

**SCALE-OUT AND STABILITY OF MICROREACTOR STACKS
FOR SYNGAS PRODUCTION**

by

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ABSTRACT

Computational fluid dynamics (CFD) simulations are used to simulate stacks of different sizes in order to understand nonlinear effects which arise in scale-out of microchemical systems. As an example process, syngas production from methane is studied using a multifunctional, parallel plate reactor with alternating combustion and steam reforming channels. A scale-out strategy is proposed which creates larger stacks from a base-unit. Stacks are evaluated in terms of efficiency, maximum wall temperature and stability under external heat loss for both high and moderate wall thermal conductivities. We find that smaller stacks are unstable under laboratory heat loss conditions. Stacks with high wall thermal conductivities are more stable than those with moderate wall conductivities under our conditions. At high heat loss coefficients, significant transverse thermal gradients exist between interior and edge channels of the stacks that result in significant loss of efficiency. A transition from all ignited to some ignited and extinguished and finally to all extinguished channels is discovered as criticality is approached in moderate size stacks. Microsystems provide one to three orders of magnitude larger volumetric and gravimetric throughputs than conventional technology irrespective of model uncertainty, and such intensification is central to portable and distributed processing.

They exhibit energy efficiency that is a strong function of size and heat loss but can outperform conventional processing under many conditions. However, they result in higher cost per unit syngas volume unless system optimization is carried out.

Stability improvement techniques such as different reactor sizes, reducing wall thermal conductivity, increasing the Pt catalyst loading and burning hydrogen rather than methane in the outermost channels are investigated. To simulate fuel-lean hydrogen combustion in a computationally efficient manner, a single step rate expression for hydrogen combustion on Pt is derived from a previously published microkinetic model. The most effective means for improving stability is found to be combusting hydrogen or increasing the Pt catalyst loading in the outermost combustion channel.

CHAPTER 1

INTRODUCTION

1.1. Global Energy Supply and Demand

Recently, energy has become a topic of concern for governments worldwide as consumption is predicted to continue to increase in the near future (Figure 1-1). While increases in energy demand within the United States are projected to be minimal over the next 20 years, growth in the developing world will push global energy consumption to historic highs. An increase in consumption is significant because traditional fossil fuel energy resources are being depleted at an increasing rate and the supplies are limited in quantity. Energy forecasts predict that global energy demand will increase by approximately 35% over the next 20 years (Figure 1-1), with the majority of this coming from fossil fuels (which currently make up 85% of total energy consumption). This is because at present renewable sources make up only a small fraction of global consumption (~7%) and would likely be unable to supply the world with the energy it requires (Figure 1-2). This large increase in demand will therefore inflict undesired strain on the global energy delivery system. In the short term, this strain on the energy market can be eased by developing technologies based on two objectives: (1) to produce and utilize energy more efficiently and (2) to develop unconventional energy resources. Process intensification using microreactors can make

an important contribution to achieving both of these objectives, and is studied in-depth in this thesis.

1.2. Portable and Distributed Fuel Processing

Portable power for small scale consumption, such as for laptops and cell phones, has traditionally relied on batteries for energy storage. Meanwhile, in the case of automobiles, power has conventionally been supplied by petroleum using the internal combustion engine. Both of these energy storage methods have allowed for unprecedented development and personal luxuries in the past 100 or so years. Despite the benefits produced by these technologies, more efficient methods for portable power delivery are needed to reduce energy consumption and increase duration of operation. In addition, capping on underutilized energy sources, such as natural gas in remote and offshore locations, and biomass in isolated areas presents a true opportunity for increasing energy supplies.

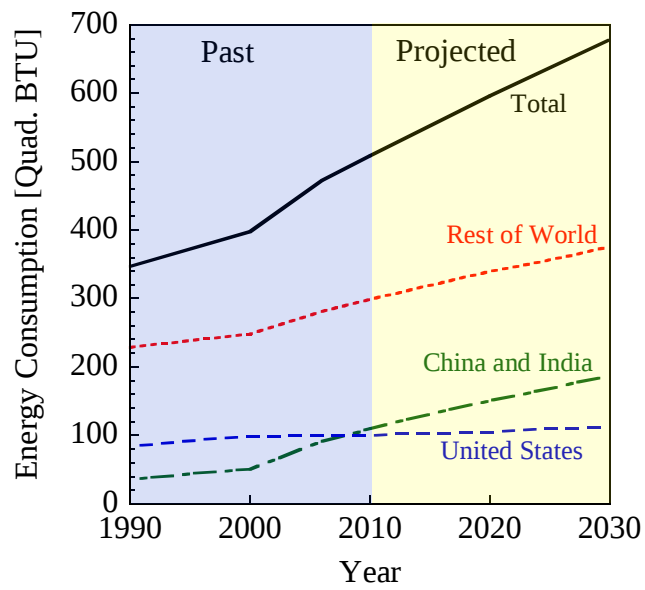


Figure 1-1. Past, present and future global energy consumption (all sources) reported by the U.S. Department of Energy. Redrawn from [1].

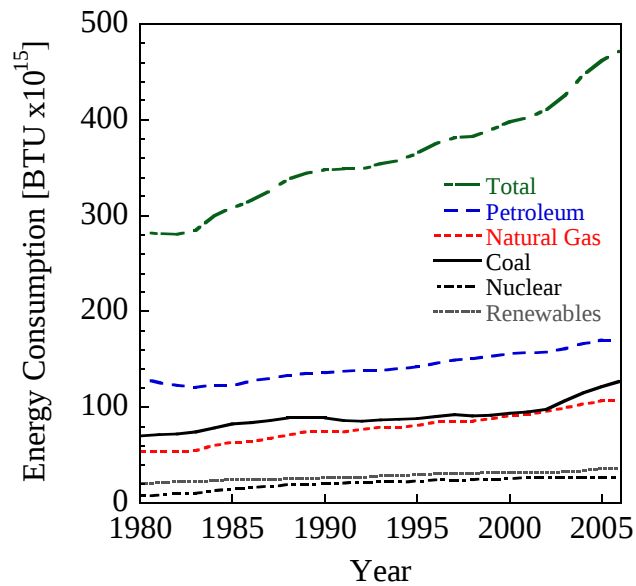


Figure 1-2. Global energy consumption by source. Redrawn from [2].

Research has been underway in recent years on replacements for both batteries and internal combustion engines; yet, little has been done to change portable power paradigms on a global consumer scale. Recently, thermoelectric elements using heat generated in microchannel combustors were investigated as a potential replacement for batteries [3] in addition to their traditional use as heat scavengers. Alternatives to conventional internal combustion engines have largely centered on the use of fuel processors integrated with hydrogen fuel cells. In this technology, the hydrocarbon fuel is reformed to produce syngas (hydrogen and carbon monoxide). Following the removal of carbon monoxide, hydrogen is consumed in a fuel cell to produce electricity. Benefits from this technology arise as integrated fuel processor/fuel cell systems can be more efficient and smaller than traditional internal combustion engines, although cost is still hindering wide scale commercialization [4].

In addition to more efficient portable and automotive energy devices, distributed processing of underutilized remote energy resources can alleviate the strain on energy markets. One example of such resources is remote and associated natural gas, which is often flared or vented and therefore its energy value is wasted [5]. Natural gas could be used as a feedstock to produce hydrogen, liquid fuels or other useful chemicals. Currently, this is not possible because conventional equipment is too large for remote and decentralized natural gas processing. Future utilization of such resources requires the development of novel processes, which are smaller relative to conventional systems.

1.3. Process Intensification

Process intensification is the modification of systems such that the resulting process is smaller, less polluting and/or more efficient. Intensification is generally associated with engineering improvements rather than changes to feedstocks or products [6]. While important for any process, intensification is especially valuable for portable and distributed energy systems, where power density is of the upmost importance.

Figure 1-3 shows the process intensification methodology. Intensification concepts are based on (I) improving equipment or (II) modifying processing methods (i.e., redesigning the flow sheet to add or integrate process units). One example of the first approach (I) is to replace a conventional packed bed reactor with a monolith reactor. For many processes, this improves catalyst utilization and reduces size [7]. The second approach (II) generally integrates multiple process elements making the design of such systems nontrivial. For example, membrane reactors combine reaction and separation elements into a single unit and synergetic effects often lead to improved performance. For perspective, real-world examples for the two approaches (I and II) are listed in Figure 1-3. Overlap between (I) and (II) often exists because equipment must be improved or redesigned when changing processing methods. For the systems studied in this thesis (microreactors for methane steam reforming), both approaches to process intensification are used. Specifically, improved reactor technology (microreactors) allows for heat producing (combustors) and heat consuming (reformers) process elements to be integrated into a single device consisting of two reactors integrated with heat exchange elements (thereby changing the processing method).

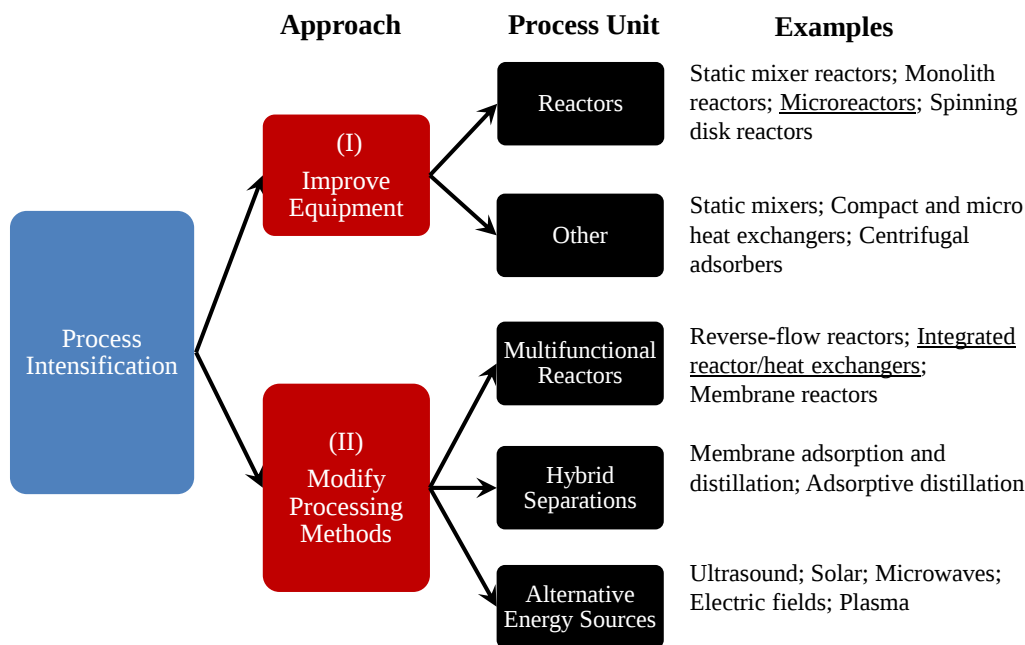


Figure 1-3. Process intensification methodology (adapted from Stankiewicz and Moulijn [6]). Underlined examples reflect topics studied in this thesis.

1.4. Microreactor Technology

While many process intensification technologies exist, this thesis focuses on microreactors. In catalytic systems, microreactors enhance heat and mass transfer to and from the catalyst bed by decreasing the distance over which transport processes occur. Significant improvement in performance can be obtained when production rates are controlled by heat or mass transport to the catalytic surface. Such is the case for methane steam reformers, where the conventional process is based on packed-bed reactors and catalysts are supported using pellets or raschig rings. In a typical packed

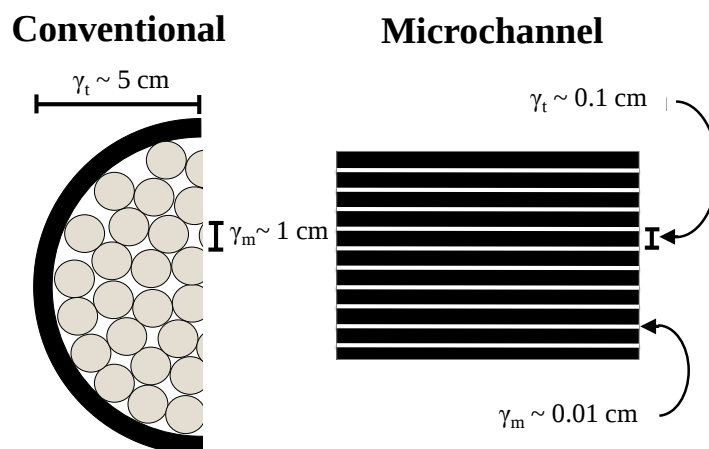


Figure 1-4. Thermal (γ_t) and mass (γ_m) transport length scales for the conventional packed bed reactor and microchannel process. Dimensions listed are order of magnitude estimates for methane steam reformers [8-13].

bed reactor, heat must be transported across the reactor wall and through the reactor catalyst bed before being consumed in endothermic reactions or sensible heating of process fluids (reactants, products or inert fluids). Conversely, in microreactors, heat is generated and consumed in adjacent microchannels allowing for fast heat transfer via a shared wall. The thermal transport length scale (γ_t) is typically a millimeter or less in microreactors [8-11], while for conventional packed bed reformers, this distance is usually several centimeters (Figure 1-4) [12]. Mass transfer in microchannel units is also fast as channels are generally on the order of 0.1 mm [8-11]. Conventional mass transport length scales are on the order of centimeters due to the catalyst support geometry [13]. For processes limited by transport, lower thermal and mass transport distances in microreactors provide one to two orders of magnitude reduction in size.

1.5. Thesis Objectives

The objective of this thesis was to develop design principles for microreactor stacks used to intensify industrial processes. In this work, steam reforming of methane was studied in microchannel reactors with the goal of developing portable and distributed syngas production systems. Stack performance (efficiency, power output, maximum temperature and stability to external heat loss) was studied as a function of size (scale-out) because the number of microchannels varies considerably with application. The instability of microreactor stacks in the presence of external heat loss was demonstrated and then techniques for solving this problem were investigated. This is an important contribution of this thesis because smaller microreactor stacks used in portable applications were found to be highly unstable under laboratory heat loss conditions.

1.6. Thesis Approach

The starting point of this work was the discovery that the generally accepted reactor model used to design microreactor stacks (infinite stack) cannot account for the effect of edge heat loss that significantly affects performance. In this work, stacks of different sizes were simulated using the computational fluid dynamics software FLUENT®. The code is fully two dimensional and no assumptions regarding dominant transport mechanisms were made. Using CFD in conjunction with

experimentally validated, fundamentally based reaction kinetics produce reliable modeling results.

1.7. Thesis Scope

This thesis includes two parts: the first studies stack performance as a function of scale-out (system size) and introduces the issue of stack stability while the second investigates several methods for stability enhancement.

Chapter 2 introduces the CFD model used in this work and then examines performance as a function of scale-out. Microreactor stack performance is benchmarked against conventional indices developed in this work. Next, the issue of stability is addressed in smaller stacks operating with experimental heat loss coefficients. Finally, mechanisms for stack failure are determined for several stack sizes and different wall materials.

In Chapter 3, methods of stability improvement are studied. Options are evaluated on their impact on stability and performance. Additionally, the effect of stability improvement options on performance is examined. A reduced microkinetic model and a simple rate expression for catalytic combustion of hydrogen on Pt catalyst were developed as part of this work.

Chapter 4 offers concluding remarks regarding the accomplishments of the thesis and also suggests potential topics for future study.

Supporting work is included in Appendices A-D.

CHAPTER 2

SCALE-OUT OF MICROREACTOR STACKS FOR SYNGAS PRODUCTION

2.1. Introduction

Microreactors have gained widespread attention in application areas, such as catalyst and drug testing, portable power generation and chemical production. For many industrial processes, there can be significant advantages in replacing conventional large-scale reactors with microreactors [6, 8, 10, 14-24]. Small length scales, characteristic of microreactors, can render processes safer [16]. The sub-millimeter distances enhance heat transfer and minimize hot spot formation [6, 17, 24]. This is desirable in highly exothermic processes as well as systems where isothermal conditions are needed. In the unfortunate event of an explosion or chemical release, lower hold-up volumes within microreactors can reduce the magnitude of any harmful impact [15, 17, 18]. Syntheses involving hazardous chemicals have been demonstrated many years ago using microreactors by researchers at DuPont [18]. Finally, for processes where production rates are limited by transport, microtechnology can lead to drastic reductions in equipment sizes with concomitant reduction in capital cost and enhanced energy efficiency [6, 8, 10, 14, 17, 19, 21, 22, 25].

The small size of microreactors inherently limits the quantity of product that may be produced from a single channel. In order to meet the demand for a chemical product in the marketplace, microreactor units are “scaled-out” or “numbered-up” to form larger stacks. Several scale-out issues, such as stack fabrication [26] and flow distribution [27-29], have been addressed in the literature. One issue that has not been evaluated is how laboratory throughput rates and performance scale with the number of channels. In published experimental work, a single microreactor stack size is studied and thought to be representative of larger process unit behavior (e.g., [11, 21]). This is done to reduce costs as fabrication of stacks is time consuming and expensive. Literature microreactor stack models are developed with a similar philosophy. Full microreactor stacks have been modeled by Schouten and co-workers [30] using a simplified reactor model assuming uniform fluid and metal temperatures in the direction perpendicular to the microstructured plate and instantaneous hydrogen combustion on the burner side. Modeling a complete stack is not the typical approach. Usually, a small number of channels are simulated to minimize computational cost. Periodic boundary conditions (see Appendix A) can be employed to essentially study an infinite stack (with no edges)[8, 22, 31, 32].

To connect literature modeling and experimental work to the commercial scale, designers assume that all channels in a stack behave similarly, and therefore, production increases linearly with the number of channels in a stack. The linear scale-out model is illustrated in Figure 2-1 for methane and methanol steam reforming (SR),

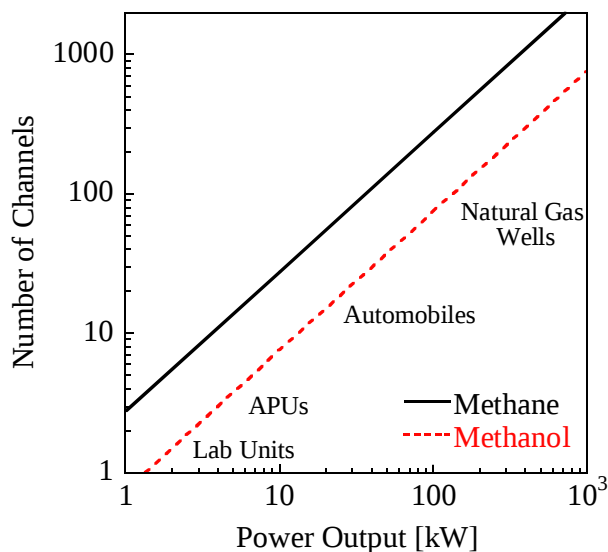


Figure 2-1. Stack size as a function of power output based on a linear scale-out model. Methanol and methane reforming data is taken from recent work [34] using an infinite stack geometry (see Appendix A) and a stack width of 10 cm is assumed.

taken here as an example for distributed and portable energy generation. As a result of the linear scale-out assumption, many authors conclude that numbering-up microreactor stacks makes for an easier transition from technical development to real-world application than conventional scale-up [8, 11, 17, 18, 21, 22, 32, 33]. The number of channels needed varies considerably with application (see Figure 2-1).

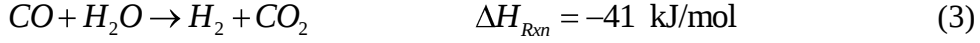
The linear scale-out model may breakdown since it has not been established that physical phenomena caused by stack edges affect all channels equally. To the best of our knowledge, the effect of stack edges on scaling-out microreactor stacks has not been studied in the literature. This work makes the first stride in

determining the effects of scaling-out microreactor stacks for an example process, methane SR. Using computational fluid dynamics (CFD), stacks of different sizes are simulated to study effects from scaling-out parallel plate reactors consisting of alternating catalytic combustion (CC) and SR channels. Efficiency, stability, temperature and conversion data are used to evaluate stacks under varying degrees of external heat loss in the first part of the paper. Comparison of the performance of the microreactors stacks to conventional methane steam reformers based on volume, efficiency, catalyst weight and catalyst cost indices makes up the second part.

2.2. Methane Steam Reforming (SR)

Methane SR has received attention recently because it is the first step in converting natural gas into liquid fuels or hydrogen for fuel cells. The importance of this comes from the desire to transition from traditional transportation power based on petroleum to renewable energy or in utilizing remote and offshore natural gas resources.

