COMBUSTION SYSTEMS FOR POWER-MEMS APPLICATIONS

by

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Abstract

As part of an effort to develop a micro-scale gas turbine engine for power generation and micropropulsion applications, this thesis presents the design, fabrication, experimental testing, and modeling of the combustion system. Two fundamentally different combustion systems are presented; an advanced homogenous gas-phase microcombustor and a heterogeneous catalytic microcombustor.

An advanced gas-phase microcombustor consisting of a primary and dilution-zone configuration is discussed and compared to a single-zone combustor arrangement. The device was micromachined from silicon using Deep Reactive Ion Etching (DRIE) and aligned fusion wafer bonding. The maximum power density achieved in the 191 mm³ device approached 1400 MW/m³ with hydrogen-air mixtures. Exit gas temperatures in excess of 1600 K and efficiencies over 90% were attained. For the same equivalence ratio and overall efficiency, the dual-zone microcombustor reached power densities nearly double that of the single zone configuration. With more practical hydrocarbon fuels such as propane and ethylene, the device performed poorly due to significantly longer reaction time-scales and inadequate fuel-air mixing achieving maximum power densities of only 150 MW/m³. Unlike large-scale combustors, the performance of the gas-phase microcombustors was more severely limited by heat transfer and chemical kinetics constraints. Using all available gas-phase microcombustor data, an empirically-based design tool was developed, important design trades identified, and recommendations for future designs presented.

Surface catalysis was identified as a possible means of obtaining higher power densities with storable hydrocarbon fuels by increasing reaction rates. Microcombustors with a similar geometry to the gas-phase devices were fitted with platinum coated foam materials of various porosity and surface area. For near stoichiometric propane-air mixtures, exit gas temperatures approaching 1100 K were achieved at mass flow rates in excess of 0.35 g/s. This corresponds to a power density of approximately 1200 MW/m³; an 8.5-fold increase over the maximum power density achieved for gas-phase propane-air combustion. Low order models including simple time-scale analyses and a one-dimensional steady-state plug flow reactor model, were developed to elucidate the underlying physics and to identify important design parameters. High power density catalytic microcombustors were found to be limited by the diffusion of fuel species to the active surface, while substrate porosity and surface area-to-volume ratio were the dominant design variables. Experiments and modeling suggest that with adequate thermal management, power densities in excess of 1500 MW/m³ and efficiencies over 90% are possible within the microengine pressure loss constraint and the material limits of the catalyst. A materials characterization study of the catalyst and its substrate revealed that metal diffusion and catalyst agglomeration were likely failure modes.

Thesis Supervisor: Professor Ian A. Waitz
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Nomenclature

Roman

\( A \) Arrhenius pre-exponential factor or area, \((m^2)\)
\( a \) Arrhenius exponent or speed of sound, \((m/s)\)
\( a_v \) surface area-to-volume ratio
\( b \) Arrhenius exponent or thin film thickness
\( Bi \) Biot number for heat transfer
\( c \) concentration
\( C_b \) molar density, \((mol/m^3)\)
\( C_p \) constant pressure specific heat, \((J/kgK)\)
\( C_v \) constant volume specific heat, \((J/kgK)\)
\( D \) diffusion coefficient, \((cm^2/s)\)
\( Da_h \) homogeneous Damköhler number
\( Da_2 \) diffusion-based Damköhler number
\( d \) diameter, \((m)\)
\( d_h \) hydraulic diameter, \((m)\)
\( E \) total energy
\( E_a \) activation energy
\( F \) molar flow rate
\( h \) convective heat transfer coefficient, \((W/m^2 K)\) or enthalpy
\( j_D \) j-factor for mass transport
\( j_H \) j-factor for heat transfer
\( K \) quasi-steady sensitivity to heat release
\( k \) thermal conductivity, \((W/m K)\), rate constant, or wave number
\( k_m \) mass transport coefficient, \((m/s)\)
\( L \) length scale, \((m)\)
\( l \) length scale, \((m)\)
\( LHV \) lower heating value
\( M \) Mach number or molecular weight
\( m \) mass, (kg)
\( \dot{m} \) mass flow rate, (kg/s)
\( n \) outward facing normal
\( Nu \) Nusselt number
\( P \) static pressure, (N/m\(^2\))
\( Pe \) Peclet number
\( Pr \) Prandtl number
\( Q \) heat, (W)
\( \dot{Q} \) heat flux, (W/m\(^2\))
\( R \) gas constant, (J/kgK) or reaction rate
\( Re \) Reynolds number
\( Sc \) Schmidt number
\( S_f \) shape factor
\( St \) Stanton number or Strouhal number
\( Sh \) Sherwood number
\( T \) temperature, (K)
\( t \) time, (s)
\( u \) velocity vector, (m/s)
\( UHC \) unburned hydrocarbons
\( V \) volume
\( v \) velocity, (m/s) or diffusion volume
\( w \) thickness, (m)
\( x \) location, (m)
\( Y \) mole fraction
\( z \) axial location (m)

**Greek**

\( \alpha \) porosity or flame correction coefficient
\( \beta \) temperature exponent in Arrhenius rate constant or transmission matrix
\( \Gamma \) circulation
\( \gamma \)  
- ratio of specific heats, \( C_p/C_v \)

\( \lambda \)  
- wave length, (m)

\( \phi \)  
- equivalence ratio

\( \eta \)  
- efficiency

\( \mu \)  
- viscosity, (Ns/m\(^2\))

\( \pi \)  
- pressure ratio

\( \rho \)  
- density, (kg/m\(^3\))

\( \tau \)  
- characteristic time, (s) or temperature ratio

\( \omega \)  
- vorticity or frequency, (Hz)

**Subscripts**

- \( a \)  
  - air
- \( ad \)  
  - adiabatic
- \( ave \)  
  - average
- \( b \)  
  - bulk flow
- \( c \)  
  - combustor or cross-section
- \( chem \)  
  - chemical
- \( comp \)  
  - compressor
- \( CV \)  
  - control volume
- \( eq \)  
  - equivalent
- \( f \)  
  - fuel
- \( INJ \)  
  - injectors
- \( NGV \)  
  - nozzle guide vane
- \( qs \)  
  - quasi-steady
- \( res \)  
  - residence
- \( s \)  
  - surface
- \( t \)  
  - total or stagnation quantities
- \( therm \)  
  - thermal
- \( TOT \)  
  - total
- \( turb \)  
  - turbine
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Chapter 1

Introduction

1.1 The Power-MEMS Concept

Advances in micromachining of silicon for integrated circuit technology applications spawned the field of Micro-ElectroMechanical Systems (MEMS) more than twenty years ago. Today the research and development of micro sensors and actuators, biological-MEMS, microfluidics, optical-MEMS, and power-MEMS is well established and growing. It is the last of these that is the subject of this thesis.

Power-MEMS consists of utilizing microfabrication techniques to develop compact power sources. These power sources can be generators for electrical power, engines for thrust power, or pumps for fluid handling. This includes the miniaturization of conventional power sources such as gas turbines, internal combustion engines, and rockets as well as the development of less common systems, which may perform better at the micro-scale such as thermoelectric generators and thermo-photovoltaics (TPVs). Figure 1.1 shows some of these large-scale power systems and their corresponding MEMS equivalent.

Figure 1.1 Conventional power systems and corresponding micro-scale power systems.
1.1.1 Motivation: Portable Power

Increasing energy needs for portable consumer electronics such as cellular phones and laptop computers motivates the development of compact power sources. Demand for these products has increased every year with an approximate doubling in total sales expected for both items in the next 2 years. In addition, the advancement of features and capabilities of consumer electronics will continue and result in a need for more power. Currently, battery technology has been able to keep up with these requirements. However, it is unclear if the rapidly growing power requirements will outpace advancements in battery technology. As a result, other compact power sources are being developed as potential alternatives. Power-MEMS devices constitute a large fraction of the research into new small-scale power sources for this application. These devices offer the potential for extremely high power densities when compared to batteries. This is largely a result of the high energy density of combustible hydrocarbon fuels on which these systems are often based.

The U.S. military services have a similar need for advanced portable power systems. As the Army moves toward a more sophisticated and digitally-enhanced ground force, the individual soldier will be equipped with wearable electronic equipment such as communications hardware, infrared night vision goggles, and navigation and guidance systems. All of these systems will require power sources. Current military batteries are large, heavy, and generally cumbersome. A power system that can provide tens of Watts of electrical power in a package smaller and lighter weight than current batteries would enable significant improvements in war-fighting capability.

1.1.2 Motivation: Micro Flight Vehicles

In addition to the portable power application of power-MEMS, these devices can be used for thrust power. Micro gas turbine engines, microrockets, micro internal combustion engines, and micro colloidal thrusters for example, can be utilized for the propulsion of air or spacecraft. Significant interest in these applications has been shown by the Defense Advanced Research Projects Agency (DARPA) and the National Aeronautics and Space Administration (NASA). Specifically, DARPA has been
interested in an unmanned micro air vehicle (μUAV) for tactical battlefield reconnaissance while NASA’s interest is in space propulsion. Figure 1.2 shows a schematic of a potential μUAV under development at MIT.

![Figure 1.2 Three view drawing of MIT micro air vehicle (courtesy M. Drela).](image)

### 1.2 The MIT Micro Gas Turbine Engine

The primary motivation of the work presented in this thesis is the development of a micro gas turbine engine, which is capable of delivering 10-50 Watts of electrical power or approximately 10 grams of thrust. Epstein et al. [1] and Grosheny [2] have reported the design for a silicon-based micro gas turbine generator capable of providing this level of power in a volume less than 1 cm³ while consuming approximately seven grams of fuel per hour. This represents a ten-fold increase in power density over current battery technology. Like their larger counterparts, an engine of the type shown in Figures 1.3 and 1.4 requires a high temperature combustion system to convert chemical energy into fluid thermal and kinetic energy.

27
The detailed design and functionality of this engine are discussed in references [3,4]. The single-spool turbojet consists of a single-stage centrifugal compressor with a pressure ratio of approximately 2:1 and a radial inflow turbine mated on a single silicon disk. The overall dimensions of the device are approximately 21 mm x 21 mm x 3.8 mm. Air enters the device axially through an inlet and makes a right angle turn prior to passing through the impeller. Fuel is then injected and mixes in the duct, which wraps around the chip called the *rectirculation* or *cooling jacket*. The fuel-air mixture passes into the annular combustion chamber where it ignites and burns. Finally, the hot gases expand through the turbine where work is extracted then make another right angle turn and exhaust from the chip. For power generation applications, an electrostatic induction
generator would be incorporated on the top face of the compressor shroud; for thrust applications the turbine exhaust would be passed through a nozzle and used for propulsion. Figure 1.5 shows a demonstration microengine. Systems studies for both of these applications have been performed and the micro gas turbine engine has been shown to be a promising technology with substantial performance benefits over competitors [3].

![Figure 1.5](image_url)

**Figure 1.5** (a) Top view of demo engine and compressor, (b) Bottom view of demo engine and turbine, (c) Cross-section of demo engine (courtesy Nicholas Savoulides).

In comparison to conventional engines, this micro gas turbine offers the potential for more power per unit weight. This can be explained via the *cube-square law*. The weight of the engine scales with its volume (the cube of a characteristic length scale). However, the power scales with mass flow rate through engine, which is a function of the inlet area (the square of a characteristic length scale). As a result, if all else is equal, the power-to-weight ratio of an engine scales with the inverse of its size. Consequently, smaller engines have higher power-to-weight ratios and a microengine could offer a 10-100-fold improvement [3].

The development strategy for this MEMS-based engine involves concurrently developing component technologies such as microcompressors, gas bearings, and microcombustors. The work presented here is part of this broader effort and seeks to
elucidate the underlying physics unique to the micro-scale combustion system, which is required. This is accomplished via a combination of experimental, analytical, and computational investigations.

1.3 Primary Technical Challenges

The MIT microengine is faced with a host of challenging technical problems. Chief among these include turbomachinery performance, bearings and rotor-dynamics, combustion, fabrication, and packaging. The difficulties associated with these topics are briefly outlined below.

- **Turbomachinery:** Due to limitations in state-of-the-art microfabrication techniques, the microengine turbomachinery must consist of only two-dimensional extruded geometries. As a result, a single-stage centrifugal compressor and a radial inflow turbine, both with constant blade height, are all that is manufacturable to date. Although a group at the University of Maryland is working in conjunction with MIT to fabricate variable span blades, this technology is not yet ready for practical application [5]. In addition, due to the small length scales involved, Reynolds numbers are low causing high viscous losses. As result, microengine turbomachinery performance is poor when compared to its large-scale counterparts and compressor and turbine adiabatic efficiencies are on the order of 60% and 65% respectively. Finally, due to the fact that the compressor and turbine comprise a single isothermal silicon disk, there is significant heat transferred from the hot turbine to the compressor. This can further degrade compressor performance by over 20 efficiency points. For additional details on these topics references [3,4,6,7] should be consulted.

- **Bearings and rotor-dynamics:** The radial turbomachinery discussed above requires a blade tip speed in the 400-600 m/s range. As the diameter of a rotating component decreases, the angular velocity must increase to maintain the appropriate tip velocity. As a result, the required rotational speed of the microengine rotor is approximately 1.2 million RPM. At these extremely high rotational speeds very low friction bearings are required. Hydrostatic gas film thrust and journal bearings have been selected to support the microengine rotor. Rotordynamic stability with this type of
bearing at these speeds is both a complex fluid dynamics problem and difficult to test in the laboratory. Passing through natural frequencies and mapping out stability boundaries can cause the rotor to contact the wall. At such high rotational speeds this is often catastrophic resulting in devices, which required significant fabrication resources, to be single use. Details of these models and experiments can be found in [3,4,8,9,10].

- **Combustion:** The microengine requires a combustion system that can efficiently convert chemical energy to fluid thermal and kinetic energy. In order to maintain the high power density of the device, a relatively large mass flow rate must be passed through a small volume. This results in combustor residence times that can be significantly smaller than chemical reaction time scales, which do not vary with geometry, ultimately causing incomplete combustion and/or flame blowout. In addition to this, the silicon structure and short heat conduction paths result in very low Biot numbers and non-adiabatic operation, further lowering efficiencies. Finally, these chemical and thermal effects are negatively coupled, exacerbating the situation. These challenges are reviewed in detail in Chapter 2, as well as throughout this thesis and in [11,12,13,14,15,16,17,18].

- **Fabrication:** The tolerances required for a device like the microengine are very stringent and difficult to achieve with current microfabrication techniques. Among the most difficult fabrication challenges is the journal bearing trench which requires an etch approximately 300 μm deep and 15 μm wide. Aspect ratios on the order of 20 are difficult to achieve with DRIE. Etch uniformity is also a critical issue. For such high-speed rotors, a well-balanced disk is needed. Etch non-uniformity can unbalance the rotor shifting the stability boundary to lower rotational speeds. Wafer alignment can also affect rotor balance. The turbine and compressor sides of the disk are fabricated on separate wafers and bonded. If the bond alignment is poor, rotor balance can be negatively impacted as well. Finally, wafer bonding in general is difficult. Any particles on the bonding surfaces can cause poor local bonding and leakage paths from the device. Critical microfabrication techniques are reviewed in Section 2.5 and additional detail can be found in [3,4,19,20,21].
• **Packaging:** Following successful fabrication, a method of packaging the devices into a suitable test rig had to be devised. Connecting the silicon chip to external fluid feed systems and sensors has proven challenging. A method utilizing glass beads to hermetically seal Kovar tubing to the silicon surface was developed by Harrison and London [22,23]. It was further advanced for the microcombustor test rig by Mehra [11]. However, glass seal packaging is still not a robust process and is especially challenging for higher-pressure devices like the microrocket [24].

### 1.4 Review of Previous MIT Microengine Combustor Research

Combustion phenomenon at microengine scales was first investigated by Tzeng and Waitz [12,13]. A flame tube was used to map the flammability boundaries of hydrogen-air mixtures and to establish the conditions under which a stable flame can be sustained inside a small diameter tube. The burning of low equivalence ratio hydrogen-air mixtures in a millimeter-scale tube was demonstrated and found to be limited by heat loss.

Using the knowledge gained from the flame tube experiments, the first microcombustor compatible with a microengine geometry was developed. This combustor was 0.13 cm$^3$ and conventionally machined out of steel. Premixed hydrogen-air combustion was stabilized and the results from this device laid the foundation for the development of the first silicon microfabricated combustors for the microengine [13].

Mehra and Waitz went on to develop this first silicon microcombustor for integration with an engine geometry [11]. This three-wafer combustor, shown in Figure 1.6 and 1.7, was 0.066 cm$^3$ in volume and was designed to operate on the lean, premixed strategy previously studied however the device also included a fuel injection scheme.
The combustor was tested over a range of equivalence ratios spanning from 0.4 to 1.6 for a fixed mass flow rate of 0.045 g/s and atmospheric pressure. This resulted in a residence time of approximately 0.5 ms. For premixed hydrogen-air operation, exit gas temperatures in excess of 1800 K were achieved with combustor efficiencies of up to 70%. For non-premixed operation, peak exit gas temperatures were approximately 100 K
lower with efficiencies above 65%. This reduced performance indicated that there was inadequate fuel-air mixing upstream of the combustion chamber.

Low combustor efficiencies were attributed to poor thermal isolation of the device. Chemical conversion was estimated at nearly 100% while heat transfer from the combustion chamber to the surroundings lowered the overall efficiency. The power density of the device was approximately 1200 MW/m$^3$. The device also maintained its structural integrity over tens of hours of operation. Reference [11] contains more detail regarding this combustor.

Mehra went on to develop a six-wafer microcombustor based on the engine layout shown in Figures 1.3 and 1.4. Several flame holding geometries, fuel injection schemes, and fuels were evaluated in this device. References [11,17] and Section 3.1 of this thesis review the details of these findings combined with more recent developments.

1.5 Review of Other Microcombustion Systems

There are many compact power research initiatives throughout the world, both in academia and industry. These efforts range from batteries and fuel cells, to other silicon-based engines and generators. The combustion systems of some of these compact engines are reviewed here.

Several groups are attempting to fabricate and test micro gas turbines which are similar in design to the MIT device presented here. A group at Tohoku University and Ishikawajima-Harima Heavy Industries (IHI) are working on conventionally machined small-scale combustors for a micro gas turbine engine. Several geometries have been tested including a radial device similar to that presented here and a canister geometry. Combustion efficiencies over 99% have been obtained with hydrogen fuel in a 2 cm$^3$ volume and with methane in a 15 cm$^3$ chamber both in a canister shaped chamber. This geometry was found to have reduced heat loss when compared to the radial combustor [25,26].

Researchers at the University of Tokyo are attempting to fabricate an ultra micro gas turbine engine. This device also includes radial turbomachinery and a radial combustion chamber. Initial devices were 10 times larger than design and the test
The combustor consisted of a canister geometry. This combustor achieved a temperature rise on the order of 1300 K at mass flow rates around 10 g/s. Ultimately, the design calls for a radial geometry similar to the MIT microcombustors presented here [27].

An ongoing power-MEMS initiative at the University of California, Berkley includes development of a silicon micromachined rotary engine. Initial larger test devices were fabricated via electro discharge machining of steel. Combustion consisted of gas-phase hydrogen-air mixtures ignited with either a spark or a glow plug and power output was as high as 4 W with a 13 mm diameter rotor [28,29].

Still other research groups are involved in developing MEMS-based internal combustion engines. At the Korea Advanced Institute of Science and Technology, a prototype of a micro reciprocating engine with a 1 mm³ combustion chamber has been pursued. Using premixed hydrogen-air and “one-shot” combustion, a piston was displaced nearly 2 mm [30,31].

There are also many power-MEMS devices which required combustion but are not heat engines. These include thermoelectric generators, thermo-photovoltaic generators, and fuel cells. Generally, combustors for these devices utilize heterogeneous catalytic combustion. Several of these are reviewed in Section 5.4 of this thesis.

1.6 Research Contributions

The specific contributions outlined in this thesis can be broken down into two categories: those pertaining to homogeneous gas-phase microcombustors, and those involving heterogeneous surface catalysis. These contributions are listed below.

- **Homogeneous gas-phase microcombustors:**
     i. Design and fabrication of a dual-zone microcombustor, which operates with a primary and secondary combustion zone, similar to conventional combustors.
     ii. Experimental evaluation of several geometries, device pressure loss, and fuel types.
iii. Experimentally mapped operating space and identified limits such as blowout and structural boundaries.

iv. Demonstrated improved mass flow capability over baseline single-zone microcombustors.

2. Synthesis of all existing gas-phase microcombustor data.
   i. Identified practical limits of gas-phase microcombustor operation in terms of required volume for a given fuel type and flow conditions.
   ii. Developed an empirically based design tool and applied this tool to provide initial assessments of combustors for future microengines.
   iii. Established firm design guidelines for gas-phase microcombustors.

3. Analytically predicted the emissions of hydrocarbon-fueled gas-phase microcombustors and identified the primary detrimental exhaust species as unburned hydrocarbons. NOx emissions were found to be minimal.

4. A thermo-acoustic stability analysis of hydrocarbon-fueled gas-phase microcombustors indicated that instability is unlikely.

- **Heterogeneous catalytic microcombustors:**
  1. Designed, fabricated, and tested first catalytic microcombustor for a micro gas turbine engine.
     i. Experimental evaluation of several geometries, catalyst substrate materials, and device pressure loss.
     ii. Experimentally mapped the operating space and identified important limits such as ignition hysteresis and conditions required for autothermal surface reactions.
  2. Identified potential catalyst failure modes via a materials characterization study.
     i. Catalyst/substrate metal diffusion during high temperature fabrication and operation was found to reduce the amount of catalyst material at the surface.
     ii. Catalyst agglomeration on metal oxide substrates during high temperature fabrication and operation was found to reduce active surface area.
  3. Developed low-order analytical models to explain performance trends and guide future designs.
i. Identified important non-dimensional parameters, which govern micro-
    scale catalytic combustion phenomenon.

ii. Identified two regimes of potential operation; kinetically limited and
diffusion limited. High power density catalytic microcombustors were
found to be diffusion-controlled.

iii. Catalyst surface area-to-volume ratio, which is a function of substrate area
and porosity, was shown to be a critical design variable for high power
density catalytic microcombustor design.

iv. Model results were synthesized in a non-dimensional operating space and
design recommendations were made.

1.7 Organization of the Thesis

This thesis is divided into two major sections relating to homogeneous gas-phase
microcombustors (Chapters 2, 3, 4) and heterogeneous catalytic microcombustors
(Chapters 5, 6, 7, 8).

This introduction is followed by Chapter 2, which outlines the primary challenges
that are faced when reducing the size of combustion systems. Residence time constraints,
heat loss issues, materials constraints, and a microfabrication overview are presented
here.

