Process Intensification for Hydrogen Generation using Micro-Channel Steam Reforming

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1. Abstract. Today, the advantages of micro-channel technology for next generation steam reforming have been demonstrated on a pilot scale. Modeling and experimental efforts are reported in the context of Power & Energy, Inc's (P&E) development of a radial tube-in-tube microreactor (TTμR) for efficient, scalable production of hydrogen (H_2) and/or synthesis gas (CO, H_2) from natural gas at competitive costs. The novel radial micro-channel reactor allows manipulating heat- and mass-transport phenomena in catalytic-wall heat-exchanger microreactors to achieve increased catalyst utilization, process intensification and reactor stability. Using similar time proven production methods as used in hydrogen purifier manufacturing, a successful commercialization of the novel microreactor technology is expected with the potential to achieve transformative breakthroughs in system cost, durability and thermal efficiency as compared to existing planar μreactor systems.

2. Introduction. The efficient catalytic conversion of hydrocarbons, including natural gas or methane, to synthesis gas remains a critical challenge for both emerging clean energy industries and existing petrochemical and natural gas markets.[1,2,3,4,5,6,7,8] Hydrogen gas represents a universal energy currency, in that it may be harvested from myriad hydrocarbon resources. Hydrogen can be utilized in electrochemical power systems capable of exceeding Carnot-Cycle thermodynamic limits on efficiency. Process intensification strategies have been employed in the design of next-generation methane reformers where closely coupling of endothermic steam reforming with exothermic combustion,[9,10] yields breakthroughs in thermal efficiency. Potential integration with gas purification via membrane[11,12] or adsorption[13,14] systems further enhances the reaction conversion process while providing a pure hydrogen product. Thanks to pioneering efforts of companies like the Battelle, Velocys and the Institut fur Mikrotechnik Mainz (IMM), micro-reactor technologies have been identified as a potentially transformative technology for realizing next-generation methane reformers for several markets.

Microchemical systems have been demonstrated as a promising technology for chemical processing, with (i) improved heat and mass transport owing to reduced characteristic lengths in microchannels, (ii) resulting enhanced control of reaction temperature and hot-spot formation, and (iii) their potential for integrating multiple processes within one compact unit for unrivalled process intensification and portability.[15] Enhancement of heat and mass transport rates within micro-channels has fueled significant research towards developing thermally-integrated μreactor systems capable of combining multiple endothermic and exothermic catalytic and/or physical processes within a compact, efficient device. To-date, several μreactor designs have been reported for integrating catalytic combustion with endothermic steam reforming of hydrocarbons[16, 17] and subsequently with water-gas-shift[18] and/or membrane separations[19,20] for further cleanup of hydrogen product.

Fabrication of μreactors traditionally involved machining two-dimensional patterns into individual silicon,[18] metal[7,21] or ceramic[22,23] plates via chemical etching or laser cutting, followed by sealing and packaging of a "stack" of such plates to achieve the desired total reactor volume.[24,15] This approach results in a near-linear cost of scale-up,[15] which has limited the market penetration of μreactors to the research and niche-chemical markets. Recently, the extension of mass-production techniques such as roll-embossing and laser cutting of individual metal plates has enabled the production of industrial-scale μreactors at competitive costs[25,26,7]

The planar μreactor design is a major achievement, it has demonstrated the potential of micro-channel technology, but it does not capture the true potential that micro-channels offer. It suffers inherent drawbacks in terms of thermal efficiency for heat-exchanger applications. In the planar μreactor design, the multitude of individual reaction channels are embedded in a single monolithic substrate, allowing significant thermal "cross-talk" between individual microchannels; more importantly, this means that each microchannel is provided with a direct conductive pathway to the outer surface of the micro-reactor. These drawbacks have been shown to play a significant role in reducing the effectiveness of micro-reactors.[27,28,29,30] Current solutions to this challenge involve the combustion of additional hydrogen and/or fuel to compensate for heat losses at the external surface of the micro-reactor system.[28] In addition to transverse or radial heat dispersion, solid-phase axial heat conduction further limits the thermal efficiency of planar microreactors. Analysis of microchannel heat-exchangers [31, 32] demonstrate the importance of maintaining significant axial thermal gradients within the solid phase to ensure maximum driving force for heat transfer between fluid volumes along the entire axial length of the exchanger. However, the high substrate-to-process volume ratios of existing planar systems result in significant axial dispersion of process heat by the solid phase, such that the lower limit of an isothermal slab is approached with commiserate losses in heat-exchanger efficiency.