Industrial steam reformers are large with methane throughputs typically on the order of $100,000 \text{ N m}^3/\text{h}$. Methane SR and water-gas-shift (WGS) reactions generally take place in multiple packed-bed tubular reactors operated in parallel and encompassed by methane-fired furnaces [35]. These reactors usually operate with low effectiveness factors, as reaction rates are controlled by interparticle heat transfer limitations in the catalyst bed [36]. Overall reactions for the process are:



Because microreactors substantially reduce transport limitations, significant benefit is gained in replacing the conventional nickel-based SR in fixed beds catalyst with a high activity rhodium-based one in alternating parallel plate microreactors. This intensification step yields a two order of magnitude reduction in reactor size [8, 10, 23] and facilitates the use of methane for on-board hydrogen production [23] and remote natural gas conversion to syngas and then to liquid fuels [37].

2.3. Model

2.3.1. Computational Fluid Dynamics (CFD) Modeling

Two-dimensional microreactor stack geometries were simulated using the CFD software package FLUENT® and meshes were generated in GAMBIT® [38]. The third dimension (width) is assumed to be long enough compared to the stack height to ensure 2D validity. In all simulations, 40 nodes per cm are used in the axial direction and 670 and 750 nodes per cm were used in the transverse direction for combustion and SR channels, respectively. Because walls have small thermal gradients, only 100 transverse nodes per cm were used in this domain in order to

reduce simulation time. Prior to performing these calculations, simulation results for a reactor with the above grid were compared to an identical reactor with double the number nodes (transverse and axial) to confirm grid independence. A first-order upwind discretization scheme is used for momentum, species and energy equations. All under-relaxation factors are set to FLUENT default values (0.7 for momentum and 1 for species equations), except for the energy equation, which is varied between 0.985 and 0.995. Simulations are considered converged when all relative residuals are less than 10^{-9} and stable (i.e., minimal oscillation). Catalytic surface reaction rates for methane combustion on Pt/Al₂O₃ and SR and WGS on Rh/Al₂O₃ were input as boundary conditions at the channel-wall interfaces as seen in Figure 2-2. Single-step rate expressions for these reactions are taken from recently published kinetics derived from microkinetic modeling and contain coverage-dependent activation energies [39, 40]. The equations describing the rates are:

$$r_{CH_4}^{comb} = SAF_{Pt} \frac{\gamma_6 C_{CH_4}}{(1 + \gamma_7 \sqrt{C_{O_2}})^2} \quad (4)$$

$$r_{CH_4}^{sr} = SAF_{Rh} \frac{\gamma_4 C_{CH_4}}{(1 + \gamma_1 \sqrt{C_{H_2}})(1 + \gamma_2 \sqrt{C_{H_2}} + \gamma_3 C_{CO})^2} (1 - \eta_{sr}) \quad (5)$$

$$r^{wgs} = SAF_{Rh} \frac{\gamma_5 C_{H_2O}}{(1 + \gamma_2 \sqrt{C_{H_2}} + \gamma_3 C_{CO})^2} (1 - \eta_{wgs}) \quad (6)$$

The rate parameters (γ_i) in the above equations represent combinations of elementary reaction rate constants taken from microkinetic models [39, 40]. The activation energy

for methane adsorption on platinum is taken to be 10 kcal/mol for consistency with previous work [8]. Surface area factors for platinum (SAF_{Pt}) and rhodium (SAF_{Rh}) catalysts are used to relate the effective catalytic surface area, which lumps the effect of active sites and diffusion within the supported catalyst, to the geometric surface area of the channel wall. The general definition for SAF is:

$$SAF = \frac{\text{Effective Catalyst Surface Area}}{\text{Geometric Surface Area}} \quad (7)$$

This definition for SAF implies that an increase in weight loading of a catalyst does not necessarily induce a linear increase in reaction rate. The SAF value for supported platinum is 1.7 [41] and for rhodium is 1.0 for consistency with previous work [8, 23]. In order to account for the thermodynamic limitations of SR and WGS reactions, the approach to equilibrium (η) is used. For the SR process, the approach to equilibrium is defined as:

$$\eta_{sr} = \frac{K_{sr}}{K_{equilibrium, sr}} \quad (8)$$

where

$$K_{sr} = \frac{P_{H_2}^3 P_{CO}}{P_{CH_4} P_{H_2O}} \quad (9)$$

$$K_{equilibrium, sr} = \exp\left(-\frac{\Delta G_{SR}^0(T)}{RT}\right) \quad (10)$$

$\Delta G^0_{\text{SR}}(T)$ is calculated from thermodynamic relationships using temperature-dependent heat capacities [42]. The approach to equilibrium for WGS can be written as:

$$\eta_{\text{wgs}} = \frac{K_{\text{wgs}}}{K_{\text{equilibrium,wgs}}} \quad (11)$$

Here K_{wgs} and $K_{\text{equilibrium,wgs}}$ are calculated in a similar manner as is done for η_{sr} in (9) and (10).

2.3.2. Scale-out Methodology

A scale-out model is proposed which keeps several reactor parameters constant in order to appropriately compare stacks of different sizes. Stack flow rates and catalyst placement on different walls are fixed using information from infinite stack and two channel reactor (2CR) simulations, respectively (see Appendix A and Appendix B). Our scale-out strategy is based on two additional design principles: (I) SR channels are positioned at the stack edges in order to insulate combustion channels from external heat losses and (II) the SR heat duty per combustion channel is the same for all stack sizes. Other designs, such as placing combustion channels at the edges or using different throughputs for inner and outer channels, are also possible (and in some instances preferable). For example, simulations of three (3CR) and nine (9CR) channel reactors indicate that the differences in stability and performance of placing

the combustion channels in the exterior are within usually 10-20% of the design used here, and thus, other designs are not further discussed here.

The starting point of this scale-out study is the three channel reactor (3CR) which is comprised of a central catalytic combustion channel (CC1) encompassed by two SR channels (Figure 2-2). This configuration satisfies (I) as the outer SR channels insulate CC1 from edge heat loss. Both interior surfaces of CC1 are catalytic (indicated by red lines in color version) and the reduced rate expression for methane combustion on Pt/Al₂O₃ (4) is applied at these faces. The two outer SR channels have only one catalytic surface, and kinetics for SR (5) and WGS (6) on Rh/Al₂O₃ are implemented at the inner SR channel wall face (adjacent to CC1). Since the outer SR channel wall is closer to the stack edge, where heat losses are prevalent, temperatures are lower and no catalyst is placed there. This choice is motivated from our 2CR simulations that indicate that exothermic and endothermic catalytic surfaces should be placed on opposite wall faces in order to maximize methane conversion and minimize hot spot formation (see Appendix B).

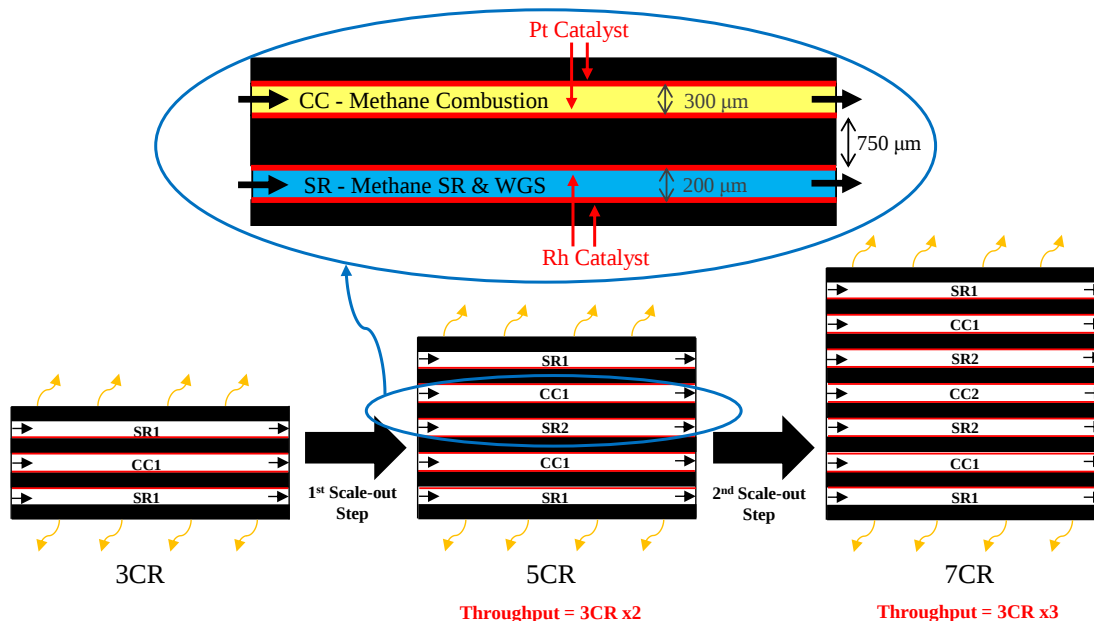


Figure 2-2. Microreactor scale-out strategy. Gap sizes and wall thicknesses are shown in the enlarged (circled) section. All stacks are 5 cm in length. Red lines indicate catalytic surfaces.

In the first scale-out step, one combustion and one SR channel are added to the 3CR to form a five channel reactor (5CR). In order to accomplish objective (II) and keep the SR load per combustion channel constant, the inlet velocity of the inner SR channel of the 5CR (SR2) is increased by a factor of two. This is done because SR2 consumes heat generated in combustion channels both above and below it while the outer SR channel (SR1) can only draw heat from one combustion channel. Similarly, as we scale-out, SR1 has only one catalytic surface (at the innermost wall) while all inner channels (SR2, CC1, CC2 in Figure 2-2) have two.

The inlet equivalence ratio for the combustion channels is 0.92 while $\text{H}_2\text{O}:\text{CH}_4$ is set at 2:1 with 1% N_2 (molar) for SR channels. The steam to methane ratio is chosen to represent the inlet composition of industrial methane steam reformers [35]. Inlet velocities of 6.1 and 3.05 m/s are used in combustion channels for high and mid wall thermal conductivities, respectively, based on the fact that under adiabatic heat transfer conditions, greater than 99.99 % methane conversion is achieved (see Appendix A). These are in the range of flow velocities used in previous CFD simulations of catalytic combustion systems [23, 41, 43, 44]. For the SR channels, two sets of outer/inner channel inlet velocities are employed: 2.0/4.0 m/s for the high wall thermal conductivity case, and 1.15/2.3 m/s for the moderate conductivity value, as shown in Table 2-1. The SR flow rates are determined from infinite stack simulations, as explained in Appendix A. Combustion and SR gap sizes are constant in all simulations at 300 μm and 200 μm , respectively. For all stacks, wall thicknesses are fixed at 750 μm and channels are 5 cm in length. With these channel gap sizes, inlet compositions and flow rates, roughly 40% of methane feed is burned in the combustion channels while the remainder is sent to the SR channels.

Table 2-1. Stack flow parameters for both inner and outer channels for wall thermal conductivities of 100 and 23 W/m-K.

Flow Parameter	k=100 W/m-K		k=23 W/m-K	
	Inner Chnls.	Outer Chnls.	Inner Chnls.	Outer Chnls.
Inlet velocity [m/s] (CC)	6.1	6.1	3.05	3.05
Inlet velocity [m/s] (SR)	4.0	2.0	2.3	1.15
Equivalence Ratio (CC)	0.92	0.92	0.92	0.92
H ₂ O:CH ₄ (SR)	2	2	2	2

2.3.3. Performance Metrics

Several metrics can be used to compare microreactor stacks. Energy efficiency should be maximized. Material of construction is also important as it significantly affects performance (hot spots, conversion, etc.) and cost. A final metric is the stability of the stack under increasing external heat loss. All of these metrics will be addressed, but stack stability and material choice will receive special attention as they are especially challenging for methane SR.

2.3.3.1. External Heat Loss

Heat losses were modeled using Newton's law of cooling:

$$Q = h \int_A \Delta T dA \quad (12)$$

Heat transfer from the stack to the ambient can be varied through the heat loss coefficient (h) at the external walls. The integral is evaluated over the external surface of the reactor, Q is the total power transferred from walls to the ambient and ΔT is the temperature difference between the reactor wall and the ambient (ΔT). The stability of different stacks can be compared using the critical heat loss coefficient. As h is increased at the stack edges, the system reaches a point where any further increase causes heat loss to the ambient to be too large and combustion processes within the stack cease. Once combustion reactions stop, the stack thermally equilibrates with the ambient and no syngas is produced. For larger stacks (i.e., the 15CR), we find a partially ignited mode for intermediate heat loss coefficients, where inner combustion channels function at high conversion after the outer channels fail. Failure of the outer combustion channels reduces efficiency and throughput. This phenomenon is discussed further in section 2.6.2. In order to connect the stability of the different simulated stacks with laboratory microsystems, the critical heat loss coefficient of a stack is compared to an estimate of the laboratory heat loss coefficient. In previous work, the laboratory heat loss coefficient was estimated to be $64.5 \text{ W/m}^2\text{-K}$ using a 2D pseudo-homogeneous model with the kinetics used herein[41]. This value lumps convective and radiant phenomena and includes the effects of laboratory equipment (insulation, nuts, bolts, piping, etc.). The laboratory heat loss coefficient was also independently estimated by simulating an experimental microreactor (at various heat loss coefficients) at full conversion from an overall energy balance and then

comparing the model results to experimental data. A value of $60 \pm 20 \text{ W/m}^2\text{-K}$ was found. Given these estimates, the laboratory heat loss coefficient is taken to be $60 \text{ W/m}^2\text{-K}$.

2.3.3.2. Stack Construction Materials

Two wall thermal conductivities are modeled. A moderate conductivity value of 23 W/m-K is chosen that is similar to the value for stainless steel. A second, higher value of 100 W/m-K is employed that is near reported values for highly conductive materials such as silicon carbide, low-alloy steels and copper alloys [45]. Silicon carbide has high chemical and mechanical stability at high temperatures, but it is 1-2 orders of magnitude more expensive than stainless steel [46]. Low alloy steels and copper alloys are inexpensive but have reduced thermal stability compared to stainless steel [45]. In this work, we ignore such downsides in order to explore the effect of wall thermal conductivity on performance.

2.3.3.3. Energy Efficiency

The efficiency of the stacks is calculated based on the methane input and syngas product. The energy content of the methane feed is calculated based on the heat of combustion at 300 K (-803 kJ/mol). Similarly, the power produced in the form of syngas is determined from the lower heating value (LHV) of hydrogen and carbon

monoxide (-241 kJ/mol and -283 kJ/mol, respectively). The efficiency (η) can be calculated from the following equation:

$$\eta = \frac{F_{\text{CO}} \text{LHV}_{\text{CO}} + F_{\text{H}_2} \text{LHV}_{\text{H}_2} \text{out}}{F_{\text{Me}} \text{LHV}_{\text{Me}} \text{in}} \quad (13)$$

In (13), F_i represents the total molar flow rate of species i into or out of the stack.

2.4. Evaluation of the 3-Channel Reactor (3CR)

First, the behavior of the base-unit stack, the 3CR, is studied as a function of edge heat loss. Figure 2-3 indicates that the efficiency (a) and maximum wall temperature (b) decrease linearly with increased heat loss coefficient, whereas the ambient power loss (a) increases linearly with increased heat loss coefficient. On the contrary, methane conversion within the combustion channel is a nonlinear function of heat loss coefficient (Figure 2-3 (c)). Interestingly, methane conversion in this channel is greater than 95% even at the critical heat loss coefficient. On the other hand, the methane conversion in SR channels drops significantly with increasing heat loss (Figure 2-3(c)).

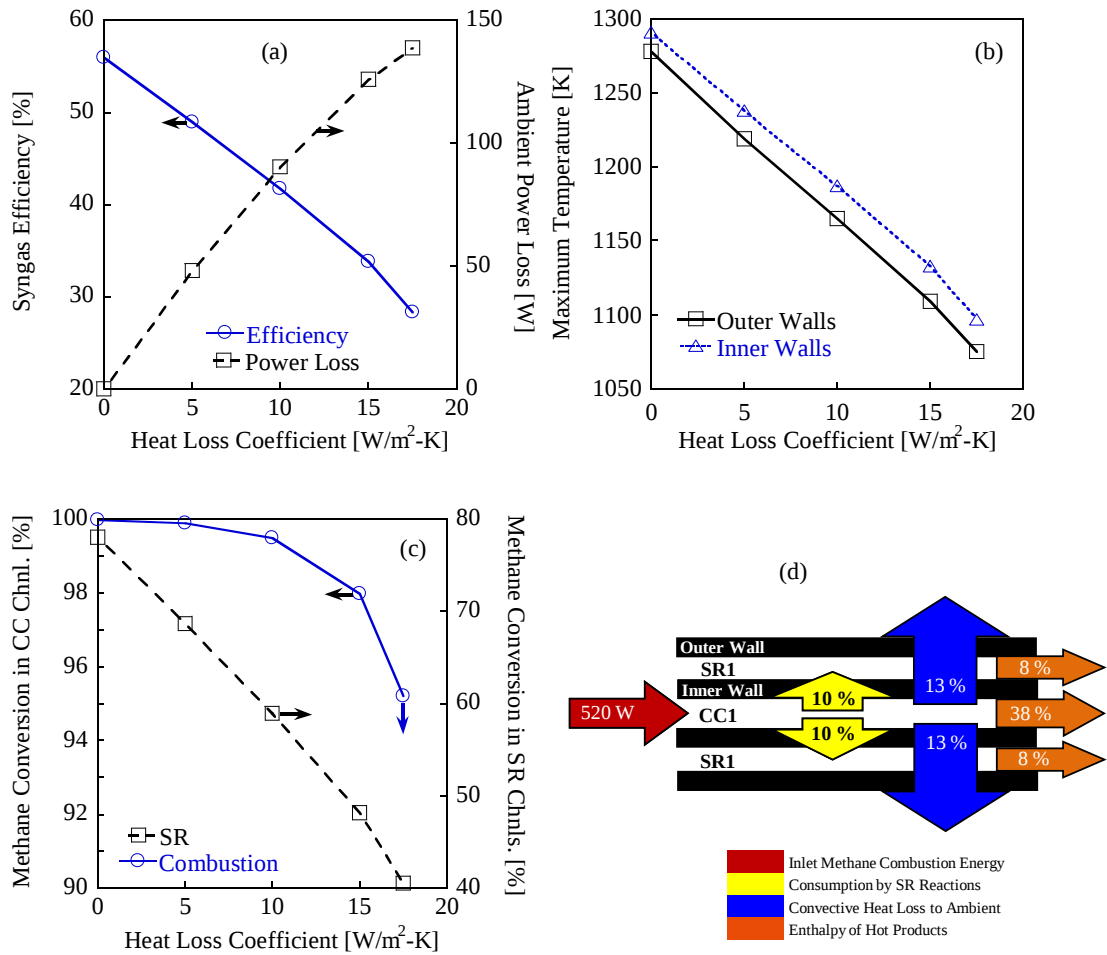


Figure 2-3. Performance of the base-unit three channel reactor (3CR) in terms of efficiency (circles, (a)), power loss to ambient (squares, (a)), maximum wall temperature (b), and methane conversion in combustion and SR channels (c). Additionally, the energy flow for the 3CR at the critical heat loss coefficient (17.5 W/m²-K) is shown in (d). The (blue) vertical arrow in (c) indicates the critical heat loss coefficient for the 3CR. All data is for a wall thermal conductivity of 100 W/m-K. Power calculations (a and d) are based on a 10 cm wide stack.

The critical heat transfer coefficient of the 3CR is only $17.5 \text{ W/m}^2\text{-K}$ (indicated by the vertical arrow in Figure 2-3 (c)), much less than the laboratory estimate of $60 \text{ W/m}^2\text{-K}$. This indicates that the 3CR cannot function in the lab. One reason for the low critical heat transfer coefficient value is that the external surface area to volume ratio (A/V) of the 3CR is higher (580 m^{-1}) than that used in industrial steam reformers (40 m^{-1}) [35]. High A/V within microreactors is often beneficial as it allows for faster heat and mass transfer within and between channels. However, as is seen in the case of the 3CR, external heat loss to the ambient is increased as well. Also, methane powered microreactors are less stable than microcombustors powered with larger hydrocarbons as methane has a higher energy barrier for adsorption on $\text{Pt/Al}_2\text{O}_3$ [40].

In order to better understand energy utilization in the 3CR, the destination of inlet methane combustion energy is indicated in Figure 2-3(d). At the critical heat transfer coefficient for the 3CR ($17.5 \text{ W/m}^2\text{-K}$), about half of the inlet chemical energy is lost in the form of hot products. An additional quarter is transferred from the stack walls to the ambient. Therefore, only 20% of the inlet combustion energy is utilized in SR reactions to produce syngas. These values can be compared to those of an (adiabatic) infinite stack, where 29% of the inlet energy is utilized in SR reactions and the remainder leaves via hot products (see Appendix A).

With this understanding of performance and stability of the base-unit stack, the edge and material effects are studied next as the 3CR is scaled-out to larger stacks.