Chapter 3 begins with a detailed review of the “baseline” microcombustor test
and analysis results. This is followed by presentation of the detailed design and
fabrication of the advanced “dual-zone” microcombustor. The experimental results
obtained from this device are discussed in the context of the previously presented
baseline results. Hydrocarbon fuels were also tested and are discussed. Finally, the
chapter concludes with an analysis of the potential turbine cooling benefit of a dual-zone
microcombustor.

Chapter 4 synthesizes all homogeneous gas-phase microcombustor data, which
has been acquired. These data include those obtained from the baseline device, the dual-
zone microcombustor, as well as the three-wafer microcombustor, which was discussed
in Section 1.4. This data synthesis manifests itself as an engine operator’s performance
map and a non-dimensional operating space, which captures the primary physics of the system. This is also shown to be useful as a design tool and several examples are given followed by a synopsis of microcombustor design recommendations.

Chapter 5 introduces the concept of a catalytic microcombustor. This work is motivated by the gas-phase results with hydrocarbon fuels. A review of previous catalytic combustor work is also presented here.

A host of catalytic microcombustor experiments are presented in Chapter 6. A simple three-wafer catalytic microcombustor test-bed is discussed first. The promising results obtained from this device led to the development of a six-wafer catalytic microcombustor. The catalyst and substrate materials as well as the fabrication process are then reviewed. This is followed by a presentation of the experimental results for these combustors including a discussion of ignition characteristics and procedures and comparisons of different devices.

Chapter 7 attempts to explain the performance trends observed in the experiments via low order modeling. These modeling efforts include pressure loss correlations, simple time scale analyses, and a one-dimensional isothermal plug flow reactor model. The development of this model and experimental comparison are presented. Finally, the model is used to suggest key design variables and a non-dimensional operating space is developed.

A catalytic materials characterization study is presented in Chapter 8. Many of the combustors developed did not perform to expectations while others did. This chapter presents probable failure modes. Materials characterization and analysis techniques are presented followed by results for the various catalytic materials and their corresponding substrates before and after high temperature exposure. Results indicated that metal diffusion and catalyst agglomeration are likely candidates for the sporadic performance of the devices. This section concludes with catalytic microcombustor design recommendations incorporating results from combustor experiments and modeling.

Finally the main body of the thesis concludes in Chapter 9. The research is summarized and the contributions reviewed. Recommendations for future work are also presented.
Appendices A, B, C, and D include the photolithography mask set which was used for most device fabrication, various chemical mechanisms that were used throughout the work, gas-phase microcombustor emissions predictions, and a thermo-acoustic stability analysis for gas-phase microcombustors.
Chapter 2

Microcombustion Challenges

The functional requirements of a microcombustor are similar to those of a conventional gas turbine combustor. These include the efficient conversion of chemical energy to fluid thermal and kinetic energy with low total pressure loss, reliable ignition, and wide flammability limits. However, the obstacles to satisfying these requirements are different for a micro-scale device. As first described by Waitz et al. [12] a micro-scale combustor is more highly constrained by inadequate residence time for complete combustion and high rates of heat transfer from the combustor. Microcombustor development also faces unique challenges due to material and thermodynamic cycle constraints. These constraints are reviewed in the following sections, which also include a review of microfabrication techniques.

2.1 Time-scale Considerations

For the energy conversion applications we are interested in, power density is the most important metric. As shown in Table 2.1, the high power density of a microcombustor directly results from high mass flow per unit volume. Since chemical reaction times do not scale with mass flow rate or combustor volume, the realization of this high power density is contingent upon completing the combustion process within a shorter combustor through-flow time.

This fundamental time constraint can be quantified in terms of a homogeneous Damköhler number; the ratio of the residence time to the characteristic chemical reaction time.

\[ Da_h = \frac{\tau_{\text{residence}}}{\tau_{\text{reaction}}} \]  \hspace{1cm} (2.1)
Table 2.1 Comparison of operating parameters and requirements for a microengine combustor with those estimated for a conventional GE90 combustor.

<table>
<thead>
<tr>
<th></th>
<th>Conventional Combustor</th>
<th>Micro-combustor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>0.2 m</td>
<td>0.001 m</td>
</tr>
<tr>
<td>Volume</td>
<td>0.073 m$^3$</td>
<td>6.6x10$^{-8}$ m$^3$</td>
</tr>
<tr>
<td>Cross-sectional area</td>
<td>0.36 m$^2$</td>
<td>6x10$^{-5}$ m$^2$</td>
</tr>
<tr>
<td>Inlet total pressure</td>
<td>37.5 atm</td>
<td>4 atm</td>
</tr>
<tr>
<td>Inlet total temperature</td>
<td>870 K</td>
<td>500 K</td>
</tr>
<tr>
<td>Mass flow rate</td>
<td>140 kg/s</td>
<td>1.8x10$^{-4}$ kg/s</td>
</tr>
<tr>
<td>Residence time</td>
<td>~7 ms</td>
<td>~0.5 ms</td>
</tr>
<tr>
<td>Efficiency</td>
<td>&gt;99%</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>Pressure ratio</td>
<td>&gt;0.95</td>
<td>&gt;0.95</td>
</tr>
<tr>
<td>Exit temperature</td>
<td>1800 K</td>
<td>1600 K</td>
</tr>
<tr>
<td>Power Density</td>
<td>1960 MW/m$^3$</td>
<td>3000 MW/m$^3$</td>
</tr>
</tbody>
</table>

(Note: residence times are calculated using inlet pressure and an average flow temperature of 1000 K.)

To ensure a $Da_h$ greater than unity (and complete combustion), a designer of a microcombustor can either increase the flow residence time or decrease the chemical reaction time. The characteristic combustor residence time is given by the bulk flow through the combustor volume.

$$\tau_{\text{residence}} \approx \frac{\text{volume}}{\text{volumetric flow rate}} = \frac{VP}{\dot{m}RT}$$  \hspace{1cm} (2.2)

Residence time can be increased by increasing the size of the chamber, reducing the mass flow rate, or increasing the operating pressure. A chemical reaction time can be approximated by an Arrhenius type expression.

$$\tau_{\text{reaction}} \approx \frac{[\text{fuel}]_0}{A[\text{fuel}]^a [O_2]^b e^{-\frac{E_a}{RT_0}}}$$  \hspace{1cm} (2.3)

Reaction time is primarily a function of fuel properties and the mixture temperature and pressure.
Since high power density requirements mandate high mass flow rates through small chamber volumes, the mass flow rate per unit volume cannot be reduced without compromising device power density. Hence, there is a basic tradeoff between power density and flow residence time.

\[
\text{Power density} \propto \frac{\dot{m}}{V} \propto \frac{\dot{m}_{LHV}}{V} \propto \frac{\rho}{\tau_{\text{residence}}} \tag{2.4}
\]

For a given operating pressure (and thus density), and assuming a Da of unity, reducing the chemical reaction time and thus required residence time is the only means of ensuring complete combustion without compromising the high power density of the device.

Mixing time-scales are also critical in microcombustion systems. Due to the small length-scales there is little time for fuel-air mixing and inadequate mixing can also lead to chemical inefficiency.

### 2.2 Heat Transfer Effects and Fluid Structure Coupling

Energy loss due to heat transfer at the walls of the combustion chamber in a conventional gas turbine is typically neglected. However, for a microcombustor this is an important factor. The surface area-to-volume ratio for a micro-scale combustor is approximately 500 m\(^{-1}\), or two orders of magnitude larger than that of a typical combustor.

Waitz et al. [12] have shown that the ratio of heat lost to that generated scales with the hydraulic diameter as follows:

\[
\frac{E''}{E} \propto \frac{1}{d_h^{1/2}} \tag{2.5}
\]

The hydraulic diameter of a microcombustor is on the order of millimeters, hundreds of times smaller than that of a typical combustor. Therefore, the ratio of heat lost to that generated may be as much as two orders of magnitude greater than that of a large-scale combustor.
The effect of this large surface heat loss on combustion is two-fold. First, large thermal losses have a direct impact on overall combustor efficiency. Therefore, typical large-scale combustor efficiencies of greater than 99% are not feasible. Second, they can increase kinetic times and narrow flammability limits through lowering reaction temperatures. This can exacerbate the constraints of short residence time.

2.3 Materials Constraints

There are also several material constraints imposed upon a silicon microcombustion system. The most critical requirement is a wall temperature limit of less than 950 K. At temperatures above this level, silicon begins to soften and lose its structural integrity. However, high surface heat transfer and the high thermal conductivity of silicon are beneficial in this case. Combustor wall temperatures can be kept below the 950 K requirement by conduction of heat through the structure to the ambient. In addition, the rotating components of the microengine must maintain even lower wall temperatures, below 900 K, due to creep considerations.

2.4 Design Space

While time scale, heat transfer, and material constraints are important, the most limiting are those imposed by the engine thermodynamic cycle. Figure 2.1 shows a typical design space for a hydrogen-fueled micro-scale combustor. Equivalence ratio is plotted on the x-axis versus heat rejected on the y-axis. A turbine inlet temperature between 1600 and 1800 K is required for the cycle proposed for this engine. In Figure 2.1 the flame stability limit represents the stable operation of a non-adiabatic perfectly stirred reactor. The thermal stress constraint indicates the material limits of the all silicon structure of a micromachined combustion system. The design space is further bounded by the desire to burn lean and the flammability limits of hydrogen-air combustion.
2.5 Fabrication Overview

Fabrication of silicon micro-devices such as the microcombustors presented here is enabled by three fundamental technologies; photolithography, Deep Reactive Ion Etching (DRIE), and aligned fusion wafer bonding. Devices typically consist of two-dimensional extruded geometries formed by photolithography and DRIE on single crystal silicon wafers. Multiple wafers with various structures are then aligned and fusion bonded to form a quasi three-dimensional device. Microfabrication is generally a batch process and typically several devices can be fabricated at once (up to 10 per 4 inch wafer in the case of the microcombustor). For the microcombustors presented in this work, there are six silicon wafer levels, 11 photomasks, and 10 deep etches. Figure 2.2 shows a schematic of the fabrication assembly. The three critical processes are described in more detail below and in references [19,20,21].
2.5.1 Photolithography

Photolithography consists of coating a wafer with a layer of photosensitive polymer called photoresist (in this case, positive photoresist is used). For the microcombustors of interest here, this layer is typically ~20 μm and is considered to be very thick. The optical template used to define the two-dimensional features, which are to be etched, is called a photomask. This mask is aligned with the coated wafer and exposed to an ultra-violet light source for approximately three minutes. After exposure, the wafer is soaked in developer for several minutes and the photoresist areas, which were exposed to the light, are removed from the surface of the wafer and the pattern is exposed. The remaining photoresist protects the wafer while the exposed silicon is etched. This entire process is known as photolithography and a schematic is shown in Figure 2.3. The photomask set used for fabrication of the dual-zone microcombustor can be found in Appendix A.
2.5.2 Deep Reactive Ion Etching (DRIE)

The formation of deep, straight-walled structures in silicon is based on Bosch’s patented technique for time-multiplexed deep etching (TMDE) [32]. The high aspect ratio, complex fluid paths required for a microcombustor and microengine can only be micromachined to the necessary tolerances using this method. The anisotropic etch uses a time-multiplexed inductively coupled plasma of SF$_6$ as the etchant and C$_4$F$_8$ as the sidewall passivating polymer. The process involves alternating between etching and deposition of the protective passivating layer. The C$_4$F$_8$ protects the sidewalls from the etchant while allowing the SF$_6$ plasma to attack the lower, perpendicular surface. This technique is capable of attaining aspect ratios in excess of 20 such as those required for the microengine journal bearing which is a trench 15 μm wide by 300 μm deep. Surface Technology System Corporation’s (STS) Inductively Coupled Plasma (ICP) multiplexed etchers are used for this process.

2.5.3 Aligned Fusion Wafer Bonding

Wafer bonding is the process of combining the individual wafers to form a single, multilevel device. This procedure requires that the wafers have minimal bow and after
all etching is complete they are thoroughly cleaned of all residues and particles. Typical cleaning procedures are listed below [21]:

1. 10 minute Pirahna (1 part hydrogen peroxide + 3 parts sulfuric acid) dip to remove photoresist
2. One hour plasma ashing to remove excess fluorocarbons from the DRIE
3. 10 minute Pirahna dip to remove contaminants from asher
4. 10 minute hydrofluoric acid dip to remove protective layer of silicon dioxide and any other defects/particles which have adhered to the surface
5. RCA cleaned to ensure surfaces are pristine [33]

The single crystal silicon wafers are then aligned and contacted. Van der Waals forces cause the wafers to stick together. After applying some pressure (approximately 4 atm) and annealing the stack in a nitrogen tube furnace at 1100°C for one hour, the individual silicon wafers diffuse into each other forming a single piece of silicon. Figure 2.4 shows a schematic of the individual combustor layers before and after contacting and bonding. Figure 2.5 shows an infrared image of a bonded six-wafer stack. Optical fringe patterns in the image indicate poorly bonded areas.
2.6 Chapter Summary

This chapter described the fundamental challenges faced when designing, fabricating, and operating a micro-scale combustion system. Microcombustors were compared and contrasted to conventional combustion systems and found to differ significantly in potential heat loss and residence time. The most limiting functional requirements and constraints for a microcombustion system include the microengine thermodynamic cycle constraints and the geometric restrictions imposed by microfabrication. The chapter concluded by reviewing these fabrication techniques.
Chapter 3

Dual-zone Microcombustors

This chapter begins with a review of the baseline six-wafer microcombustor and the primary conclusions derived from performance testing. This is done because later comparisons, design choices, and data synthesis will refer to these initial results, which were obtained by Mehra [11]. These sections are followed by a description of the design, testing, and operation of a dual-zone microcombustor. This device consists of a simple modification to the baseline design but represents a significant change in operating mode. Both devices discussed here include all non-rotating components of the MIT microengine such as, fuel plenums, fuel injectors, and pressure ports, as well as compressor and turbine static airfoils. Finally, the chapter concludes with a discussion of potential systems benefits of the dual-zone microcombustor. Additional analyses of gas-phase microcombustor emissions and thermo-acoustic stability can be found in Appendices C and D respectively.

3.1 Review of Baseline Microcombustor Design and Results

A schematic of the six-wafer micro-combustor is shown in Figure 3.1 while a scanning electron micrograph (SEM) of a cross-section of the device can be seen in Figure 3.2. The combustor is referred to as the six-stack due to its six silicon wafer levels required for fabrication. Air, or premixed fuel-air, enters the device axially followed by a 90° turn prior to entering the compressor. For this non-rotating test device, swirl vanes were included to replicate the compressor exit flow angle of 80°. The flow then passes through a duct, which wraps around the combustion chamber. This passage is referred to as the cooling jacket and is intended to thermally isolate the combustion chamber and cool the inner walls, as well as act as a simple recuperator for preheating the reactants. This is also where fuel is injected in the non-premixed mode of operation. A set of three fuel injection ports was included to evaluate fuel-air mixing requirements.
The fuel-air mixture is then burned in the combustion chamber. Two types of chamber inlets were designed to create different flame holding recirculation zones. The first is a simple annular inlet 1.2 mm wide. The second is an array of 60 slots 2.2 mm long intended to create multiple small recirculation zones for more rapid and uniform ignition of the incoming flow. SEMs of both inlets can be seen in Figure 3.3.
the combustion products are passed through the turbine nozzle guide vanes and exit axially from the device.

![Figure 3. 3 SEMs of inlet geometries [11].](image)

3.1.1 Efficiency Definitions

Overall combustor efficiency is defined as:

\[
\eta_c = \frac{(\dot{m}_a + \dot{m}_f)h_2 - \dot{m}_a \dot{h}_t}{\dot{m}_f \dot{h}_f}
\]  

(3.1)

where station (1) refers to the combustor inlet and station (2) refers to the combustor exit.

The combustor efficiency can be written as the product of two sub-efficiencies: a chemical efficiency, and a thermal efficiency. These two efficiencies can be written as:

\[
\eta_{\text{chem}} = \frac{[(\dot{m}_a + \dot{m}_f)h_2 - \dot{m}_a \dot{h}_t] + Q_{\text{loss}}}{\dot{m}_f \dot{h}_f} = \frac{\text{total enthalpy released}}{\text{maximum enthalpy release possible}}
\]  

(3.2)

\[
\eta_{\text{therm}} = \frac{(\dot{m}_a + \dot{m}_f)h_2 - \dot{m}_a \dot{h}_t}{[(\dot{m}_a + \dot{m}_f)h_2 - \dot{m}_a \dot{h}_t] + Q_{\text{loss}}} = \frac{\text{enthalpy rise of fluid}}{\text{total enthalpy released}}
\]  

(3.3)

where \(Q_{\text{loss}}\) is the heat lost to the wall.
3.1.2 Baseline Six-Wafer Hydrogen Tests

Baseline six-wafer micro-combustor tests were performed with premixed hydrogen-air in the annular inlet geometry. Figure 3.4 shows a plot of combustor exit temperature for constant equivalence ratio and Figure 3.5 indicates overall combustor efficiency. Mass flow rate was varied by increasing the inlet pressure with a fixed exit area exhausting to atmosphere.

The combustor produced exit gas temperatures in excess of 1600 K for a mass flow rate of 0.11 g/s and an operating pressure of 1.13 atm. The overall efficiency in this case exceeded 90% and the power density was approximately 1100 MW/m³. The break in the $\phi = 0.5$ and $\phi = 0.6$ exit temperature and efficiency curves is due to a lack of measurement capabilities for gas temperatures over 1600 K. The $\phi = 0.7$ curve terminates at a mass flow rate of 0.015 g/s due to upstream burning in the cooling jacket.

The inability of the device to achieve the design point operation of 0.36 g/s and 3 atm and the general shape of the exit temperature and efficiency curves can be explained by examining the change in $Da_h$ over a constant equivalence ratio operating line. Using the previously defined residence time and a simple one step mechanism for hydrogen-air combustion

$$\tau_{reaction} = \frac{[H_2]_0}{A[H_2]^2[O_2]e^{-\frac{E_a}{RT}}},$$

with $E_a = 10950$ cal/mole and $A = 1.62 \times 10^{18}$ (cm³/mole)²·sec, an estimate of $Da_h$ can be obtained [11]. Figure 3.6 shows a plot of reaction time and residence time along with $Da_h$ versus mass flow rate. Residence time decreases more rapidly than reaction time, resulting in a $Da_h$ less than one. This leads to chemical inefficiency at high mass flow rates as well as flame blowout prior to choking the nozzle guide vanes and reaching the design point conditions.

Analysis by Mehra [11] using a 1-D heat transfer model to predict heat loss from the combustor indicates that thermal inefficiencies dominate low mass flow operation, while at high mass flows performance is limited by chemical inefficiency.
Figure 3.4 Exit gas temperature vs. mass flow rate for annular six-wafer microcombustor [11].

Figure 3.5 Overall efficiency for annular six-wafer microcombustor [11].
3.1.3 Effect of Inlet Geometry

Combustor efficiency for premixed hydrogen-air tests in the slotted-inlet geometry is plotted in Figure 3.7. Performance is similar to the annular-inlet combustor, however, the slotted-inlet device produced higher exit temperatures and efficiencies in the high mass flow, kinetically limited regime of the operating line. This is attributed to the presence of multiple recirculation zones at the inlet which rapidly and uniformly ignite the incoming mixture. The sharp drop in performance for the slotted combustor is due to the rapid extinction of the ignition zones. In the annular case shown in Figures 3.4 and 3.5, the single large recirculation zone stays lit over a wider range of mass flow rates, however, it also results in lower chemical efficiency.
Numerical simulations were performed on both inlet geometries using FLUENT v. 5.1 with a nine-species, 20-step, hydrogen-air reaction mechanism for the chemical model (see Appendix B) and an adiabatic wall boundary condition [34]. Figure 3.8a shows CFD generated contours for the combustor with the annular inlet. In Figure 3.8b contours of temperature are plotted for a 2-D cut through the combustor inlet in the $\theta$-$z$ plane. These contours show a temperature gradient from the bottom of the combustion chamber to the top and indicate the primary ignition zone is in the upper right corner of the combustor. Figures 3.9a and 3.9b show the same contour plots for a combustor with a slotted inlet. The temperature contour in the $\theta$-$z$ plane shows significantly higher temperature in the lower regions of the combustion chamber and higher overall temperatures. The shape of the contours indicates that there are small, hot ignition zones near the slotted inlet. Additional details of the numerical simulations can be found in reference [14].
3.1.4 Fuel Injection Schemes

The performance of the three sets of fuel injectors was evaluated by comparing efficiencies with the premixed case. Pre-mixed operation consisted of fuel/air injection through the primary air inlet only. Figure 3.10 plots efficiency for different equivalence ratios at a mass flow rate of 0.045 g/s. The injectors were located at radii of 4.8 mm and 8.0 mm in the cooling jacket while a set of sidewall injectors were at the base of the cooling jacket. The figure indicates that performance decreases as the injectors get closer to the combustion chamber. This is due to the decreased mixing length.
3.2 Dual-Zone Microcombustor Concept

The dual-zone micro-combustor is a modification to the six-wafer geometry, but represents a significant change in operating mode. A schematic of this device is shown in Figure 3.11. A series of holes through the inner wall have been created connecting the upper cooling jacket to the combustion chamber. These holes allow inlet air to bleed into the combustion chamber. This dilution air serves two purposes; first, it splits the combustion chamber into two zones, and second, it dilutes the hot combustion products reducing their temperature to the desired turbine inlet temperature of 1600 K. This is similar to conventional large-scale combustors. In the primary zone, the fuel-air mixture is burned near stoichiometric conditions. By burning at higher temperature, kinetic rates increase and reaction time decreases effectively increasing $Da_h$. The dilution jet also serves to strengthen recirculation zones and improve stability. The combustion chamber inlet for the dual-zone combustor is slotted as shown in Figure 3.3b. Due to the nature of
this combustor’s operation, premixed combustion is not feasible and fuel injection occurs just downstream of the dilution holes in the cooling jacket.

3.3 Dual-Zone Microcombustor Design

The dilution holes were designed to split the total mass flow in half, establishing a stoichiometric primary zone at the design point conditions. The overall equivalence ratio for the combustor in this case is 0.5. However, at off-design conditions, the flow split will deviate from the desired 50% dilution air and the primary zone will no longer operate at $\phi = 1.0$. As mass flow rate increases, the dilution flow decreases. For a fixed fuel flow rate, this results in a lean primary zone. To maintain a stoichiometric primary zone over a range of operating conditions, the fuel flow must be regulated. Figure 3.12 shows an SEM of these holes. To fabricate these holes, an additional photolithography step and a 400 µm etch was required.
Three-dimensional, adiabatic, reacting flow CFD simulations were used as the primary design tool for these devices. The dimensions and radial location of the dilution holes and fuel injectors were determined using FLUENT v 5.1 to model the primary/dilution flow splits and temperatures. Figure 3.13 shows a sample solution. For this case, the primary zone temperature reached ~2000 K and was then reduced to ~1500 K by the cool dilution air. The primary zone equivalence ratio was 1.05 resulting in an overall equivalence ratio of 0.47, near the design target of 0.5.