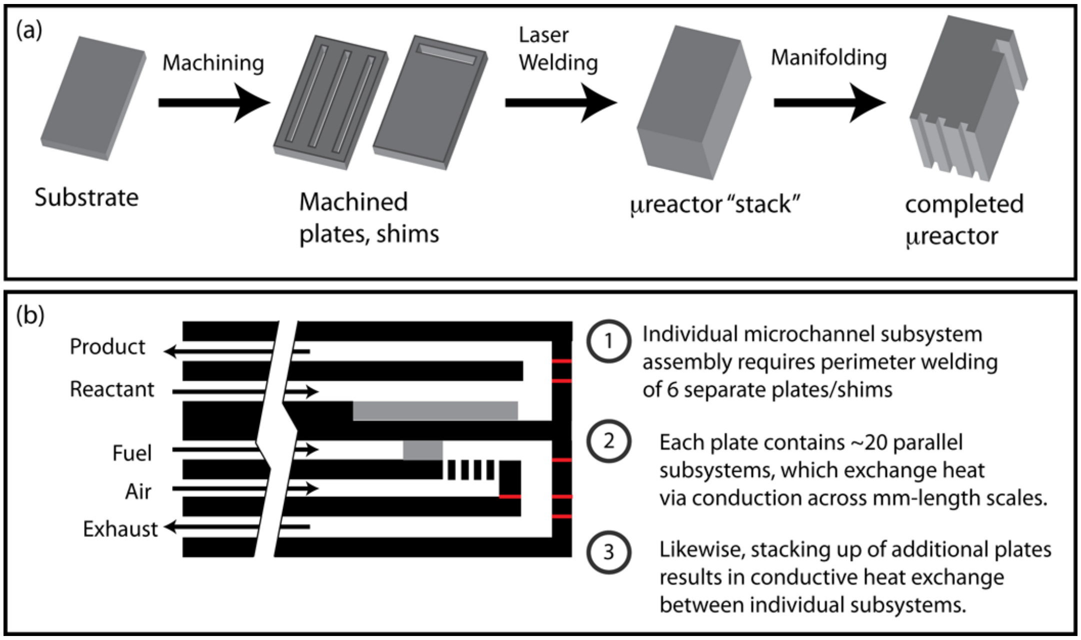

Figure 1: Illustration of a planar microreactor assembly for autothermal methane reforming to synthesis gas; (a) generalized process flow for microreactor construction, adapted from LeViness et al., 2011; (b) cross-section schematic a planar microchannel subsystem for integrated methane combustion and steam reforming, adapted from Tonkovich et al.

	Planar System*	**Tubular System****
Subsystem Volume	75 cm^3	17.9 cm^3
Process Volume	10 cm^3	9.3 cm^3
Sealing Surface	53.3 cm^2	21.4 mm^2
Heat Transfer Surface	256 cm^2	260 cm^2
Surface Area-Process Volume Ratio	~2,500 m^{-1}	~2,800 m^{-1}
Sealing Area-Process Volume Ratio	~5,000 m^{-1}	~4.6 m^{-1}
Process Volume-System Volume Ratio	0.14	0.52
Volumetric Heat Transfer Flux	65 W/cm^3 @ 4ms	840 W/cm^3 @ 5ms

*values estimated based upon dimensions and performance reported by Tonkovich et al.[53] for a single microchannel subsystem depicted in Figure 1.

**values estimated based upon nominal tube dimensions discussed in Section 3 and preliminary results for methane steam reforming.