2.5. Scale-out Effects

Using the aforementioned scale-out strategy, different stacks with high or mid wall thermal conductivity are studied as a function of heat loss coefficient. Energy efficiency is a common metric used to study microreactor stacks and power generation systems in general. Figure 2-4 (a) shows that efficiency of stacks for high wall thermal conductivity stacks ($k=100$ W/m-K) is approximately linear with respect to heat loss coefficient, with the end points of each curve representing the critical heat loss coefficient. Due to decreased A/V , syngas efficiency increases with increasing stack size as larger stacks lose a lesser fraction of inlet energy to the ambient (Figure 2-4(b)). In addition to ambient heat loss, a large fraction of the stack energy input is retained in hot products (~60%) leaving a lesser amount to fuel endothermic SR reactions. At the small scales studied here, the efficiency increases substantially with increasing stack size but is considerably lower than that of large stacks under typical laboratory heat loss. Larger stack sizes are not investigated here, but it is likely that efficiencies of these systems are near the infinite stack value (dashed line in Figure 2-4(a)).

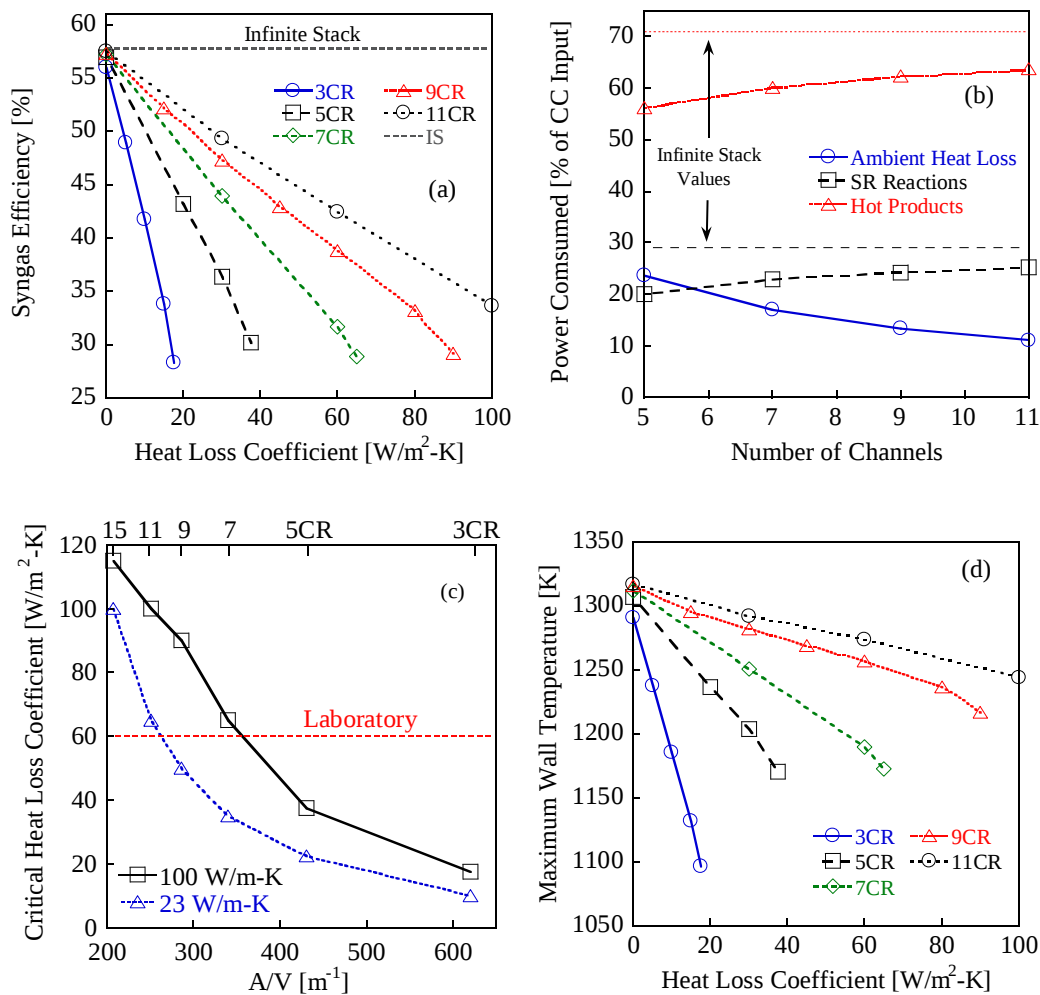


Figure 2-4. Stack performance in scale-out in terms of: (a) efficiency as a function of heat loss coefficient; (b) energy consumption pathways as a function of size (at $h=30 \text{ W/m}^2\text{-K}$); (c) stability versus A/V ; and (d) maximum wall temperature versus heat loss coefficient. The dashed (red) line in (c) indicates a typical laboratory heat loss coefficient for microreactors. A wall thermal conductivity of 100 W/m-K was used in (a), (b) and (d). In (b), energy consumption pathways for the infinite stack reactor are indicated with horizontal lines for SR reactions (dashed line) and hot products (dotted line).

For the particular conditions studied here, maximum wall temperatures are reasonable for all stack sizes and heat loss coefficients (Figure 2-4(d)). Maximum temperatures occur at the lower catalytic wall of the inner combustion channel (nearest to the center of the stack). It is clear that the inner combustion temperature of the basic unit (3CR) is very sensitive to heat loss, whereas larger sizes (5CR and up) are less sensitive.

Stability as a function of stack size is compared for various stack sizes in terms of the critical heat loss coefficient. Figure 2-4(c) shows that stability improves with stack size. This trend is partially due to reduced external surface area per volume ratio as stack size is increased, as discussed in the previous section for the 3CR. Stacks constructed from materials with mid thermal conductivities (e.g., SS) are less stable than those built from high conductivity materials (e.g., SiC) for these conditions, although the difference is less dramatic for larger stacks. Additionally, the high wall conductivity data in Figure 2-4(c) indicate that stability is not simply a linear function of A/V . Small stacks constructed from materials with a moderate thermal conductivity are not stable under laboratory heat loss conditions.

2.6. Stack Failure Analysis

2.6.1. Failure of Smaller Stacks

In order to understand how smaller stacks fail, individual channels of the 9CR are examined. The effect of edge heat loss on exit temperatures (Figure 2-5) and methane conversion (Figure 2-6(a) and (b)) is determined. Figure 2-5 illustrates that transverse thermal gradients develop as edge heat loss is increased. At the critical heat transfer coefficient of the 9CR ($90 \text{ W/m}^2\text{-K}$), a difference in exit temperature of $\sim 350 \text{ K}$ is observed between the middle channel (SR3) and the outermost channel (SR1). At the vertical midline of the 9CR (line at 2.5 cm), transverse thermal gradients are slightly larger ($\sim 450 \text{ K}$) as heat generation in interior combustion channel (CC2) occurs closer to this point. These gradients are substantial given that these channels are separated by only 4 mm. At laboratory heat loss conditions ($h=60 \text{ W/m}^2\text{-K}$), the temperature difference between pairs of adjacent combustion and SR channels in the 9CR ranges from 15 K (interior pairs, SR3/CC2) to 100 K (outer pairs, SR1/CC1). These differences are caused by edge heat losses and are larger than those predicted in infinite stack simulations, where the temperature differences between adjacent SR and combustion channels do not exceed 5 K (after entrance effects have subsided).

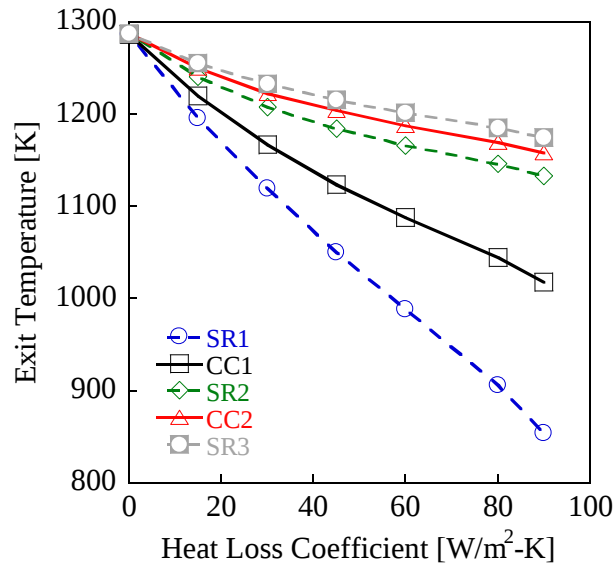


Figure 2-5. Thermal effects from edge heat loss on a nine channel reactor (9CR). Exit temperatures are shown as a function of heat loss coefficient. The wall thermal conductivity is 100 W/m-K.

The large temperature gradients observed within the stack at high heat loss cause methane conversion in outer and inner channels to be unequal. Figure 2-6(a) shows that conversion for inner SR channels (SR2 and SR3) is a weak function of heat loss coefficient. Similarly, conversion in the inner combustion channel (CC2) is greater than 98% even at the critical heat loss coefficient (Figure 2-6(b)). Additionally, Figure 2-6(a) shows that the conversion in SR1 drops from 80% under adiabatic conditions to 10% at the critical heat loss coefficient. Similarly, methane conversion in CC1 decreases from greater than 99% at low heat loss coefficients to 84% at the critical heat loss coefficient. Figure 2-6(b) implies that CC1 fails first and, because of thermal coupling, ultimately causes combustion within CC2 to cease as

well. Figure 2-7 expands on this conclusion and suggests conversion in CC1 is always less than that in CC2.

An additional effect of edge heat loss is that top and bottom catalytic walls within a single channel are not utilized equally. Figure 2-6(c) shows that top catalytic walls process less methane relative to bottom walls in both SR and combustion channels. In the outer combustion channel (CC1), the top catalytic surface (nearest edge heat loss) is much less utilized than the bottom surface. Reduced activity is a product of lower temperatures at the top surface ($T_{\max} = 900 \text{ K}$) relative to the bottom catalytic wall ($T_{\max} = \sim 1150 \text{ K}$). Edge heat loss also causes the catalytic surfaces of inner combustion channels (CC2) to be unequally utilized despite this channel having greater than 98% methane conversion at critical heat loss. As is the case with CC1, asymmetric activity of CC2 catalytic walls is due to different temperatures between top ($T_{\max} = \sim 1150 \text{ K}$) and bottom ($T_{\max} = \sim 1200 \text{ K}$) surfaces. Unused catalytic surfaces can reduce conversion and throughput. From Figure 2-6(c), one may conclude that edge heat loss can have undesired impact on catalyst utilization, an effect that penetrates to interior channels, even when these channels are operating with high conversion.

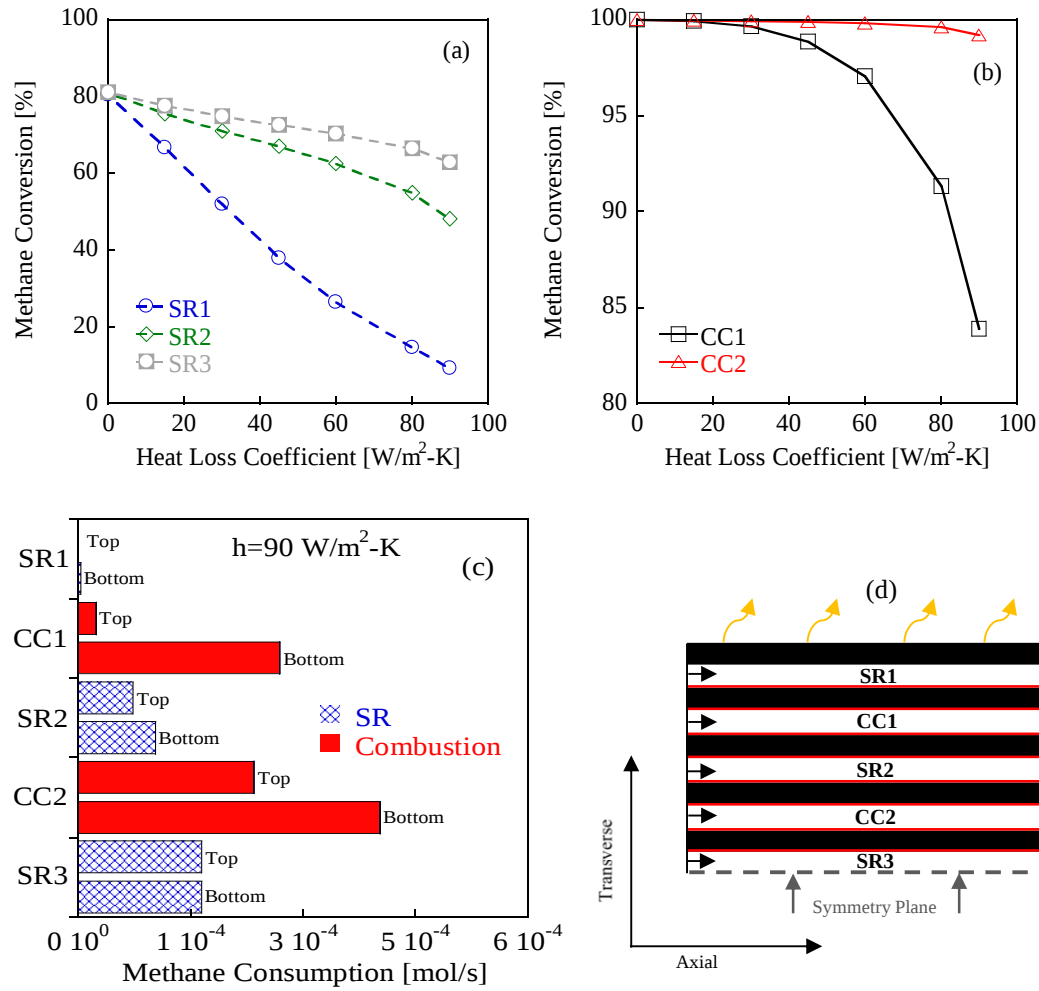


Figure 2-6. Effect of edge heat loss on conversion and catalyst surface utilization of a nine channel reactor (9CR). Exit methane conversion for combustion (a) and SR (b) channels is shown as a function of heat loss coefficient. Utilization of catalytic surfaces for SR and combustion channels at critical heat loss ($h=90 \text{ W/m}^2\text{-K}$) (c). Schematic of the 9CR (d). A wall thermal conductivity of 100 W/m-K is used.

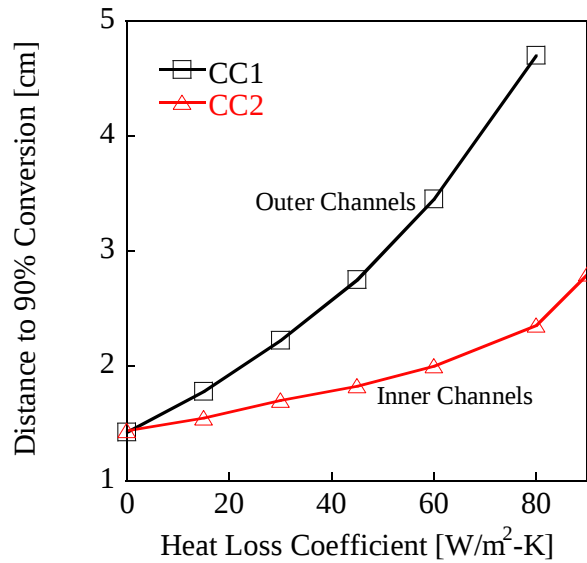


Figure 2-7. Reaction zone location within combustion channels of the nine channel reactor (9CR). Distance to 90% methane conversion is shown as a function of heat loss coefficient. Average (cup-mixing) conversion values are reported for outer (CC1) and inner (CC2) combustion channels. The wall thermal conductivity is 100 W/m-K.

The location of 90% methane conversion is used to identify the reaction zone within the combustion channels of the 9CR (Figure 2-7). As the heat loss coefficient increases, the reaction zone within CC1 moves down the reactor length while the reaction zone in CC2 is less affected by the increase in external heat loss. This indicates that at high heat loss, the CC1 reaction zone is further from the channel inlet and that CC1 causes failure.

Failure of the outer combustion channel (CC1) does not generally imply failure of the entire stack, i.e., interior combustion channel(s) (CC2) may still function even when the chemistry in CC1 dies out (as is the case with the 15CR, discussed in

the next section). However, if combustion channels within stacks possess sufficient thermal coupling, failure of one channel causes all channels to fail (as is the case for the 9CR, which we consider here). To illustrate the degree of thermal coupling between combustion channels, the energy flow within the 9CR is presented for three heat loss coefficients (Figure 2-8). Heat fluxes into and out of CC1 and CC2 (each receives 520 W as input combustion energy for a 10 cm wide stack) are shown in Figure 2-8. Combustion channels are separated by one SR channel (SR2). Figure 2-8 shows that for adiabatic conditions, the heat flux from both CC1 and CC2 to SR2 (to carry out SR reactions) is roughly equal. However, as edge heat loss increases, CC1 loses a substantial fraction of its inlet power to edge heat loss causing reduction of the heat flux from CC1 to SR2. This results in increased heat transfer from CC2 to SR2 due to the increase in the transverse temperature gradient. At critical heat loss ($h=90 \text{ W/m}^2/\text{K}$), the outer combustion channel (CC1) contributes only a small fraction of the power required to heat reactants and fuel SR reactions in SR2 (5 W at $h=90$ vs. 128 W at $h=0 \text{ W/m}^2/\text{K}$). This causes a 40% reduction in methane conversion in SR2 compared to the adiabatic case (see Figure 6a), as the increase in power transfer from CC2 is unable to make up for the reduced contribution from CC1 (CC1 decrease: 123 W, CC2 increase: 50 W).

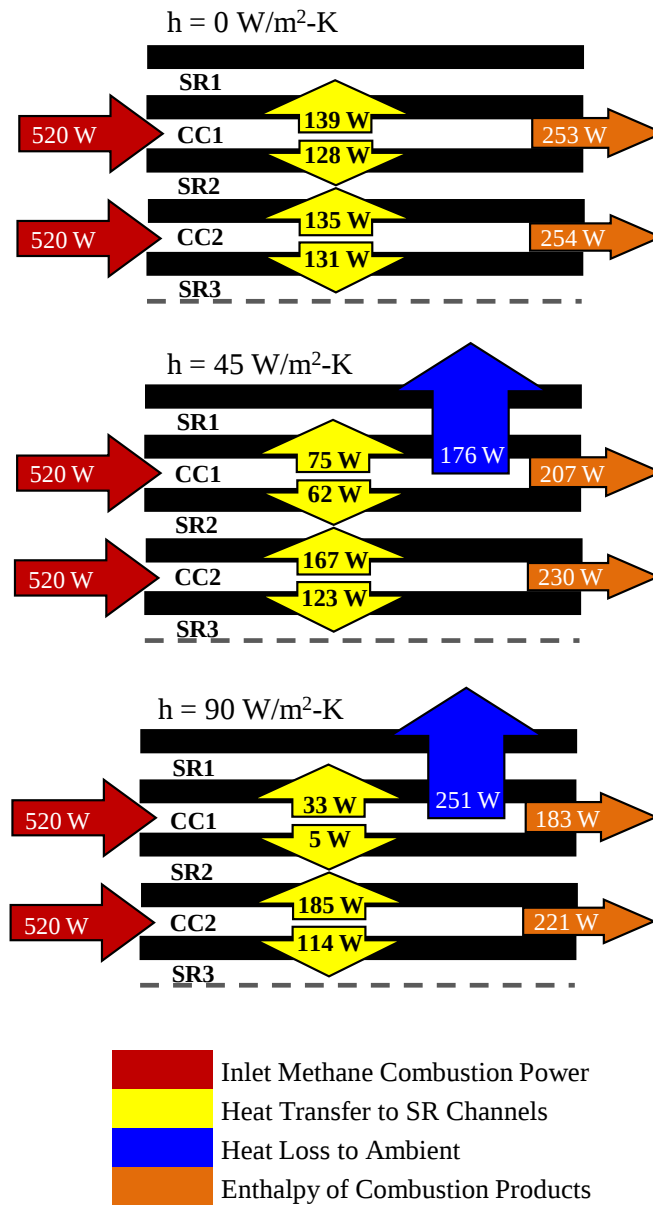


Figure 2-8. Energy flow diagrams for adiabatic, moderate ($h=45 \text{ W/m}^2\text{-K}$) and critical ($h=90 \text{ W/m}^2\text{-K}$) heat loss for the nine channel reactor (9CR). Uncombusted methane is not accounted for in the enthalpy of combustion products (orange arrows). Dashed (grey) lines indicate symmetry planes. The wall thermal conductivity is 100 W/m-K and power values are for stack width of 10 cm.