Two variations of the dual-zone combustor were fabricated and a summary of the design specifications for these devices is in Table 3.1. Radial location of the dilution holes was varied to test the effect of primary zone volume. All of the devices were designed for a mass flow rate of 0.36 g/s, $\phi_{\text{primary}} = 1$, $\phi_{\text{overall}} = 0.5$, a pressure of 3 atm, and with slotted combustion chamber inlets.
Figure 3.13 Temperature (K) profile from 3D, reacting flow CFD solution for dual-zone microcombustor.

Table 3.1 Design specifications for dual-zone microcombustors.

<table>
<thead>
<tr>
<th></th>
<th>Device 1</th>
<th>Device 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution hole diameter (μm)</td>
<td>448</td>
<td>465</td>
</tr>
<tr>
<td>Number of dilution holes</td>
<td>156</td>
<td>140</td>
</tr>
<tr>
<td>Radial location of holes (mm)</td>
<td>7.0</td>
<td>5.9</td>
</tr>
<tr>
<td>Number of NGVs</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>
3.4 Experimental Setup and Diagnostics

Prior to testing, the microcombustors were packaged into a suitable test rig. In order to connect the device's micro-scale fluid channels to a macro-scale feed system, a glass bead interconnect scheme was developed by Mehra [11]. Small diameter Kovar tubing was hermetically sealed to the silicon with glass beads and brazed to a larger kovar plate for connection to conventional fittings. A fully packaged device is shown in Figure 3.14. A more detailed description of this process can be found in references [11,22,23].

![Fully packaged microcombustor.](image)

Due to the micro-scale of the devices, it is difficult to obtain non-intrusive measurements. Therefore, diagnostics were limited. Exit gas temperature was measured using a 0.010 in. sheathed type K thermocouple. Because of the large temperature gradients along the length of the wire, an error analysis for the thermal conductivity, radiative emissivity, and calibration drifts predicted uncertainties up to ±130 K. A wall temperature measurement was also obtained with the same type thermocouple and an
uncertainty of ±12 K. In addition to the temperature diagnostics, pressure was measured upstream in the cooling jacket and in the combustion chamber itself. Flow control was accomplished with several MKS Type 1359C flow controllers with ±0.5% full-scale accuracy (±0.05 SLM for air and ±0.005 SLM for fuel). A detailed uncertainty analysis can be found in reference [11].

3.5 Performance Testing – Hydrogen-air

3.5.1 Baseline Dual-zone Testing

Baseline dual-zone testing was performed with hydrogen fuel injection through upstream fuel injectors at a radius of 8.0 mm. The dilution hole radial location was 7.0 mm. Plots of exit gas temperature and efficiency are shown in Figure 3.15 and 3.16 respectively. Figure 3.17 shows a pressure trace for the device. This combustor achieved exit gas temperatures in excess of 1600 K at mass flow rates exceeding 0.12 g/s and efficiencies over 85%.

![Figure 3.15 Exit gas temperature for dual-zone microcombustor with hydrogen-air mixtures.](image-url)
Figure 3.16 Overall efficiency for dual-zone microcombustor with hydrogen-air mixtures.

Figure 3.17 Combustor pressure for dual-zone device.
Figure 3.18 shows an efficiency breakdown for these tests. At high mass flow rates the devices is chemically limited. As mass flow rate increases, Damköhler number decreases until the flame is eventually blown out. At low mass flow rates the device is limited by heat loss and thermal efficiency is low. At very low flow rates (less than 0.02 g/s) much of the flow pass through the dilution holes and there is little heat release. As a result, the combustor is chemically limited in this regime as well.

![Efficiency breakdown for dual-zone microcombustor.](image)

**3.5.2 Effect of Primary-Zone Size**

To evaluate the effects of primary zone size, dilution holes located at radii of 5.9 mm and 7.0 mm were tested. These correspond to primary-zone volumes of 78.5 mm$^3$ (41% of total combustor volume) and 37 mm$^3$ (20% of total combustor volume) respectively. Figure 3.19 plots efficiency for the two devices operating at similar conditions. Higher mass flows were achieved with the larger primary zone. This is largely due to increased residence time in the primary zone. There was also a reduction in efficiency. This may be due to non-uniform exit temperature profiles where the measurement was made.
3.6 Performance Testing – Hydrocarbon-air

Hydrocarbon fuels were tested in the devices. For a microengine to be practical, fuels such as ethylene (C\textsubscript{2}H\textsubscript{4}) and propane (C\textsubscript{3}H\textsubscript{8}) will be required due to their high energy densities and favorable storage properties. Results from combustion tests for these two fuels in the six-wafer combustor are shown in Figure 3.20 and 3.21. The ethylene-air mixture achieved maximum power density at an equivalence ratio of 0.9 and ~1 atm pressure, with exit temperature exceeding 1400 K and efficiency of 60%. The estimated power density for these conditions is ~500 MW/m\textsuperscript{3}. The reaction rates of propane are significantly lower than ethylene and as a result, combustion could only be stabilized in the device at an equivalence ratio of 0.8. Exit temperatures of 1200 K were reached at ~1 atm with an efficiency of 55%. This corresponds to a power density of ~140 MW/m\textsuperscript{3}. Nominal residence times for ethylene-air and propane-air combustion in this device were 1.6 ms and 2.8 ms respectively. Typical reaction times are 0.5-1 ms for ethylene-air and 1-2 ms for propane-air whereas hydrogen-air reaction times are approximately 0.2 ms.
Figure 3.20 Overall efficiency for baseline microcombustor with ethylene/air.

Figure 3.21 Overall efficiency for baseline microcombustor with propane/air.
The dual-zone combustor did not provide an expected broader range of mass flow for hydrocarbon-fueled operation. This is believed to be due primarily to inadequate mixing lengths and fuel injectors that were designed for operation with hydrogen. The injection hole diameters should be re-sized to optimize jet penetration and spreading with the lower mass flow rates of hydrocarbon fuels. As a result, mass flows of only up to 0.06 g/s at approximately 1 atm and efficiencies less than 50% were achieved with ethylene. However, these combustors were operated with a wider range of equivalence ratios. This was due in part to fuel injection, which prevented upstream burning and allowed higher mixture ratios. In addition, lower equivalence ratios were possible due to the strengthened recirculation zones created by the dilution flow. Figures 3.22 and 3.23 show efficiency for both ethylene-air and propane-air combustion in a dual-zone combustor with dilution holes located 7.0 mm radially outward. The maximum power density achieved for the ethylene-air mixture was ~100 MW/m³ and 75 MW/m³ for propane-air with residence times of 2.1 ms and 3.7 ms respectively.

![Figure 3.22 Overall efficiency for dual-zone microcombustor with ethylene-air.](image_url)
3.7 Comparison of Dual-Zone and Baseline Microcombustors

The dual-zone combustor exhibited slightly lower exit gas temperatures and efficiencies than the single-zone, six-wafer combustor. However, its operating range was much wider for hydrogen-air operation. Combustion was stabilized at equivalence ratios as low as 0.2 and mass flow rates as high as 0.2 g/s. Figure 3.24 compares the dual-zone combustor efficiency to the single-zone for similar conditions.

The significant extension in operating range is largely due to strengthened recirculation zones and the hot, stable primary zone. For the same overall efficiency, the dual-zone combustor achieved a 100% increase in mass flow rate before blowout. The ability to operate at low overall equivalence ratio is a result of a higher local equivalence ratio in the primary zone. It should be noted that for the current microengine applications, combustor efficiencies of 80% or higher are acceptable. Table 3.2 summarizes the maximum power densities achieved for both devices with various fuels.
3.8 Effect on Turbine Cooling

The non-uniform exit temperature profile generated by the dual-zone combustor (as shown in CFD solutions) may be beneficial for turbine cooling. As discussed in Section 1.3, heat transfer from the turbine to the compressor can degrade compressor performance by as much as 20%-30%. Reducing the heat load on the turbine would reduce the heat transferred to the compressor and improve overall engine performance. The dual-zone combustor’s non-uniform temperature profile has the potential, if properly tailored, to provide a cooler layer of gas over the turbine disk while still maintaining a high enthalpy flow over the blades for work extraction. This section examines these potential benefits.
3.8.1 Baseline Turbine Heat Load Estimate

In order to determine the cooling effectiveness of a non-uniform temperature profile in the microengine turbine, the heat transferred to the turbine/compressor rotor for a baseline uniform temperature field must be estimated. For this case, a uniform profile of 1600 K entering the turbine nozzle guide vanes will be used and the microengine rotor will be assumed isothermal. The latter approximation is justified given that the Biot Number for heat transfer is much less than unity (≈0.01).

\[
Bi = \frac{hL}{k} = \frac{\text{resistance to conductive heat transfer}}{\text{resistance to convective heat transfer}} \ll 1 \quad (3.5)
\]

As the hot gas passes through the NGVs, there will be some heat loss to the static structure resulting in a lower inlet temperature to the turbine rotor. To estimate this, simple heat transfer correlations can be used. Approximating the passage between a pair of NGVs as a square duct can provide a simple method for calculating the heat lost. Using the actual turbine geometry as a guide, a square duct with dimensions 0.4 mm x 1.3 mm x 3.0 mm will be used.

Nusselt Number correlations from the literature can then be used to obtain an estimate for the convective heat transfer coefficient.

\[
Nu = \frac{hd}{k} \quad (3.6)
\]

For a duct with a width-to-height ratio of approximately 3 and laminar flow, the Nusselt Number is approximately 3.96 [35]. The hydraulic diameter for the duct is 6.12x10^{-4} m^2 and the thermal conductivity of the gas can be obtained from the following correlation [36]:

\[
k = 0.241 \left( \frac{T}{273} \right)^{\frac{3}{2}} \left( \frac{273 + 194}{T + 194} \right). \quad (3.7)
\]
From these relations, \( h \) is found to be 576 W/m\(^2\)K.

The heat loss through an NGV passage can now be calculated from

\[
Q_{NGV} = A_{duct}h(T_w - T_{wall})
\]  

(3.8)

with \( T_{wall} \) assumed to be 950 K, the softening point of silicon. \( Q_{NGV} \) is 3.82 W/passage. There are a total of eight NGV passages; the total heat lost in the NGVs is 30.5 W. From this, the NGV exit temperature (rotor inlet temperature) can be calculated using a power balance.

\[
\dot{m}h_{in} = \dot{m}h_{out} + Q_{lost}
\]  

(3.9)

\[
\dot{m}C_p T_{in} = \dot{m}C_p T_{out} + Q_{lost}
\]  

(3.10)

Using a mass flow rate of 0.293 g/sec, the NGV outlet temperature is 1498 K.

Next, the heat loss through the rotor and its wall temperature will be estimated using 1498 K as the inlet temperature. An efficiency and pressure ratio through the turbine of 0.6 and 2 will be assumed [6]. From

\[
\eta_{turb} = \frac{l - \tau_{turb}}{l - \tau_{turb}/(1-r)\gamma}
\]  

(3.11)

the turbine temperature ratio can be found and is 1.13. The turbine outlet temperature can be calculated and is 1326 K. The average temperature through the turbine blades and along the rotating disk can be estimated and is approximately 1412 K. This will be used as the gas temperature for the hot side of the rotor.

To estimate the heat loss through the turbine, convective heat transfer coefficients from Evans [7] can be used. These coefficients are broken down into separate values for the disk and blades and are 3077 and 4506 W/m\(^2\)K respectively and are for a mass flow rate of 0.293 g/sec and a turbine pressure ratio of 2. The following relations can be used to obtain an expression for heat loss in terms of rotor wall temperature only:
\[ Q_{\text{disk}} = A_{\text{disk}} h_{\text{disk}} \left( \bar{T}_{\text{ave}_{\text{wb}}} - T_{\text{wall}} \right) \]  

(3.12)

\[ Q_{\text{blades}} = A_{\text{blades}} h_{\text{blades}} \left( \bar{T}_{\text{ave}_{\text{wb}}} - T_{\text{wall}} \right) \]  

(3.13)

\[ Q_{\text{OUT}_{\text{wb}}} = Q_{\text{disk}} + Q_{\text{blades}}. \]  

(3.15)

The disk and blade areas are 26.2 mm\(^2\) and 27.7 mm\(^2\) respectively [7].

A corresponding expression for the compressor side of the disk can also be found. First, the compressor operating parameters must be estimated and the average gas temperature found. An efficiency of 0.5 and a pressure ratio of 2 will be used here [6].

From

\[ \eta_{\text{comp}} = \frac{\pi^{(y-1)/\gamma} - 1}{\pi_{\text{comp}}^{(y-1)/\gamma} - 1} \]  

(3.16)

the compressor temperature ratio can be found and is 1.44. Starting with an ambient inlet temperature of 300 K this results in a compressor exit temperature of 431 K and an average gas temperature of 366 K.

An expression for heat input to the compressor flow from the hot rotor is

\[ Q_{\text{IN}_{\text{comp}}} = A_{\text{comp}} h_{\text{comp}} \left( T_{\text{wall}} - \bar{T}_{\text{ave}_{\text{comp}}} \right) \]  

(3.17)

where \( h_{\text{comp}} \) is 1765 W/m\(^2\)K and \( A_{\text{comp}} \) is 103 mm\(^2\) [7]. The heat lost from the turbine flow is equal to the heat input to the compressor flow:

\[ Q_{\text{OUT}_{\text{wb}}} = Q_{\text{IN}_{\text{comp}}}. \]  

(3.18)
The only unknown left in this expression is $T_{\text{wall}}$, which can then be solved for. In this case, $T_{\text{wall}}$ is 921 K and heat transferred from the turbine to the compressor through the rotor is 101 W.

However, a correction to this solution is still required. The heat addition to the compressor flow has not been accounted for in the gas temperature. To model this effect an iterative process is required. First, the methodology developed by Gong [37] and utilized by Protz [3] and Savoulides [4], of adding all heat to the flow prior to compression will be implemented. The enthalpy rise due to the heat addition already calculated will be used to find the new compressor inlet temperature.

\[ Q_{\text{IN,comp}} = \dot{m}C_p (T_{\text{new}} - T_{\text{ambient}}) \] (3.19)

Once this new temperature is obtained, the heating due to compression is calculated from the compressor parameters and the average gas temperature is found. The wall temperature and compressor heat addition are then recalculated as previously described. After six iterations, the rotor wall temperature converged to within 2 degrees K to a value of 1059 K with heat lost from the turbine (and added to the compressor) of approximately 73 W.

3.8.2 Turbine Heat Load with Non-uniform Temperature Profile

Using the methodology laid out above in Section 3.8.1, the heat load to the rotor for a non-uniform temperature profile can be estimated. First, a temperature profile that reasonably simulates that which can be generated by a dual-zone combustor must be selected. This temperature profile must also be simplified for ease of calculation. For these reasons, a step profile will be used with a cool layer temperature of 950 K. This temperature was selected by examining CFD solutions used in the design of the dual-zone microcombustor. The size of the step will be 136 µm for a turbine with 400 µm blades. This was chosen based on the thickness of the thermal boundary layer as calculated by Philippon [6]. In order to keep the turbine work extraction constant (to first order) the free stream temperature must be calculated to maintain a mass averaged total
temperature of 1600 K. With this in mind, the free stream total temperature for the profile is 1969 K. This higher free stream gas temperature will tradeoff against the reduced area exposed to this temperature. Figure 3.25 shows a schematic of this temperature profile.

![Figure 3.25 Schematic of simplified non-uniform dual-zone microcombustor exit temperature profile.](image)

As done previously, the heat loss through the NGVs must be estimated in order to calculate the inlet temperature to the rotor. Maintaining the same static structure temperature of 950 K as in the baseline case, there is no heat transfer due to the cooling layer. The only heat loss is through the section of blades exposed to the free stream gas temperature of 1969 K. Using the methodology of Section 3.8.1 and equations 3.6 and 3.7, a new heat transfer coefficient is found to be 652 W/m²K. Scaling the heat load by the reduced area and using the new free stream gas temperature, the heat lost through the NGVs is 29.1 W resulting in a free stream rotor inlet temperature of 1874 K.

Using the same turbine performance properties (efficiency of 0.6 and a pressure ratio of 2) and equation 3.11, the average turbine free stream gas temperature is 1766 K. The heat lost through the turbine can then be written as
\[ Q_{\text{disk}} = A_{\text{disk}} h_{\text{disk}} \left( T_{\text{coolant}} - T_{\text{wall}} \right) \] (3.20)

\[ Q_{\text{blade}_\text{cool}} = \left( \frac{136}{400} \right) A_{\text{blade}} h_{\text{blade}} \left( T_{\text{coolant}} - T_{\text{wall}} \right) \] (3.21)

\[ Q_{\text{blade}_\text{hot}} = \left( 1 - \frac{136}{400} \right) A_{\text{blade}} h_{\text{blade}} \left( T_{\text{wall}} - T_{\text{wall}} \right) \] (3.22)

\[ Q_{\text{OUT}_{\text{wall}}} = Q_{\text{disk}} + Q_{\text{blade}_\text{cool}} + Q_{\text{blade}_\text{hot}} \] (3.23)

where the blade heat transfer is broken down into two components:

1. fraction of blade area exposed to coolant flow
2. fraction of blade area exposed to high free stream temperature

Heat transfer coefficients and areas are the same as those used in Section 3.8.1. The final expression for heat lost from the turbine is a function of \( T_{\text{wall}} \) only. A corresponding expression can be obtained for the compressor side of the rotor using equations 3.16 and 3.17 and the previously stated compressor performance characteristics.

By equating the heat lost from the turbine to that gained in the compressor (equation 3.18) the rotor wall temperature can be obtained. For this initial solution, the wall temperature is 849.5 K and the heat lost from the turbine (added to the compressor) is 88.2 W. However, as previously outlined in Section 3.8.1, several iterations must be performed to account for the heat addition from the rotor into the compressor inlet flow. After six iterations, the wall temperature converged to 970 K and the heat transferred is 63.6 W.

When compared to the baseline, this temperature profile resulted in a 90 K lower rotor wall temperature and reduction of heat transferred by 9.2 W. This can be best quantified by calculating a cooling effectiveness, which has been defined by Philippon [6] as

\[ \eta_{\text{cool}} = \frac{Q_{\text{without cooling}} - Q_{\text{with cooling}}}{Q_{\text{without cooling}}} \] (3.24)
For this simplified temperature profile, the cooling effectiveness was 12.6% (reduced heat load by 12.6% when compared to baseline).

### 3.8.3 Higher Order Effects

There are significant higher order effects, which are not accounted for in this analysis. To adequately capture these effects a higher fidelity model, such as a 2-D or 3-D CFD solution is required. Philippon performed many of these simulations for a film-cooled turbine. His disk cooling models involved similar temperature profiles to those discussed here. Some of the higher order effects are discussed below, however for a detailed review see reference [6]. In addition, turbine performance and structural implications are briefly discussed.

- **Aerodynamic Effects:** Vorticity and circulation will be generated by these non-uniform temperature profiles. The misalignment of the density gradient (resulting from the temperature profile) and the pressure gradient cause a baroclinic torque and vorticity and circulation form according to equations 3.25 and 3.26 respectively.

\[
\frac{D\omega}{Dt} = (\omega \cdot \nabla)u + \frac{1}{\rho^2}(\nabla \rho \times \nabla p) \quad (3.25)
\]

\[
\frac{D\Gamma}{Dt} = \int_s \frac{\nabla \rho \times \nabla p}{\rho^2} \cdot nds \quad (3.26)
\]

The tipping and stretching of these vortex lines as they pass through the curved NGV and rotor passages will result in secondary flows. These flows can affect the heat transfer characteristics in the turbine and also degrade performance (efficiency and work extraction). Secondary flows, which result from the geometry itself, such as, tip clearance and horseshoe vortices, can also impact heat flux by entraining hot gas into the boundary/cooling layer. Finally, centrifugal effects on the disk can negatively
impact the effectiveness of a cooling layer. Centrifugation of some flow in the boundary layer is nearly certain. The flow near the disk entering the rotor (the cooling layer) has low momentum and is easily centrifuged. This can result in non-uniform cooling coverage on the disk [6].

- **Turbine Performance:** The effect of a disk-cooling layer is two-fold. First, by reducing the total heat transferred from the flow to the structure, there is more enthalpy available for work extraction. Conversely, turbine performance (efficiency) will be negatively impacted by the secondary flows generated by the non-uniform profile. In addition, segments of the turbine blades themselves may be operating off design due to the varying span-wise temperature. A more detailed CFD simulation is required to evaluate the tradeoff between the aerodynamic performance penalties and the additional available enthalpy benefit [6].

- **Structural Implications:** Overall, a cooling layer should be structurally beneficial. By reducing the rotor temperature, the structure is being driven away from its creep limit. In addition, the cooling layer proposed here would cover the base of the blades, which is one of the more likely failure initiation points. The secondary flows generated due to the cooling layer could result in local hot spots, however the isothermal silicon structure cannot sustain large temperature gradients and these hot spots would tend to diffuse into the structure.

### 3.9 Chapter Summary

This chapter begins with a detailed review of the baseline gas-phase microcombustor, referred to as the six-wafer microcombustor. At low mass flow rates these devices were found to be limited by heat loss while constrained by inadequate residence time at high mass flow rates. The effects of various inlet geometries as well as different fuel injection locations were evaluated. With hydrogen fuel, these devices achieved exit gas temperatures on the order of 1800 K, efficiencies greater than 90%, and power densities in excess of 1100 MW/m^3.

A second gas-phase microcombustion device is then presented. This combustor is known as the dual-zone microcombustor. The concept and design of this device are
reviewed, followed by the results of performance testing. It was found to operate over a wider range of mass flow rates than the baseline six-wafer device but at lower overall exit gas temperatures and efficiencies. For the same operating conditions (inlet temperature, mixture ratio, and pressure) the dual-zone device was able to achieve a two-fold increase in flow rate compared to the baseline.

Hydrocarbon fuels were also tested in both devices and found to operate at significantly lower efficiencies and mass flow rates primarily due to the significant decrease in reaction rates associated with these fuels. The maximum power densities achieved with these fuels were 500 MW/m³ and 140 MW/m³ for ethylene and propane respectively.

Finally, the chapter concludes with an analysis of the potential systems-level benefits of the dual-zone microcombustor. This combustor has implications for turbine cooling. The non-uniform exit temperature profile generated creates a relatively cooler layer of fluid over the turbine disk reducing heat flux to the rotor and hence, heat transfer to the compressor. This can improve compressor and overall microengine efficiency.
Chapter 4

Gas-phase Microcombustor Data Synthesis

In this chapter, all gas-phase microcombustor data, ranging from the three-wafer device discussed in Section 1.4 to the dual-zone microcombustor of Chapter 3, is synthesized in an effort to draw general conclusions and design guidelines for heterogeneous microcombustion systems. The chapter begins with the presentation of the empirically determined operating space in a form which is useful to the microengine systems engineers, followed by a more general non-dimensional operating space, and concludes with a discussion of how to use this as a design tool and some final design recommendations.

