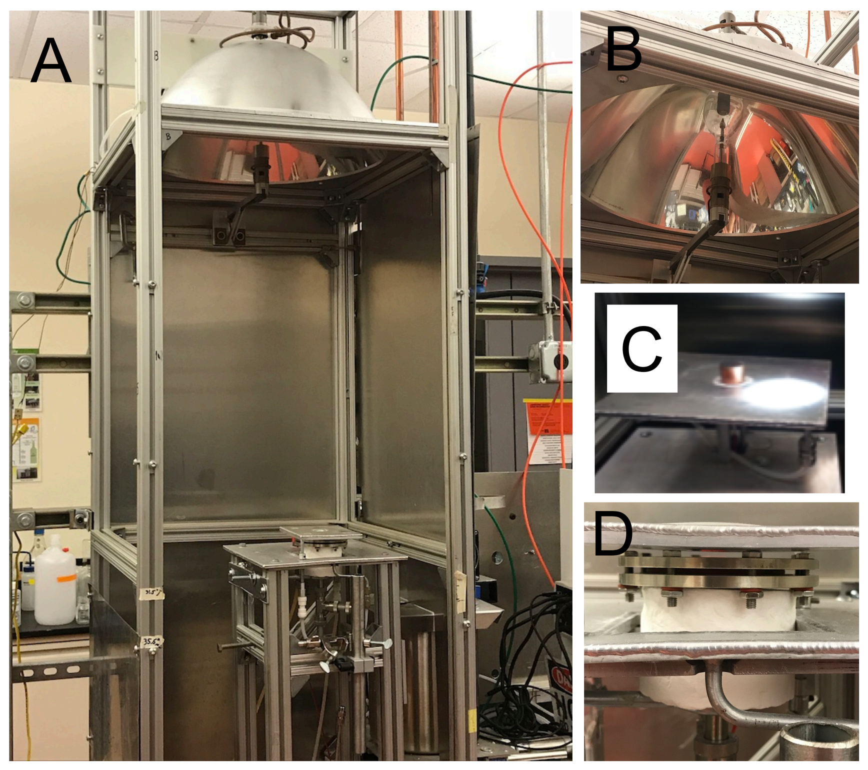


Figure 4. (A) Solar simulator showing stage and reflector. (B) Xenon arc lamp and ellipsoidal reflector. (C) Flux meter and focal area of simulator when lamp is on. (D) Milli-scale solar reactor, positioned below mask.