Next, the mechanism for stability loss in the outer combustion channel (CC1) is investigated. There are two mechanisms for loss of stability. In combustion systems plagued by blowout, the reaction zone migrates down the reactor length until it eventually leaves the reactor and combustion ceases. Reactor temperatures are typically high and residence time is crucial. On the other hand, extinction temperatures are generally low and the reaction zone is delocalized, reducing the overall reaction rate. Both failure mechanisms have been documented in gas-phase microburners [47-49]. Previous work on propane catalytic combustion microreactors lacked a clear demarcation between extinction and blowout because low activation energies lead to delocalized reaction zones [41]. Microreactor stacks studied here are powered by methane rather than propane, and therefore the combustion is slower due to high activation energy for fuel adsorption. The higher adsorption barrier causes more localized reaction zones near failure, which allows for a clearer demarcation between blowout and extinction in our stacks. At the same time, the thermal coupling between multiple channels of stacks makes analysis more difficult.

Figure 2-9(a) shows the maximum temperature for the top and bottom catalytic walls of the outer combustion channel (CC1) as a function of size at the critical heat loss coefficient of each stack, whereas Figure 2-9(b) illustrates the location of maximum temperature relative to the entrance of CC1. Figure 2-9(a) indicates that top walls (near stack edge) are cooler than bottom walls (away from stack edge) and top walls of high conductivity stacks are cooler than top walls of

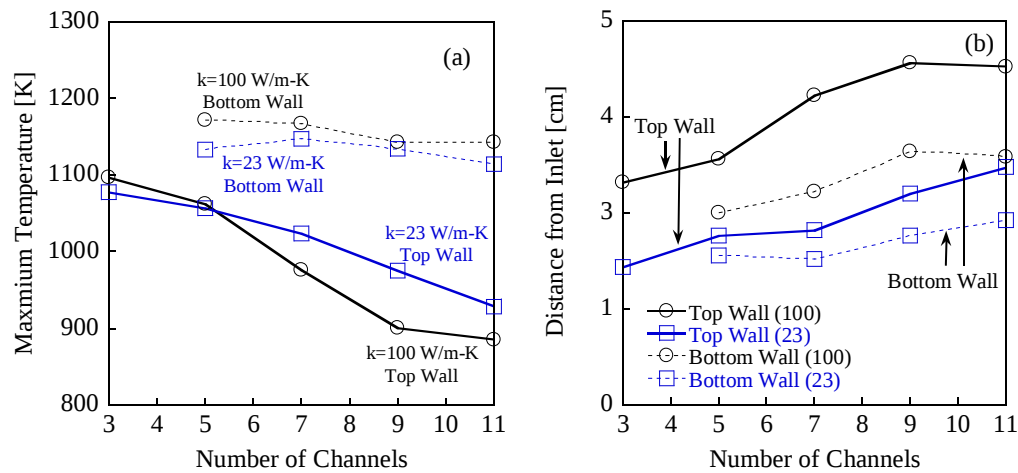


Figure 2-9. Reaction zone in the outer combustion channel (at critical heat loss) as a function of stack size. The maximum wall temperature (a) and maximum wall temperature location (b) for top and bottom walls of stacks is shown during scale-out. The three channel reactor (3CR) has only a top wall and therefore no bottom wall data is shown for this stack.

moderate conductivity stacks. This implies that top walls play a less significant role at critical heat loss for high conductivity stacks (similar to what Figure 2-6(c) data suggest).

The maximum temperature location for stacks operating at the critical heat loss coefficient (different for each stack) is shown as a function of stack size in Figure 2-9(b). The maximum temperature provides an indicator of the reaction zone within CC1. For *adiabatic* stacks with high and moderately conductive walls, the maximum temperature location is 1.4 cm and 1.0 cm from the inlet, respectively. The maximum temperature location moves away from the inlet in larger stacks indicating reaction

zone migration. This suggests that blowout could be a factor in the failure of larger stacks as the reaction zone nears the exit of the outer combustion channel.

Figure 2-10 further illustrates the reaction zone location in CC1 by depicting the axial location of 10% (left hashes) and 90% (right hashes) methane conversion at the critical heat loss coefficient (a different value for each stack). The reaction zone is larger for highly conductive walls compared to stacks with moderately conductive walls due to higher peak temperatures in the second case that increase the average reaction rate. The reaction zone for larger stacks is near the outlet of CC1 at the critical heat loss coefficient. This is due to reaction zone migration (a signature of blowout) in CC1. For small stacks (3CR and 5CR), the reaction zone is far from the CC1 exit indicating that stability is lost via extinction. Figure 2-10 supports the hypothesis that larger stacks are controlled via blowout whereas failure in smaller stacks is due to extinction.

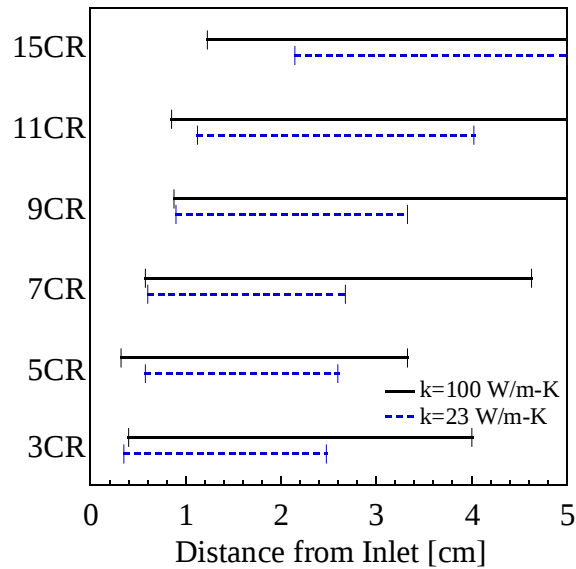


Figure 2-10. Reaction zone location in outer combustion channel (CC1) at the critical heat loss coefficient (different for each stack). Horizontal lines represent the location of the reaction zone with the distance to 10% methane conversion being the start (left vertical bars) and the distance to 90% methane conversion being the end (right vertical bars). Data is taken for five stack sizes with both high (solid black lines) and mid (dashed blue lines) wall thermal conductivities.

To test the hypothesis that outer channels in larger stacks fail because of blowout, the flow in outer combustion channels (CC1) of the 9CR was increased. An increase in flow rate increases the energy input to the stack, and if the additional methane input is combusted, stack temperatures are elevated and ultimately the critical heat loss coefficient is increased. In contrast, if a channel is controlled from blowout, the increased flow will not result in increased energy generation as the residence time is insufficient to burn the additional fuel. To benchmark increases in the critical heat loss coefficient when flow is increased to the outer combustion channel, the effect of

increased flow to the inner channels on critical h is used for comparison. A 25% increase in flow to the inner combustion channel (CC2) results in a 33% increase in critical heat loss coefficient. The same flow increase to the outer combustion channel (CC1) does not change critical h , as little of the additional methane input combusts and stack temperatures are not increased. These simulations indicate that the outer combustion channel fails because of blowout.

2.6.2. Failure of Larger Stacks

While the stability of smaller stacks (<15 channels) is bimodal (combustion channels are either all ignited or all extinguished), the 15CR exhibits more complex operation. Figure 2-11 shows conversion and outlet temperatures of the individual channels of the 15CR for a wall thermal conductivity of 100 W/m-K. For low heat loss coefficients ($h \leq 115$ W/m²-K), all combustion channels are ignited and operate at high temperature and conversion. At intermediate heat loss coefficients ($115 < h \leq 130$ W/m²-K), conversion is low (<10%) in outer combustion channels and high ($\geq 80\%$) for inner combustion channels. In this parameter range, heat from the interior of the stack is able to compensate for reduced heat generation due to the failure of the outer combustion channel (CC1). This behavior is different from smaller stacks, where combustion channels are more strongly thermally coupled and cannot function independent of one another. Finally, for high heat loss coefficients ($h > 130$ W/m²-K), both inner and outer combustion channels are extinguished and complete stack failure

occurs. The 15CR therefore represents a size where stacks transition from typical bimodal behavior (all ignited or all extinguished channels) to bimodal operation with all combustion channels being fully ignited or the outer one only being extinguished for the operating conditions studied here. For larger stack sizes (greater than 15 channels) or different operating conditions, more operational modes are possible. Such complex behavior obviously cannot be captured with a simple linear scale-out model.

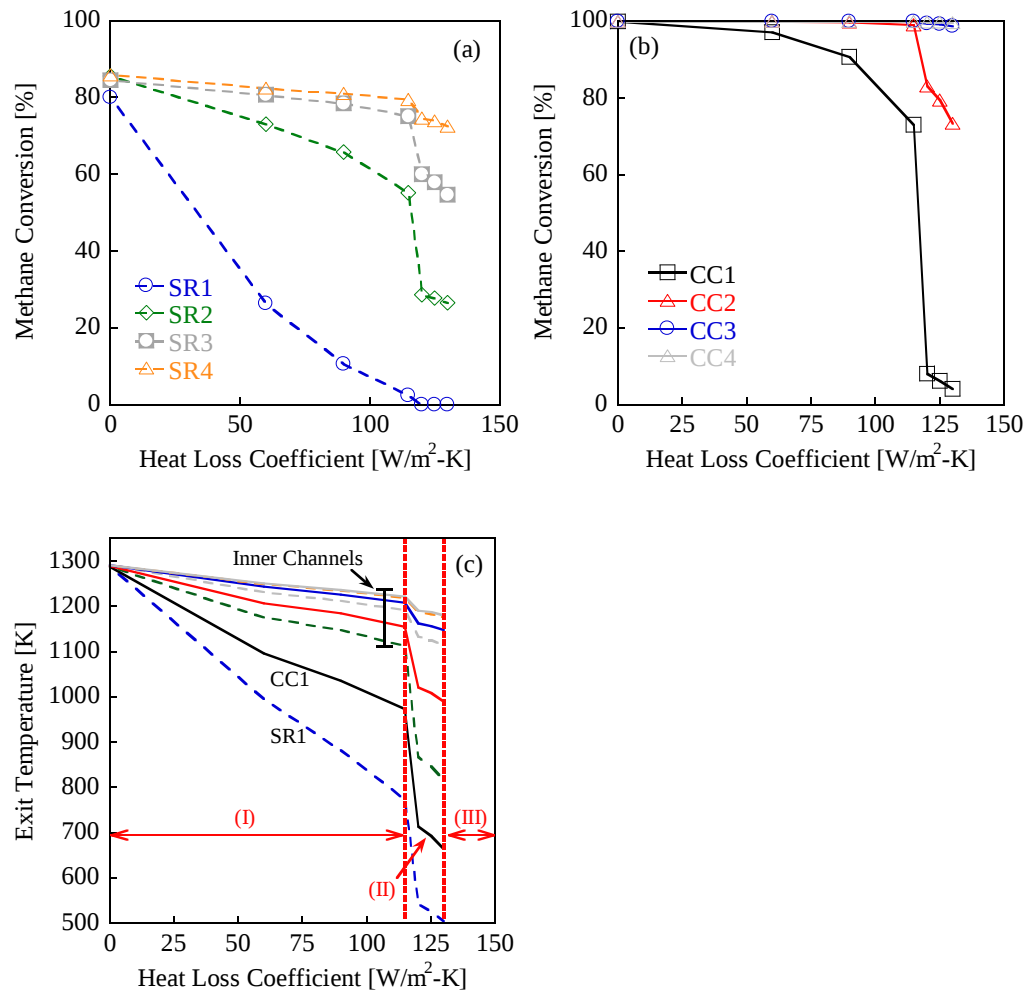


Figure 2-11. Conversion (a and b) and exit temperature (c) for 15CR channels as a function of heat loss coefficient. In (c), three operating modes are illustrated: (I) all combustion channels ignited, (II) inner channels functioning while outer ones are not, and (III) no combustion in any of the combustion channels. Data is for a wall thermal conductivity of 100 W/m-K.

2.7. Comparison to Conventional Technology

Valuable perspective can be gained by comparing the performance of microreactor stacks to conventional methane steam reformers. In this work, several indices are used to benchmark characteristics of microreactor stacks: Volume Index (VI), Efficiency Index (EI), Catalyst Weight Index (CWI) and Catalyst Cost Index (CCI). VI and CWI were used by Zafir and Gavrilidis to evaluate parallel plate steam reformers operating with Ni catalysts, but their comparison was based on methane throughput [22], whereas here we have reset the basis to be hydrogen output. Hydrogen production rates are taken from previously published plant data for the conventional case [12], whereas microtechnology throughputs are determined in this work. Additionally, inlet conditions between microreactor stacks and conventional systems are different, and the effect of this is determined in Appendix C.

2.7.1. Definition of Performance Indices

The Volume Index (VI) is defined as the ratio of microreactor and conventional specific powers or throughputs.

$$VI = \frac{Q_{H_2} V^{-1}_{\mu}}{Q_{H_2} V^{-1}_c} \quad (14)$$

Here, subscripts μ and c indicate micro and conventional systems. V is the volume of stacks and Q_{H_2} is the hydrogen power output (in terms of hydrogen combustion energy at 300 K). The volume of the conventional system is calculated from literature [12],

whereas microchannel stack volumes are determined from the scale-out model introduced in this work.

The Efficiency Index (EI) compares the energy efficiency of the stacks to that of conventional technology.

$$EI = \frac{\eta_{\mu}}{\eta_c} \quad (15)$$

Here, efficiency (η) is calculated similar to (13) with the only difference being that η_c includes hydrogen input to the plant furnace. It is important to note that heat recuperation has not been accounted for in the calculation of η_c or η_{μ} .

The Catalyst Weight Index (CWI) compares hydrogen power output per unit supported catalyst weight (M_{cat}) of micro and conventional systems.

$$CWI = \frac{Q_{H_2} M_{cat \mu}^{-1}}{Q_{H_2} M_{cat c}^{-1}} \quad (16)$$

To calculate M_{cat} (sum of support and metal masses) for stacks, properties of supported platinum and rhodium catalysts are specified (Table 2-2). Parameters used in this calculation are comparable to catalysts used in experimental catalytic microcombustors [3, 43].

Finally, the Catalyst Cost Index (CCI) is defined as the ratio of hydrogen power output per unit catalyst metal cost (C_{cat}) and provides an economic comparison of the two processes.

Table 2-2. Input parameters for performance index calculations. Nominal, improved and worse case calculations are performed for a 9CR with $k=100$ W/m-K and a heat loss coefficient of 60 W/m²-K. Combustion channels are indicated by CC.

Input Parameters (Affected Indices)	Case A (Nominal)	Case B (Improved)	Case C (Worse)	Comments
<i>Throughput:</i>				
Inlet velocity (VI, EI, CWI, CCI)	6.1 m/s (CC) 4.0 m/s (SR)	9.15 m/s (CC) 5.7 m/s (SR)	3.05 m/s (CC) 1.4 m/s (SR)	For combustion velocities above 9.15 m/s, low residence time causes reduced methane conversion.
<i>Catalyst metal properties:</i>				
Surface area factors	1.7 (CC) 1.0 (SR)	1.7 (CC)	1.7 (CC)	SAF values relate catalyst and geometric surface areas.
Particle Diameter (CCI)	100 nm (some sintering)	1.0 (SR) 10 nm (fresh catalyst)	1.0 (SR) 1000 nm (high sintering)	Metal particles are assumed to be hemispherical in shape (see Eq. (27))
<i>Support properties:</i>				
Pore diameter	500 nm	50 nm	5000 nm	Pore diameter increases with time on stream as catalysts sinter. The
[Primary diff. mechanism]	[both]	[Knudsen]	[bulk]	diffusion mechanism (bulk or Knudsen) is
Porosity	$\varepsilon = 0.3$	$\varepsilon = 0.3$	$\varepsilon = 0.3$	pore size dependent.
Tortuosity	$\tau = 1.0$	$\tau = 1.0$	$\tau = 1.0$	
Washcoat thickness (CCI, CWI)	100 μ m	10 μ m	100 μ m	

$$CCI = \frac{Q_{H_2} C_{cat}^{-1} \mu}{Q_{H_2} C_{cat}^{-1} c} \quad (17)$$

Details for calculating C_{cat} are given in Appendix C.

2.7.2. Performance Indices as a Function of Scale-out

Figure 2-13 (a-d) illustrates performance indices for nominal flow rates (see Table 2-1) and catalyst properties (see Appendix C). Indices are reported as a

function of stack size for both adiabatic and laboratory ($h = 60 \text{ W/m}^2\text{-K}$) heat loss conditions. All indices are higher under adiabatic conditions due to higher throughput (VI, CWI, and CCI) and efficiency (EI). For small stacks (3CR and 5CR) with laboratory heat loss, no values are reported in Figure 2-13 because these stacks are unstable (see Figure 2-4(c)).

Figure 2-13 (a) shows that in general the throughput per unit volume (VI) of microsystems is about two orders of magnitude greater than that of the conventional process, which is important for portable and distributed processing. The effects of stack size and heat loss are minor relative to the effect of throughput (discussed in 2.7.3). This same conclusion applies for CWI and CCI, which are also proportional to throughput. For EI, however, the effects of stack size and heat loss are important. For example, the efficiency of the 7CR under laboratory conditions is 20% less than that of conventional systems, whereas the 11CR is 10% more efficient (Figure 2-12(b)). For most applications entailing many channels, the energy efficiency will be better than that of conventional systems. Performance indices are discussed in more detail next.

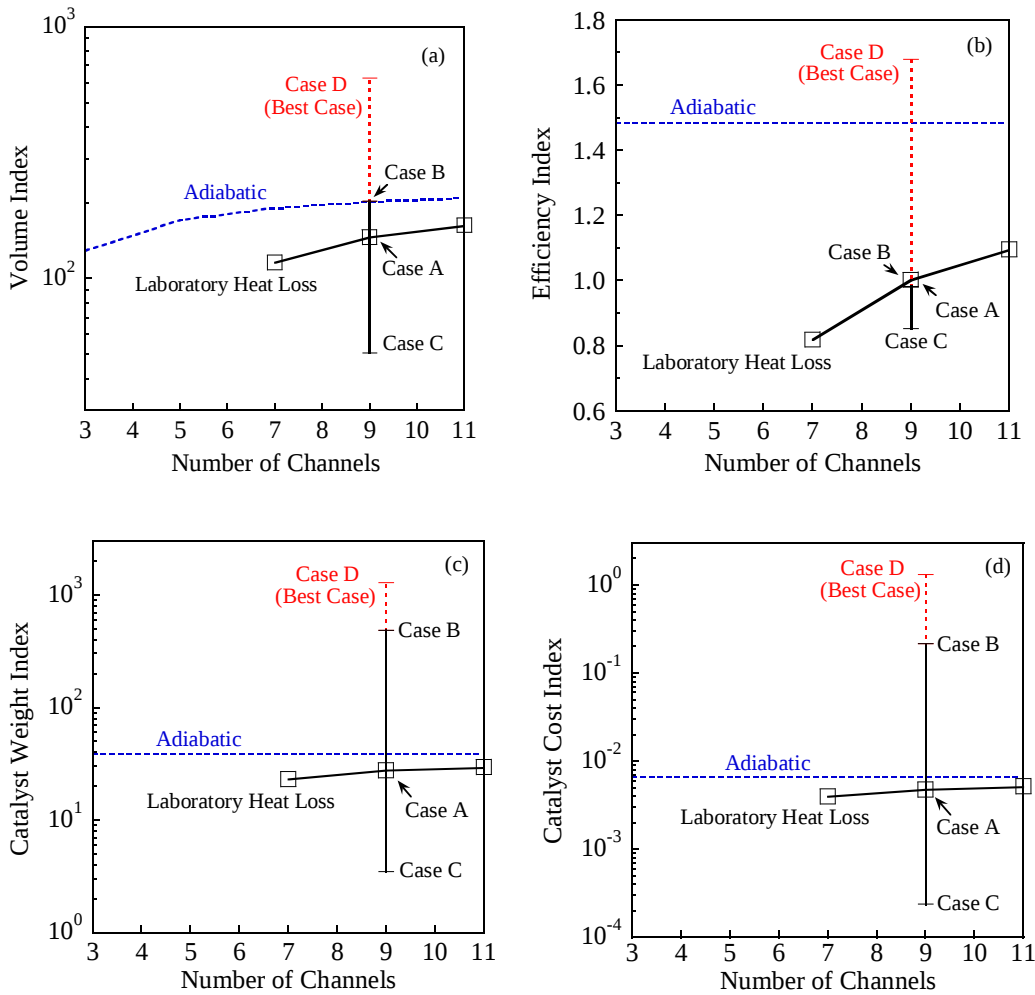


Figure 2-12. Microchannel stacks compared to a conventional reformer using performance indices. Volume Index (a), Efficiency Index (b), Catalyst Weight Index (c), and Catalyst Cost Index (d) vs. size for adiabatic (blue dashed lines) and laboratory (black lines with squares) heat loss conditions. The sensitivity of indices is indicated for two 9CR cases with laboratory heat loss (solid black error bars; cases A-C) and for a best case estimate (red dashed error bars; case D). For adiabatic (dashed, blue line) and laboratory heat loss (black line, square symbols), flow rates and catalyst properties are those of case A. Laboratory heat loss corresponds to a heat loss coefficient of $60 \text{ W/m}^2\text{-K}$. Stack wall thermal conductivity is 100 W/m-K

2.7.3. Uncertainty Analysis

Many stack parameters used in computing performance indices change with time and/or operating conditions. In portable applications, hydrogen power output can range from 0 to 100% of capacity depending on instantaneous demand. In previous work it has been shown that throughput for a single microdevice can vary by an order of magnitude [8]. In addition to throughput, catalyst metal particle size can vary with synthesis and operating conditions. Of particular importance are calcination and operating temperature. In order to determine the effect of variability on performance, a simple uncertainty analysis has been carried out.