3. Tube-in-Tube Microreactors (TTμR): A Novel Approach to Microreactor Design

P&E has developed a novel manufacturing process for realizing compact, high-efficiency radial microchannel systems with significant advantages over their planar counterparts. The heart of this technology is the use of individual tube-in-tube assemblies to realize thermally isolated μchannel subsystems (Figure 2). Individual tube-in-tube assemblies are constructed by coaxially mounting an inner stainless-steel microtube (nominally 1.47 mm OD) inside an outer stainless-steel μtube (nominally 2.03 mm ID). The outer tube is closed on one end, such that two radially-symmetric microchannels are formed by the inner diameter of the inserted tube and the annulus formed between the inner and outer tubes. Manufacturing of the tube-in-tube assembly is achieved via automated 200W continuous laser-welding system developed by P&E capable of achieving high-quality sealing at a rate of ~3 seconds/tube. Mechanical stabilization is provided at the sealed end of the outer-most tube via insertion in a “slip plate,” which minimizes transverse deflection of individual tubes while allowing axial expansion with changing temperature. The P&E TTμR design offers several unique industrial advantages over existing planar μreactor, including:

- **Reduction in manufacturing costs:** By utilizing mass-produced tubular substrates and conventional (automated laser-welding) sealing technologies, dramatic reduction in cost of scale can be achieved, as compared to planar μreactors requiring customized manufacturing of individually-patterned plates.
- **Increased Durability, Scalability:** By minimizing the packaging and sealing contact area, device durability is increased by reducing the occurrence of gas leaks, seal failure; likewise, placement of seals is such that each seal can be inspected and repaired if necessary prior to final μreactor assembly. Finally, scale-up is no longer limited by sealing challenges (discussed in Section 2), as individual tubes are not sealed directly to each other.
- **Increased Resistance to Thermal Stresses:** By anchoring the tubular μreactor at one end and allowing the other to “float”, the resulting system is capable of absorbing significant thermal gradients without the risk of failure due to thermal strain; likewise, because individual tubes are not sealed directly to each other, thermal expansion does not compromise seals.
- **Improved Power and System Density:** By minimizing substrate volumes through the use of the tube-in-tube architecture, breakthroughs in system density, portability construction costs are achieved.

- **Better Handling of High Pressure Operation:** the hoop stress advantage of, particularly, small OD cylinders allows larger pressure drops for a given wall thickness compared to planar technology. Alternatively, walls can be thinner for similar pressure differences providing better heat transport. The ability to operate at higher pressures may be particularly relevant when sequestering CO2.