Reaction Testing

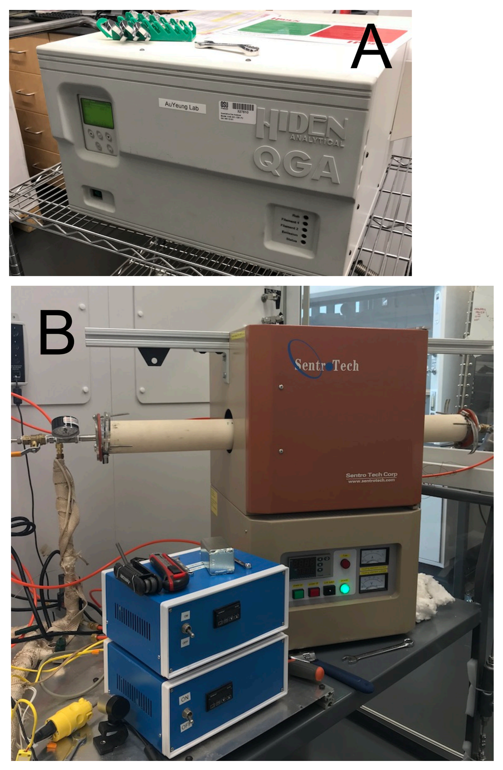


Figure 5. (A) Mass spectrometer. (B) Tube furnace and temperature controllers

Catalyst

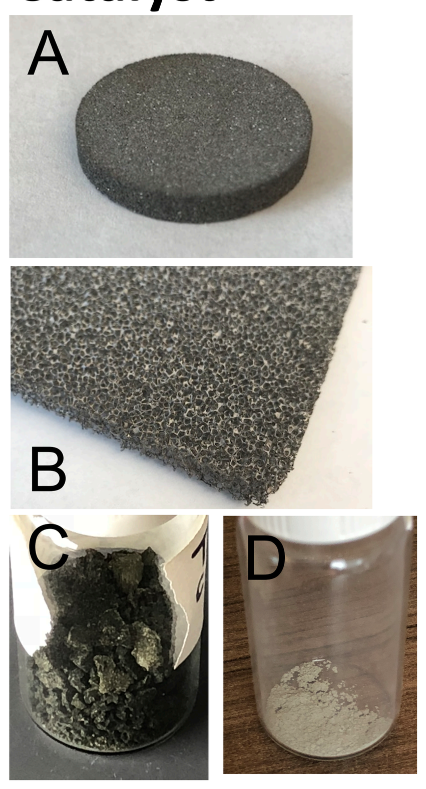


Figure 6. (A) FeCrAlY sintered felt (B) Porous, Metallic Ni foam. (C) Coprecipitated Ni/MgAlO$_x$. (D) Hydrothermally precipitated Ni-ZrO$_2$.

PI Principles

- Synergy between the two reaction processes over the same catalyst.
- PI in the spatial domain. Milli-scale reactor and micro-porous catalyst supports promote high rates of heating and improved efficiency.
- PI in the temporal domain. Periodicity; modal switching to accommodate solar intermittency.

Thermal Conductivity Enhancement for Vectorized Heat Flow

New additive manufacturing techniques enable "3D Printing" of metals, providing an opportunity to customize material properties like thermal conductivity. Microchannel heat exchangers enjoy high efficiency; however, their size is limited. As device size shrinks, the characteristic lengths for heat conduction in unwanted directions become more important relative to the heat exchange path length of interest, resulting in an isothermal condition that prevents heat transfer all together. Enhancing the conductivity of solid, geometric features that bridge the path of interest promotes a higher driving force for conduction between streams while limiting heat flow in unwanted directions. Applying this technology, more compact devices, selective heat delivery and rapid heat recuperation are imagined.

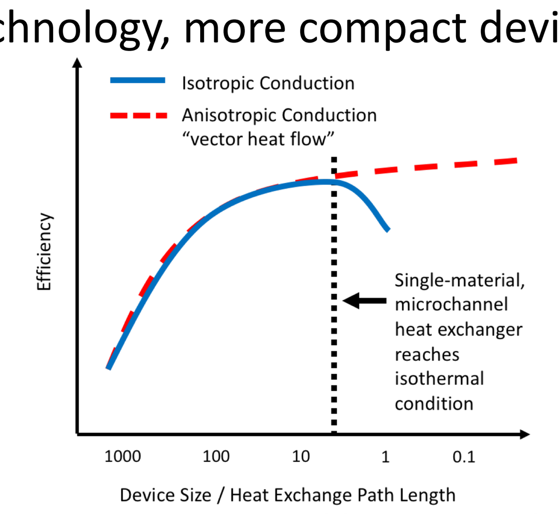


Figure 7. Unwanted heat spreading begins to limit the efficiency of single-material, microchannel heat exchangers.

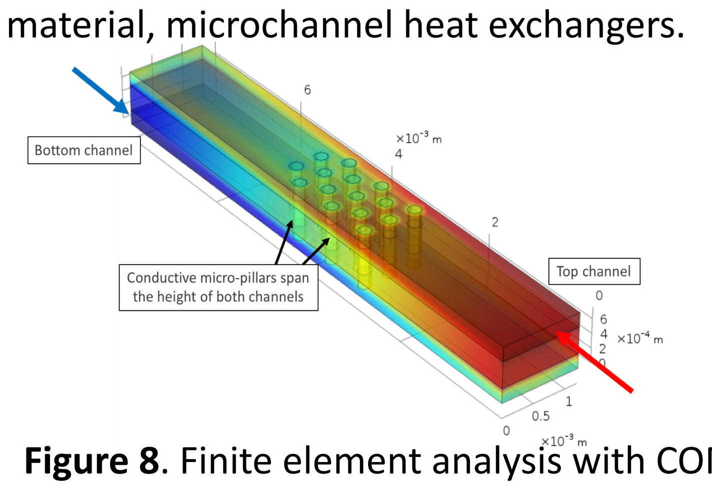


Figure 8. Finite element analysis with COMSOL's non-isothermal flow module provides rapid testing of multi-material conductivity enhancement.