Three throughput/catalyst property combinations have been considered for a 9CR (A, B and C in Table 2-2 and Table 2-3). Variability is estimated for laboratory heat loss conditions ($h=60 \text{ W/m}^2\text{-K}$) and high wall thermal conductivity (100 W/m-K). Hydrogen power is controlled by varying combustion and SR flow rates while methane conversion in SR channels is kept constant (59%) for all three cases. Case A (nominal) represents the nominal case presented in the preceding sections of this work (flow rates of Table 2-1, particle diameter of 100 nm and support pore size of 500 nm). For case B (improved performance), hydrogen power output is high, the catalyst is unsintered with low metal particle diameter (10 nm) and a reduced washcoat thickness is used (decreased from 100 to 10 μm). Recently, a method for maintaining low (precious metal alloys) particle size during high temperature processes was proposed [50] so the low diameter used here may be realized under realistic SR conditions. In

case C (worse), hydrogen power output is low and a sintered catalyst (1000 nm, with 5 μm pores) is considered. Catalyst sintering causes a reduction in surface area and increases support pore diameter. Increased pore size changes the diffusion mechanism in effectiveness factor calculations. Previous work using anodized supports reported a pore diameter of ~ 50 nm [3] which means that internal diffusion is in the Knudsen regime [51]. However, for highly sintered catalysts, support pores are larger and the internal diffusion mechanism changes (see Appendix C).

Results for cases A, B and C are illustrated with the (solid black) error bars in Figure 2-12 (a-d). For these three cases, VI and CWI are always greater than one. This means that in terms of power output per unit volume or per weight catalyst, microsystems always outperform conventional systems. In terms of cost (CCI), the conclusion is opposite. Conventional systems are preferable to microreactors ($\text{CCI} < 1$) in terms of power output per unit catalyst cost for all three cases due to the cost of noble metals relative to nickel. Finally, cases A, B and C do not predict a clear winner in terms of efficiency (EI). In case C, the efficiency of conventional systems is higher than that of stacks ($\text{EI} < 1$), whereas in A and B, the efficiency of microsystems is higher ($\text{EI} > 1$). This finding implies that details of calculations, specifically those of the catalyst (size, porous support, loading), are important and upon optimization a higher efficiency may be realized.

Table 2-3. Output parameters used in performance index calculations. Cases A, B and C are determined for a 9CR with a heat loss coefficient (h) of 60 W/m²-K. For case D, an adiabatic 9CR is considered with best case input parameters. Correspondingly, these optima output parameters yield maxima in performance indices (see text for details). Combustion channels are indicated by CC.

Output Parameter (Affected Indices)	Case A (Nominal)	Case B (Improved)	Case C (Worse)	Case D (Best Case) (Indices Independently optimized)	Comments
Methane Conversion in SR Channels	58%	58%	58%	--	Combustion and SR inlet velocities were chosen such that total SR conversion is constant within the 9CR. Conversion varies for theoretical best case.
H ₂ Power (RVI, CWI, CCI)	1470 W	2050 W	510 W	5040 W	H ₂ throughput can vary by an order of magnitude.
Syngas Efficiency (EI)	39%	38%	33%	65%	
Catalyst Support Effectiveness Factor, η_w (CCI, CWI)	0.29 (CC) 0.16 (SR)	0.86 (CC) 0.66 (SR)	0.35 (CC) 0.18 (SR)	0.86 (CC) 0.66 (SR)	Knudsen and bulk diffusion are accounted for (see Appendix C)
Required Weight Loading (CCI)	2.9% Pt 1.8% Rh	1% Pt 0.4% Rh	19.8% Pt 13.2% Rh	0.5% Pt 0.04% Rh	Weight loading is calculated using SAF, support thickness, metal particle diameter and effectiveness factor.

In addition to the three cases discussed above, a fourth case is considered (case D). Figure 2-12 (b) indicates that to increase efficiency, one has to decrease heat loss (and increase stack size if possible). Stack efficiency is also a function of combustion and SR flow rates, and choosing the proper combination to maximize efficiency is nontrivial. Figure A-2(c) shows efficiency as a function of inlet combustion flow rate for the (adiabatic) infinite stack system. For a fixed SR inlet

velocity of 0.9 m/s, efficiency is highest at low inlet combustion velocities (1.525 m/s) due to increased contact time. The resulting maximum efficiency is 65%, which results in an EI value of 1.68 (i.e., stacks are 68% more efficient than the conventional process). This higher efficiency is a result of higher methane conversion (due to higher temperatures) relative to conventional steam reformers.

Next, a maximum VI value is determined by setting the power output (Q_{H2}) to its maximum value (that of the infinite stack, according to Figure A-2(a)) and assuming methane conversion in SR channels is complete (100%). These assumptions result in a throughput 3.4 times the nominal case (A) and twice as high as the improved case (B), as shown in Figure 2-12(a). Combustion and SR flow rates may not increase beyond these high values due to blowout. Theoretically, complete SR conversion can be achieved by increasing catalyst loading (Figure 2-13) or recycling product streams (neither explicitly studied here).

Higher CCI and CWI values occur when throughput is maximized and the amount of catalyst metal is minimized. The minimum catalyst loading is estimated using SAF values and best case catalyst properties (B in Table 2-2). Reduced SAF values are estimated by determining the minimum catalyst loading for Pt (combustion) and Rh (SR) surfaces by independently varying combustion and SR SAFs in infinite stack simulations (adiabatic, with nominal combustion and SR flow rates). Figure 2-13 shows the effect of combustion and SR SAFs on methane conversion. For combustion channels, the minimum SAF (~ 0.85) is the point where combustion fails and stacks do

not function. Figure 2-13 also shows that methane conversion in SR channels decreases nonlinearly with Rh SAF. Even for an order of magnitude reduction in Rh SAF (from 1 to 0.1), methane conversion is still relatively high (>40%) and similar to the nominal case (A). These results for Pt and Rh catalysts suggest that SAF can be reduced by factors of 2 and 10, respectively, with minimal reduction in throughput. Such reductions in SAF can be achieved by keeping catalyst metal particles small. These lower SAF values (0.85 for Pt and 0.1 for Rh) are then used (along with the catalyst properties of Case B and the theoretical maximum power) to calculate values of CWI and CCI (case D). For CWI, this calculation does not change previous conclusions regarding the preference of microtechnology on the basis of catalyst weight. From an economic perspective, microchannel reactors become competitive with conventional systems (i.e., CCI = 1) by simultaneously minimizing the required catalyst loading and maximizing the throughput (Figure 2-13(d)). It should be noted here that in our analysis we do not account for the shorter life-time of the commercial Ni catalyst, compared to Rh, due to coke formation, which disfavors the economics of the industrial process. Finally, our economic estimates consider only the cost of the catalyst, rather than that of the entire process, which should be included in more detailed designs.

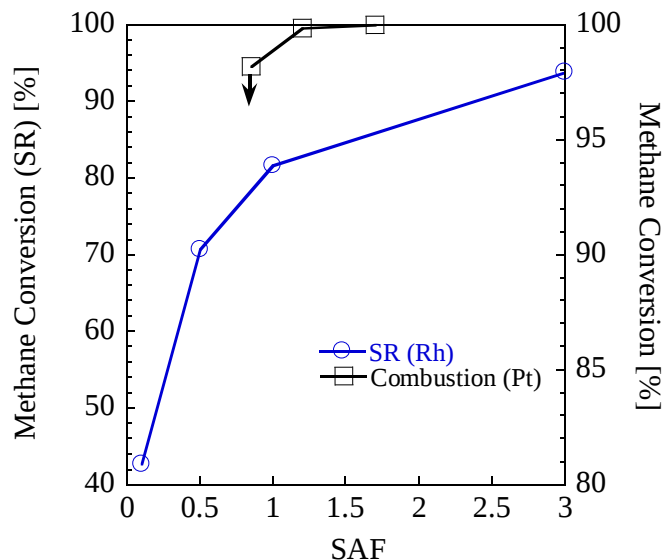


Figure 2-13. Methane conversion in combustion and SR channels as a function of surface area factor (SAF). Calculations for a wall thermal conductivity of 100 W/m-K and nominal inlet flow rates.

In summary, the uncertainty analysis performed here is meant to illustrate the variability of the performance indices due to throughput and catalyst properties. Uncertainty can be significant, and defines the competitiveness of microtechnology in terms of efficiency and catalyst cost. In terms of volumetric and gravimetric throughputs, microtechnology always outperforms conventional technology irrespective of uncertainty.

2.8. Conclusions

In this work, a strategy for scaling out microreactor stacks which couple exothermic and endothermic processes is proposed and evaluated for methane steam

reforming. Stacks have been evaluated for high and mid wall thermal conductivities in terms of efficiency, maximum wall temperature and stability. Smaller stacks have critical heat loss coefficients well below typical laboratory values, indicating that these stacks would not function in the lab. It is found that stacks with moderate wall thermal conductivities (23 W/m-K) are less stable in the presence of heat loss than those with more conductive walls (100 W/m-K) under our operating conditions.

Low temperatures in the outmost combustion channel, due to edge heat loss, cause combustion in this channel to cease. For smaller stacks, significant thermal coupling exists between combustion channels and interior combustion channels cannot power the stack alone and ultimately fail as well. In the case of the 15CR (the largest stack studied here), thermal coupling is weaker, and for sufficiently high heat loss coefficients, the interior channels function despite the failure of the outer combustion channels. For larger stacks, the reaction zone of outer combustion channels expands and partially leaves the stack (blowout). In smaller stacks, the reaction zone in the outer combustion channel is far from the outlet and therefore failure is due to extinction. Performance indices are used to compare stacks to conventional technology for adiabatic and laboratory heat loss conditions. It is found that parallel plate stacks have one to two orders of magnitude higher volume index and catalyst weight index relative to conventional technology. This is essential for portable and distributed processing and is independent of stack size, heat loss, flow rates and catalyst properties. Heat loss is critical in determining efficiency of small stacks. Efficiencies

of small stacks are roughly equal to those of industrial reformers but larger stacks are more efficient. Finally, the cost of nickel (per unit hydrogen production) in the conventional process is in most cases at least one order of magnitude less than that of microreactors with precious metals. However, our uncertainty indicates that with optimization of throughput and catalyst (size, catalyst loading, support), it may be possible for microreactors to be cost-competitive with the conventional process.

Our work indicates that scaling-out microreactor stacks can produce highly nonlinear behavior. Fundamentally, this trend is caused by edge heat losses which affect outer and inner channels differently. Such nonlinearities cannot be captured with a linear scale-out model and point to the complex behavior of microsystems. Understanding nonlinear behavior can help microtechnology increase its commercial foothold.

CHAPTER 3

STABILITY ENHANCEMENT OF MICROREACTOR STACKS

3.1. Introduction

Parallel plate microreactor stacks are an attractive means to intensify exothermic and endothermic process elements by enhancing mass and heat transfer rates over conventional reforming processes, where reaction rates are limited by heat transfer to the catalyst bed [36]. Parallel plate microreactors have been investigated for this purpose experimentally [10, 11, 21] and numerically [8-10, 23, 30, 32]. It is generally believed that results from a small number of channels can be used to linearly scale-out stacks to meet application-scale throughputs [8, 9, 11, 21, 52]. This design principle tacitly ignores finite size effects and heat losses.

In recent work, we have studied the effect of edge heat loss as a function of size for syngas production in small microreactor stacks [53]. Our stacks consist of alternating methane steam reforming (SR) and catalytic combustion (CC) microchannels. It was found that small stacks cannot function under typical laboratory heat loss conditions. Figure 3-1 summarizes previous stability results and shows that small stacks with moderately conductive walls (corresponding to stainless steel) are unstable under laboratory heat loss conditions.

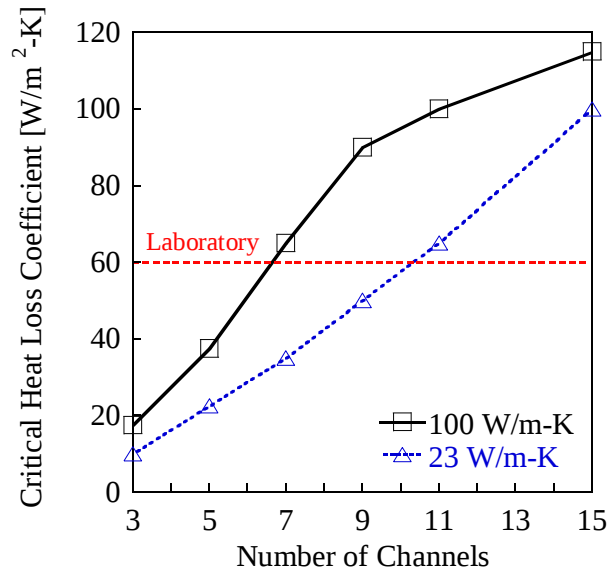


Figure 3-1. Stability as a function of stack size for stacks with highly (100 W/m-K) and moderately (23 W/m-K) conductive walls. Redrawn from [53]. The critical heat loss coefficient is the maximum h where combustion within stacks is sustained.

In order to improve stability, especially of small stacks for low power or throughput applications, several methods are explored that can lead to stability enhancement: (1) increase the net power input, (2) modify dimensions and wall materials, (3) increase catalyst loading, and (4) change combustion fuel in some of the channels. Stability enhancement methods are evaluated using computational fluid dynamics (CFD) simulations of a nine channel reactor (9CR).

3.2. Model

3.2.1. Nine Channel Reactor (9CR)

The parallel plate 9CR consists of alternating SR and CC channels, as shown in Figure 3-2. The 9CR represents a middle ground in terms of stability where high wall thermal conductivity stacks are stable under laboratory heat loss conditions while stacks with moderately conductive walls are not. The 9CR is preferred over smaller stacks because inner and outmost combustion channels can be independently modified (in terms of flow rate, catalyst loading, etc.) to improve stability (in smaller stacks this cannot be done as combustion channels are equidistant from edges and thus respond identically to design changes). Simulations are conducted for a 9CR with highly conductive walls (100 W/m-K), which is characteristic of silicon carbide and low-alloy steels, and moderately conductive walls (23 W/m-K), which represents stainless steel [45]. In this work, SR channels are placed closest to edges in order to insulate combustion channels from heat losses. Different designs can also be considered. Dimensions of the channels and walls are indicated in Figure 3-2 and are the same as in previous work [8, 53]. Inlet flow rates for combustion and steam reforming channels (shown in Table 2-1) are determined from infinite stack simulations and produce high SR throughput while maintaining moderate wall temperatures. Throughput in outmost SR channels (closest to stack edges) is half that of interior SR channels because outmost SR channels are adjacent to one combustion

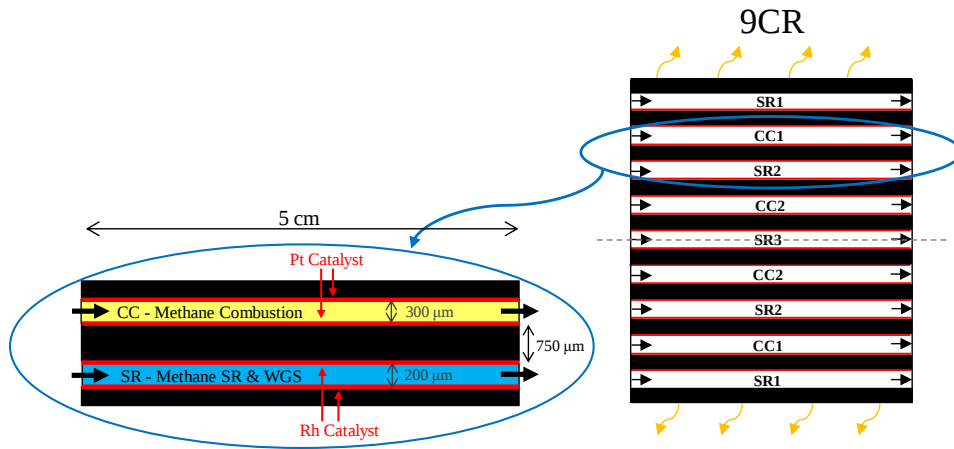


Figure 3-2. Schematic of the 9CR. Red lines indicate catalytic surfaces in steam reforming (SR) and catalytic combustion (CC) channels. The dashed (grey) line represents a symmetry plane.

channel whereas inner SR channels are sandwiched between two (thereby receiving twice as much heat). For inner SR channels (and all combustion channels), both walls are catalytic while for outmost SR channels, only the lower wall (furthest from edge heat loss) is catalytic. Placing catalyst in this manner keeps contact time the same for inner and outmost SR channels and also leads to an acceptable compromise in terms of (increasing) stability and (decreasing) hot spots [53]. Methane-fueled combustion channels operate with an inlet equivalence ratio of 0.92 while SR channels employ an inlet H_2O to CH_4 ratio of 2:1.

3.2.2. Quantifying Stability

The heat lost (Q) through stack edges is given by Newton's law of cooling:

$$Q = h \int_A (T - T_a) dA \quad (18)$$

Here, T and T_a are wall and ambient temperatures, respectively, and h is the external heat loss coefficient. In our model, the latter parameter lumps convective and radiant heat loss from all exterior surfaces. A heat loss coefficient of zero corresponds to an adiabatic stack. The critical heat loss coefficient (h_c) is defined as the maximum possible heat loss coefficient, above which stacks are no longer autothermal. Our previous work has shown that high heat losses cause small stacks to fail because of low temperatures and reduced reaction rates in the combustion channel nearest the stack edge [53]. Single channel microburners (not stacks) fail as a result of either extinction or blowout. The demarcation between these mechanisms depends on operating conditions and device design [48, 49, 54]. Our recent work with methane SR microreactor stacks revealed that the failure mechanism is more complicated and is size-dependent where small stacks fail because of extinction and larger stacks due to blowout under certain conditions [53]. The failure mechanism suggests combustion flow rates (for inner and outmost channels) can be modified to improve stability, as discussed below.

The relative stability improvement is defined as the ratio of critical heat loss coefficient (h_c) of improved over that of the nominal case.

$$\text{Relative Stability Improvement} = \frac{h_c(\text{improved})}{h_c(\text{nominal})} \quad (19)$$

The nominal h_c values for the 9CR are $90 \text{ W/m}^2\text{-K}$ and $50 \text{ W/m}^2\text{-K}$ for highly and moderately conductive walls, respectively (Figure 3-1). In our previous work, the 9CR was found to be bistable, i.e., it is either ignited with all combustion channels operating at high temperature ($>1000 \text{ K}$) and conversion ($>50\%$) or extinguished with all channels thermally equilibrated with the ambient (zero methane conversion). Partially ignited stacks, where inner combustion channels are ignited and outmost ones are extinguished, were observed only for larger stacks (i.e., ≥ 15 channels). In the simulations of this work, the 9CR is found to be bistable, except for the case of combusting hydrogen (rather than methane) in outmost combustion channels. Because hydrogen is a more reactive fuel than methane, the outmost combustion channels (powered by hydrogen) function while the inner ones (powered by methane) may not. Such partially ignited stacks are (energy) inefficient, and thus, the critical heat loss coefficient is defined as the maximum value where all combustion channels function with high conversion ($>50\%$).

3.2.3. Computational Fluid Dynamics (CFD) Model

Stacks are simulated using FLUENT® CFD software [38]. To model catalytic surface reactions, published single step rate expressions, derived from microkinetic models for methane combustion on Pt (Pt) [40] and methane SR and water-gas shift (WGS) on rhodium (Rh) [39], are used. For hydrogen combustion on

Pt, a reduced rate expression is derived in this work (Appendix D) from a previously published microkinetic model [55].

3.3. Stability Enhancement

3.3.1. Effect of Inlet Power

Stability enhancement options are summarized in Table 3-1. Due to lower temperatures in the outmost channels, an increase in the net power input over that utilized for reforming may stabilize the system. This can be achieved by increasing combustion channel flow rates (cases A, B and C in Table 3-1), decreasing the SR flow rate (case D) or elevating inlet temperatures (cases E and F). Increasing combustion channel flow rates may reduce thermal efficiency because a larger fraction of the fuel is burned (rather than reformed). Increasing inlet temperature accounts implicitly for the effect of heat recirculation. Both approaches can selectively increase power to one or more channels. This is advantageous because previous work indicates that low temperatures in outmost combustion channels cause stack failure [53]. To perform a fair comparison, the net power input to the stack (Q_{in}) is increased by the same amount for all six cases.

$$Q_{in} = Q_p + Q_c - Q_{sr} \quad (20)$$

Here, Q_p represents the inlet energy flow in the form of reactant preheating (relative to 300 K), Q_c is the power content of combustion feeds, and Q_{sr} is the power required to

Table 3-1. Summary of stability improvement options (inlet power). Inlet power parameters (P) are reported for both high and mid wall thermal conductivity stacks (k_{high} / k_{mid}). The change in inlet power (Q_{in}) is kept constant in all cases (for a given wall thermal conductivity). Channel labels (CC1 and CC2) are indicated in Figure 3-2.