4.1 Empirically Determined Operating Space

Figure 4.1 plots the empirically identified operating space for the baseline six-stack and the dual-zone microcombustors burning hydrogen. The operating boundaries include:

1. The lean blowout limit.
2. The upstream burning limit where combustion in the cooling jacket occurred.
3. The structural limit.
4. The $1600 \, \text{K}$ $T_{14}$ microengine cycle limit (assuming 80% combustor efficiency).

A narrow operating corridor exists between the lean blowout limit and the upstream burning limit, however, as previously discussed, the design mass flow rate of 0.36 g/s was not reached. As a result, initial engine designs will have reduced flow (225 $\mu$m compressor blade height instead of 400 $\mu$m blade height).

The dual-zone combustor has a broader operating space due to the stable, hot primary zone. The most notable features of this operating space are: the lower lean blowout limit and the absence of an upstream burning limit due to non-premixed operation.
Figure 4.1 Operating space for six-wafer and dual-zone microcombustor.

Figure 4.2 shows data for all of the combustors, including the three-wafer device mentioned in Section 1.4, presented in a plot of Damköhler number versus chemical efficiency. The wall temperature measurements along with a simple 1-D heat transfer model were used to estimate the heat loss from the devices enabling a calculation of chemical efficiency [11]. The residence time was calculated using the exit gas temperature measurements while Chemkin III, a reaction kinetics software package, was used to compute chemical time-scales. The nine species, 20-step hydrogen-air reaction mechanism used for the CFD simulations was utilized as the chemical model [34]. For hydrocarbon-air cases GRIMech 3.0 was used (see Appendix B) [38]. As Damköhler number increases, chemical efficiency asymptotically approaches unity. Points to the far left with low chemical efficiency are a result of the combustor approaching blow-out in the high mass flow regions of the operating space.
4.2 Non-dimensional Operating Space

Although Figure 4.2 shows high chemical efficiency over a range of Damköhler numbers, the performance of these devices was found to be a function of both chemical and thermal losses. In this case performance is quantified in terms of non-dimensional power density, or actual power density normalized by the maximum possible power density at those conditions (function of mass flow rate and fuel type).

If it is assumed that there is adequate fuel-air mixing and rapid, uniform ignition, this quantity is a function of only two parameters; Damköhler number and non-dimensional heat loss. Damköhler number was estimated as previously described using exit gas temperature measurements for residence time calculations and Chemkin III for chemical time approximations. Heat loss can be cast in non-dimensional terms by normalizing the actual heat lost from the device by the maximum possible heat that can be generated at a given operating condition. Again, the actual heat lost was estimated using a 1-D heat transfer model [11].

Figure 4.2 Damköhler number vs. chemical efficiency for several microcombsutors.
Figure 4.3 plots this non-dimensional power density for all of the combustors in three-parameter space. The plot includes all three fuels tested (hydrogen, ethylene and propane). The heat loss parameter and homogenous Damköhler number are on the x and y-axes, respectively. A second order, least squares surface fit was used to generate contours of non-dimensional power density (the fit explains 65% of the variance in the data).

Thermal efficiency in these devices is inversely proportional to heat loss while chemical efficiency is directly proportional to Damköhler number. Hence, optimum performance is achieved at low levels of heat loss and high Damköhler number as indicated in Figure 4.3.

This non-dimensional operating space further explains the operating line considerations of a micro-combustor. Conditions of increasing mass flow for constant equivalence ratio move from the upper right side of the operating space to the lower left. In the low mass flow region of the space, performance is limited by heat loss, while at
high mass flow Damköhler number falls and performance is limited by chemical inefficiency. In the area of moderate mass flow, the center of the operating space, the highest power densities are achieved. This is consistent with the data presented in Chapter 3 where the highest overall efficiencies were found to be at moderate mass flow rates.

Figure 4.3 also indicates that the microcombustor’s evolutionary design changes improved overall performance. The three-wafer combustor suffered from high heat loss (primarily due to packaging) and lies to the lower right in the operating space. The largest performance enhancement came with the implementation of the cooling jacket for thermal isolation of the combustion chamber and the glass seal packaging scheme. The six-wafer data lies much farther to the left (low heat loss region) and also has higher Damköhler numbers. The dual-zone combustors provided a hot stable flame-zone, which resulted in higher Damköhler numbers and improved performance over a range of conditions.

4.3 Design Tool – Case Studies

4.3.1 Propane-air Combustion for Demo Engine

The non-dimensional operating space of Figure 4.3 can also be useful in the design process. For example, a good estimate of the volume required for a propane-air microcombustor suitable for a micro gas turbine can be obtained. If similar conditions to those run here are assumed (1600 K exit gas temperature, 1 atm pressure, and mass flow of 0.15 g/s) and an equivalence ratio of $\phi = 0.8$ is selected, the non-dimensional power density can be computed and is approximately 60%. The heat loss from the device can be assumed to be approximately 5% based on previous data with thermal management techniques such as the cooling jacket. From Figure 4.3, the desired Damköhler number can be found and is approximately 5.5. The chemical time can be computed using Chemkin III or any other suitable technique and the desired residence time found from the Damköhler number. This results in a residence time of 1.44 ms and a volume of 950 mm$^3$, or about a five-fold increase in volume compared to those combustors presented here.
4.3.2 Propane-air Combustion for Advanced Engine Designs

The methodology presented here for estimating gas-phase microcombustor volume has been utilized for possible future microengine designs. These advanced engine designs would include higher mass flow rates, improved turbomachinery, and increased turbine inlet temperatures. The devices would be microfabricated out of silicon and fueled by a propane-air mixture. Table 4.1 shows the critical design parameters for each engine and the corresponding combustor parameters. The overall combustor volume required for the design point is shown at the end of the table along with the percent increase over the current baseline design of 191 mm³. All engine parameters were obtained from Sirakov [39].

Table 4.1 Design parameters for advanced microengines.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Engine #1</th>
<th>Engine #2</th>
<th>Engine #3</th>
<th>Engine #4</th>
<th>Engine #5</th>
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<tbody>
<tr>
<td>(m)</td>
<td>g/s</td>
<td>0.5</td>
<td>0.6</td>
<td>0.5</td>
<td>1.15</td>
<td>0.7</td>
</tr>
<tr>
<td>(T_{\text{inlet}})</td>
<td>K</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>(P_{\text{inlet}})</td>
<td>atm</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>(\eta_{\text{comp}})</td>
<td>%</td>
<td>0.75</td>
<td>0.78</td>
<td>0.78</td>
<td>0.78</td>
<td>0.78</td>
</tr>
<tr>
<td>(\pi_{\text{comp}})</td>
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<td>2.5</td>
<td>2.9</td>
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<td>4.5</td>
</tr>
<tr>
<td>(T_{\text{r4}})</td>
<td>K</td>
<td>1600</td>
<td>1600</td>
<td>1700</td>
<td>1700</td>
<td>1800</td>
</tr>
<tr>
<td>(\eta_{\text{burner}})</td>
<td>%</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>95</td>
</tr>
<tr>
<td>(\pi_{\text{burner}})</td>
<td>n/a</td>
<td>0.95</td>
<td>0.95</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>fuel</td>
<td>n/a</td>
<td>(\text{C}_3\text{H}_8)</td>
<td>(\text{C}_3\text{H}_8)</td>
<td>(\text{C}_3\text{H}_8)</td>
<td>(\text{C}_3\text{H}_8)</td>
<td>(\text{C}_3\text{H}_8)</td>
</tr>
<tr>
<td>(\phi)</td>
<td>n/a</td>
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<td>0.55</td>
<td>0.55</td>
<td>0.58</td>
<td>0.63</td>
</tr>
<tr>
<td>(Da_h)</td>
<td>n/a</td>
<td>8.5</td>
<td>8.5</td>
<td>8.5</td>
<td>8.5</td>
<td>9.0</td>
</tr>
<tr>
<td>(\tau_{\text{chem}})</td>
<td>ms</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>(\tau_{\text{res}})</td>
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<td>2.55</td>
<td>1.7</td>
<td>0.90</td>
</tr>
<tr>
<td>volume</td>
<td>mm³</td>
<td>2310</td>
<td>2390</td>
<td>2046</td>
<td>2413</td>
<td>715</td>
</tr>
<tr>
<td>% increase</td>
<td>%</td>
<td>1210</td>
<td>1250</td>
<td>1070</td>
<td>1260</td>
<td>375</td>
</tr>
</tbody>
</table>
When reviewing Table 4.1 it is important to note that these results are for design point operation only. The same operating line issues, which manifested themselves in the gas-phase microcombustor experiments, need to be kept in mind here. Namely, the combustors will likely reach a minimum Damköhler number at which blow-out may occur, prior to reaching the design mass flow rate. To account for this, the combustor volume should be sized for this off design operating condition or a scheme for igniting the device at high mass flow rate (choked conditions) should be devised.

4.4 Gas-Phase Microcombustor Design Recommendations

The following design trades and recommendations for microcombustion systems have been identified:

1. The high power density requirements of a microcombustor mandate high mass flow rates per unit volume. However, this results in low residence time and Damköhler numbers of order unity. Microcombustion systems are fundamentally limited by this trade-off between high power density and efficient combustion.

2. The large surface area-to-volume ratio of a microcombustor makes non-adiabatic operation intrinsic to its design. The coupling between heat transfer and chemical kinetics is a critical element of the design process. Strategies such as the cooling jacket presented here are effective solutions. While keeping the inner wall cool, it acts as a fuel-air pre-heater to improve kinetic rates, offsetting the effect of lower wall temperatures.

3. Recirculation zones are critical for rapid and uniform ignition of incoming reactants. However, if these ignition zones are too large, the effective volume of the combustion chamber will be significantly reduced resulting in decreased residence time and $Da_h$.

4. Fuel injection for non-premixed operation should occur as far upstream of the combustion chamber as possible to provide adequate mixing length.

5. It is not sufficient to design a microcombustor exclusively for design point operation. Operating line issues need to be considered. For the combustors
presented here, the minimum $Da_h$ occurs at mass flows and pressures corresponding to operation prior to choking of the nozzle guide vanes.

4.5 Chapter Summary

In this chapter, all gas-phase microcombustor data is synthesized in an effort to develop an empirically based design tool and to draw general conclusions and design guidelines. A non-dimensional operating space incorporating data from all devices with various fuels was used as this design tool. Estimates for potential future combustors operating under different conditions were made using the methodology presented here. It was found that for propane-air combustion in more aggressive microengine designs, combustor volume increases on the order of 1000% are required. The chapter concludes with a review of recommended design guidelines.
Chapter 5
Catalytic Microcombustor Concept

5.1 Motivation and Objective

The work presented thus far has focused on homogeneous gas-phase combustion. It has resulted in an understanding of the combustor volume required for a practical device given requirements for mass flow, turbine inlet temperature, and fuel type. This has also provided an understanding of the operating behavior and performance of a microcombustor with homogeneous gas-phase hydrocarbon-air mixtures. Experimental results described in Chapter 3 and the prediction tool developed in Chapter 4 suggest that a combustor volume of approximately 950 mm$^3$ would be required for a propane-air microcombustor, compared to the baseline volume of 191 mm$^3$ for hydrogen-air mixtures. A sample of experimental results is shown in Figure 5.1 for both hydrogen-air and propane-air combustion to underscore this point. Note the factor of five difference in mass flow range for the two fuels. The difference is attributable to the difference in chemical kinetic rates of the two different fuels.

![Figure 5.1 Performance comparison for different fuel types in gas-phase microcombustor.](image)
Ultimately, it is the goal of the microengine project to develop a power system which operates on practical hydrocarbon fuels such as propane or ethylene. To utilize these fuels without increasing combustor volume or temperature, chemical conversion rates must be increased significantly. Surface catalysis has been identified as a means of increasing reaction rates. Heterogeneous reactions of hydrocarbon-air mixtures over noble metal catalysts are known to be faster than those occurring in the gas-phase. For this basic reason, the development of catalytic microcombustors was pursued. A review of other catalytic combustor work, at the macro and micro-scale, can be found in Sections 5.3 and 5.4 respectively.

5.2 Catalytic Microcombustor Challenges

Although the development of a catalytic microcombustor for a micro gas turbine engine may provide significant performance enhancements over gas-phase devices, there are a host of new challenges and constraints that must be overcome. These include additional time-scale constraints, increased heat loss, increased total pressure loss, and new materials and fabrication issues.

5.2.1 Typical Catalytic Combustor Operation

Catalytic combustors for gas turbines are typically used in aero-derivative ground-based power applications for emissions control rather than to increase reaction rates as required for a microcombustor. These combustors can be designed for very low NOx operation. Due to the increased weight, pressure loss, and narrow operability limits associated with a catalytic combustor, these devices are not yet found on flight engines.

A typical design would consist of a monolith structure (a set of parallel channels) coated with an active catalyst material. Common catalyst materials included noble metals such platinum and palladium as well as more exotic and proprietary metal oxides. The fuel and air flow through the channels and diffuse to the active surface. When a fuel molecule and an oxygen molecule reach the surface they are adsorbed and react releasing heat. The products of the reaction are then desorbed and flow out of the channel. The
heat that has been liberated from the reaction is transferred both conductively through the solid and convectively to the fluid. Eventually, the remaining fuel-air mixture can get hot enough to ignite in the gas-phase. Figure 5.2 shows a schematic of a typical catalytic combustor.

![Schematic of typical catalytic combustor](image)

**Figure 5.2** Schematic of typical catalytic combustor [40].

### 5.2.2 Time-scale Considerations

For catalytic combustors there is an additional time-scale to consider. The reaction time and residence time are still important parameters, however diffusion time must also be accounted for. The time required for a fuel and oxidizer molecule to come into contact with the active catalytic surface can govern the operation of the device.

As a result there are several non-dimensional parameters that can be examined to determine which process governs performance. Combustor residence time and reaction time can be estimated in the same fashion as done in the gas-phase case. Reaction mechanisms for some catalytic reactions can be found in Appendix B. The Damköhler number is the ratio of these two quantities and indicates their relative importance.

\[
Da_h = \frac{\tau_{\text{residence}}}{\tau_{\text{reaction}}} \quad (5.1)
\]
With the additional diffusion time-scale, a second Damköhler number can be defined. This parameter is the ratio of the diffusion time to the reaction time and indicates the relative rates of these two processes.

\[ Da_2 = \frac{\tau_{\text{diffusion}}}{\tau_{\text{reaction}}} \]  

(5.2)

Finally, there is a third ratio of time-scales, which can be examined. The ratio of diffusion time to residence time is known as the Peclet number. For large Peclet numbers (\(>>1\)) reactants do not have time to diffuse to the active surface and simply pass through the combustor unreacted. A device operating under these conditions is said to be mass transfer controlled or diffusion limited.

\[ Pe = \frac{\tau_{\text{diffusion}}}{\tau_{\text{residence}}} \]  

(5.3)

For low Peclet numbers (\(<<1\)), the chemical reaction may be controlling the combustion process and the two Damköhler numbers must be examined. If they are both \(<<1\), then the device is kinetically limited or reaction-controlled.

For the micro-scale devices of interest here, power density has been the primary performance metric. As discussed in Chapter 2, high power density requires high mass flow rates through small chamber volumes resulting in the following relation:

\[ \text{Power density} \propto \frac{\dot{m}}{V} \propto \frac{\rho}{\tau_{\text{residence}}} \]  

(5.4)

Note that at the flow rates and volumes of interest, residence time will be very small and catalytic reaction rates are generally fast when compared to other processes. As a result these devices will likely be diffusion-controlled. Peclet number must then be considered and power density can be rewritten as
Power density \( \propto \frac{\rho Pe}{\tau_{\text{diffusion}}} \). \hspace{1cm} (5.5)

Hence, there is a basic tradeoff between power density and diffusion time. Noting that Peclet number can also be written as a ratio of mass transfer rate to diffusion rate

\[
P_{e} = \frac{Lv}{D} \hspace{1cm} (5.6)
\]

where \( L \) is reactor length and \( v \) is velocity, power density can again be re-written.

\[
\text{Power density} \propto \frac{\rho L v}{D \tau_{\text{diffusion}}} \hspace{1cm} (5.7)
\]

For a given operating pressure and temperature (thus density) and reactant species, reducing diffusion times will increase the power density of the device and improve performance.

5.2.3 Heat Transfer Effects

Heat transfer effects in a gas-phase microcombustor are significant due primarily to the high surface area-to-volume ratios and high thermal conductivity of the silicon structure. In a catalytic device, the heat loss problem becomes worse. Because the reaction and heat release process occurs on the solid surface of the catalyst, there is potentially a direct conduction path out of the device. In the case of the gas-phase microcombustor, there was a thermal boundary layer between the hot reacting gases and the wall helping to limit heat loss. In a catalytic device, the thermal boundary layer acts to isolate the hot wall from the relatively cooler free-stream flow. In addition, surface area-to-volume ratios are likely to be even higher in a catalytic combustor due to the need to fill the chamber with a monolith or porous substance coated with the active catalytic material.
5.2.4 Total Pressure Loss

The thermodynamic cycle constraints of the microengine system require that combustor total pressure loss be less than about 5%. The combustor must be filled with a monolith, a porous substance, or some other substrate material, which is coated with the active catalytic material. Structures such as these in the combustion chamber will increase the total pressure loss. Furthermore, as shown in Section 5.2.2, the power density of a diffusion-controlled device is inversely proportional to the diffusion time. An effective means of reducing diffusion time-scales is to utilize catalyst substrate materials with small diffusion distances and larger surface-area-to-volume ratios (e.g. a monolith with smaller channel diameters or a more dense porous substance). However, these solutions will increase total pressure loss and the desire for high power density must be balanced with this constraint.

5.2.5 Materials and Fabrication Constraints

There are several materials and fabrication issues which arise when developing a catalytic microcombustor. First, the catalyst material itself can be problematic. For noble metals such as platinum, agglomeration of thin layers can occur at elevated temperatures. This phenomenon has been shown to occur at temperatures on the order of 1000 K [41,42]. This is not only a potential problem during the actual combustion process, but also during the high temperature fabrication steps such as the bonding anneal and the glass seal packaging process which both occur at temperatures approaching 1350 K. Agglomeration will reduce the active surface area and negatively impact performance. The substrate material on which the active catalyst is deposited must be also chosen with care. It should be a material with a temperature limit at least as high as that of the catalyst itself and be inert with respect to the catalyst. Finally, thermal shock of the catalyst and substrate material must be considered, especially if ceramic substrates are used.

Catalyst fouling during operation must also be considered. A common deactivation mechanism is for excess carbon from the reactant species to be deposited on the catalyst surface and is known as coking. Carbon deposits cover the active surface and
reactants can no longer adsorb to the catalyst surface thus reducing the activity of the catalyst and performance of the device. This occurs most often with noble metal catalysts operating with rich hydrocarbon mixtures. For the microcombustor, this is not expected to be an issue due to the desire to operate with lean mixture ratios.

The primary fabrication challenge for a catalytic microcombustor is to incorporate the catalyst into the process flow and/or the bonding. A noble metal catalyst material can be deposited directly onto the silicon structure using e-beam deposition or sputtering. However, there must be a high surface area-to-volume ratio structure (approximately an order of magnitude larger than a similar gas-phase device) on which to deposit the layer. This would require an etch in the silicon of some micro-channels or post type structures. An alternate method of fabrication could be to utilize a foreign substance as the substrate material. This substance could then be coated with a catalytic material and fit into the combustion chamber. This would cause difficulties with the bonding process if the baseline silicon structure were kept approximately the same. If these foreign objects were dirty or mishandled while implanting them into the combustion chamber they could destroy the integrity of the bonding surface.

5.3 Review of Conventional Catalytic Combustor Work

Catalytic combustors for conventional gas turbine engines have been a topic of research and development for several decades. The primary focus was (and still is today) reducing NO\textsubscript{x} emissions for ground-based power applications. Pfefferle et. al. spearheaded much of this early work in the mid-1970’s and showed that by using surface catalysis of hydrocarbon fuels over noble metals, low equivalence ratio operation would reduce maximum temperatures and could significantly reduce NO\textsubscript{x} [43]. Various configurations such as staged or hybrid catalytic/gas-phase combustors and graded-cell (varying diameter of monolith channels along flow path) geometries are also presented. This work was followed by researchers at NASA and General Electric who built and tested a catalytic combustor with various monolith structures and active materials (predominantly proprietary catalysts) achieving high combustion efficiencies with ultra-
low NO\textsubscript{x} emissions [44,45,46]. Much of this early work is summarized in a paper by Trimm and includes catalytic reactors for other applications as well [47].

The mid-1990's has brought additional advancement in the field of catalytic combustors for gas turbines, primarily by a group at Catalytica Inc. lead by Dalla Betta and in conjunction with several large gas turbine manufacturers such as General Electric and Allison. These researchers have built and tested multiple catalytic combustors with monolith type structures and advanced catalyst materials. They have used the staged catalytic combustor concept to achieve high exit gas temperatures with low wall temperatures and NO\textsubscript{x} emissions less than 3 ppm [48,49,50,51]. This concept is shown schematically in Figure 5.3. In additional, they have developed a catalyst material, which oxidizes at high temperatures effectively shutting itself off and preventing the combustor from exceeding material temperature limits [52,53]. Similar programs have been developed in Japan at the Institute of Electric Power Industry and at Volvo Aero Corporation in Sweden [54,55].

![Figure 5.3 Schematic of staged catalytic combustion system [49].](image)

Ignition and extinction characteristics for multiple noble metal catalysts and a wide array of fuels are well documented in the work of the Schmidt group at the University of Minnesota. Catalytic ignition, extinction, and the onset of homogenous
combustion have been experimentally mapped for metal foils with impingement flows. The metal catalyst is typically heated resistively while a fuel-air mixture flows directing into the structure. Hydrocarbon fuels ranging from methane to butane in both lean and rich mixture ratios are examined. Active materials include platinum, palladium, iridium, and nickel. For propane-air heterogeneous reactions platinum was shown to operate over the widest range of conditions while nickel showed minimal catalytic activity [56,57,58,59].

5.4 Review of Previous Catalytic Microcombustor Work

Several research groups worldwide have conducted work in the area of micro-scale catalytic reaction devices. This includes the Jensen group at MIT whose work consists of a thermoelectric generator involving a catalytic combustor for a heat source. This combustor is comprised of a channel-type geometry coated with platinum burning butane-air mixtures [60]. Also as part of this research group, Arana developed a suspended tube micro-reactor, which shows an innovative means of managing the heat transfer problems associated with a catalytic microcombustor. In this device, a serpentine tube was fabricated and cantilevered in an open cavity. This open space was evacuated eliminating the convective heat transfer path. All thermal energy leaving the device was either radiated through the cavity or conducted down the length of the small tube. Propane-air mixtures were reacted over a platinum washcoat-type catalyst [61].