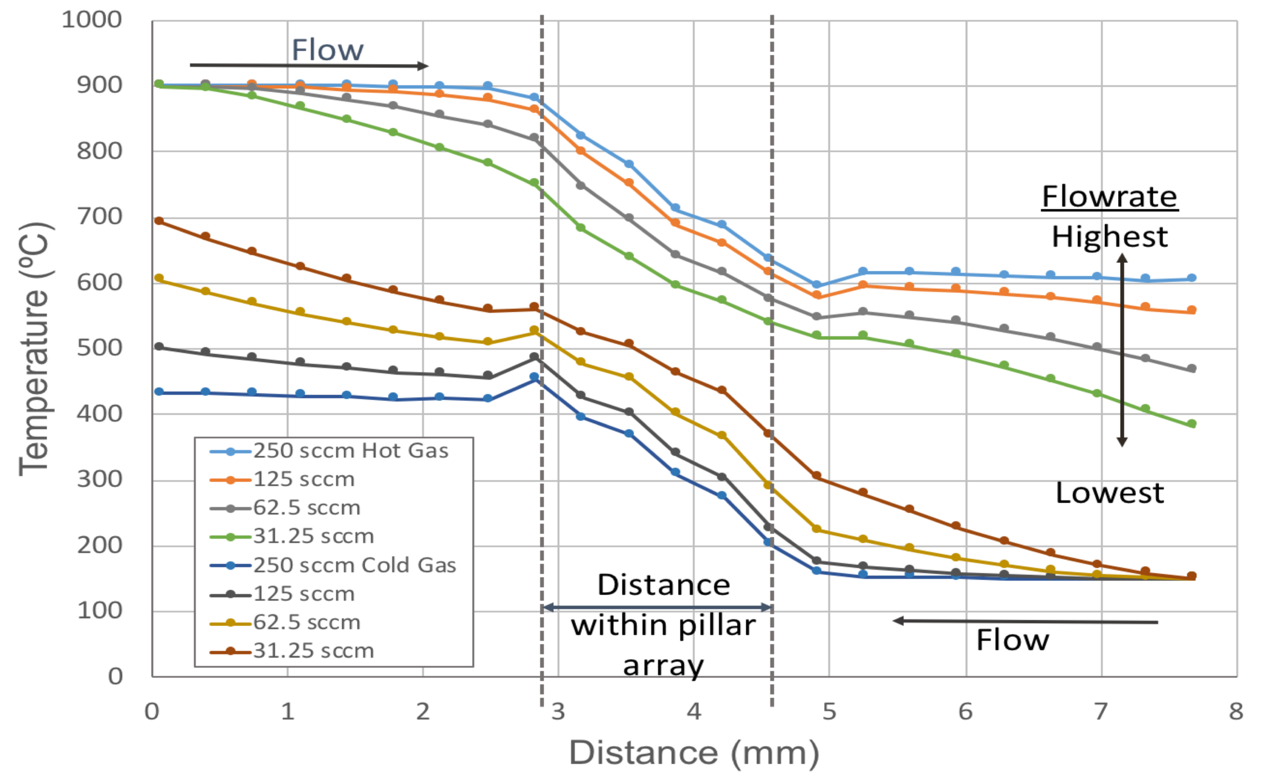


Figure 9. Temperature profiles along heat exchanger channel centers. A significant increase in the slope of the temperature profile is observed, especially at higher flowrates where conduction through the dividing wall is a limiting phenomena. The model has demonstrated multi-material pillars to provide heat flux twice as great as single material pillars and eight times greater than channels with no pillars.

PI Principles

- PI in the thermodynamic domain. Judicious control of the flow of energy in the system.