Inlet Parameter (P)	Case	Nominal Case	Improved Stability	Change in Inlet Power
		$P(k_{\text{high}})/P(k_{\text{mid}})$	$P(k_{\text{high}})/P(k_{\text{mid}})$	$P(k_{\text{high}})/P(k_{\text{mid}})$
Combustion inlet velocity [m/s]				
<i>Increase flow in:</i>				
CC1	A	6.1 / 3.05	7.63 / 3.75	262 / 120
CC2	B	6.1 / 3.05	7.63 / 3.75	262 / 120
CC1/2 (split flow increase)	C	6.1 / 3.05	6.87 / 3.4	262 / 120
SR inlet velocity [m/s]				
SR1/2/3 (split flow decrease)	D	4.0 / 2.3	2.3 / 1.5	262 / 120
Inlet Temperature [K]				
<i>Increase for CC1</i>	E	300 / 300	855 / 800 ^a	262 / 120
<i>Increase for all channels</i>	F	400 / 400 ^b	535 / 510 ^a	262 / 120

^aIn the case of reactant preheating, inlet velocity is increased to keep inlet molar flux constant.
^bNominal inlet temperatures are 300 K and 400 K for combustion and SR channels, respectively.

reform all of the SR feed (absolute value). Q_{in} is increased by 18% (for both high and moderate wall conductivity stacks).

Figure 3-3 shows the relative stability improvement for increased net inlet power (cases A-F, outlined in Table 3-1). For a given increase in net power input (Q_{in}), stability is improved more through reactant preheating (cases E and F) rather than by increasing combustion flow rates (cases A, B and C). Stability is moderately improved by reducing flow rates in SR channels (case D). The critical heat loss coefficient

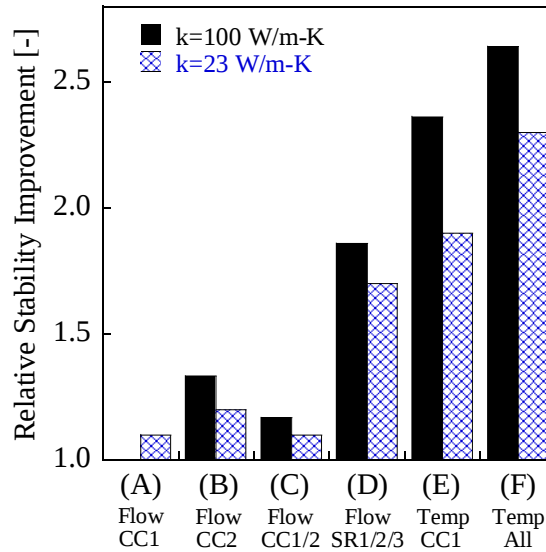


Figure 3-3. Relative stability improvement due increased net power input. Modified parameters and affected channels are indicated for ease of interpretation (for detailed descriptions see Table 3-1).

approximately doubles when the inlet temperature is increased for only the outmost combustion channels (case E) or when the same amount of preheat is distributed among all 9CR channels (case F). Increasing combustion flow rates (cases A, B and C) improves stability less because 60% of the additional methane is used to heat the increased combustion gases at the inlet (principally nitrogen). On the other hand, when preheating the inlet gases, the sensible heating requirement is reduced.

The best option among cases A-C is to increase the flow to the inner combustion channels (Figure 3-3(B)). This is counterintuitive since one would expect that increasing net power input to the outmost (less stable) channels would elevate temperatures locally and therefore improve stability. Yet, in outmost combustion

channels the reaction zone is closer to the outlet, and thus, increasing the flow of these channels results in blowout, which in turn causes failure of the stack. Conversely, the reaction zone for inner channels is localized near the inlet and therefore blowout is not a factor; as a result, an increased flow rate results in enhanced stability.

3.3.2. Effect of Stack Design

In cases H-K, we modify stack design (Table 3-2). Results are shown in Figure 3-4. Thermal transport can be influenced by modifying gap sizes and reducing wall thermal conductivity. The gap size of the outmost channels (SR1) is increased (from 0.2 mm to 1.0 mm) (case H) to limit heat transfer from the interior of the stack to edges. Additionally, the gap size of SR2 can be reduced to improve heat transfer between outmost (less stable) and inner (more stable) combustion channels. Finally, the thermal conductivity of the outmost wall may be reduced to limit heat transfer between the stack and the environment, thereby increasing temperatures and stabilizing combustion. Previous work on heat recirculating combustion microburners indicates that reducing the thermal conductivity of outmost walls has little effect on stability when inner walls are moderately or highly conductive [48]. However, these simulations were performed without SR channels using different gap sizes and wall thicknesses. Therefore, it is not clear if previous findings hold for multifunctional microreactors. To investigate the effect of having more insulating outmost walls, the outmost wall conductivity is reduced to 3 W/m-K while keeping inner walls highly

Table 3-2. Summary of stability improvement options (stack design and fuel type). Channel labels (CC1, SR1 etc.) are shown in Figure 3-2.

Parameter	Case	Nominal Case	Improved Stability	Potential Issues with Implementation
Outmost wall thermal conductivity [W/m-K]	G	100 or 23	3	Low conductivity materials such as glass are fragile
Gap size [μm]				
SR1	H	200	1000	Reduces conversion
SR2	I	200	50	
Combustion catalyst surface area factor [-]				
CC1: Bottom wall	J	1.7	8.5	Increases catalyst loading and cost
CC1: Bottom and top walls	K	1.7	8.5	
Changing combustible in outmost channels only [-]				
CC1: Low flow	L	Methane	Hydrogen	Reduction in system efficiency and formation of hot spots
CC1: High flow	M	Methane	Hydrogen	

(100 W/m-K) or moderately (23 W/m-K) conductive (case G). Quartz and silicates are examples of low conductivity materials.

Reducing the thermal conductivity of the outmost wall is found to have a negligible influence on stability (Figure 3-4G). This finding is consistent with previous work on heat recirculating microburners [48]. Increasing the outmost channel (SR1) gap size, however, moderately increases the critical heat loss coefficient (Figure 3-4H). Simple thermal resistance calculations indicate that decreasing the outer wall conductivity to 3 W/m-K (case G) increases the thermal resistance between the stack

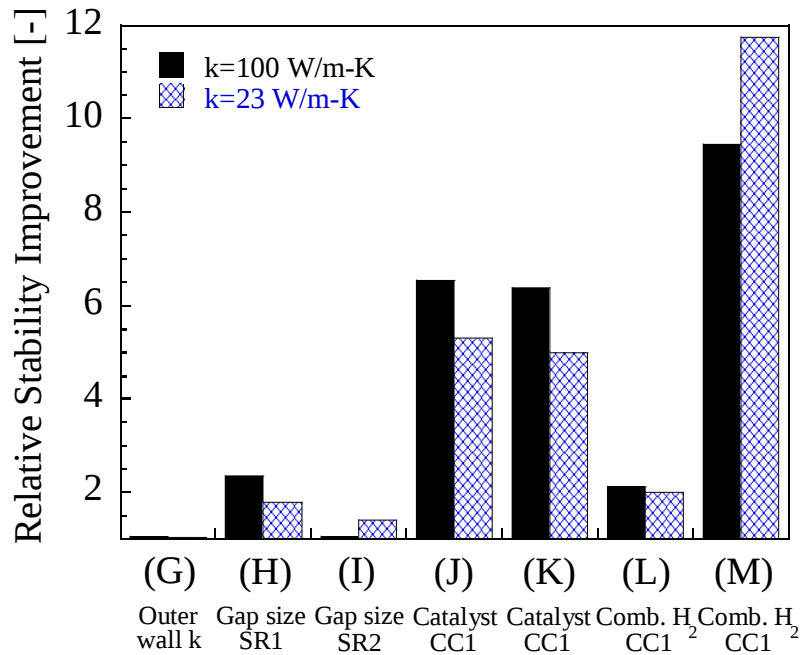


Figure 3-4. Relative stability improvement due to change of stack design (cases F-J) or fuel type (cases K and L). For a detailed description of F-L, see Table 3-2.

interior and the edge by 25%; in contrast, increasing SR1 gap size (case H) increases the thermal resistance by 500%. This calculation explains why increased SR1 gap size improves stability much more than reduced thermal conductivity. In case I, reduction of the SR2 gap size only slightly improves stability which indicates that thermal coupling of channels can play only a limited role in stability enhancement.

3.3.3. Effect of Catalyst Loading (in Outmost Channels)

As mentioned previously, low temperatures in the outmost combustion channels reduce reaction rates and ultimately cause stack failure. At low temperatures,

combustion becomes kinetically controlled and the amount of catalyst is important. Under kinetic limitations, reaction rates scale linearly with catalyst surface area. Computationally, catalyst loading is varied through the surface area factor (SAF), which is the ratio of the available catalyst surface area to the geometric surface area of the catalytic wall. It effectively lumps any diffusion limitations within the support and the number of surface sites available for reaction. In order to study the effect of increased catalyst, SAF is increased from 1.7 (nominal) to 8.5. The nominal SAF (1.7) is typical of experimental catalytic microburners [41], but higher values (~100) are possible when no sintering or internal diffusion limitations are present [43].

Increasing catalyst loading results in a marked improvement in stability relative to changing wall material (case G) or channel dimensions (cases H and I). Figure 3-4 shows that increasing catalyst at only the bottom wall (case J) or both bottom and top walls (case K) results in nearly identical stability improvement. The bottom wall is farther from edges, and therefore is at a higher temperature and more active than the top catalytic surface [53]. While increasing catalyst loading improves stability, this option can lead to increased cost, especially for precious metal-based materials considered in this work.

3.3.4. Effect of Combustion Fuel (in Outmost Channels)

Another method for improving stability is to burn a more reactive fuel, such as hydrogen or syngas, rather than methane in the outmost combustion channels

(cases L and M in Table 3-2). In fuel cell applications, hydrogen is available from the anode off-gas. In this work, a H_2 /air mixture with equivalence ratio of 0.4 is used to reduce the likelihood of hot spot formation. While such fuel-lean hydrogen combustion is better for wall and catalyst material integrity, operating at low equivalence ratios reduces the efficiency of stacks (the combustion stream has excess air). Despite these downsides, combusting hydrogen in the outmost channels is an attractive option because this reaction occurs at much lower temperatures (relative to catalytic methane combustion) and hydrogen can be burned down to the leanest compositions [56, 57]. Hydrogen is so much more reactive, that at high heat loss coefficients when all methane combustion channels have failed, the hydrogen combustion channels still operate with >99% conversion (Figure 3-5).

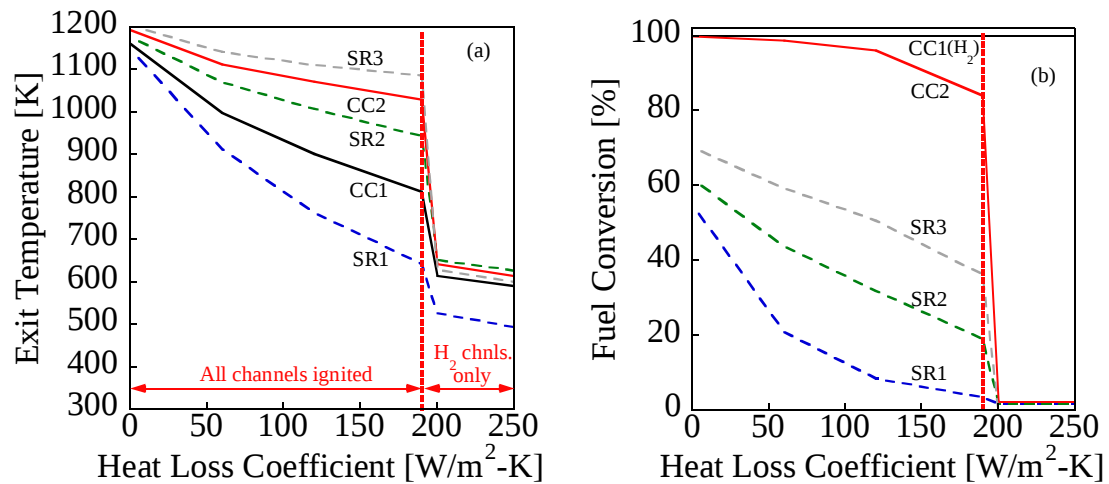


Figure 3-5. Temperature (a) and fuel conversion (b) versus heat loss coefficient for the 9CR with hydrogen combustion in outmost channels (case L). Methane combustion and SR channels extinguish at a critical heat loss coefficient (190 $\text{W/m}^2\text{-K}$, indicated by dotted vertical line) while outmost channels (CC1) powered with hydrogen remain ignited.

For the purposes of this work, hydrogen combustion on Pt is simulated using a reduced rate expression for an oxygen covered Pt surface (derived in Appendix A). CFD simulations show that for an equivalence ratio of 0.4, the hydrogen mole fraction directly above the catalyst surface is low and that the surface is oxygen covered (Appendix D, Figure D-2). Two inlet flow rates are considered for combusting hydrogen in the outmost channels: low flow ($v=12.4$ m/s for stacks with highly conductive walls), where the inlet enthalpy is the same as that of the nominal methane combustion channels, and fast flow ($v=32$ m/s for stacks with highly conductive walls) where the net power input is substantially higher than the nominal combustion flow rate. Figure 3-4 shows the relative stability for low (case L) and high (case M)

hydrogen flow rates. Both cases enhance stability, but the high flow case has a more profound effect (3 times as great) because stack temperatures are higher. With high hydrogen flow (case M), stability is improved due to using a more reactive fuel and increasing net power input. Use of hydrogen prevents blowout and allows the outmost combustion channels to operate with higher flow rates relative to the inner channels, which are fueled with methane.

3.4. Effect of Stability Enhancement on Performance

The best approaches to improving stability entail increasing catalyst loading (cases J and K) and combusting hydrogen rather than methane in the outmost channels (cases L and M). If only a slight improvement in stability is needed or significant design modification is undesired (such as increasing catalyst or changing the fuel type), reactant preheating (cases E and F) is an attractive option.

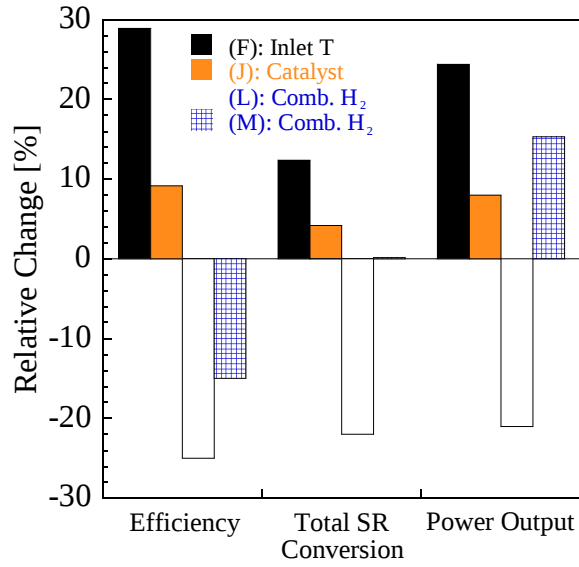


Figure 3-6. Relative changes in efficiency, methane conversion (SR channels) and hydrogen power output for select approaches (F, J, L and M in Table 3-1 and Table 3-2). The heat loss coefficient is 60 W/m²-K. Percent change is reported relative to the nominal case. Nominal values: efficiency-39%, SR conversion-58%, power output-147 W/cm stack width.

Figure 3-6 shows the effect of four stability improvement options (cases F, J, L, and M) on efficiency (η), conversion (X) and power output (Q_{out}), which are defined in (21), (22) and (23).

$$\eta = \frac{F_{H_2} LHV_{H_2} + F_{CO} LHV_{CO} \text{ }_{out}}{F_{CH_4} LHV_{CH_4} \text{ }_{in}} \quad (21)$$

$$X = \frac{F_{CH_4} \text{ }_{in} - F_{CH_4} \text{ }_{out}}{F_{CH_4} \text{ }_{in}} \times 100\% \quad (22)$$

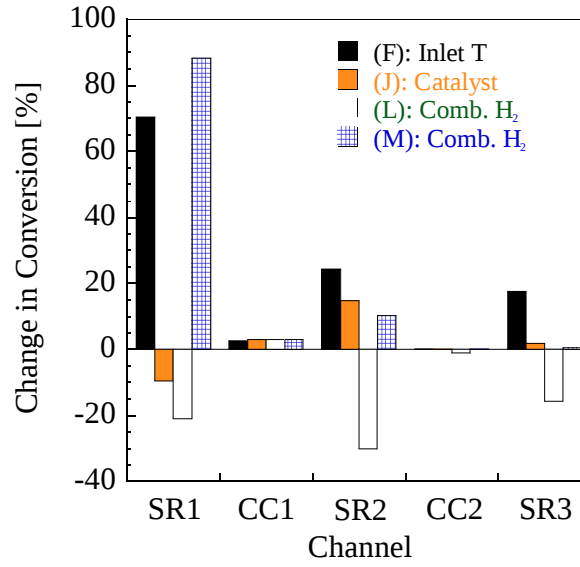


Figure 3-7. Change in methane conversion (relative to the nominal case) for specific channels of the 9CR for four stability improvement cases (F, J, L and M in Table 3-1 and Table 3-2) with $h=60 \text{ W/m}^2\text{-K}$.

$$Q_{out} = F_{H_2} LHV_{H_2 \text{ out}} \quad (23)$$

In Eqs. (21)-(23), F_i is the total molar flow rate (sum of all channels) of species i and LHV_i is the lower heating value. These metrics are discussed in more detail elsewhere [53].

Performance is evaluated at a typical laboratory heat loss coefficient ($60 \text{ W/m}^2\text{-K}$) [53]. Increased preheating (case F) increases overall stack efficiency and throughput because temperatures in both inner and outer channels are higher (Figure 3-8), which results in increased methane conversion in SR channels (Figure 3-7F). Figure 3-6J shows that increasing catalyst loading (case J) also improves stack

performance, but to a lesser degree relative to reactant preheating (case F) because overall stack temperatures (Figure 3-8) and SR conversions are lower (Figure 3-7J). Figure 3-8 shows that increasing catalyst loading increases axial thermal gradients as the temperatures are higher near the inlet (relative to the nominal profile in Figure 3-8). This phenomenon stabilizes combustion near the inlet of the outmost combustion channel and therefore increases the critical heat loss coefficient substantially. However, it should be noted that large temperature gradients can cause catalyst and wall materials to breakdown. This localized high temperature region has little effect on stack performance as temperatures in inner channels are unchanged (Figure 3-8b). Finally, combusting hydrogen in outmost channels results in reduced efficiency for high flow rates (case M) and in decreased efficiency and throughput for low flow rates (case L). Stack temperatures are reduced for the low hydrogen flow (case L) relative to the nominal case (Figure 3-8a and b) because the flux of unreacted gases (N_2 and O_2) into the outmost combustion channel is higher. At high hydrogen flow rates, greater enthalpy input results in higher temperatures and greater throughput. In summary, performance is improved only when temperatures are increased in combustion and SR channels, which only occurs when the net power input is increased (cases F and M).

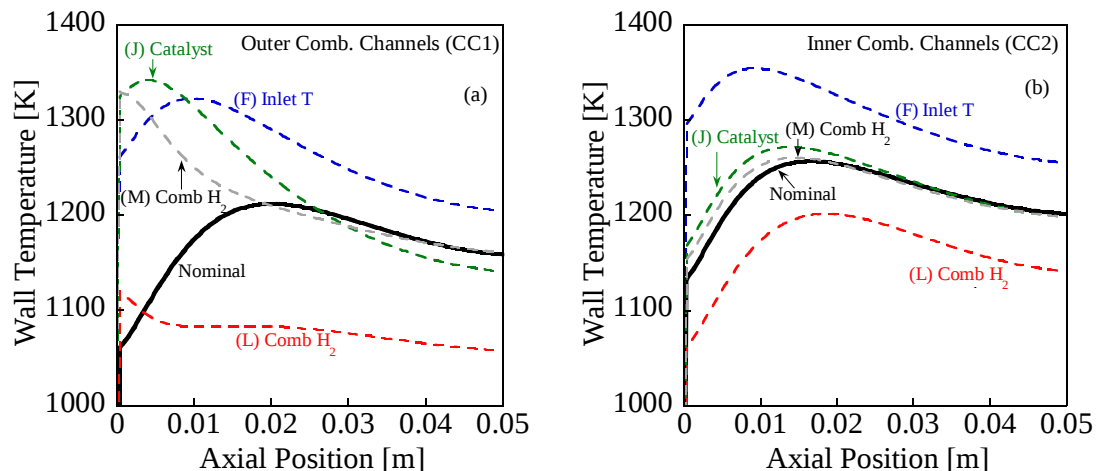


Figure 3-8. Temperature as a function of axial position for outer (a) and inner (b) combustion channels of the 9CR. Temperatures are measured at the lower catalytic wall (furthest from edge heat loss). The wall thermal conductivity is 100 W/m-K and the heat loss coefficient is 60 W/m²-K. Short labels are provided in the legend for cases F, J, L and M; for detailed descriptions see Table 3-1 and Table 3-2.