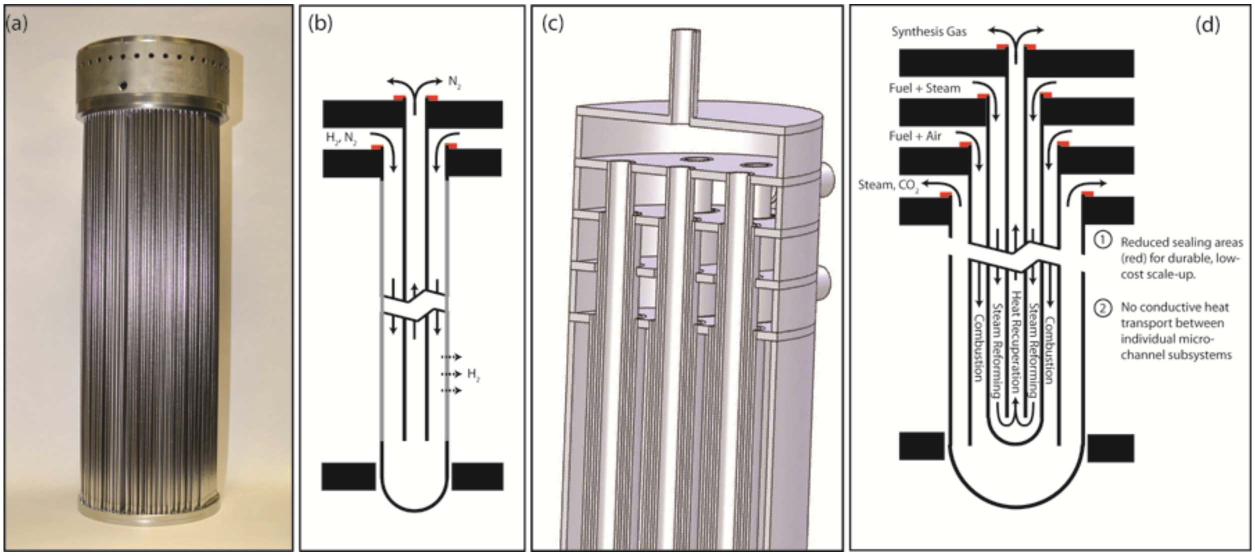

Figure 2: P&E tube-in-tube μchannel technology; (a) tube-in-tube Pd-μmembrane system, 6" x 12.5" containing 1400 individual μmembrane subsystems; (b) schematic of individual tube-in-tube μmembrane subsystem; (c) CAD drawing of proposed μreactor system showing packaging strategy; (d) schematic of planned μreactor system for coupling methane combustion with steam/autothermal reforming for compact production of hydrogen and/or synthesis gas.

4. Experimental

4.1. Manufacturing of TTμRs

A video will be shown of existing automated manufacturing methods currently employed in the production of commercial hydrogen Palladium membrane purifiers that is largely similar in the methods used to fabricate the novel tube-in-tube micro-channel devices. Hereunder, are various pictures showing tools and parts of the latter process.

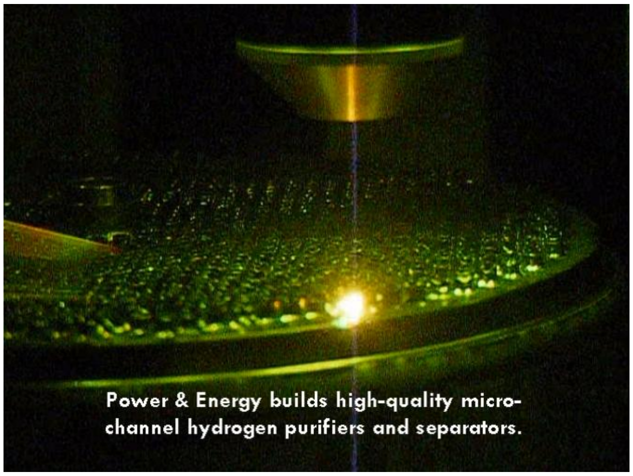

Fig. 6, laser welding connecting tubes on one end only.

2800 tube-in-tube Pd-alloy micro-channels

Fig. 7, large parallel tubes assemblies

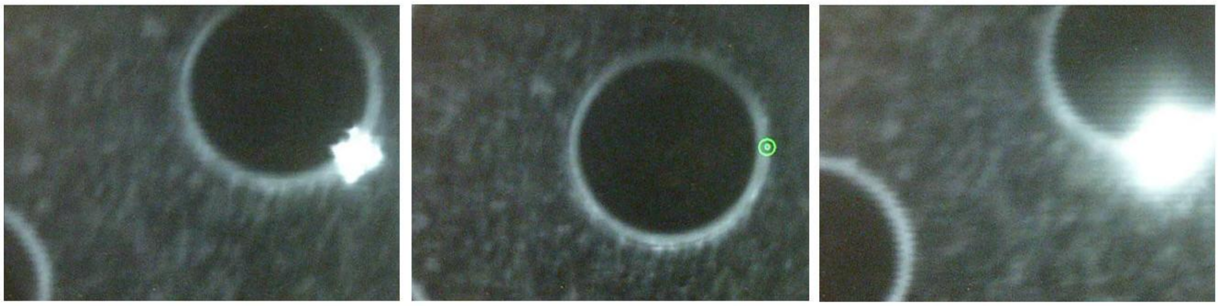

Figure 8 Automated laser welding positioning with computer vision software.

Figure 9 traditional hand weld attempt.