At the University of Tokyo, Suzuki et al. have been studying catalytic oxidation reactions in small diameter tubes. These researchers have developed a wall coating of Pt/Al₂O₃ with micro-pore structures. In a tube of diameter 0.6 mm they have observed butane-air ignition at 250°C and power densities of 710 MW/m³ while the apparatus was submerged in a solder bath ranging from 190-400°C. In addition, a silicon-based MEMS fabricated micro-tube catalytic combustion device with the same Pt/alumina catalyst is under development. Initial results have indicated lower power densities due to added heat loss and inadequate catalyst coverage. A concurrent modeling effort has identified the combustor as diffusion-controlled [62].
Ronney et al. at the University of Southern California have developed a "swiss-roll" combustion system from which thermal energy is converted to electrical energy via a thermopile. This device consists of a toroidal shaped tube containing "rolled-up" microchannels, which act as a recuperator and fuel-air preheater. A platinum catalyzed reaction takes place at the center of the device to generate the heat from which electrical power is extracted [63].

Peterson et al. at the Oregon State University have developed a catalytic microcombustion system and have burned both hydrogen-air and propane-air mixtures. This device is arranged in a counterflow configuration and uses platinum wire as the catalyst material. With this device, they have reported the smallest self-sustaining combustion device known with a heat release of 0.25 Watts in a volume of 0.050mm³ with hydrogen fuel. Sub-watt heat release was also achieved with propane-air mixtures [64,65].

5.5 Chapter Summary

This chapter introduces the catalytic microcombustor concept. For the microengine application, catalytic combustion could provide improved combustor performance with hydrocarbon fuels by increasing reaction rates. However, new challenges such as additional time-scale constraints, added heat and total pressure loss, and materials and fabrication complications must be overcome. The chapter concludes with a brief review of catalytic combustion systems for both conventional gas turbines and for micro-scale systems.
Chapter 6

Catalytic Microcombustor Experiments

This chapter presents the data obtained from all catalytic microcombustor experiments. It begins with experiments performed with a simple three-wafer device. This was chosen as an initial test-bed to show feasibility of a catalytic device due to its relative ease of fabrication and assembly. A readily available substrate material coated with platinum acted as the active catalytic material. Upon successful completion of these tests, a six-wafer catalytic microcombustor compatible with the microengine geometry was pursued. The first version of this consisted of the same catalyst substrate material coated with platinum. Following these tests, a second set of catalytic microcombustors with different substrate materials was fabricated and tested. Results of these experiments are presented along with details of the fabrication process.

6.1 Three-wafer Catalytic Microcombustor Test-bed

Initial feasibility tests were carried out on the three-wafer level combustor shown in Figure 6.1. Nickel foam (~95% porous) was selected as a convenient catalyst support material and was conventionally machined to fit in the combustion chamber. An electron-beam deposition process was used to coat the substrate with platinum, which serves as the active catalytic surface. The combustor’s packaging scheme consists of placing the silicon between two conventionally machined invar plates. As a result, inserting catalyst material into the combustion chamber can be done outside of the clean room environment. Figure 6.2 shows an exploded view of the three-wafer combustor, the surrounding invar plates, and the catalytic insert. Figure 6.3 shows a photograph of the nickel foam support as it is fit into a three-wafer device.
Figure 6.1 Schematic of three-wafer microcombustor [11].

Figure 6.2 Exploded view of combustor, catalytic insert, and invar plates for packaging [11].
Figure 6.3 Three-wafer combustor and catalytic insert. (a) SEM cross-section of three-wafer microcombustor. (b) Catalyst substrate prior to insertion into combustion chamber. (c) Catalyst substrate inside combustion chamber.
6.2 Three-wafer Catalytic Microcombustor Performance Testing

Previous gas-phase experiments with the three-wafer combustor showed that hydrocarbon combustion could not be sustained in the device due to insufficient residence time and significant heat loss from the structure [11]. With the catalytic foam piece, combustion of both propane and ethylene was achieved. Figure 6.4 shows the overall combustor efficiencies achieved for both fuels in this device over a range of mixture ratios. Efficiencies in excess of 40% were attained in both cases. This experiment represented the first stable hydrocarbon combustion in this device. In addition, it is important to note that hydrocarbon combustion was stabilized at the same mass flow rate as in the gas-phase hydrogen-air combustion case. This resulted in power densities approximately half of that obtained with gas-phase hydrogen-air combustion rather than the 5 to 50-fold decrease expected for hydrocarbon-air reactions (due to their slower reaction rates) indicating that there was significant catalysis occurring.

![Figure 6.4](image)

Figure 6.4 Three-wafer catalytic microcombustor efficiency. (a) Propane; (b) Ethylene.
6.3 Six-wafer Catalytic Microcombustor Concept

The three-wafer catalytic microcombustor tests led to the pursuit of a six-wafer device with catalyst. The use of foam substrate materials coated with platinum was adopted for these combustors. This would result in minimal fabrication changes to the silicon structure but a significant change to the bonding process.

The baseline six-wafer level microcombustion system compatible with the current microengine design is shown in Figure 6.5. This system includes the previously discussed improved thermal management and a 191 mm$^3$ combustion chamber. For this device, the platinum-coated foam inserts must be placed into the existing design during the fabrication process in the clean room environment. This poses several challenges due to cleanliness of the inserts, particulate contamination of bonding surfaces, and damage to bonding surfaces via mishandling.

![Diagram of baseline microcombustor](image)

Figure 6.5 Baseline microcombustor to be fitted with catalytic insert piece.
6.4 Fabrication Process

In fabricating the six-wafer catalytic microcombustors, several new processes were introduced, however, none of these involved new etches in the primary silicon components. The photolithography masks are nearly identical to those used for the dual-zone microcombustor and can be found in Appendix A. The primary difference is that there are no dilution holes in the catalytic devices. The new processes used include the methods of coating the substrate materials with platinum and the bonding procedure. Both are reviewed below.

6.4.1 Catalyst Substrate Materials

Several catalyst substrate materials were used in the six-wafer devices. For the initial set of catalytic microcombustors, the same nickel foam material used in the three-wafer test-bed was utilized. The porosity of this material is approximately 95%, or the open volume constitutes 95% of the total volume. This parameter will be referred to as $\alpha$ and can be written as

$$\alpha = \frac{V_{\text{open}}}{V_{\text{total}}}.$$  (6.1)

This nickel foam material is shown in Figures 6.6a and 6.6b, which are a photograph and SEM respectively.

The second set of devices consisted of two types catalytic microcombustors. The first contains a foam substrate material made of FeCrAlY with a porosity of approximately 88.5%. This is shown in Figures 6.7a and 6.7b. The other type consists of a porous foam material made of Inconel-625 with a porosity of approximately 78%. Figures 6.8a and 6.8b show this material.
Figure 6.6 Nickel foam substrate material (~95% porosity); (a) Photograph; (b) SEM (50X).

Figure 6.7 FeCrAlY foam substrate material (~88.5% porosity); (a) Photograph; (b) SEM (50X).

Figure 6.8 Inconel-625 foam substrate material (~78% porosity); (a) Photograph; (b) SEM (50X).
6.4.2 Preparation of Pt Coated Catalyst Insert

After machining to the size and shape of the combustion chamber, the foam substrate required a platinum coating, which covered the entire foam piece. Two methods were utilized to produce these layers. The first involved dipping the substrate in a chloroplatinic acid solution while the second consisted of using ionic plasma deposition. The first technique was performed on the 95% porous nickel substrate and the second technique on the FeCrAlY and Inconel-625 substrates (88.5% and 78% porous respectively).

Unsupported metal catalysts can be deposited onto a substrate using a solution of metal salt. In this procedure, the metal salt (H₂PtCl₆ in this case) is dissolved in deionized water. The substrate pieces are soaked in this solution then placed in a small tube furnace. The water is then evaporated followed by reacting the remaining compound with hydrogen at elevated temperature to remove the Cl in the form of HCl leaving only platinum on the surface. The nickel foam pieces of the 1st generation devices were coated using this technique and typically increased in weight by approximately 3%-5% creating layers approximately 2-3 µm thick. The procedure used is listed below.

1. Start with dihydrogen hexachloroplatinate salt (H₂PtCl₆).
2. Mix approximately 2.5 g of H₂PtCl₆ with about 20 ml of deionized water to form H₂PtCl₆·H₂O (~10% Pt-salt solution).
3. Soak nickel foam pieces in solution for approximately 1 hour.
4. Insert pieces into tube furnace.
5. Flow approximately 100 sccm of N₂ at >100°C for ~2 hour.
6. Flow approximately 100 sccm of H₂ at ~300°C for ~3 hours.

The substrate materials for the second set of combustors were coated using ionic plasma deposition. This is a proprietary process developed by Ionic Fusion Corporation and involves propelling atoms of a given material by ionic acceleration and ballistically impregnating a substrate. It is a high energy, low temperature process that provides good penetration into porous substances [66]. The foam pieces were first coated with 2-3 µm of either Al₂O₃ or ZrO₂ followed by 2-3 µm of platinum. The FeCrAlY and Inconel-625
pieces increased in weight by approximately 4% and 2% respectively. The reasons for the ceramic inter-layers are discussed in Chapter 8.

6.4.3 Wafer Bonding Process

To protect the bonding surfaces from the inserts, a "shield wafer" was fabricated. This wafer was etched through with the shape of the inserts and silicon dioxide was deposited on its surface via plasma-enhanced chemical vapor deposition (PECVD). The fourth, fifth, and sixth wafer levels were fusion bonded prior to inserting the catalyst. The shield wafer was then aligned and contacted with these three levels. While in contact, the catalytic pieces were placed into the bonded 4-5-6 wafer stack through the shield wafer. Finally, the protective shield wafer was carefully removed. The PECVD oxide prevented the shield wafer from adhering to the 4-5-6 stack. Insertion of the catalytic pieces can be seen in Figure 6.9.

Figure 6.9 Catalytic pieces being inserted into the six-wafer microcombustor during fabrication
For the first attempt at this bonding process, wafer levels one, two, and three were fusion-bonded forming another three-wafer stack. The final bonding of the two three-wafer stacks was unsuccessful due to the thick, stiff nature of the wafers combined with a small amount of bow. As a result, a new bonding sequence was developed. Rather than bonding two thick three-wafer stacks together, the level three wafer was individually contacted to the 4-5-6 stack with the catalytic pieces. This was followed by individually contacting and bonding the level two and one wafers. As a result, wafer bonding of the first set of devices resulted in good bond quality over most of the wafer. This assembly/bonding process is shown in Figure 6.10. Note that special care should be taken to ensure that the inserts fit well into the opening so that significant quantities of particles are not generated upon insertion of the foam pieces.

Figure 6.10 Fabrication, assembly, and bonding process for six-wafer catalytic microcombustor.

Figure 6.11a shows an infrared image of the six-wafer stack (with 95% porous nickel foam coated with platinum) immediately after contact. A small, well-contacted region can be seen in the center of the wafers. After several hours of room temperature pressing at 4 atm followed by a 500°C thermal-press also at 4 atm, the bond-front propagated radially outward, resulting in 70% device yield. An infrared image after the room temperature press and prior to the thermal-press is shown in Figure 6.11b, while the final bonded stack is shown in Figure 6.11c.
The second set of devices were bonded using the same process. However, an additional difficulty was encountered. The materials used in these devices were much denser (lower porosity) than the nickel used in the first set of combustors. This is especially true for the 78% porous Inconel-625 foam. If these insert pieces protruded above the level of the bonding surface, significant difficulties were encountered. In the case of the nickel, it was compliant enough to undergo some amount of compression during the contacting and bonding process. This was not the case with the denser inserts and proved to be problematic. Even the slightest protrusion above the bonding level by an Inconel piece could prevent bonding and crack the level three wafer. As a result, special care had to be taken to ensure that all pieces were below the bonding surface. Figures 6.12a through 6.12d show the bond progression for the second set of catalytic microcombustors. Note that some cracking in the level three wafer can be seen in the images. Later tests described in Sections 6.7.2 and 6.7.3 indicated that these cracks did not result in leakage from the devices.
Figure 6.12 Infrared images of the catalytic microcombustors with 88.5% porous FeCrAlY-Pt and 78% porous Inconel-Pt: (a) After initial contact; (b) After room temperature press; (c) After thermal-press; (e) After final anneal.
6.5 Ignition Characteristics

To ignite the catalytic microcombustors the catalyst has to be heated to a suitable ignition temperature. Once reaching this temperature, a hydrogen-air mixture was passed through the device and over the platinum catalyst. Initiation of the surface reaction would ensue and both the wall and gas temperatures would rise to some steady-state value. To accomplish this in the microcombustors, the entire chip was preheated with an external heater [15]. After achieving ignition, the heater could be powered down and the device would continue to operate with auto-thermal combustion of the hydrogen-air mixture over platinum. Typically, a catalytic combustor will exhibit an ignition/extinction hysteresis similar to that shown by Schmidt et al. [56,57,58,59]. For the 95% porous nickel foam and the 88.5% porous FeCrAlY foam this is shown in Figure 6.13. Wall temperature is plotted against heater power and ignition occurs at a heater power of approximately 20%-30% (around 80-100°C). This figure is intended only to qualitatively show the ignition process and to illustrate the hysteresis. The heater power parameter is not an appropriate metric for comparison and no specific conclusions regarding a device’s ignition performance or comparison to other devices should be made.

Figure 6.13 Ignition characteristics for catalytic microcombustors.
6.6 Propane Ignition Procedure

Although the catalytic microcombustors initially ignite with a hydrogen-air mixture, ultimately, the goal is to achieve auto-thermal combustion of propane-air mixtures over the platinum catalyst. To accomplish this, the device must be brought to a high enough temperature to initiate propane-air catalytic reactions. This ignition temperature is significantly higher than that required for the hydrogen-air mixture and is on the order of 600 K [59]. This temperature is not attainable with the external heater. However, the heater can be used to ignite a hydrogen-air mixture that can heat the catalyst to the required level for propane mixtures. Propane is then added in small quantities until its ignition is observed via an additional temperature rise. At this point, the hydrogen concentration is lowered while propane is added to the mixture until there is only propane and air. This ignition procedure and conversion to propane-air operation is summarized in the steps listed below.

1. Heat the entire device to ~400 K with the external heater.
2. Flow a hydrogen-air mixture at an equivalence ratio of 0.5 and an air flow rate of 0.02 g/s through the device.
3. Observe ignition of hydrogen-air mixture and wait several minutes for steady state. Temperature should exceed 700 K.
4. Power down heater and achieve auto-thermal operation with hydrogen.
5. Introduce propane at an equivalence ratio of approximately 0.7 and observe temperature rise.
6. Reduce hydrogen concentration and increase propane until no hydrogen is left and auto-thermal catalytic combustion of propane is achieved.
7. Set desired operating conditions and conduct tests.

6.7 Performance Testing

The following sections review the test results for two types of catalytic microcombustors. Pressure loss, exit gas temperature, wall temperature, and efficiencies will be presented and discussed.
6.7.1 Nickel Foam Substrate (95% porosity)

Initial tests in the first set of devices were performed on combustors which were fabricated without platinum on the nickel foam surface. This was done to isolate the effect of the foam structure itself inside the combustion chamber. Figure 6.14 shows the exit gas temperature for such a device operating with propane-air combustion. The temperatures and flow rates are comparable to that achieved in the gas-phase devices and indicates that there is no catalytic activity and minimal effect from the foam itself.

![Figure 6.14 Exit gas temperature plot for microcombustor with non-catalytic foam.](image)

In the case of the microcombustors with platinum, plots of exit gas temperature and overall combustor efficiency for a range of mixture ratios are shown in Figures 6.15 and 6.16 respectively. Figure 6.17 shows a pressure trace. Maximum exit gas temperature achieved was approximately 850-900 K over a wide range of flow rates and efficiencies were up to 30%. The sharp drop in performance at 0.35 g/s was a result of transients from the mass flow controllers that were operating at maximum flow levels. Although these temperatures and efficiencies are quite low, the mass flow rates achieved were in excess of 0.4 g/s, well beyond the design mass flow rates for the microengine. These mass flow rates of interest are noted on the figures with a vertical dashed line. The
maximum power density achieved was approximately 1050 MW/m³, which is a 7.5-fold increase over gas-phase propane-air power densities and about 95% of that for gas-phase hydrogen-air mixtures.

Figure 6.15 Exit gas temperature plot for a catalytic microcombustor with Ni-Pt.

Figure 6.16 Overall combustor efficiency for a catalytic microcombustor with Ni-Pt.
Figure 6.17 Combustor pressure for 95% porous nickel foam substrate material.

Figure 6.18 shows the wall and gas temperatures for an equivalence ratio of unity. As mass flow rate increases, the recirculation jacket becomes more effective at retaining the heat in the primary flow as shown by the divergence of the wall and gas temperature. The overall combustor efficiency can be broken down into its thermal and chemical components. The wall temperature measurement combined with a 1-D heat transfer model reveal that although heat loss is greater than in the gas-phase case, losses are dominated by chemical inefficiency. Figure 6.19 shows a breakdown of the efficiencies in the device for a stoichiometric mixture ratio.

Another interesting feature of these devices is their performance at low mass flow rates. In the gas-phase case, mass flow rates could be driven very close to zero prior to extinguishing of the flame. The catalytic surface reaction appears to be much more sensitive to heat loss at low mass flow rate. Figure 6.20 shows the wall and gas temperatures for catalytic propane-air combustion at an equivalence ratio of 0.8. The reaction extinguishes at a mass flow rate of approximately 0.06 g/s, which is significantly greater than in the gas-phase devices due to increased heat loss.
Figure 6.18 Wall and gas temperatures for catalytic microcombustor with Ni-Pt, $\phi=1.0$.

Figure 6.19 Efficiency breakdown for catalytic microcombustor with Ni-Pt, $\phi=1.0$. 
Figure 6.20 Temperatures for catalytic microcombustor with Ni-Pt at $\phi=0.8$. Mass flow rate was decreased until flame extinguished.

Pressure drop through the combustor is also a critical parameter for the overall engine design. Due to thermodynamic cycle constraints for engine operation, total pressure loss must be limited to less than 5%. Figure 6.21 shows that the pressure drop through the catalytic microcombustor is between 1%-3% for mass flow rates of interest. This was based on estimates of the Mach number and pressure measurements far upstream in the recirculation jacket and in the combustion chamber itself.
Figure 6.21 Total pressure loss for catalytic microcombustor with Ni-Pt.

Another important feature to note regarding these microcombustors is that nearly all of the data presented here was obtained from one device. This combustor was operated for a total of approximately 13 hours of hot test time and underwent nine ignition cycles and three auto-thermal propane runs. However, of the other devices that were tested, none performed at the same level. Most ignited with hydrogen and only some of the devices could successfully be converted to propane operation. Of those able to operate with propane, none achieved the same temperature levels or efficiencies as those presented here. Possible reasons for this variable performance are discussed in Chapter 8.

6.7.2 FeCrAlY Foam Substrate (88.5% porosity)

The catalytic microcombustors with FeCrAlY (88.5% porous) were lit using the hydrogen and propane ignition procedures described in Sections 6.5 and 6.6. Plots of exit gas temperature and overall combustor efficiency for a range of equivalence ratios are shown in Figures 6.22 and 6.23 respectively. Figure 6.24 shows a pressure trace for this
device. Maximum exit gas temperatures achieved were in excess of 1050 K and efficiencies approached 40%. The mass flow rates achieved were greater than 0.35 g/s and in the range of the design mass flow rate of the microengine as indicated by the dashed lines. The maximum power density achieved was 1200 MW/m³, which is approximately an 8.5-fold increase over gas-phase propane-air power densities and about a 10% increase over that achieved by the gas-phase hydrogen-air device. In addition, no leaks were detected in the silicon due to the cracks shown in Section 6.4.3.

Figure 6.22 Exit gas temperature plot for a catalytic microcombustor with FeCrAlY-Pt.
Figure 6.23 Overall combustor efficiency for a catalytic microcombustor with FeCrAlY-Pt.

Figure 6.24 Combustor pressure for 88.5% porous FeCrAlY foam substrate material.
Figure 6.25 shows the wall and gas temperatures for this device operating with an equivalence ratio of 0.9. As in the case of the 95% porous Ni-Pt device, at higher mass flow rate the recirculation jacket is more effective as indicated by the declining wall temperature. Figure 6.26 is a plot of the efficiency breakdown for an equivalence ratio of unity. Again, losses are dominated by chemical inefficiency with a maximum chemical efficiency near 45%.

Pressure losses can be seen in Figure 6.27. Again, for the flow rates of interest (as indicated by the dashed lines), the pressure loss is less than the 5% constraint and is between 1%-3.5%. As done previously, the pressure loss calculations are based on estimates of the Mach number and pressure measurements far upstream in the recirculation jacket and in the combustion chamber itself.

![Figure 6.25 Wall and gas temperatures for catalytic microcombustor with FeCrAlY-Pt, φ=0.9.](image)
Figure 6.26 Efficiency breakdown for catalytic microcombustor with FeCrAlY-Pt, $\phi$=1.0.

Figure 6.27 Total pressure loss for catalytic microcombustor with FeCrAlY-Pt.
6.7.3 Inconel-625 Foam Substrate (78% porosity)

The testing of the catalytic microcombustors with Inconel-625 foam was not as successful as with the nickel and FeCrAlY foams. Three devices were packaged and tested. None of these combustors would ignite with hydrogen-air or propane-air mixtures. The typical ignition procedures were attempted followed by higher heater settings and various flow rates and equivalence ratios. None of these variations on the startup procedure were successful. However, cold flow pressure data could be obtained. Figure 6.28 shows the cold flow pressure loss for all three of the Inconel-625 devices that were tested. Note that device #2 had lower pressure loss primarily due to a leak in the glass seal packaging while devices #1 and #3 are approaching 4% total pressure loss. The inability to light these combustors may be due to the fuel-air mixture channeling around the foam rather than through it. Significant gaps may have been present around the foam due to the need to ensure that it easily fit into the combustion chamber for bonding purposes. Other possible failure mechanisms include platinum agglomeration during high temperature processing and inadequate platinum coverage inside the foam.

![Graph showing cold flow total pressure loss for catalytic microcombustors with Inconel-Pt.](image)
6.8 Device Comparisons

Figures 6.29 and 6.30 show exit gas temperatures and overall combustor efficiency comparisons for the nickel foam and FeCrAlY foam devices both operating at a stoichiometric equivalence ratio. The lower porosity FeCrAlY combustor achieved exit gas temperatures over 150 K higher than the 1st generation combustor. This corresponds to an approximately 2%-10% higher efficiency over a range of mass flow rates. To further illustrate the performance improvement achieved by the 88.5% porous foam device, Figure 6.31 shows an efficiency comparison of the two combustors operating at an equivalence ratio of 0.9. The FeCrAlY device is superior in efficiency and mass flow rate capability.