3.5. Conclusions

Several approaches for improving the stability of small microreactor stacks converting natural gas to syngas have been examined and evaluated in terms of stability, efficiency, and throughput. The best approaches to improving stability entail the increase of catalyst loading or combusting a more reactive fuel, such as hydrogen (studied herein) or syngas (not explicitly studied herein), both in the outmost channels only. Increased catalyst loading has a minor effect on efficiency and throughput, whereas increased inlet temperatures (via heat recirculation) significantly increase

efficiency and throughput. Finally, combusting hydrogen in the outmost channels improves stability the most, albeit at the expense of efficiency.

CHAPTER 4

CONCLUSIONS

4.1. Summary

Microreactors are an attractive option to intensify conventional steam reformers and can be an important component in the next generation of portable and distributed energy systems. Different from previous approaches, microreactor stacks which account for edge heat losses were simulated in this work. The inclusion of edge effects allowed for scale-out and stability to be studied.

In Chapter 2, the performance of microreactor stacks was examined as a function of size. Stability was found to be a problem for smaller stacks, especially those constructed of stainless steel. Stack failure was found to be a result of low temperatures and low conversion in only the outer combustion channels. The performance of stacks in terms of efficiency, volume, catalyst weight and catalyst cost was benchmarked against a conventional steam reformer. It was found that even with reduced throughputs and less desirable catalyst properties, microreactors outperform conventional technology in terms of power output per unit volume and catalyst weight. From an efficiency standpoint, stacks were found to be preferable to the conventional process except for small stacks and low throughputs. Finally, it was found that the catalyst cost for microreactors is always higher than that of the conventional system,

except in the case of large adiabatic stacks with optimal catalyst properties and maximum throughput.

Chapter 3 focused on enhancing the stability of stacks to external heat losses. Using the stack failure mechanisms determined in Chapter 2, several stability improvement methods were examined. The best methods for improving stability were found to be increasing catalyst loading and combusting a more stable fuel (relative to methane) in the outer channels. While these two options are attractive from a stability standpoint, increasing the amount of catalyst is expensive and combusting a more reactive fuel reduces efficiency.

4.2. Future Work and Outlook

Future work with microreactor stacks should involve experimental validation, new model development and extension of the scale-out study to other processes. Thermal gradients within stacks reduce performance and radial temperature measurements in experimental microreactors could validate this finding. Also, similar to the CFD work presented here, stacks of different stack sizes could be fabricated to experimentally determine the effect of edges. A separate but equally important endeavor is to simulate large stacks (i.e., 100s or 1000s of channels) in order to understand the dynamics of commercial-scale microreactors. Two-dimensional CFD is computationally expensive and is not a realistic option for such large stacks. Therefore, a simplified stack model which is less computationally expensive is required. One option is to reduce the dimensionality of the governing transport equations by approximating transverse heat and mass transfer terms using transport coefficients, as done in previous work for single channel [41] and infinite stack reactors [8]. Finally,

the effect of edge heat loss should be examined for low temperature microchannel processes, such as methanol reforming. Integrated systems with methanol reformers and fuel cells have been considered as a replacement for conventional batteries [58]. Similar to methane SR, previous modeling work on microchannel methanol reformers has centered on the infinite stack geometry [34], and therefore the effect of edge heat loss and size on performance has not been determined.

APPENDIX A

INFINITE STACK REACTOR

The starting point of this work is the infinite stack reactor (shown in Figure A-1) which has been studied for coupling exothermic and endothermic systems both by our group [8, 31, 59] and others [22, 52]. The infinite stack reactor is comprised of two half-channels (bordered above and below by symmetry planes) separated by a single wall, all of which are infinitely far away from stack edges and thus unaffected by external heat losses. Gap sizes, wall thicknesses and inlet compositions are the same as in the main paper.

Figure A-2 shows H_2 power output (a) and maximum wall temperature (b) as a function of inlet combustion velocity along three operating lines: (i) the materials stability limit, (ii) the breakthrough point, and (iii) the maximum power output. These three operating points were introduced in previous work [8, 59] and are determined for each combustion channel inlet velocity by incrementally increasing the SR flow rate from low values. The materials stability limit occurs at low SR flow rates, where much more heat is produced via combustion than is consumed in SR processes resulting in high temperatures (1500 K for this work). Breakthrough is defined as the operating point where 99% methane conversion is achieved in the SR channel and it occurs at a moderate SR channel flow rate. Upon increasing the SR inlet velocity further, H_2 yield increases due to high throughput leading to a maximum power output value. Any further increase in SR flow rate causes a decrease in H_2 power output as low temperatures hinder reforming reactions.

Figure A-2(a) indicates that by changing only inlet velocities, the H_2 power output (defined in (24)) can range from 100 W up to 1000 W with only one SR and one CC channel.

$$H_2 \text{ Power Output} = F_{H_2} LHV_{H_2 \text{ out}} \quad (24)$$

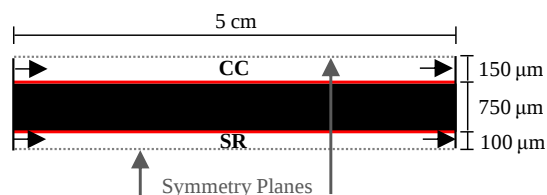


Figure A-1. Schematic of the infinite stack reactor. Red lines indicate catalytic surfaces. Dimensions for catalytic combustion (CC) and steam reforming (SR) channels are in terms of half-gap sizes and symmetry planes are indicated by gray dotted lines.

Despite the low SR conversions observed at maximum power (Figure A-2(d)), one advantage of this operating line is that maximum wall temperatures are significantly lower (Figure A-2(b)) allowing for greater operational flexibility. At the materials stability limit, a larger fraction of the inlet combustion energy is wasted in the form of hot products. This can be contrasted with the maximum power limit, where energy is underutilized because low temperatures reduce reaction rates and cause incomplete conversions within SR channels. In terms of efficiency, it is preferred to operate near the breakthrough line (Figure A-2(c)) as it represents a compromise between high SR conversions and high throughput.

The principal link between the infinite stack reactor and the scale-out study of this work is that the infinite stack reactor provides a computationally efficient means to determine CC and SR channel flow rates that can be used in simulations of larger stacks. For a wall thermal conductivity of 100 W/m-K, the CC inlet velocity was chosen to be 6.1 m/s (Figure A-2(e)). An acceptable operating point is found for a SR inlet velocity of 4.0 m/s where this pair of flow rates lies between the breakthrough and maximum power cases as indicated by the (green) “x” in Figure A-2(a)-(e). This point represents the combination of CC and SR flow rates with reasonable methane conversion and maximum wall temperature (used in the proposed scale-out model). A similar analysis was done to determine CC and SR flow rates in stacks with a wall thermal conductivity of 23 W/m-K (not shown).

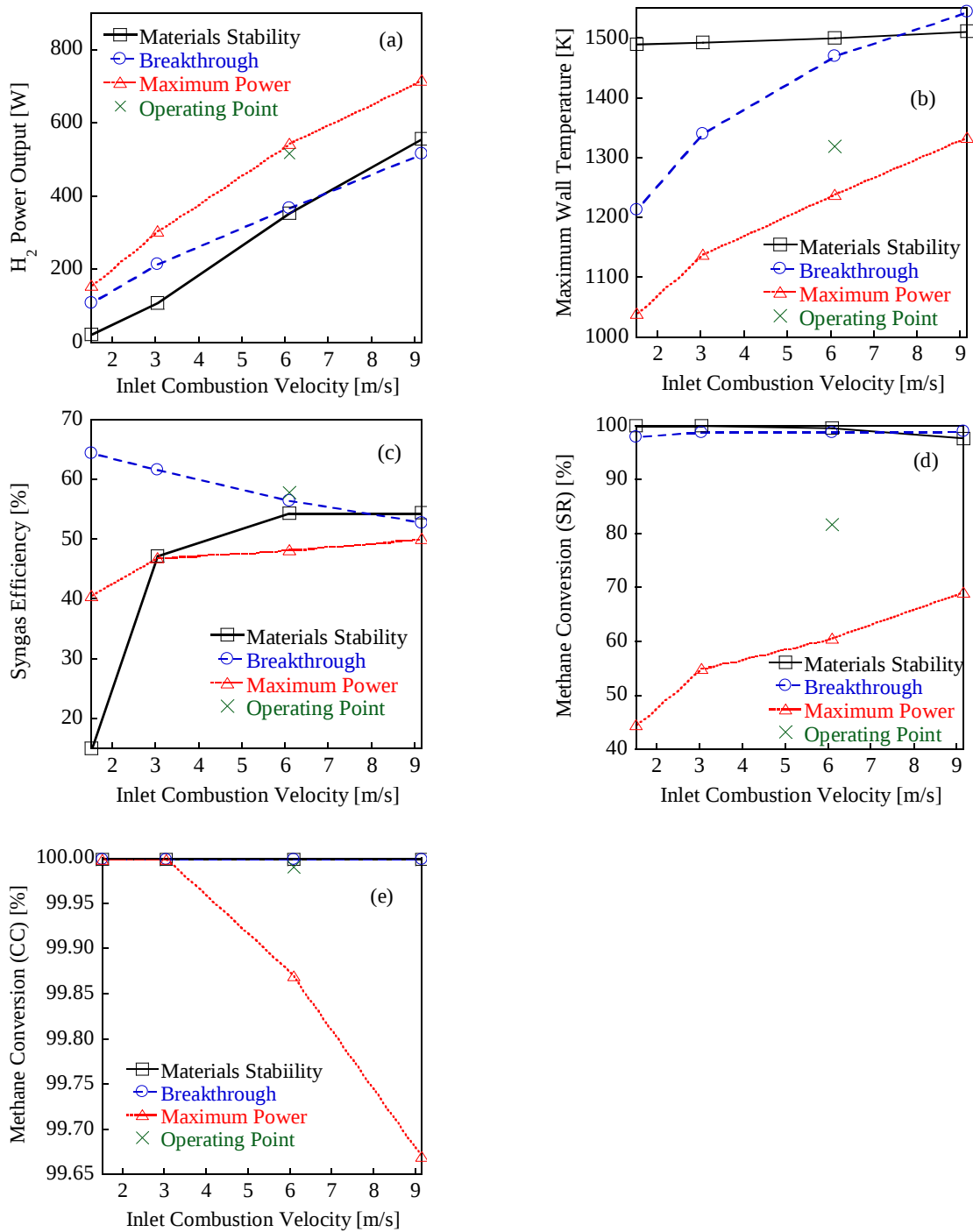


Figure A-2. Performance of the infinite stack model (adiabatic). Performance is evaluated in terms of (a) H₂ power output, (b) maximum wall temperature, (c) syngas efficiency, (d) SR methane conversion and (e) CC methane conversion at three operating lines: materials stability limit (solid line, squares), breakthrough (dashed line, circles) and maximum H₂ power output (dotted lines, triangles). All calculations are for a wall thermal conductivity of 100 W/m-K. Power outputs are based on a 10 cm stack width.

APPENDIX B

TWO CHANNEL REACTOR

The two channel reactor (2CR), shown in Figure B-1, is the smallest stack that can be fabricated using the parallel plate design. The 2CR consists of 1 SR channel, 1 CC channel and 3 walls and unlike the infinite stack reactor, it does not employ symmetry planes. External heat losses are included in the 2CR, as indicated by curved (orange) arrows in Figure B-1. The major design issue to the 2CR is how the catalyst should be placed in the CC and SR channels. Solid (red) lines at wall faces indicate surfaces which are catalytic in all simulations, while the dotted red lines represent surfaces which are catalytic only in some simulations.

The catalyst surface area within the 2CR is related to the geometric surface area through the surface area factor (SAF, defined in Chapter 2, eq. (7)). In order to examine the effect of catalyst placement, the total SAF within a single channel (both wall faces) is kept constant at 3.4 and 2.0 (twice the value of stated estimates) for CC and SR channels, respectively. The SAF is then varied between the top and bottom walls for both CC and SR channels.

The effect of catalyst placement is determined by simultaneously changing the catalyst fraction on the bottom and top walls while keeping the total catalyst

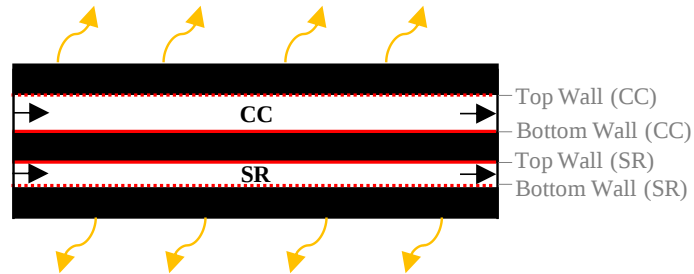


Figure B-1. Schematic of the two channel reactor (2CR). Solid red lines at faces indicate surfaces are catalytic in all simulations, while dotted red lines represent surfaces which are catalytic in only select cases. External heat losses are indicated by orange arrows. Gap sizes and wall thicknesses are the same as those in the infinite stack reactor (Appendix A).

surface area factor fixed. In order to examine only the effect of catalyst placement within the CC, the catalyst in the SR channel is placed entirely (SAF=2.0) at the top wall of the SR channel while the combustion catalyst placement is varied. In the first simulation, the combustion catalyst is put entirely at the bottom wall. This produces a highly isothermal system, as illustrated in Figure B-2(b), with a low critical heat loss coefficient (Figure B-2(a), circles). One reason for the low critical heat loss coefficient is that the 2CR has a high surface area to volume (A/V) ratio (767 m^{-1}) relative to conventional reactors (40 m^{-1}) [35].

As catalyst is gradually removed from the bottom wall and placed on the top wall, an initial reduction in the critical heat loss coefficient and maximum wall temperature is observed (Figure B-2(a)) as reaction rates at the bottom wall are

delocalized. This decrease in stability is observed down to 75% catalyst at the bottom wall, where the minimum critical heat loss coefficient is observed. As catalyst is further removed from the bottom wall, the trend reverses, and the critical heat loss coefficient reaches a maximum when the catalyst is equally split between the surfaces (50%). Figure B-2(a) and (b) indicate that the increase in stability corresponds to hot spot formation in the combustion channel. The important conclusion of this work is that catalytic combustion surfaces not balanced by reforming surfaces (at the opposite wall face) cause hot spot formation that in turn leads to a higher critical heat loss coefficient. Despite this increase in stability, it is more important to prevent hot spot formation (and ensure the reactor operated in a safe manner) and therefore, catalytic combustion surfaces should be balanced by reforming surfaces. The minimum in Figure B-2(a) indicates the nonlinear behavior of this system and that a rigorous optimization of catalyst placement may be desirable for commercial units.

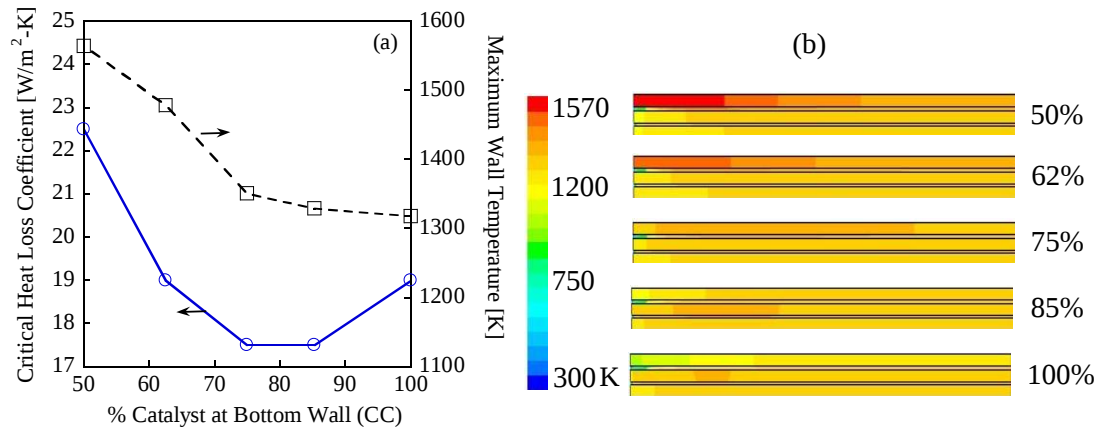


Figure B-2. Stability and maximum wall temperature (a) and thermal profiles (b) of the two channel reactor ($k=100$ W/m-K) as a function of combustion channel catalyst placement. Temperature contours for an adiabatic 2CR are shown in (b) for various catalyst fractions at the bottom wall of the combustion channel (to the right of contours).

Two simulations are run to determine how the SR channel catalyst should be placed. In the first case, the Rh catalyst is put entirely at the top wall. In the second configuration, the catalyst is split evenly between the top and bottom wall of the SR channel. In both cases the SAF in the SR channel is kept constant at 2.0. Simulations are conducted for an adiabatic 2CR with a wall thermal conductivity of 100 W/m-K. It is found that splitting the catalyst between the walls produces a slightly lower exit methane conversion (0.5% lower). Also, temperatures of the middle wall are slightly higher (20 K higher) as less SR reaction proceeds at the top wall (wall face adjacent to combustion catalyst). Therefore, it is concluded that the steam reforming catalyst should be placed only on SR channel wall faces adjacent to catalytic combustion surfaces so that conversion is maximized and wall temperatures are minimized. Unlike

the combustion channel, these improvements due to catalyst placement are rather minor.

APPENDIX C

PERFORMANCE INDICES SUPPLEMENTAL

C.1. Difference in Inlet Streams

While combustion feed streams are similar for conventional and micro technologies, inlet conditions in SR elements are different for the industrial reformer considered here. Our stacks operate with a lower inlet $\text{H}_2\text{O}:\text{CH}_4$ ratio (2 versus 3.4), inlet temperature (400 K versus 793 K) and system pressure (1 atm versus 25 atm). Stack simulations indicate that the conventional inlet $\text{H}_2\text{O}:\text{CH}_4$ and temperature result in a minor change in hydrogen production rate (a 24% increase) indicating that these differences may not significantly change our conclusions. The effect of system pressure is not determined in this work, but at 1200 K (typical stack exit temperature), equilibrium methane conversion shows a decrease from 99% at 1 atm to 84% at 25 atm (plant pressure). The difference in methane conversion between atmospheric and high pressure cases is more substantial at lower temperatures, but because we operate stacks at higher temperatures, the effect of elevated pressure on equilibrium conversion is less significant.

C.2. Catalyst Cost Calculations

In the denominator of CCI, the cost for the conventional process is calculated using catalyst structure and composition information published by Xu and Froment [13]. Catalyst cost (C_{cat}) is related to the precious metal price (P_m), the precious metal weight fraction (Y_m) and the total mass of the supported catalyst (support (M_s) plus metal (M_m)). Precious metal and nickel prices are the average value for July 2009 [60, 61].

$$C_{cat} = P_m Y_m (M_s + M_m) \quad (25)$$

Metal weight loading (Y_m) is defined as:

$$Y_m = \frac{M_m}{M_m + M_s} \quad (26)$$

Here, M_s is the mass of the catalyst support and M_m is the mass of the catalyst metal. For stacks, metal content is calculated assuming Pt and rhodium nanoparticles are hemispherical in shape. Catalyst metal mass is related to simulation kinetics by the surface area factor (SAF) and can be calculated given a washcoat effectiveness factor (η_w) and metal particle diameter (D_p). Particle size is a strong function of time on stream and operating conditions. Particle diameters for supported precious metal catalysts can range for nanometers (fresh catalysts) to micrometers (heavily sintered catalysts) [62]. The nominal particle radius is taken to be 100 nm, but the effect of particle size on CCI is determined in the uncertainty analysis section of this work.

$$M_m = \frac{1}{\eta_w} N_p M_p = \frac{1}{\eta_w} \left(\frac{2(\text{SAF})LW}{\pi D_p^2} \right) \left(\rho_m \frac{1}{12} \pi D_p^3 \right) \quad (27)$$

Here, N_p is the number of nanoparticles and is the ratio total catalyst surface area to the surface area of a single particle. M_p is the mass of a single catalyst particle ($\rho_m 1/12 \pi D_p^3$) and SAF is the surface area factor used in simulations. L and W refer to the length (5 cm) and width (10 cm) of catalytic walls, respectively.