Fig. 10, laser weld result.

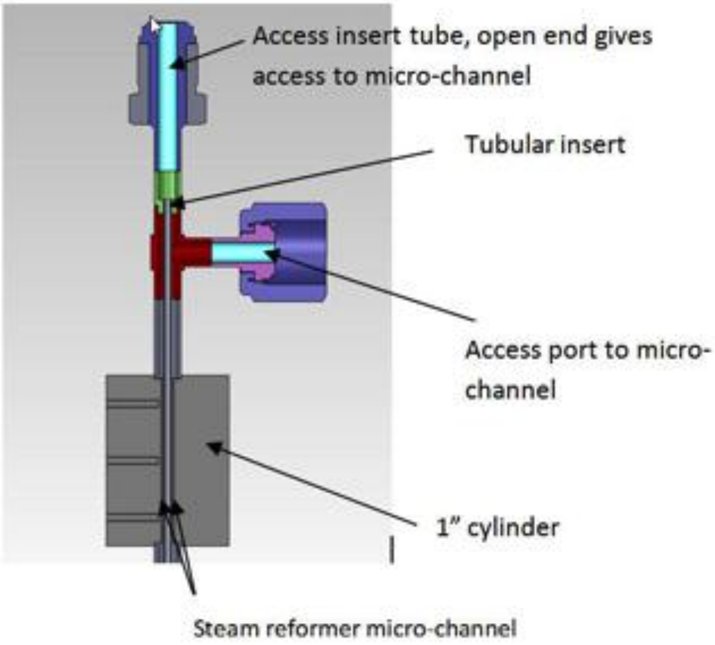

Figure 3: Experimental single cylindrical micro reactor systems developed by **P&E**, which allows the unique ability to precisely monitor heat flux and temperature in a single, isolated microchannel.

4.2. Prototype TTμR for Methane Steam Reforming

P&E's researchers have constructed a bench-scale TTμR system for evaluating heat transfer and reaction rates of individual micro-channel processes. This single TTμR system is comprised of a band heater attached to the outside of a 1" OD Aluchrom tube with bore diameter machined to match that of final tube-in-tube μreactor designs, see figure 3. The band heater allows accurate control of reactor temperature, to within +/- 0.1 K. The inner wall of the bore is coated with steam reforming catalyst and an insert tube is coaxially mounted within the bore to complete the TTμR geometry. Reactor temperatures are measured by thermocouples placed approx. 0.03” from the inner surface of the micro-channel. Heat flux from the band heater to the catalyst wall can then be accurately determined via geometry. Multiple cylindrical reactors are put in series with individual power control and samples can be extracted on either end of any of the reactors. This enables detailed and precise studies of reaction dynamics of the fuel, steam and catalyst in a test setup that has the essential internal features of TTμR based production systems. This apparatus provides, for the first time, operation of individual microchannels with precise monitoring and/or control of heat flux to the microchannel volume and inner-wall surface temperature while minimizing heat losses common to planar single-channel systems.

4.3. Two-Dimensional Simulations of P&E system using COMSOL

Detailed simulations of laboratory-scale single-tube μreactor described above were implemented using the COMSOL multiphysics programming environment. Gas velocity through individual μchannels was described using the Navier-Stokes equation assuming weakly compressible fluids in tandem with the continuity equation while mass transfer of individual species is described by Maxwell-Stefan multicomponent diffusion.[33] Fluid density (ρ) was calculated assuming ideal gas law and dynamic viscosity of the gas mixture is evaluated as a function of composition and temperature using the semiempirical formula developed by C.R.Wilke[34] with all values for Lennard-Jones parameters taken from Bird et al. (2006).[35] Fluid-phase heat transport was described by conduction and convection, assuming negligible radiative heat transport within the μchannel. Fluid-phase thermal properties were taken from physical property databases.[36] The resulting 2-dimensional, radially-symmetric computational fluid-dynamic (CFD) model is identical to models previously implemented by Vlachos’ and Vacarro’s research groups.[27,28,29,30,37]