Integrated Reactor/Solar-Receiver/Heat Exchanger

In-situ gas recuperation and thermally coupled endothermic and exothermic reactions are implemented in this device to increase solar-to-chemical efficiency without the need for an external high temperature recuperator. Feeding gas to the perimeter cools sealing features below their melting point, and conductive micro-pillars facilitate rapid gas recuperation to heat the feed to reaction temperatures before delivery to the methane reforming catalyst. Addition of a exothermic reaction in series – positioned radially in the correct temperature range – will provide additional heat to the feed stream, boosting efficiency further and converting syngas into more practical liquid fuels.

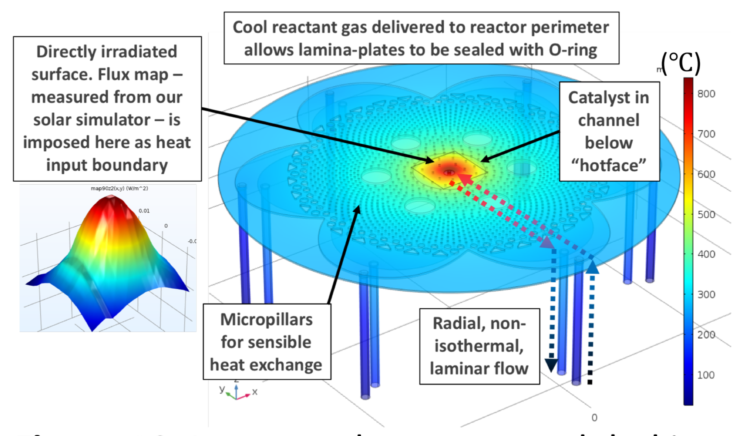


Figure 10. Integrated reactor, modeled in COMSOL using non-isothermal flow and coefficient form PDE modules. To simulate ***steam reforming*** on a catalyst surface, a first-order rate expression was adapted to become a mass flux boundary condition.