The catalyst support properties used in catalyst cost calculations are those of supported Pt/Al₂O₃ employed in catalytic combustion microsystems. Supported catalysts are prepared by anodizing a 100 μm thick aluminum foil to form a semi-ordered pore network. SEM micrographs indicate the porosity (ϵ) of the supported catalyst is ~ 0.3 and pores are straight and the tortuosity factor (τ) is unity [3, 43]. Using this information, the effective diffusivity within the porous catalyst bed (D_{eA}) is calculated using the dusty gas model, which accounts for bulk (D_A) and Knudsen (D_{Kn}) diffusivities [63].

$$D_{eA} = \frac{\epsilon}{\tau} \left(\frac{1}{D_A} + \frac{1}{D_{Kn}} \right)^{-1} \quad (28)$$

At atmospheric pressure and temperatures typical of SR processes (1200 K), Knudsen diffusion dominates for smaller pore sizes (50-500 nm) typical of unsintered experimental catalysts [43]. In larger pores ($\sim 1 \mu\text{m}$), bulk diffusion is prevalent and Knudsen diffusivity may be neglected. For simplicity, we assume the bulk diffusivity (D_A) to be that of nitrogen. Using D_{eA} and the catalyst washcoat thickness (H_c ,

nominally 100 μm), the Thiele modulus (ϕ) and effectiveness factor (η_w) are determined.

$$\phi_{\text{irreversible}} = H_c \sqrt{\frac{k_e}{D_{eA}}} \quad (29)$$

$$\phi_{\text{reversible}} = H_c \sqrt{\frac{k_e}{D_{eA}} \left(\frac{1 + K_{\text{eqm}}}{K_{\text{eqm}}} \right)} \quad (30)$$

$$\eta_w = \frac{\tanh \phi}{\phi} \quad (31)$$

The Thiele modulus is shown for first-order irreversible (29) and reversible (30) reactions [51]. These expressions do not account for volume change (present in SR reactions), but previous work indicates that for the inlet composition used here and SR stoichiometry, the effectiveness factor would not significantly change (<15%) [64]. The kinetics employed in this work is not simple first-order. The rate expressions are negative order with respect to certain co-reactants and products for combustion (4) and SR (5) reactions. This complexity is addressed in our calculations by using an effective rate constant (k_e) which lumps kinetic parameters in the numerator and denominator of the Langmuir-type rate expressions introduced in the modeling section of the work. Combustion or SR effective rate constants are calculated for Pt and Rh catalysts and for simplicity the catalyst temperature is taken to be 1200 K. This catalyst temperature is reasonable for methane SR processes, and operating at a higher temperature (1300 K) was found to have a relatively small effect (~20%) on effectiveness factors for both combustion and SR supported catalysts. Additionally, the effectiveness factor is a

function of gas-phase composition for both Pt and rhodium supported catalysts. To account for this, η_w is averaged over a range of methane conversions (5%-95%) for combustion and SR reactions. The average η_w is then used in (27). Effectiveness factors (for the conditions studied here) was found to be a weak function of methane conversion and varied only 25% over a range of conversions considered.

APPENDIX D

DERIVATION OF A REDUCED MODEL FOR HYDROGEN COMBUSTION ON PT

In order to carry out CFD simulations, it is preferred to have an accurate, one-step rate expression for hydrogen combustion. A recently published, thermodynamically consistent microkinetic model for water-gas shift on Pt contains the required reactions and species for hydrogen oxidation [55]. This mechanism is comprised of 46 irreversible elementary reactions with 10 gas-phase and 8 surface species. For hydrogen combustion, reactions involving carbon can be removed, thereby resulting in a mechanism of 18 reactions, with 6 gas-phase species, and 4 surface species.

Prior to developing a reduced rate expression, the dynamics of hydrogen combustion in air over Pt is examined using the microkinetic model in an isothermal plug-flow reactor (PFR). Simulations show that, prior to ignition, the dominant surface species changes with gas-phase composition. At higher equivalent ratios (Φ), hydrogen is the most abundant reaction intermediate (MARI), whereas at low Φ , atomic oxygen covers the surface. In the post-reaction zone for fuel-lean combustion, the platinum surface is O-covered as the gas-phase contains only O_2 , N_2 and H_2O . H- and O-

covered surfaces were reported in previous work [65-67]. The transition from one regime to the next occurs at $\Phi \sim 0.1$ ($x_{H_2} \sim 0.04$) and is nearly independent of temperature (Figure D-1). For Φ higher than 0.1, hydrogen covers the surface and the reaction is limited by oxygen adsorption (not studied here). In the oxygen covered regime ($\Phi < 0.1$), oxygen blocks surface sites and the overall reaction is controlled by hydrogen adsorption. Previous work by Bui et al. found that this transition occurs at $x_{H_2} = 0.003$, but their model had fewer reactions, coverage independent activation energies and unoptimized sticking coefficients and pre-exponentials [66]. The most important difference between the model used here and the model of Bui et al. is the sticking coefficient for hydrogen (s_{H_2}), where Bui et al. used a value of 1.0 while we employ $s_{H_2} = 0.129$. The high value employed by Bui et al. causes H to dominate the surface down to lower H_2 mole fractions. No experimental data is available to tune parameters to predict the transition accurately.

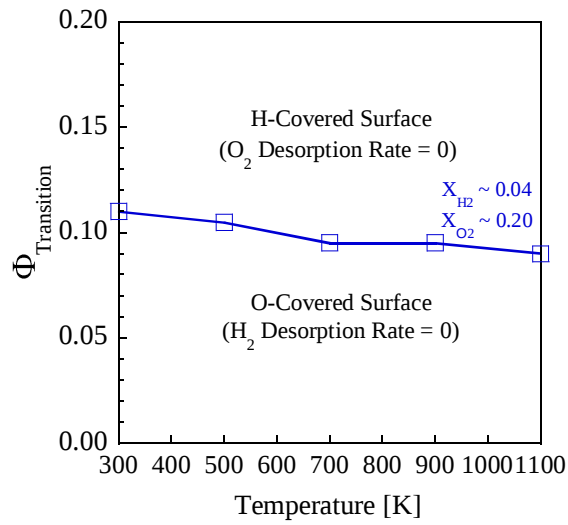


Figure D-1. O and H-covered regimes for hydrogen combustion on Pt. The transition equivalence ratio ($\Phi_{\text{Transition}}$) separates oxygen and hydrogen covered surfaces. Appropriate assumptions for O and H surfaces are indicated in parentheses.

CFD simulations indicate that under fuel-lean inlet conditions, the hydrogen mole fraction directly above the catalytic surfaces is low (<0.04) and therefore, only kinetics for O-covered Pt is relevant. The low hydrogen mole fraction at the catalytic surface is due to the fast kinetics of hydrogen combustion on Pt, and this finding is consistent with previous work by Mantzaras and co-workers [68]. In the combustion zone, hydrogen rapidly adsorbs on the surface and then reacts with surface oxygen. Figure D-2a and b show the surface hydrogen mole fraction and the temperature, respectively, from CFD simulations of hydrogen combustion in microchannels (using the rate expression developed in this work). For three flow rates

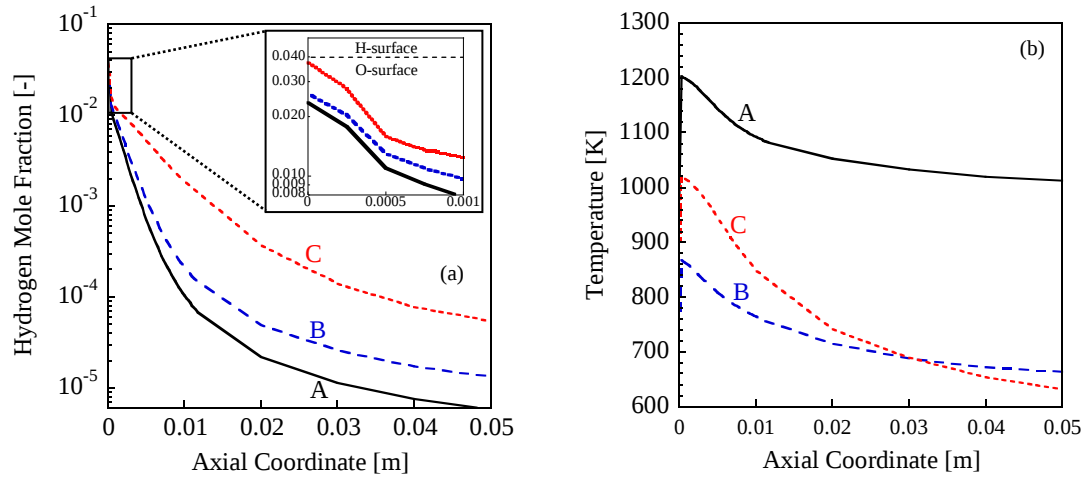


Figure D-2. Hydrogen mole fraction (a) and temperature (b) profiles directly above the Pt surface determined by CFD modeling of microchannels. Simulations are performed using reduced kinetics derived in this work: (A) low flow ($v=12.4$ m/s) and low heat loss ($h=60$ W/m²-K); (B) low flow ($v=12.4$ m/s) and critical heat loss ($h=250$ W/m²-K); and (C) high flow ($v=32$ m/s) and critical heat loss ($h=750$ W/m²-K).

(all with $\Phi=0.40$) and heat loss coefficients (indicated in Figure D-2), the maximum surface hydrogen mole fraction (which occurs at the inlet) is always less than 0.04.

A single step rate expression is derived from the full microkinetic model using rate of production information. This method has been used previously to obtain single step expressions from microkinetic models [39, 66, 69, 70]. A reduced rate expression for hydrogen combustion on Pt was published by Bui et al., but this reduction was based on a different microkinetic model (as discussed above). The model used in this work allows for more accurate predictions.

The mechanism is now reduced using published methodology. Using the reactions in Table D-1, steady state balances for θ_O , θ_H , θ_{OH} , and θ_{H_2O} are written as:

$$\frac{d\theta_O}{dt} = 2r_3 - 2r_4 + r_5 - r_6 - r_9 + r_{10} + r_{17} - r_{18} = 0 \quad (32)$$

$$\frac{d\theta_H}{dt} = 2r_1 - 2r_2 + r_5 - r_6 + r_7 - r_8 + r_{15} - r_{16} = 0 \quad (33)$$

$$\frac{d\theta_{OH}}{dt} = r_5 - r_6 + r_7 - r_8 + 2r_9 - 2r_{10} + r_{11} - r_{12} = 0 \quad (34)$$

$$\frac{d\theta_{H_2O}}{dt} = -r_7 + r_8 - r_9 + r_{10} + r_{13} - r_{14} = 0 \quad (35)$$

The terms r_2 , r_5 , r_7 , r_9 - r_{13} , and r_{15} - r_{18} are neglected because they always contribute less than 5% of the rate of formation or consumption of all surface species (Figure D-3).

Using simplifications based on rate of production, Eqs.(32), (33) and (34) are rewritten as:

$$\frac{d\theta_O}{dt} = 2r_3 - 2r_4 - r_6 = 2k_3c_{O_2}\theta_{vac}^2 - 2k_4\theta_O^2 - k_6\theta_O\theta_H = 0 \quad (36)$$

$$\frac{d\theta_H}{dt} = 2r_1 - r_6 - r_8 = 2k_1c_{H_2}\theta_{vac}^2 - k_6\theta_O\theta_H - k_8\theta_{OH}\theta_H = 0 \quad (37)$$

$$\frac{d\theta_{OH}}{dt} = r_6 - r_8 = k_6\theta_O\theta_H - k_8\theta_{OH}\theta_H = 0 \quad (38)$$

Because the surface is O-covered, θ_{vac} may be defined in terms of only θ_O .

$$\theta_{vac} = 1 - \theta_O \quad (39)$$

Using Eqs. (37), (38) and (39), expressions for θ_H and θ_{OH} in terms of only θ_O are determined:

$$\theta_H = \frac{k_1c_{H_2}(1-\theta_O)^2}{k_6\theta_O} \quad (40)$$

Table D-1. Microkinetic model for hydrogen combustion on Pt [55].

No.	Reaction	Sticking coefficient [-] or pre-exponential [s ⁻¹]	Temperature exponent β	Activation Energy [kcal/mol]
R ₁	H ₂ +2* → 2H*	0.129	0.858	0.0
R ₂	2H* → H ₂ +2*	7.95e12	-0.001	19.8 - 6 θ_H + f(T)
R ₃	O ₂ +2* → 2O*	0.054	0.766	0.0
R ₄	2O* → O ₂ +2*	8.41e12	-0.796	50.9-32 θ_O + f(T)
R ₅	OH* → H*+O*	1.95e12	1.872	27.1 + f(θ_O , θ_H , θ_{H_2O} , T)
R ₆	H*+O* → OH*	6.33e12	0.624	8.8 + f(θ_O , θ_H , θ_{H_2O} , T)
R ₇	H ₂ O* → H*+OH*	9.36e12	-0.118	17.8 + f(θ_O , θ_H , θ_{OH} , θ_{H_2O} , T)
R ₈	H*+OH* → H ₂ O*	9.99e12	-1.049	13.5 + f(θ_O , θ_H , θ_{OH} , θ_{H_2O} , T)
R ₉	H ₂ O*+O* → 2OH*	4.32e9	0.082	8.8 + f(θ_O , θ_H , θ_{OH} , θ_{H_2O} , T)
R ₁₀	2OH* → H ₂ O*+O*	1.7e9	0.325	22.7 + f(θ_O , θ_{OH} , θ_{H_2O} , T)
R ₁₁	OH+* → OH*	0.999	2.000	0.0
R ₁₂	OH* → OH+*	1.44e14	2.000	63.0 - 33 θ_O + 25 θ_H + f(T)
R ₁₃	H ₂ O+* → H ₂ O*	0.108	1.162	0.0
R ₁₄	H ₂ O* → H ₂ O+*	2.03e12	1.372	10.0 - 2.5 θ_{H_2O} + 25 θ_{OH} + f(T)
R ₁₅	H+* → H*	0.384	1.832	0.0
R ₁₆	H* → H+*	4.37e13	1.890	62.0 - 3 θ_H + f(T)
R ₁₇	O+* → O*	0.049	0.250	0.0
R ₁₈	O* → O+*	1.44e13	-0.250	85.0 - 16 θ_O + f(T)

Reaction rate constants are calculated using the modified Arrhenius expression,

$$k = \frac{A}{\sigma^{n-1}} \left(\frac{T}{T_0} \right)^\beta e^{-E_a/RT} \text{ or } k = \frac{s}{\sigma^n} \sqrt{\frac{RT}{2\pi M}} \left(\frac{T}{T_0} \right)^\beta e^{-E_a/RT}$$

where A is the preexponential, s is the sticking coefficient, σ is the site density, n is the reaction order, β is the temperature exponent, E_a is the activation energy, R is the ideal gas constant and T is the absolute temperature.

$$\theta_{OH} = \frac{k_6 \theta_O}{k_8} \quad (41)$$

The oxygen balance (36) is then used to solve for θ_O explicitly using the quadratic formula.

$$\theta_O = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (42)$$

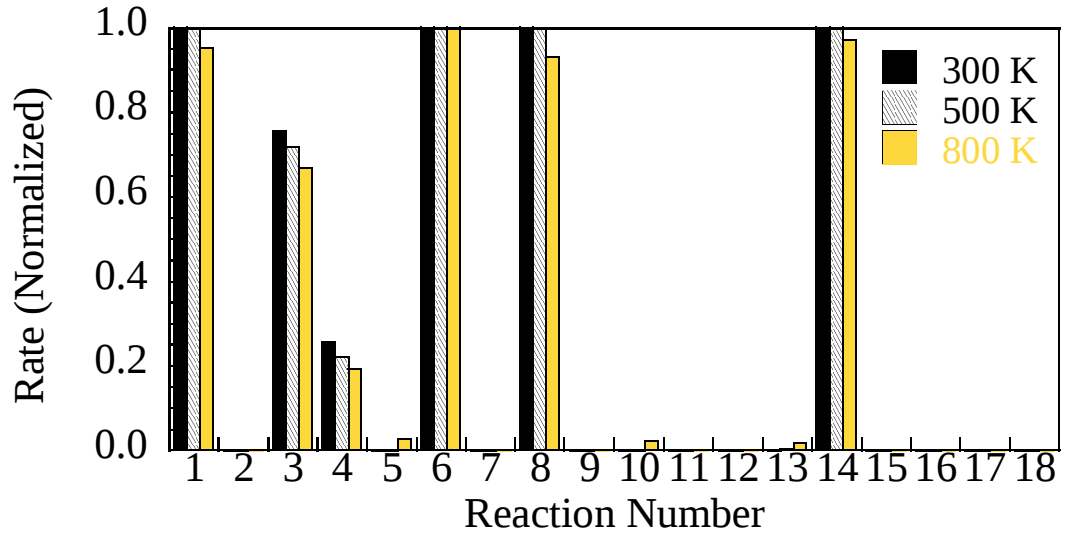


Figure D-3. Rates of production for reactions of the full microkinetic model at three temperatures. All rates are normalized by the largest value in each dataset. Data is taken for an equivalence ratio of 0.07 and low hydrogen conversion (<10%). Numbers refer to the reactions in Table D-1.

Here, only the negative root results in physical coverage values. Parameters a, b and c can be calculated using only rate constants and mol fractions.

$$a = 2k_3c_{O_2} - 2k_4 - k_1c_{H_2} \quad (43)$$

$$b = -4k_3c_{O_2} + 2k_1c_{H_2} \quad (44)$$

$$c = 2k_3c_{O_2} - k_1c_{H_2} \quad (45)$$

Now that relevant surface coverages can be calculated for the oxygen covered surface, a global rate expression can be derived. Since hydrogen desorption does not occur to a significant extent (Figure D-3), we can assume that all adsorbed hydrogen oxidizes to

Table D-2. Rate constants for the reduced rate expression (47). Parameters are calculated from the full microkinetic model (Table D-1) and are listed below for convenience. A good approximation is $\theta_O=0.6$, although in this work we use coverage balances to solve for this parameter.

Rate Constant	Expression	Units
k_1	$2.48 T^{1.358}$	cm/s
k_3	$0.4424 T^{1.2656}$	cm/s
k_4	$1.962 \times 10^6 T^{-0.796} e^{-49.9 - 32\theta_O / RT}$	mol/cm ² -s

form water. Therefore, the global rate of hydrogen consumption can be written in terms of hydrogen adsorption as:

$$\sigma_{comb}^{H_2} = k_1 c_{H_2} (1 - \theta_O)^2 \quad (46)$$

The final single step rate expression in terms of only rate constants and gas-phase concentrations is written as:

$$\sigma_{comb}^{H_2} = k_1 c_{H_2} \left(1 - \frac{4k_3 c_{O_2} - 2k_1 c_{H_2} - \sqrt{-4k_3 c_{O_2} + 2k_1 c_{H_2}^2 - 4k_3 c_{O_2} - 2k_4 - k_1 c_{H_2}}}{4k_3 c_{O_2} - 4k_4 - 2k_1 c_{H_2}} \right)^2 \quad (47)$$

Equation (47) constitutes a computationally efficient means to calculate the rate of hydrogen consumption on an oxygen covered Pt surface. Relevant rate constants are listed in Table D-2. Figure D-4 shows that the reduced expression accurately predicts full model results.

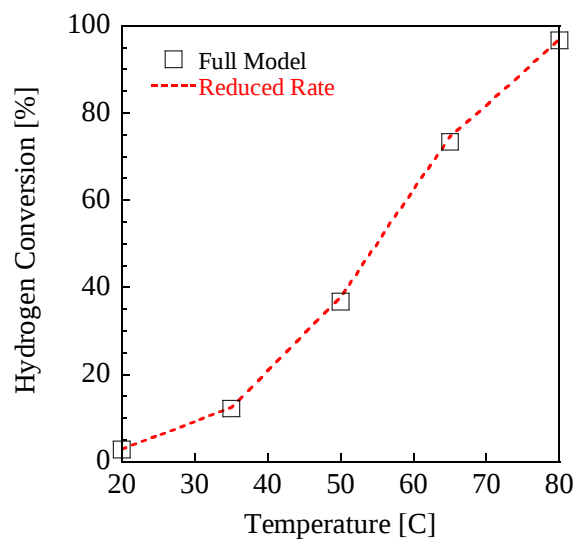


Figure D-4. Evaluation of reduced rate expression for hydrogen combustion on an O-covered Pt surface. Inlet composition is $x_{H_2}=0.025$, $x_{O_2}=0.15$ with balance N_2 . PFR parameters: $L=1$ cm, $area/volume=1600$ cm^{-1} and $v=83$ cm/s.

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