Reaction, mass diffusion and heat conduction within the catalyst film was modeled assuming a combination of Darcy’s Law (to describe convective transport in porous media) and Maxwell-Stefan diffusion and reaction. The resulting reaction-diffusion model has recently been shown to be capable of comparable accuracy to the more rigorous dusty-gas model of Jackson[38,39,40] for pore diameters > 500 μm.[41,42] Kinetics of methane pyrolysis and water-gas-shift provided in the literature for a $Ni/MgAl_2O_4$ catalyst by Xu and Froment[43] were employed. By imposing a constant temperature boundary condition at the catalyst-μreactor wall interface, i.e. the inner boundary of the catalyst layer, numerical solutions to the above system of partial differential equations predict extent of catalytic reaction as well as the total heat duty required to maintain the externally-imposed μreactor wall temperature.

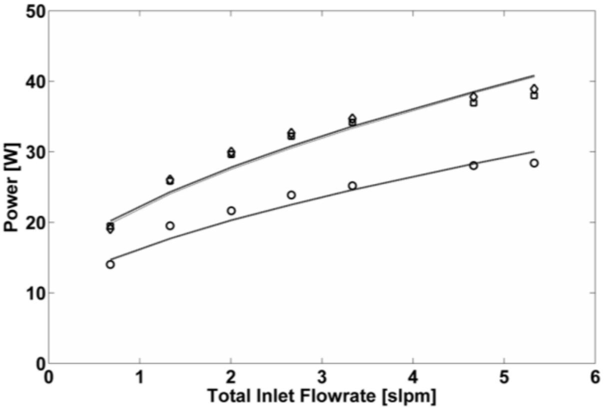

Figure 4: Comparison of preliminary simulation results (lines) of the net power entered into the reaction with experimental data points for single-tube microreactor provided by P&E; feed composition 25% CH_4:75%H_2O at 10bar and (o) 600^{o}C, (□) 650^{o}C and (◇) 700^{o}C.

5. Preliminary Results

Experimental data was initially obtained using a proprietary methane steam reforming catalyst washcoated within a single 1” μchannel system (described in Section 4.2) over a range of inlet gas superficial velocities of 25% methane, 75% steam in terms of the total heat supply added to the reactor to maintain a designated reactor-wall temperature (Figure 4). For the single TTμR described here, heat duties approaching 40W correspond to a volumetric heat flux of > 800W/cm^3, more than an order-of-magnitude improvement over competing planar designs.

Simulations using the model described above showed good agreement between COMSOL predictions and experimental data provided by

P&E relating heat duty vs. process flowrate for the 1” single-channel μreformer (Figure 4). Validation of the COMSOL design model allows theoretical exploration of different catalyst and/or reactor configurations for further improvement in process intensification. Additional experimental and simulation results will be presented in this talk.

6. Conclusion/outlook

Today, the advantages of micro-channel technology for next generation steam reforming have been demonstrated on a pilot scale. A radial microreactor is presented for efficient, scalable production of hydrogen and/or synthesis gas from natural gas at competitive costs. Modeling and experimental tools are introduced that provide, for the first time, operation of individual microchannels with precise monitoring and/or control of heat flux to the microchannel volume and the inner-wall surface temperature while minimizing heat losses common to planar single-channel systems. Simulation, in the absence of any refinement of kinetics or transport properties, showed good agreement between COMSOL predictions and experimental data relating heat duty vs. process flowrate. The presentation shows some of the tools of commercial production methods used for micro-channel hydrogen purifier manufacturing. These tools are very similar to tools needed for radial microreactor manufacturing and successful commercialization of this technology has the potential to achieve transformative breakthroughs in system cost, durability and thermal efficiency as compared to existing planar microreactor systems.

Future work is planned to provide the possibilities and limitations of the radial micro-channel reactor such as: the exceptionally low operational stresses, the possibility of manipulate heat- and mass-transport phenomena in catalytic-wall heat-exchanger microreactors to achieve transformational breakthroughs in catalyst utilization, process intensification and reactor stability.

7. Acknowledgement

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