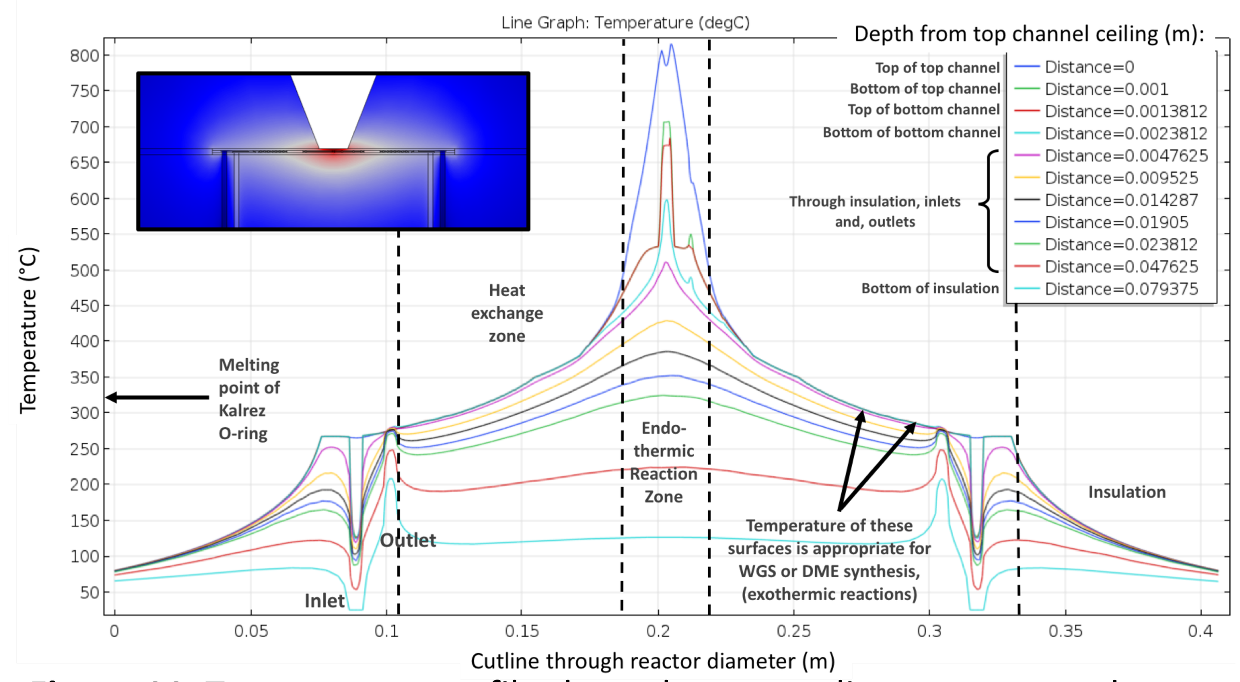
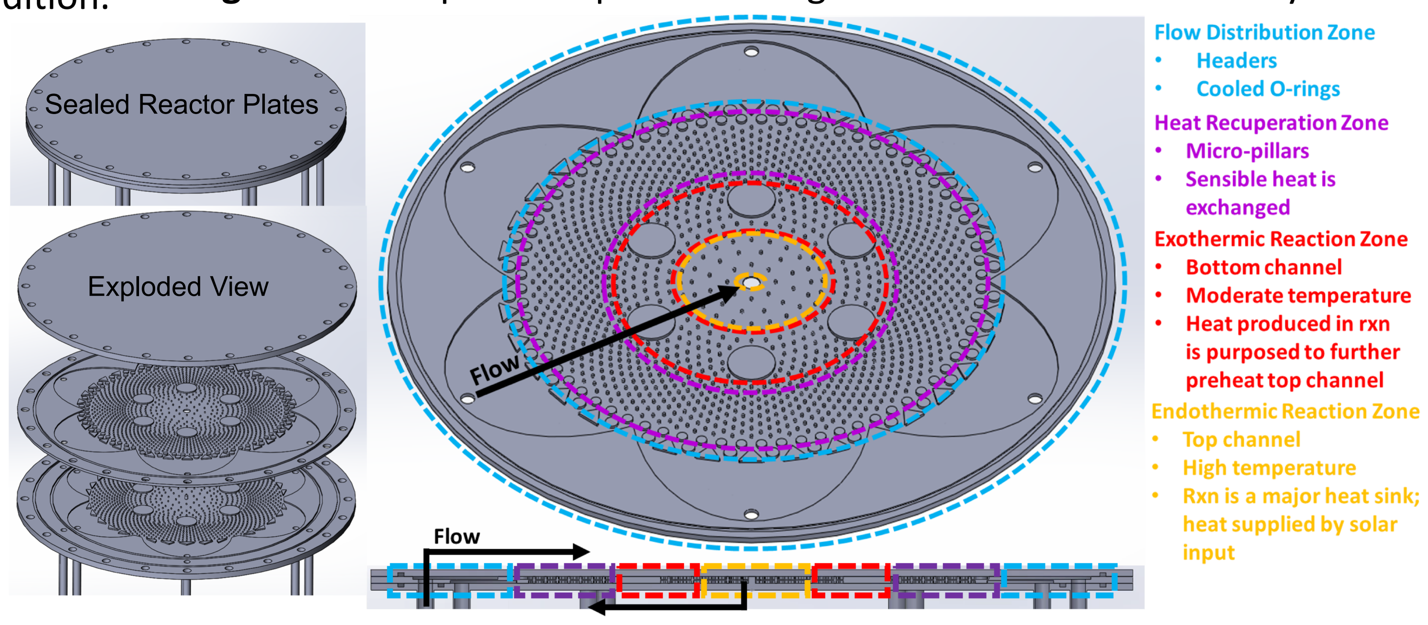


Figure 11. Temperature profile through reactor diameter at steady-state.

Figure 12 (right). Illustration of lamina plate assembly and integrated microreactor concept, showing radial arrangement of unit-operations.



PI Principles

- PI in the spatial domain. Microchannel reactor design facilitates intensified heat and mass transfer.
- Synergy is maximized by integrating components in a single, compact device.
- PI in the thermodynamic domain. Thermally coupled reactions reduce external heating duty.