![Exit gas temperature plot comparing Ni-Pt and FeCrAlY-Pt devices for φ=1.](image-url)
Figure 6.30 Overall combustor efficiency plot comparing Ni-Pt and FeCrAlY-Pt devices for $\phi=1$.

Figure 6.31 Overall combustor efficiency plot comparing Ni-Pt and FeCrAlY-Pt devices for $\phi=0.9$. 
The efficiency breakdown for both devices indicates that they are severely limited by chemical losses. Because these chemical inefficiencies seem to dominate performance, a comparison of this parameter between the two devices is shown in Figure 6.32. This Figure indicates that the lower porosity FeCrAlY foam material provides a 2%-10% improvement in chemical efficiency over a range of flow rates. This may be due to shorter diffusion distances and higher surface area-to-volume ratios of the active catalytic surface. These potential explanations of the improved performance are further explored in Chapter 7. In addition, this improvement is consistent with results shown by Peck in a conventionally machined, small-scale catalytic combustor [15].

Finally, the pressure losses from the two devices are compared in Figure 6.33. The lower porosity (higher density) FeCrAlY material exhibits higher pressure loss as expected. However, both devices are below the 5% total pressure loss desired by the thermodynamic cycle of the microengine.

![Chemical efficiency plot comparing Ni-Pt and FeCrAlY-Pt devices for φ=1.](image)

Figure 6.32 Chemical efficiency plot comparing Ni-Pt and FeCrAlY-Pt devices for φ=1.
6.9 Chapter Summary

This chapter has presented all of the catalytic microcombustor experiments for the microengine. An initial three-wafer proof of concept device was fabricated and tested. This combustor indicated that using platinum deposited on 95% porous nickel foam could provide improved combustion performance of propane-air mixtures over that achieved in the gas-phase devices.

A six-wafer catalytic microcombustor compatible with the microengine geometry was then pursued. The fabrication of these devices is presented with attention given to the substrate materials, platinum coating processes, and the wafer bonding process. The devices with platinum deposited on 95% porous nickel foam operated at exit gas temperatures in excess of 850 K, combustor efficiencies of approximately 30%, and mass flow rates above the engine design value of 0.35 g/s with propane-air mixtures. This performance corresponds to a power density of 1050 MW/m³ or a 7.5-fold increase over the gas-phase propane-air microcombustor experiments.
A second set of catalytic microcombustors using the same bonding process but different substrate materials and platinum coating processes was fabricated. The catalytic microcombustor with a catalyst substrate of 88.5% porous FeCrAlY operated with exit temperatures over 1050 K, efficiencies approaching 40%, and mass flow rates above 0.35 g/s with propane-air mixtures. This corresponds to a power density of 1200 MW/m$^3$ or an 8.5-fold increase over the gas-phase case. Similar devices with 78% porous Inconel-625 would not ignite.

An efficiency breakdown indicated that both combustors were dominated by chemical losses. Chemical efficiencies were approximately 30% for the 95% porous nickel-platinum device and 5%-8% higher for the 88.5% FeCrAlY-platinum combustor operating at the same conditions. Other direct comparisons of the two combustors showed that the device with the less porous (more dense) substrate material operated at higher temperatures and overall efficiencies but had greater pressure loss.
Chapter 7

Catalytic Microcombustor Modeling

Several levels of modeling have been pursued to better understand the operation of a catalytic microcombustor and to develop design tools and recommendations. A pressure loss correlation has been utilized to estimate the drop in stagnation pressure through a given catalyst substrate. Time-scale analyses have identified the limiting factors and important non-dimensional parameters, which govern high power density catalytic combustor performance. A one-dimensional isothermal plug flow reactor model was developed to further explore combustor performance over a range of conditions and catalyst geometries. This parametric study is synthesized in a model-based non-dimensional operating map.

7.1 Time-Scale Analysis

To determine which phenomena control the combustion process in a catalytic microcombustor, relevant physical time-scales (or velocities) can be evaluated. These include, reaction time, residence time, diffusion time of the fuel species, and diffusion time of the oxidizer. Residence time can be estimated from the volume, mass flow rate, pressure, and bulk gas temperature as in the gas-phase case.

\[ \tau_{\text{residence}} \approx \frac{VP}{mRT} \]  

(7.1)

Reaction rate can be obtained from an Arrhenius type rate expression. For a propane-air reaction on a platinum catalyst, the following mechanism can be used [36]

\[ (-R_{C_3H_8}) = k_s [C_3H_8] \]  

(7.2)
where the rate constant is

\[ k_s = 2.4 \times 10^5 \exp \left( -\frac{1.08 \times 10^4}{T} \right). \]  

(7.3)

Additional reaction mechanisms can be found in Appendix B. Molecular diffusion coefficients for propane and oxygen diffusion through air can be obtained from the Fuller correlation [36]:

\[ D_{AB} = \frac{1.013 \times 10^{-2} T^{1.75} \left( \frac{I}{M_A} + \frac{I}{M_B} \right)^{\frac{3}{2}}}{P \left[ \left( \sum v_i \frac{\sqrt{3}}{2} \right)^2 + \left( \sum v_i \frac{\sqrt{3}}{2} \right)^2 \right]^2}. \]  

(7.4)

\( M_A \) and \( M_B \) are the molecular weights of the species and \( v_i \) is the diffusion volume of each atom in the molecule. A table of diffusion volumes is shown below. This correlation is based on collision theory and \( D_{AB} \) is in units of \( \text{m}^2/\text{s} \).

**Table 7.1** Diffusion volumes of various atoms and simple molecules [36].

<table>
<thead>
<tr>
<th>Species</th>
<th>Diffusion Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>16.5</td>
</tr>
<tr>
<td>H</td>
<td>1.98</td>
</tr>
<tr>
<td>O</td>
<td>5.48</td>
</tr>
<tr>
<td>N</td>
<td>5.69</td>
</tr>
<tr>
<td>H₂</td>
<td>7.07</td>
</tr>
<tr>
<td>N₂</td>
<td>17.9</td>
</tr>
<tr>
<td>O₂</td>
<td>16.6</td>
</tr>
<tr>
<td>Air</td>
<td>20.1</td>
</tr>
<tr>
<td>CO</td>
<td>18.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>26.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>12.7</td>
</tr>
</tbody>
</table>
Using estimates of these various time-scales, non-dimensional parameters can be calculated and used to determine the governing physical phenomena. These parameters and their approximate values for a catalytic microcombustor are summarized below in Table 7.2. From this simple time-scale analysis, it is clear that diffusion of reactants to the surface is a controlling parameter. The second Damköhler number indicates that the surface reaction rate is much faster than the rate of diffusion to the surface. The Peclet number indicates that reactants can flow through the device without coming into contact with the active catalytic surface and number less than unity are desired. The longest time-scale in the system is the diffusion time.

Table 7.2 Summary of non-dimensional parameters.

<table>
<thead>
<tr>
<th>Non-dimensional parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damköhler number for</td>
<td></td>
</tr>
<tr>
<td>residence time</td>
<td>( Da_h = \frac{\tau_{\text{residence}}}{\tau_{\text{reaction}}} )</td>
</tr>
<tr>
<td>Damköhler number for</td>
<td></td>
</tr>
<tr>
<td>diffusion time</td>
<td>( Da_2 = \frac{\tau_{\text{diffusion}}}{\tau_{\text{reaction}}} )</td>
</tr>
<tr>
<td>Peclet number</td>
<td>( Pe = \frac{\tau_{\text{diffusion}}}{\tau_{\text{residence}}} )</td>
</tr>
</tbody>
</table>

If a tubular plug flow reactor is assumed, the Peclet number can be estimated and shown to be a strong function of geometry. For a given set of flow conditions (pressure, temperature, and mass flow rate) Peclet number can be calculated for a range of diameters (or pore sizes). In this case, the gas velocity through the tube and the length of the tube are based on the actual micro-combustor. Figure 7.1 shows this parameter for \( P = 2 \) atm, \( T = 1000 \) K, and a mass flow rate = 0.3 g/s for both propane and oxygen. For the diameters (or pore sizes) of interest (\(~0.2-0.6\) mm for the 95% porous nickel foam that was used in the first set of catalytic microcombustors) the Peclet number is significantly larger than unity. It is also important to note that propane diffuses more slowly than oxygen due to its larger molecule. This results in a larger Peclet number and indicates that propane diffusion to the active surface is the governing phenomenon.
7.2 Pressure Loss Analysis

Pressure loss through a porous substrate can be estimated from the Ergun equation for Reynolds numbers less than 300 (based on the thickness of a fiber or diameter of a catalyst particle) [36]:

$$\frac{dP}{dz} = \frac{-\nu (1-\alpha)^{\frac{1}{2}}}{l \alpha^\frac{1}{2}} \left[ \frac{150 \mu (1-\alpha)}{l} + 1.75 \rho \nu \right],$$

where $\mu$ is the viscosity, $\nu$ is velocity through the porous media, and $l$ is a characteristic length scale, usually the width of a foam fiber or diameter of a particle in a packed bed. For the substrates of interest, Reynolds numbers are approximately 200-300. The porosity of the substrate is denoted by $\alpha$ and is defined as the ratio of the open volume to total volume:
\[ \alpha = \frac{V_{\text{open}}}{V_{\text{total}}} \]  

(7.6)

Figure 7.2 shows an estimate of pressure loss through the nickel foam (95% porous) and the FeCrAlY foam (88.5% porous) used in the catalytic microcombustors. The thickness of a foam fiber was approximately 80-100 μm measured using a scanning electron microscope. The actual pressure vs. mass flow characteristic from the catalytic microcombustor experiments was used as an input. The temperature was held constant at 1000 K. The pressure drop associated with this material is very low according to the Ergun calculation while the measured pressure drop in the experiment was significantly higher, in the range of 1%-3%. However, the experiment measures the loss through the entire device not just the foam. If the measured pressure loss through the device without catalyst material is subtracted from that measured in this set of experiments, the loss attributable to the foam can be estimated. Total pressure loss from the original gas-phase device can be found in reference [11]. The data points at the bottom of Figure 7.2 are obtained by subtracting the total pressure loss of the gas-phase device from that of the catalytic micro-combustor.

![Figure 7.2](image)

**Figure 7.2** Pressure loss versus mass flow rate for porous media, comparing estimates from equation 7.5 and experimental data.
The additional curves shown on Figure 7.2 indicate the estimated pressure loss (based on equation 7.5) for lower porosity substrates (more dense foams). The same pressure vs. mass flow characteristic, reactor temperature, and fiber thickness was used. The stagnation pressure loss through the foam increases as porosity decreases. However, the chart indicates that a significant decrease in porosity (and increase in catalytic material) can be introduced into the reactor without violating the maximum allowable combustor pressure loss of 5%. If the 1%-3% system pressure loss is included with this estimate of catalyst pressure loss, a substrate with a porosity of approximately 80%-85% could be used in the device.

### 7.3 Isothermal Tubular Plug Flow Reactor Model

A steady state, one-dimensional, isothermal, plug flow reactor model has been developed to examine important trends in performance. A tubular or porous media geometry can be incorporated into the model. The following sections discuss the model development, including the derivation of the governing equations and solution method, as well as the results of the model over a variety of geometries and flow conditions.

#### 7.3.1 Governing Equations – Tubular Reactor

The equations developed here will be for a tubular reactor. In later sections these expressions will be modified to account for a porous media reactor. The model consists primarily of two ordinary differential equations and one algebraic equation, which are derived from a control volume analysis. These equations coupled with the isothermal assumption will yield trends in fuel conversion and bulk gas temperature rise through the reactor as a function of flow conditions and geometry.

A steady state gas-phase mole balance across the control volume shown in Figure 7.3 will yield the first equation. The Peclet number analysis indicated that the diffusion of propane is the governing phenomenon, therefore only the mass transport and consumption of the fuel species is taken into account in all subsequent derivations. Homogeneous gas-phase reactions will be neglected and the catalytic reaction mechanism shown in Section 7.1 will be utilized for all further analyses.
The gas-phase mole balance can generally be written as

\[
\begin{bmatrix}
\text{moles transported into volume} \\
\text{moles transported out of volume}
\end{bmatrix}
- \begin{bmatrix}
\text{moles reacted in gas phase} \\
\text{moles transported to Pt surface}
\end{bmatrix}
= 0
\] (7.7)

The third term, moles reacted in gas-phase, is equal to zero because homogeneous reactions are being neglected. The first two terms can be written as a molar flow rate of fuel species (propane in this case).

\[
\begin{bmatrix}
\text{moles transported into volume} \\
\text{moles transported out of volume}
\end{bmatrix}
= \left( F_{\text{fuel}} \right)_z - \left( F_{\text{fuel}} \right)_{z+\Delta z}
= -\Delta F_{\text{fuel}}
\] (7.8)

The fourth term, which describes the transport of fuel species out of the control volume to the catalyst surface, can be written as

\[
\begin{bmatrix}
\text{moles transported to Pt surface}
\end{bmatrix}
= k_m C_b \left( Y_{\text{fuel,b}} - Y_{\text{fuel,S}} \right) \Delta A_S
\] (7.9)
where \( k_m \) is a mass transport coefficient, \( C_b \) is the molar density, \( Y_{\text{fuel,b}} \) is the mole fraction of fuel in the bulk gas stream, \( Y_{\text{fuel,S}} \) is the mole fraction of fuel at the surface, and \( \Delta A_S \) is the incremental surface area. The transport of fuel species is driven by the concentration gradient.

Combining all of the terms from above, the expression for the gas-phase mole balance over the control volume becomes

\[
\Delta F_{\text{fuel}} + k_mC_b(Y_{\text{fuel,b}} - Y_{\text{fuel,S}})\Delta A_S = 0. \tag{7.10}
\]

Noting that

\[
\Delta F_{\text{fuel}} = C_b \nu Y_{\text{fuel,b}} \tag{7.11}
\]

where \( \nu \) is the bulk gas velocity and normalizing by

\[
\Delta V = A_C \Delta z \tag{7.12}
\]

the expression can be written as

\[
\frac{\Delta(C_b \nu Y_{\text{fuel,b}})}{\Delta z} + \frac{4}{d_h} k_mC_b(Y_{\text{fuel,b}} - Y_{\text{fuel,S}}) = 0. \tag{7.13}
\]

Finally, assuming that the control volume is a differential element, the following first order differential equation is obtained.

\[
C_b \nu \frac{dY_{\text{fuel,b}}}{dz} + \frac{4}{d_h} k_mC_b(Y_{\text{fuel,b}} - Y_{\text{fuel,S}}) = 0 \tag{7.14}
\]

The mass transport coefficient is analogous to the heat transfer coefficient and can be written as
where \(D_{AB}\) is the diffusion coefficient for propane in air and can be found using the Fuller correlation as shown in Section 7.1, \(d\) is the tube diameter, and \(Sh\) is the Sherwood number. The Sherwood number is similar to the Nusselt number for heat transfer and for laminar flow in a duct; the following correlation can be used [35].

\[
Sh = 3.66 \left[ 1 + 0.095 \left( \frac{d}{L} \right) Re Sc \right]^{0.45} \tag{7.16}
\]

\(L\) is the reactor length and \(Re\) and \(Sc\) are the Reynolds and Schmidt numbers respectively.

\[
Re = \frac{\rho vd}{\mu} \tag{7.17}
\]

\[
Sc = \frac{\mu}{\rho D_{AB}} \tag{7.18}
\]

A similar molar balance can be conducted at the catalyst surface. Assuming that all fuel species, which come into contact with catalyst react, the moles transported to the surface must equal the moles reacted on the surface.

\[
\begin{bmatrix}
\text{moles transported to Pt surface}
\end{bmatrix} = 
\begin{bmatrix}
\text{moles reacted on Pt surface}
\end{bmatrix} \tag{7.19}
\]

The transport term is the same as in the gas-phase mole balance. The surface reaction term can be written as

\[
\begin{bmatrix}
\text{moles reacted on Pt surface}
\end{bmatrix} = (-R_{\text{fuel}})_S \Delta A_S \tag{7.20}
\]
where \((-R_{\text{fuel}})_{S}\) is the reaction rate obtained from the mechanism in Section 7.1 and \(\Delta A_{S}\) is the incremental surface area. The mole balance can then be written as

\[
k_m C_b (Y_{\text{fuel},b} - Y_{\text{fuel},S}) \Delta A_S = (- R_{\text{fuel}})_{S} \Delta A_S.
\]  

(7.21)

Canceling the surface area results in the algebraic equation

\[
k_m C_b (Y_{\text{fuel},b} - Y_{\text{fuel},S}) = (- R_{\text{fuel}})_{S}.
\]

(7.22)

The mass transport coefficient is found in the same manner as that described above for the gas-phase mole balance.

The third and final equation (second ordinary differential equation) can be obtained by performing a gas-phase energy balance across the fluid element shown in Figure 7.3. In general terms, this energy balance is

\[
\begin{bmatrix}
\text{enthalpy rise from heat addition} \\
\text{heat added from surface}
\end{bmatrix} = \begin{bmatrix}
\text{heat added from gas-phase reaction}
\end{bmatrix}.
\]

(7.23)

The gas-phase reaction term is zero because only catalytic reactions are being considered in this model. The enthalpy rise (left hand side of the expression) can be written as

\[
\begin{bmatrix}
\text{enthalpy rise from heat addition}
\end{bmatrix} = \dot{m} C_p \Delta T_b
\]

(7.24)

where \(\dot{m}\) is the mass flow rate, \(C_p\) is the specific heat of the gas, and \(T_b\) is the bulk gas temperature. The heat generated from the surface reaction is transferred to the gas stream and can be expressed as
where \( h \) is the heat transfer coefficient and \( T_s \) is the catalyst surface temperature. All other variables are the same as in previous sections. The energy balance then becomes

\[
-h \cdot C_p \Delta T_b + \Delta A_s h(T_s - T_b) = 0. \tag{7.26}
\]

Again normalizing by

\[
\Delta V = A_c \Delta z \tag{7.27}
\]

and taking the control volume to be a differential element, an ordinary differential equation is obtained.

\[
- \rho C_p \frac{dT_b}{dz} + \frac{4}{d_h} h(T_s - T_b) = 0 \tag{7.28}
\]

The heat transfer coefficient \( h \) can be written as

\[
h = \frac{Nu \cdot k_b}{d} \tag{7.29}
\]

where \( Nu \) is the Nusselt number and \( k_b \) is the thermal conductivity of the bulk fluid. These quantities can be estimated from the following correlations [35].

\[
Nu = 3.66 \left[ 1 + 0.095 \left( \frac{d}{L} \right) Re \ Pr \right]^{0.45} \tag{7.30}
\]

\[
k_b = 1.679 \times 10^{-2} + 5.073 \times 10^{-5} T_b \tag{7.31}
\]
The Prandtl number is approximately 0.7 for gases and can be found from

\[ Pr = \frac{\mu C_p}{k_b}. \]  \hfill (7.32)

### 7.3.2 Solution Method

The two differential equations have analytical solutions or can be solved numerically by discretizing and implementing a solution algorithm such as a Newton-Raphson technique. The bulk gas temperature, bulk gas fuel mole fraction, and the surface mole fraction can be found as a function of reactor axial location. Analytical expressions for these parameters are:

\[
T_b(z) = T_S + \left[ T_b(0) - T_S \right] e^{-\frac{\theta}{\rho C_p}} z \]  \hfill (7.33)

\[
Y_{fuel,b}(z) = Y_{fuel,b}(0) + \left[ Y_{fuel,b}(0) - Y_{fuel,b}(z) \right] e^{-\frac{\theta}{\rho C_p}} z \]  \hfill (7.34)

\[
Y_{fuel,S}(z) = \left[ k_m Y_{fuel,b}(z) \right] \left( k_m + k_s \right) \]  \hfill (7.35)

The boundary conditions required to run the model include the inlet bulk gas temperature, the inlet bulk gas fuel mole fraction (obtained from equivalence ratio), and the inlet surface mole fraction. The catalyst surface temperature also must be specified and due to the isothermal condition is constant throughout the reactor. A typical set of boundary conditions is shown in Table 7.3.

**Table 7.3 Typical boundary conditions for reactor inlet in 1-D isothermal plug flow model.**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_b$</td>
<td>500 K</td>
</tr>
<tr>
<td>$T_S$</td>
<td>1000 K</td>
</tr>
<tr>
<td>$Y_{fuel,b}$ (from $\phi$)</td>
<td>0.04 ($\phi=1.0$)</td>
</tr>
<tr>
<td>$Y_{fuel,S}$</td>
<td>0.00</td>
</tr>
</tbody>
</table>
7.3.3 Results – Tubular Reactor

The model can be used to estimate performance for a set of flow conditions and geometry approximating the actual catalytic microcombustor. Figure 7.4 shows the axial wall temperature and bulk gas temperature profiles through the plug flow reactor for an inlet gas temperature of 500 K, a wall temperature of 1000 K, a pressure of 2 atm, an equivalence ratio of 1.0, and a mass flow rate of 0.3 g/s. As the gas moves along the length of the tube it approaches the wall temperature. Figure 7.5 shows conversion along the tube and indicates that the final conversion of fuel is approximately 60%. Figure 7.6 is the axial concentration profile of propane in the bulk gas and at the wall up to 5 mm downstream (selected based on length of actual device).

Figure 7.4 Axial temperature profile along plug flow reactor.
Figure 7.5 Axial conversion profile along plug flow reactor.

Figure 7.6 Axial fuel concentration profile along plug flow reactor.
If the model is run for a constant geometry and catalyst temperature over a range of mass flow rates and pressures similar to those in the actual microcombustor, a trend in conversion vs. mass flow rate can be generated. Figure 7.7 shows fuel conversion plotted against mass flow rate for this situation. Although the values obtained here are significantly higher than the chemical efficiencies from the experiment, the trend is similar. After an initial high rate of conversion at low mass flow rate, the conversion begins to drop. However, at higher mass flow rates the level of fuel conversion seems to stabilize around 65%. This can be explained by considering the Peclet number. At low mass flow rates residence times are high and diffusion of fuel to the surface can easily take place. As mass flow rate increases, residence time decreases resulting in less time for diffusion. However, when the device becomes choked, pressure increases linearly with mass flow rate. As a result, residence time becomes relatively constant over a range of mass flow rates. For these temperatures and pressures, the diffusion time-scale does not vary significantly and the Peclet number is approximately constant.

![Graph showing propane conversion versus mass flow rate for constant geometry and wall temperature.](image.png)

Figure 7.7 Propane conversion versus mass flow rate for constant geometry and wall temperature.
7.4 Isothermal Porous Media Plug Flow Reactor Model

7.4.1 Governing Equations – Porous Media Reactor

The three governing equations for the tubular reactor must be modified to account for a consolidated porous substrate. Generally, the derivations proceed in the same manner but have different geometric parameters. For the fluid mole balance, the \(4/d_h\) parameter is replaced with the surface area-to-volume ratio

\[
a_v = \frac{\Delta SA}{\Delta V} = \frac{SA}{V}
\]  

(7.36)

and the expressions becomes

\[
C_b \nu \frac{dY_{\text{fuel},b}}{dz} + a_v k_m C_b (Y_{\text{fuel},b} - Y_{\text{fuel},S}) = 0.
\]

(7.37)

The surface area-to-volume ratio can also be written in terms of porosity and foam fiber thickness as

\[
a_v = \frac{4(1-\alpha)}{w}.
\]

(7.38)

The catalyst surface mole balance becomes

\[
k_m C_b \left(Y_{\text{fuel},b} - Y_{\text{fuel},S}\right) = \left(-R_{\text{fuel},S}\right) (1-\alpha).
\]

(7.39)

Finally, the geometric parameter in the fluid energy balance equation is modified and the differential equation becomes

\[
- \rho C_p \nu \frac{dT_b}{dz} + a_v h (T_s - T_b) = 0.
\]

(7.40)
Correlations for gases in packed bed reactors have been used to approximate the heat and mass transfer coefficients in porous substrates. These transport coefficients are given in terms of non-dimensional $j$ factors; $j_D$ for mass transfer and $j_H$ for heat transfer.

$$j_D = \frac{k_m}{v}Sc^{2/3} \quad (7.41)$$

$$j_H = \frac{h}{C_p \rho v}Pr^{2/3} \quad (7.42)$$

These $j$ factors can be estimated using the following correlations [36].

$$j_D = j_H = 0.91 Re_j^{0.51} S_f \quad \text{Re}_j < 50 \quad (7.43)$$

$$j_D = j_H = 0.91 Re_j^{0.41} S_f \quad \text{Re}_j > 50 \quad (7.44)$$

$s_f$ is the shape factor and for this analysis a value of 0.79 was used (shape factor for ring-type structures). The Reynolds number used here can be found from

$$Re = \frac{\rho w}{6(l - \alpha) \mu S_f} \quad (7.45)$$

where $w$ is the thickness of a fiber in the foam substrate.

### 7.4.2 Solution Method – Porous Media Reactor

The expressions for the porous media reactor can be solved in the same manner as in the tubular case. The analytical solutions are shown below.

$$T_b(z) = T_S + [T_b(0) - T_S]e^{-\frac{a_h}{C_p v} z} \quad (7.46)$$

$$Y_{fuel,h}(z) = Y_{fuel,S} + [Y_{fuel,h}(0) - Y_{fuel,S}]e^{-\frac{a_s \alpha_n}{v} z} \quad (7.47)$$
\[ Y_{\text{fuel, S}}(z) = \frac{k_m Y_{\text{fuel, b}}(z)}{k_m + k_s (I - \alpha)} \] (7.48)

Boundary conditions for these cases are the same as those used for the tubular reactor.

### 7.4.3 Results – Porous Media Reactor

The same conditions as in the tubular reactor were run for the porous model. These include an inlet temperature of 500 K, a wall temperature of 1000 K, a pressure of 2 atm, an equivalence ratio of 1.0, and a mass flow rate of 0.3 g/s. The substrate porosity is 95% which is the same as that used in the catalytic microcombustors with the nickel foam substrate. The foam fiber thickness is 80-100 μm. Figure 7.8 shows the wall and bulk gas axial temperature profiles. Figure 7.9 is the fuel conversion along the length of the reactor and figure 7.10 shows the concentration profiles. Note that the final conversion achieved for these conditions is approximately 25%, which compares well with the 30% achieved in the experiment.

![Figure 7.8 Axial temperature profile along porous media plug flow reactor.](image)

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Figure 7.9 Axial conversion profile along porous media plug flow reactor.

Figure 7.10 Axial fuel concentration profile along porous media plug flow reactor.
As was done in the tubular reactor case, the model can be run for a constant geometry and wall temperature over a range of mass flow rates and pressures similar to those in the experiment. Figure 7.11 shows fuel conversion versus mass flow rate for this situation with a porosity of 95%. The trend is similar to that generated in the tubular case and in the experiment, however the values compare well with the experiment for this case. The actual catalytic microcombustor operated at ~28% chemical efficiency over a broad range of flow rates while the model shows a conversion of ~25% over a similar flow range. Again, a relatively constant Peclet number in the high mass flow range can explain the flat trend in conversion.

![Figure 7.11 Propane conversion versus mass flow rate for constant geometry and wall temperature in a porous media reactor.](image-url)
7.5 Effect of Heat Loss

Heat loss from the catalytic microcombustor can significantly impact performance. To illustrate this point, consider a case at constant flow conditions with varying levels of heat loss. The heat loss will primarily affect the system by lowering the catalyst wall temperature. For a mass flow rate of 0.25 g/s, an inlet gas temperature of 500 K, and an equivalence ratio of unity with a catalyst substrate similar to the nickel foam, Figure 7.12 shows the wall and bulk gas fuel mole fractions for various catalyst temperatures. These temperatures range from 1500 K to 800 K. At higher temperatures it is clear that the system is diffusion-controlled. The bulk gas mole fraction is much higher than that at the wall indicating that the transport of fuel molecules to the surface is slow. As the temperature is lowered (via increased heat loss for example) the curves approach each other. At an 800 K wall temperature they track very closely indicating that the system is no longer diffusion-controlled. In this case the reactor is dominated by slow reaction time-scales and has changed regimes to a kinetically limited case.

![Figure 7.12 Mole fractions for varying catalyst wall temperature.](image)
At lower catalyst wall temperatures the system becomes reaction-controlled and the governing parameter is no longer the Peclet number. The second Damköhler number is now the parameter of interest and compares the diffusion time to the reaction time. With very slow reaction time-scales, this parameter can be below unity. At some minimum level of catalyst temperature, the reaction will cease and the combustor will extinguish. In the reaction-controlled regime, the model validity becomes suspect, as it is highly dependent on the quality of the reaction mechanism being used.

This shift in controlling phenomenon at low temperature and high heat loss can also explain the catalytic microcombustor's poor performance at low equivalence ratio. At low equivalence ratios the heat release and catalyst wall temperature are lower and the device may be operating in the reaction-controlled regime. In this regime, as mass flow rate increases, the device will perform similarly to a gas-phase device where the first Damköhler number governs the process. At high mass flow rates the combustor will simply blow out due to low residence times.

### 7.6 Comparison to Experiments

Figure 7.13 shows a comparison of the model results to that obtained in the experiments for both the 95% and 88.5% porous substrates. Fuel conversion is the parameter being compared. The approximate geometries of the substrate materials were used as well as the actual pressure and mass flow rates from the experiment. The model replicates the trends shown in the experiments. These trends include a relatively constant fuel conversion over a broad mass flow range and the lower porosity material resulting in higher conversions and exit gas temperatures. However, the model does not predict overall levels well. Likely reasons for this are unknowns in the substrate geometry and the platinum coverage as well as flow leakage around the foam material. The surface area-to-volume ratio was calculated using equation 7.38, the manufacturers' specification for porosity, and SEM length measurements for the width of a fiber. This width is only an estimate and varies throughout the foam. In addition, the platinum layer may not cover the entire substrate surface as the model assumes. This could be due to a poor initial coating or loss of the catalyst layer during high temperature fabrication processes.
A model sensitivity study was performed and indicated that a variation of 20% in surface area-to-volume ratio would result in an approximately a 10% change in fuel conversion. Figure 7.14 shows these results. The sensitivity to leakage flow around the foam substrate material can also be estimated. The conversion for a reduced flow rate can be mass averaged with an unreacted leakage flow to simulate this scenario. Figure 7.15 shows results for 20% and 40% leakage flow. The fuel conversion changes by approximately 7% with each 20% increment in leakage.
Figure 7.14 Model sensitivity to surface area-to-volume ratio.

Figure 7.15 Model sensitivity to leakage flow around foam substrate material.
7.7 Key Design Variables

With this porous media reactor model, the effect of porosity and surface area can be further examined. For constant flow conditions, the model can produce fuel conversion profiles for various porosity materials. Figure 7.16 shows the effect of porosity for an inlet temperature of 500 K, a catalyst wall temperature of 1000 K, a pressure of 2 atm, an equivalence ratio of unity, and a constant foam fiber thickness of 0.1 mm. The profiles generated indicate that lower porosity substrates will significantly improve fuel conversion. This is due to both the decreased diffusion distances and increased catalyst surface area-to-volume ratio. However, a change in porosity does not necessarily imply an improvement in performance. If the foam fiber width changes, then the surface area-to-volume ratio may be lower for a lower porosity material. As a result, surface area-to-volume ratio is a more general and useful design variable if it can be well estimated. Figure 7.17 shows trends in fuel conversion for increasing surface area-to-volume ratios.

![Figure 7.16 Fuel conversion profiles for various porosities in a porous media plug flow reactor.](image)
7.7 Operating Space

The 1-D isothermal plug flow model can also be used to visualize a catalytic microcombustor’s operating space. Figure 7.18 shows lines of constant combustor efficiency on a plot of total pressure loss through the device versus catalyst temperature for an equivalence ratio of unity. The total pressure loss is estimated by adding the pressure loss through the substrate material as predicted by equation 7.5 to an estimate of the pressure loss due to the silicon structure. The overall combustor efficiency is obtained from the exit gas temperature predicted by the model. Figure 7.18 indicates that at higher pressure loss (higher surface area-to-volume ratio) and higher catalyst temperatures, combustor performance improves. It is also clear that by loosening the pressure loss constraint and utilizing a catalyst which can survive at higher temperatures, the available operating space will broaden. The current microengine constraint of less than 5% total pressure loss is indicated by the black line and gray shaded area. The
shaded area above a 1400 K catalyst temperature represents an estimated failure
temperature for the catalyst layer. Data from experiments presented in Chapter 6 are also
shown for comparison. Although the catalyst temperature is not directly measured, it can
be estimated using the model and the known exit gas temperature. The broad trend in the
experimental data is similar to that generated by the model. Combustor efficiency
increases with pressure loss and catalyst temperature. Figure 7.19 shows similar trends
but with lines of constant power density.

The model also shows that for a fixed thermal efficiency, there is an optimal
equivalence ratio that will maximize combustor efficiency. Figure 7.20 shows lines of
constant thermal efficiency plotted on a pressure loss versus equivalence ratio axis.
These curves also correspond to the locus of maximum attainable efficiencies for a given
heat loss. The optimal equivalence ratio decreases as pressure loss increases indicating
the increase in surface area-to-volume ratio required to react the mixture. As equivalence
ratio is lowered, a higher chemical efficiency is required to maximize the overall
efficiency. To achieve this, a larger surface area-to-volume ratio (and pressure loss) is
required. The equivalence ratio asymptotes to a value which will result in a catalyst wall
temperature near the adiabatic flame temperature of the mixture.

Figure 7.21 shows a plot of catalyst temperature versus pressure loss for optimal
equivalence ratio conditions (maximum overall combustor efficiency). The curves for
varying thermal efficiency collapse to a single line. To optimize equivalence ratio for
overall combustor efficiency at a fixed thermal efficiency and catalyst temperature, the
surface area-to-volume ratio is increased until chemical efficiency is greater than 99%.
The surface area-to-volume ratio (and pressure loss) required for this optimization is
primarily a function of catalyst temperature and not equivalence ratio. The curve
indicates that at lower catalyst temperatures, a higher pressure loss must be sustained to
obtain the optimal condition in terms of overall combustor efficiency.
Figure 7.18 Operating space for catalytic microcombustor; lines of constant combustor efficiency.

Figure 7.19 Operating space for catalytic microcombustor; lines of constant power density.
Figure 7.20 Equivalence ratio versus pressure loss for maximum combustor efficiency.

Figure 7.21 Catalyst temperature versus pressure loss for maximum combustor efficiency.
The catalytic microcombustor's operating space can be viewed more generally by plotting non-dimensional parameters. Figure 7.22 shows lines of constant combustor efficiency on a chart with Peclet number versus thermal efficiency. As Peclet number decreases, combustor efficiency increases due to the time available for diffusion of the reactant species to the active surface. However, as heat is lost from the system (lower thermal efficiency), the overall efficiency decreases. Figure 7.23 again plots lines of constant combustor efficiency, but for Peclet number versus diffusion-based Damköhler number. The same trend with Peclet number is shown here. The trend with Damköhler number indicates that as either reaction rates get faster or diffusion times-scales get longer and Da$_2$ gets larger, there is little change in efficiency. In order to take advantage of increased reaction rates, the system must have reduced diffusion times and lower Peclet numbers.

Figure 7.22 Non-dimensional operating space; Peclet number versus thermal efficiency.
7.8 Chapter Summary

Low-order modeling of catalytic combustion systems has been undertaken in an effort to understand performance trends and suggest future designs. A pressure drop correlation for porous media was used to estimate the potential pressure loss through various catalyst substrates. A simple time-scale analysis was used to identify the governing parameters of the system and a one-dimensional, steady state, isothermal, plug flow reactor model was developed to identify the parameters which will have the largest impact on future devices.

The pressure loss correlation indicated that in the catalytic microcombustors that were tested, the catalyst substrate accounted for minimal pressure loss. Most of the losses associated with this device can be attributed to inlet swirl dissipation and the flow-path through the silicon. The catalyst substrate materials were approximately 95% and 88.5% porous. A significant decrease in porosity (increase in surface area and catalytic
material) can be introduced without exceeding the 5% pressure loss limit, which has been imposed by the microengine thermodynamic cycle.

Reaction, residence, and diffusion time-scales have been estimated and used to identify the controlling process in a high power density catalytic microcombustor. The longest time-scale in the system is the fuel diffusion time indicating that the limiting phenomenon is the diffusion of the fuel species to the surface of the catalyst. The Peclet number, which compares the diffusion time to the residence time, was shown to be significantly larger than unity.

A one-dimensional, isothermal, plug flow reactor model was developed to identify performance trends and high impact design variables. Both tubular and porous media geometries were examined. Similar trends in fuel conversion were shown in the model and the experiment and the diffusion of fuel species was found to be the governing phenomenon. Substrate porosity and surface area-to-volume ratio were identified as the design parameters that have the greatest impact on performance. The model was also used to examine the operating space of these devices.
Chapter 8

Catalytic Materials Characterization

As a result of the inconsistent performance of many of the catalytic microcombustors described in Chapter 6, a materials characterization of the catalyst and substrate material was performed. This characterization included pre and post-fabrication surface structure and elemental analysis, and the identification of metal inter-diffusion and platinum agglomeration as potential failure mechanisms. Analysis techniques utilized were Scanning Electron Microscopy (SEM) for surface structure imaging including use of the backscatter detector, and Energy Dispersive X-ray Spectroscopy (EDX or EDS) for elemental analysis. The following sections review this materials characterization. The chapter ends with catalytic microcombustor design recommendations based on this materials characterization as well as the previously reviewed experiments and modeling.

8.1 Characterization Techniques

8.1.1 SEM Imaging

A Scanning Electron Microscope has been used to obtain topographical images and elemental data from the catalyst layers and substrate materials. The SEM is able to provide high resolution, high magnification images with excellent depth of field by rastering an electron beam across the sample. This beam is generated from an electron gun, which includes a tungsten filament that is electrically heated and acts as a cathode. An anode, which is positively charged with respect to the filament, provides an attractive force for electrons. The resulting flow of electrons is passed over the sample to be imaged and electrons from the specimen are ejected. A schematic of a typical SEM can be seen in Figure 8.1.
There are two types of electron detectors in the SEM. The first is called a secondary electron detector. Secondary electrons are specimen electrons, which obtain energy from inelastic collisions with the incoming beam electrons. These electrons are scattered and collected by the detector. Secondary electron detection provides high quality surface imaging.

The second type is called backscatter electron detection. The incident electrons from the beam themselves can be scattered and collected. A small number of these electrons will elastically scatter as a result of interaction with the nucleus of an atom. These can be detected and used for both surface imaging and limited elemental analysis. The number of backscattered electrons will vary based on the size of the nucleus, which they are interacting with. As a result, a larger atom with a higher atomic number will backscatter more electrons. If the various elements present on a sample have significantly different atomic number (a difference greater than approximately 10) then backscatter detection can distinguish between the elements. This technique has proven
useful in visualizing platinum catalysts on substrate materials with lower atomic numbers.

### 8.1.2 EDS Elemental Analysis

A third type of signal is emitted from the sample in the SEM. The incident electrons cause x-rays to be scattered. The SEM also includes a detector to collect these x-rays as part of an Energy Dispersive X-ray Spectrometer, which is capable of providing elemental analysis of the sample. EDS measures the energy and intensity distribution of these signals. Each element scatters a unique x-ray spectrum. The EDS system is capable of distinguishing between elements and providing a quantitative measure of the amount of each element present (~5% relative accuracy by weight [68]). Any point on the SEM image can be selected for elemental analysis. The EDS then collects x-rays from an area of approximately 1μm² and can detect elements up to 1μm deep [68].

### 8.2 High Temperature Exposure of Catalytic Microcombustor Materials

Prior to the final fabrication and bonding procedures for the second set of catalytic microcombustors, the substrate materials with platinum coatings were tested for high temperature durability. These initial insert pieces consisted of the FeCrAlY and Inconel foams with approximately a 1 μm platinum layer deposited via ionic plasma impregnation. In addition, several nickel foam pieces were fabricated and coated as well to simulate the first set of devices. These pieces were examined with the SEM and the EDS tool for elemental analysis. Next they were exposed to high temperature in a small electrically heated N₂ tube furnace. To simulate the high temperatures of the bonding furnace and the packaging furnace, the pieces were exposed for approximately 1 hour at 1100°C and were at elevated temperatures for an additional 2 hours due to the furnace ramp up/down time. After this exposure, the pieces were re-examined with the SEM and EDS. Results are discussed below.
8.2.1 Nickel-Pt Prior to High Temperature Exposure

Figures 8.2 and 8.3 show the nickel foam substrate material at 200X magnification and the x-ray spectrum respectively. As expected, the material is predominantly nickel. Measurement points can be seen on the SEM and are indicated by the ‘+’ marks. Table 8.1 lists the elemental analysis from the EDS.

Figure 8.2 Nickel foam at 200X magnification.

Figure 8.3 EDS spectrum for nickel foam.
Table 8.1 EDS analysis of nickel foam.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.27</td>
<td>14.910</td>
<td>3.494</td>
</tr>
<tr>
<td>O</td>
<td>0.34</td>
<td>1.136</td>
<td>0.355</td>
</tr>
<tr>
<td>Ni</td>
<td>209.06</td>
<td>83.954</td>
<td>96.151</td>
</tr>
</tbody>
</table>

This same nickel foam coated with approximately 1 μm of platinum can be seen in Figure 8.4. Figure 8.5 is the EDS spectrum and the platinum spike can be clearly seen. Table 8.2 lists the value from the elemental analysis. Quantities of platinum approaching 50% have been found indicating adequate coverage. The nickel below the platinum layer is also still evident in the analysis.

Figure 8.4 Ni-Pt at 100X magnification.
Figure 8.5 EDS spectrum for Ni-Pt.

Table 8.2 EDS analysis of Ni-Pt.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.12</td>
<td>49.546</td>
<td>11.587</td>
</tr>
<tr>
<td>O</td>
<td>0.90</td>
<td>1.764</td>
<td>0.550</td>
</tr>
<tr>
<td>Ni</td>
<td>224.23</td>
<td>36.557</td>
<td>41.778</td>
</tr>
<tr>
<td>Pt</td>
<td>28.61</td>
<td>12.133</td>
<td>46.085</td>
</tr>
</tbody>
</table>

8.3.2 Nickel-Pt Post High Temperature Exposure

The coated nickel piece was exposed to 1100°C in the tube furnace for 1 hour in addition to the ramp up/down time at elevated temperature. Upon re-evaluating the piece it was discovered that the quantity of platinum remaining was greatly reduced. Figures 8.6 and 8.7 show an SEM of this sample and the corresponding EDS spectrum respectively. Table 8.3 lists the elemental analysis and it can be seen that the platinum level has been reduced to less than 2% by weight. This disappearance of the catalyst layer at high temperatures is a likely cause for the sporadic performance of the nickel-platinum foam devices. As result, the materials used in the second set of combustors were examined in the same way prior to bonding and packaging.
Figure 8.6 Ni-Pt at 100X magnification post high temperature exposure.

Figure 8.7 EDS spectrum for Ni-Pt post high temperature exposure.
8.3.1 FeCrAlY-Pt Prior to High Temperature Exposure

Figures 8.8 and 8.9 show the FeCrAlY foam without a platinum coating at 200X magnification and the associated EDS spectrum. Large iron, chromium, and aluminum spikes can be seen along with smaller yttrium spikes. Table 8.4 lists the quantities of each element found.

![Figure 8.8 FeCrAlY foam at 200X magnification.](image-url)
Figure 8.9 EDS spectrum for FeCrAlY foam.

Table 8.4 EDS analysis of FeCrAlY foam.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
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<td>C</td>
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<td>12.861</td>
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<tr>
<td>O</td>
<td>3.83</td>
<td>5.476</td>
<td>2.505</td>
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<tr>
<td>Al</td>
<td>33.93</td>
<td>6.696</td>
<td>5.164</td>
</tr>
<tr>
<td>Cr</td>
<td>105.08</td>
<td>9.334</td>
<td>13.874</td>
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<tr>
<td>Fe</td>
<td>287.99</td>
<td>40.934</td>
<td>65.345</td>
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<tr>
<td>Y</td>
<td>0.67</td>
<td>0.099</td>
<td>0.251</td>
</tr>
</tbody>
</table>

The FeCrAlY foam with a 1 μm platinum layer can be seen in Figure 8.10 at 100X magnification. The surface is well covered with platinum and the associated EDS spectrum and analysis can be seen in Figure 8.11 and Table 8.5 respectively. Platinum concentrations are very high, exceeding 80% by weight indicating good surface coverage. The other elements present in FeCrAlY can be seen in trace quantities.
Figure 8.10 FeCrAlY-Pt at 100X magnification.

Figure 8.11 EDS spectrum for FeCrAlY-Pt.
Table 8.5 EDS analysis of FeCrAlY-Pt.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
<th>Atomic %</th>
<th>Weight %</th>
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<tr>
<td>C</td>
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<tr>
<td>O</td>
<td>0.93</td>
<td>2.663</td>
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<td>Al</td>
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<td>Pt</td>
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8.3.2 FeCrAlY-Pt Post High Temperature Exposure

After exposure to 1100°C in the N₂ furnace for 1 hour plus the associated ramp up/down time at elevated temperature, the platinum layer appears to have been significantly reduced. Figure 8.12 shows an SEM image of the piece while Figure 8.13 shows the EDS spectrum. The elemental analysis showed a similar result as that done for the nickel case and can be found in Table 8.6. The analysis indicates that the platinum has been reduced to less than 3%.

Figure 8.12 FeCrAlY-Pt at 200X magnification post high temperature exposure.
Table 8.6 EDS analysis of FeCrAlY-Pt post high temperature exposure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
<th>Atomic %</th>
<th>Weight %</th>
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<tr>
<td>C</td>
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<tr>
<td>O</td>
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<tr>
<td>Al</td>
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<td>Pt</td>
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8.3.3 Inconel-Pt Prior to High Temperature Exposure

Figures 8.14 and 8.15 show an SEM image and EDS spectrum for the Iconel-625 foam respectively. Table 8.7 lists the results of the EDS analysis. The typical components of the Inconel high temperature alloy are found. These include significant amounts of nickel, chromium, molybdenum, iron, and niobium.
Figure 8.14 Inconel-625 foam at 200X magnification.

Figure 8.15 EDS spectrum for Inconel-625 foam.
Table 8.7 EDS analysis of Inconel-625 foam.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
<th>Atomic %</th>
<th>Weight %</th>
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<tr>
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<tr>
<td>Mo</td>
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<td>14.144</td>
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</table>

The corresponding figures and table for the Inconel-625 foam coated with 1 μm of platinum prior to high temperature exposure are shown in Figures 8.16, 8.17, and Table 8.8. Significant platinum spikes can be seen and concentrations are on the order of 40% by weight.

Figure 8.16 Inconel-Pt at 100X magnification.
Figure 8.17 EDS spectrum for Inconel-Pt.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
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<tr>
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</tr>
<tr>
<td>Nb</td>
<td>1.81</td>
<td>0.359</td>
<td>0.809</td>
</tr>
<tr>
<td>Mo</td>
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</tr>
<tr>
<td>Pt</td>
<td>43.085</td>
<td>9.103</td>
<td>43.085</td>
</tr>
</tbody>
</table>

8.3.4 Inconel-Pt Post High Temperature Exposure

After high temperature exposure in the N₂ tube furnace, the Inconel foam coated with platinum exhibited the same characteristics as that found in the other materials. The platinum layer was reduced to less than 2% by weight as detected by the EDS system. Figures 8.18, 8.19, and Table 8.9 summarize these findings.
Table 8.8 EDS analysis of Inconel-Pt.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
<th>Atomic %</th>
<th>Weight %</th>
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<tr>
<td>Cr</td>
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<tr>
<td>Fe</td>
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<td>0.809</td>
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<tr>
<td>Mo</td>
<td>0.00</td>
<td>0.000</td>
<td>0.000</td>
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<tr>
<td>Pt</td>
<td>43.085</td>
<td>9.103</td>
<td>43.085</td>
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8.3.4 Inconel-Pt Post High Temperature Exposure

After high temperature exposure in the N₂ tube furnace, the Inconel foam coated with platinum exhibited the same characteristics as that found in the other materials. The platinum layer was reduced to less than 2% by weight as detected by the EDS system. Figures 8.18, 8.19, and Table 8.9 summarize these findings.
Table 8.9 EDS analysis of Inconel-Pt post high temperature exposure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
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<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
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<tr>
<td>Pt</td>
<td>0.39</td>
<td>0.207</td>
<td>1.351</td>
</tr>
</tbody>
</table>

8.4 Solid Diffusion Experiment

The disappearance of the platinum layers at high temperature is likely due to inter-diffusion between the layer and the metal substrate material. In the following sections, a short loop experiment and analysis intended to verify this possibility are described. This verification involved fabricating solid nickel sample pieces and coating them with layers of platinum and chromium to simulate both the nickel and Inconel foam substrates. These test coupons were cross-sectioned and analyzed using the SEM backscatter detector and the EDS system. They were then exposed to 1100°C in the N\textsubscript{2} tube furnace in the same manner as done with the foam pieces. Finally, after high temperature exposure, the coupons were again cross-sectioned and examined revealing the diffusion of the platinum layer into the substrate material.

8.4.1 Nickel Test Coupons Prior to High Temperature Exposure

Nickel-100 alloy was used as base material for the test coupons. This was the purest and most readily available nickel alloy, which could be found and is approximately 99% nickel. The coupons were machined from a 1/16 inch thick sheet of nickel-100 into 1 x 1/2 inch rectangles.

Plasma sputtering was used to coat the coupons with both platinum and chromium layers. One set of coupons was coated with approximately 1 μm of platinum only, while a second set was first coated with a 0.5 μm layer of chromium followed by a 1 μm layer.
of platinum to better simulate the Inconel substrate material. Figures 8.20 and 8.22 show cross-sections of both the Ni-Pt and Ni-Cr-Pt coupons using the SEM backscatter detector. The bright stripe indicates the platinum layer while the dark base material is the nickel. Figures 8.21 and 8.23 are the EDS spectra and Tables 8.10 and 8.11 list the elemental analysis and show platinum levels approaching 90% by weight.

Figure 8. 20  Cross-section of Ni-Pt coupon at 2500X magnification (backscatter).

Figure 8. 21  EDS spectrum for Ni-Pt coupon.
Table 8.10 EDS analysis of Ni-Pt coupon.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
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<th>Weight %</th>
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<tr>
<td>Pt</td>
<td>63.12</td>
<td>36.801</td>
<td>88.729</td>
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</table>

Figure 8.22 Cross-section of Ni-Cr-Pt coupon at 2500X magnification (backscatter).

Figure 8.23 EDS spectrum for Ni-Cr-Pt coupon.
Table 8.11 EDS analysis of Ni-Cr-Pt coupon.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity (count/s)</th>
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<th>Weight %</th>
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<tr>
<td>Ni</td>
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<tr>
<td>Pt</td>
<td>64.12</td>
<td>44.150</td>
<td>90.935</td>
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</table>

8.4.2 Nickel Test Coupons Post High Temperature Exposure

Both the Ni-Pt and Ni-Cr-Pt test coupons were exposed to 1100°C for 1 hour in the tube furnace. After SEM inspection and EDS analysis, it was clear that the platinum layer diffused into the nickel substrate material. Figures 8.24 and 8.26 show SEM backscatter images of cross-sections of the two test coupons and the bright platinum has spread deep into the nickel substrate. The platinum was detected up to 7 μm deep. Figures 8.25 and 8.27 show the EDS spectra for the two coupons as viewed from above (perpendicular to cross-sections). Platinum percentages found on this top surface have been reduced from approximately 90% to less than 10% by weight. These concentrations are listed in Tables 8.12 and 8.13.

![Cross-section of Ni-Pt coupon at 2500X magnification after high temperature exposure (backscatter).](image)
Figure 8.25 EDS spectrum for Ni-Pt coupon after high temperature exposure.

Table 8.12 EDS analysis of Ni-Pt coupon after high temperature exposure.

<table>
<thead>
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<th>Element</th>
<th>Intensity (count/s)</th>
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<tr>
<td>Pt</td>
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</table>

Figure 8.26 Cross-section of Ni-Cr-Pt coupon at 2500X magnification post high temperature exposure (backscatter).
Figure 8.27 EDS spectrum for Ni-Cr-Pt coupon after high temperature exposure.

Table 8.13 EDS analysis of Ni-Cr-Pt coupon after high temperature exposure.

<table>
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<tr>
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<tr>
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<td>3.20</td>
<td>1.582</td>
<td>8.974</td>
</tr>
</tbody>
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8.4.3 Comparison to Solid Diffusion Model

In addition to the 1 hour high temperature exposures of the test coupons, the Ni-Pt coupons were also exposed to 1100°C and examined after only 6 minutes. Because the metal diffusion process is expected to occur exponentially with time, data from a significantly shorter test run will provide additional confirmation of the diffusion process. EDS measurements were taken at various depths in the samples (using the cross-sectional view) to obtain a concentration profile. The profile obtained from the samples at 6 minutes and 60 minutes can then be compared to a metal diffusion model using diffusion coefficients from the literature.
The diffusion of one solid metal species within another is driven by the concentration gradient. The diffusion equation for this scenario with a constant diffusion coefficient can be written as

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \tag{8.1}
\]

There are several solutions to this equation. For thin films, the concentration profile as a function of location and time is

\[
c(x,t) = \frac{bc_0}{2\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \tag{8.2}
\]

where \(c_0\) is the initial concentration and \(b\) is the initial thickness \([69,70]\). For this thin film solution to apply it is subject to the constraint

\[
b < \sqrt{Dt}. \tag{8.3}
\]

\(D\) is the diffusion coefficient for the diffusion of one element into another and can be written as a function of temperature in an Arrhenius form.

\[
D = Ae^{(-E_r/RT)} \tag{8.4}
\]

These parameters for a given temperature range and elemental composition can be found in the literature \([71]\). If the thin film constraint does not hold, then the semi-infinite solid solution to the diffusion equation can be utilized \([69,70]\).

\[
c(x,t) = \frac{c_0}{2} \left[ 1 + \text{erf}\left( \frac{x}{2\sqrt{Dt}} \right) \right] \tag{8.5}
\]
For the Ni-Pt system of interest here, the diffusion coefficient used was 1.39e-11 cm²/s and can be found in references [71]. This parameter corresponds to a 100% platinum layer diffusing into nickel at 1100°C. Curves for diffusion of Pt into Ni at 1100°C at times 0 minutes, 6 minutes, and 60 minutes are plotted in Figure 8.28. For the curve representing 6 minutes, \( b \approx \sqrt{Dt} \). As a result, the thin film and the semi-infinite solid solutions were averaged. For the 60 minute case, \( b < \sqrt{Dt} \) and the thin film solution can be used. The initial conditions are represented by the time = 0 curve indicating a platinum layer of 1 μm prior to diffusion. The data points on the plot are from EDS measurements on the cross-sections of the coupons. Due to the tendency of the EDS system to average data over a 1 μm³ volume, sharp gradients are difficult to measure. The agreement between the diffusion model and the data supports the assertion that the platinum layer is lost via diffusion into the metal substrate.

Figure 8.28 Comparison of diffusion model to EDS concentration profiles.
8.5 Catalyst Substrate with Diffusion Barrier

As a result of the high temperature tests on the platinum coated foam materials and the test coupons, it was determined that a diffusion barrier material was a possible solution. Ceramics such as alumina (Al₂O₃) and zirconia (ZrO₂) are often used for this purpose. Both of these materials were coated in 2-3 μm layers onto the FeCrAlY and Inconel foam substrate materials via the ionic plasma process prior to deposition of 2-3 μm of platinum. Before bonding these pieces into the six-wafer stack to form the combustors, these samples were tested via high temperature exposure in the N₂ tube furnace. They were subsequently examined with the SEM backscatter detector and the EDS system as done previously to ensure platinum durability.

8.5.1 Substrate Materials with Diffusion Barriers

Both the alumina and zirconia diffusion barriers seem to have been effective in preventing the diffusion of the platinum layer into the metal substrate material. Figures 8.29 and 8.30 show an SEM backscatter image and an EDS spectrum respectively for the Inconel foam with a zirconia diffusion barrier and a platinum layer, after high temperature exposure. It is clear from both figures that the platinum is still present on the surface. However, the SEM backscatter image shows some agglomeration occurring. The platinum layer has begun to coalesce reducing the active surface area. This was expected as it is a common failure mode for platinum layers and is well documented in the literature [41,42]. EDS measurements on the bright areas show large platinum spikes as indicated by Figure 8.30. Table 8.14 lists the results of the EDS analysis for a measurement location on one of these bright areas. Subsequent EDS spectra from the dark areas showed very little platinum and large spikes of Zr, O, and Ni. Results for the FeCrAlY with diffusion barriers and platinum after high temperature exposure were very similar.
Figure 8.29 Inconel-Pt with diffusion barrier at 1000X magnification after high temperature exposure (backscatter).

Figure 8.30 EDS spectrum for Inconel-Pt with diffusion barrier after high temperature exposure.
Table 8.14 EDS analysis of Inconel-Pt with diffusion barrier after high temperature exposure.

<table>
<thead>
<tr>
<th>Element</th>
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</table>

8.6 Design Recommendations

Design recommendations for catalytic microcombustion systems are listed below. These recommendations are based on the experiments presented in Chapter 6, the low order modeling in Chapter 7, and the materials characterization described in this chapter.

1. High power density catalytic microcombustors are diffusion-controlled. A designer should seek to approach the high temperature reaction-controlled regime to maximize performance. This can be achieved by implementing the following:
   a. Utilize the most thermally durable catalytic materials to achieve higher temperature operation.
   b. Utilize the highest surface area-to-volume ratio substrate material available, which does not violate the system pressure loss constraint.
   c. Push the total pressure loss constraint as far as the thermodynamic cycle will permit.

2. Searching for a more active catalytic material is not required unless:
   a. The ignition transient is of concern.
   b. The overall design lies in the reaction-controlled regime.

3. Although thermal management was not a problem in the devices tested here due to poor thermal contact of the catalyst to the silicon, leakage paths around the catalyst material, and the recirculation jacket, a more intimately contacted catalyst material operating at higher temperatures will likely suffer from thermal losses. A materials solution such as a thermal barrier combined with a concept similar to the recirculation jacket may mitigate these losses.
4. Due to high temperature processing and operation, substrate materials for noble metal catalysts should be resistant to solid diffusion or include a diffusion barrier layer.

5. Catalytic materials, which are less likely to agglomerate at high temperatures, should be used.

6. A robust fabrication and assembly process, which does not result in leakage paths around the catalyst material, should be considered when designing the device.

8.6 Chapter Summary

This chapter discusses the characterization of the materials used in the catalytic microcombustors. This includes the measurement of substrate surface area, the elemental analysis of these materials and the catalyst layers, as well as an experiment, which showed catalyst diffusion and agglomeration possible failure modes.

These materials were also examined using the SEM and EDS x-ray detection system for elemental analysis. The composition of each material was determined. The samples were then coated with platinum and re-examined with these tools. This was followed by exposure to 1100°C in a tube furnace and another examination with the SEM and EDS system. It was found that the platinum layers were severely depleted.

As a result of these findings, an experiment was devised to determine if metal diffusion was responsible for the loss of platinum. Nickel test coupons were fabricated and coated with chromium and platinum. These test pieces were exposed to high temperatures and examined with the SEM backscatter detector and the EDS system. Cross-sections of the samples revealed diffusion of the platinum layer into the substrate material. This was compared to solutions of the diffusion equation with diffusion coefficients from the literature and showed good agreement.

Finally, diffusion barriers of zirconia and alumina were coated onto the substrate materials prior to platinum deposition. These pieces were then checked using the same procedure of high temperature exposure followed by SEM and EDS analysis. The diffusion barriers were successful in preventing the loss of the catalyst layer via diffusion but revealed platinum agglomeration as another possible failure mode.
Chapter 9

Summary and Conclusions

This chapter summarizes the research in this thesis and presents conclusions and recommendations for future work.

9.1 Summary of Research

As part of an effort to develop a micro-scale gas turbine engine using MEMS fabrication techniques, this thesis has presented work regarding the combustion system. Two types of microcombustion systems were reviewed; homogeneous gas-phase microcombustors and catalytic microcombustors. Research focused on obtaining high power density operation with practical hydrocarbon fuels such as propane.

The first half of the thesis concerns work on gas-phase microcombustors. This research is an extension of that conducted by Mehra [11]. Mehra’s hydrogen-fueled devices were reviewed in detail and used as a baseline for comparison. An advanced gas-phase microcombustor was developed and presented. This combustor is referred to as the dual-zone microcombustor because it diverts some flow from the recirculation jacket and splits the combustion chamber into two zones; a hot primary zone followed by a secondary or dilution zone.

Design and testing of the dual-zone microcombustor is presented in Chapter 3. Device design involved utilizing CFD tools to determine primary/secondary flow splits and the geometry of the dilution holes. Testing revealed improved performance over the baseline device with hydrogen-air mixtures. For certain conditions, the dual-zone microcombustor exceeded the baseline device by a factor of two in mass flow capability. In addition, it operated over a more broad range of fuel-air mixture ratios due to the improved local stability provided by the hot primary-zone. However, the dual-zone device did not show any improvement in performance with hydrocarbon fuels, which have reaction times 5-50 times slower than hydrogen. An analysis of the impact of the non-uniform exit temperature profile generated by the dual-zone device revealed a
potential benefit for turbine cooling. The exit temperature profile is such that a relatively cooler layer of gas covers the turbine disk while hot gases pass over the blades. This can result in up to a 12% reduction in heat transfer to the rotor improving turbomachinery performance.

The data obtained from the dual-zone device was combined with all other gas-phase microcombustor data including Mehra’s baseline six-wafer device and his three-wafer combustor. All data was plotted in non-dimensional three-parameter space. This resulted in a useful empirically based design tool. This tool provided estimates for required gas-phase combustor volume for various fuels and engine parameters.

Due to the poor performance with hydrocarbon fuels as a result of significantly slower reaction rates, a strategy of heterogeneous surface catalysis was pursued. This offered the potential to increase hydrocarbon microcombustor power density by directly increasing reaction rates. An initial test-bed device comprised of the three-wafer microcombustor fitted with platinum coated foam material showed stable propane-air combustion where previously it was not possible. A more sophisticated catalytic six-wafer device compatible with the microengine geometry was then developed.

This device also consisted of filling the combustion chamber with a foam material coated with platinum as the active catalytic surface. However, this constituted a significant fabrication challenge with respect to the bonding process. This was overcome by utilizing a protective non-bondable “shield wafer” while inserting the catalytic material during the bonding process.

Several catalyst substrate materials were utilized in these devices. The first catalytic microcombustors consisted of a foam substrate material made of nickel and were 95% porous. A second set of catalytic microcombustors consisted of either an 88.5% porous FeCrAlY foam or a 78% porous Inconel-625 foam. The combustors were ignited via preheating the entire chip and flowing a hydrogen-air mixture through the device. After catalytic ignition of the hydrogen-air mixture, operation was converted to propane-air autothermal combustion.

The 95% porous foam devices achieved exit gas temperatures in excess of 850 K and efficiencies of approximately 30% with propane. Although the efficiency and gas temperatures were quite low, this combustor operated at high mass flow rates compared
to the gas-phase combustors. Mass flow rates over 0.4 g/s were achieved and power density was a 7-fold increase over propane-air gas-phase operation. The devices with 88.5% porous FeCrAlY foam achieved exit gas temperatures approaching 1100 K and efficiencies near 40%. The power density of this device was an 8.5-fold increase over the comparable gas-phase microcombustor. Low order modeling including time-scale analyses and a 1-D isothermal plug flow reactor model indicated the high power density operation is diffusion-controlled and the relatively lower porosity and higher surface area-to-volume ratio of the FeCrAlY foam device was responsible for the improved performance. The microcombustors with the Inconel-625 foam would not ignite primarily due to leakage paths around the foam material created during the fabrication and bonding process.

Due to the sporadic performance of the 95% porous nickel-platinum devices and difference between the model and the results of the 88.5% porous FeCrAlY-platinum devices, a materials characterization analysis was performed. The results of this analysis strongly indicate that the platinum layer in the nickel-platinum devices was depleted due to diffusion into the nickel substrate material during the high temperature bonding anneal and packaging process. As a result, later combustors were fabricated with a ceramic diffusion barrier. This analysis also revealed that with the diffusion barrier, the platinum surface area was reduced by agglomeration during high temperature processing steps thus negatively impacting performance.

9.2 Review of Contributions

The primary contributions as a result of the gas-phase microcombustor work are summarized below:

1. Design, fabrication, packaging, and testing of an advanced dual-zone microcombustor. Specific contributions include:
   a. Demonstration of a microcombustion system operating with two reaction zones; a hot primary-zone and cooler dilution-zone. Device power density exceeded 1100 MW/m³ with hydrogen-air mixtures and under certain
conditions achieved a 2-fold increase in mass flow rate capability over the baseline device.

b. Experimental evaluation of device pressure loss, various fuel types, and several geometries.

c. Experimentally mapped operating space and identified critical limits.

2. Synthesis of all available gas-phase microcombustor data. Specific contributions include:
   a. Identified practical limits of gas-phase microcombustors in terms of required volume for a given fuel type and operating condition.
   b. Developed an empirically based design tool and applied this tool to future microengine designs.
   c. Established design guidelines for gas-phase microcombustors.

The second half of the thesis consists of work regarding catalytic microcombustors. The primary contributions from this portion of the research can be summarized as:

1. Design, fabrication, packaging, and testing of the first catalytic microcombustors for a micro gas turbine engine. Specific contributions are:
   a. Experimental evaluation of several geometries, catalyst substrate materials, and device pressure loss.
   b. Experimentally mapped the operating space and identified important limits and trends such as catalytic ignition characteristics and the procedure and conditions for heterogeneous autothermal propane-air operation.

2. Developed low order analytical models to explain performance trends and suggest future designs. Specifically:
   a. Identified important non-dimensional parameters that govern the operation of a catalytic microcombustor.
   b. Identified potential regimes of operation including kinetically limited and mass transport limited; for high power density operation as is required for the microengine, a catalytic microcombustor is mass transport limited.
c. Catalyst substrate porosity and surface area-to-volume ratio were identified as key design variables. To improve performance lower porosities and higher surface area-to-volume ratios were recommended at the expense of total pressure loss.

3. Potential failure mechanisms for catalytic microcombustors with platinum surfaces were evaluated via a materials characterization process. Specifics include:
   a. Platinum diffusion into the metal foam substrate during high temperature processing was identified as a likely failure mode due to reduction of the active catalytic component at the surface.
   b. Ceramic diffusion barriers were identified and utilized to prevent metal inter-diffusion.
   c. Platinum agglomeration was found to occur during high temperature processing reducing the active surface area and negatively impacting performance.

Additional contributions include:
1. Gas-phase microcombustor emissions predictions (Appendix C). Due to the low residence times inherent in micro-scale combustion systems, NO\textsubscript{x} emissions are expected to be low while unburned hydrocarbon emissions are high.
2. Thermo-acoustic stability analysis of gas-phase microcombustors (Appendix D). For propane-air mixtures, it was found that thermo-acoustic instabilities resulting from equivalence ratio fluctuations at the fuel injectors are not likely to occur.

9.3 Recommendations for Future Work

Based on the results of this work, additional research has been suggested. These topics are briefly addressed in the following sections.
9.3.1 Catalytic Ignition Schemes

Although the ignition procedure described in Sections 6.5 and 6.6 was effective for these bench-top catalytic microcombustor experiments, a more robust and self-contained system would be optimal for a practical device. A simple and effective means of achieving catalytic ignition of hydrocarbons over noble metal catalysts is to resistively heat the catalyst material itself [56,57,58,59]. By bringing the catalyst temperature up to the ignition temperature required for propane-air mixtures, the external preheating and hydrogen ignition procedure could be completely eliminated. In order to accomplish this in a device like the six-wafer microcombustors presented here, there would need to be significant fabrication changes. This would involve incorporating multi-level electrical interconnects into the device and contacting them to the metal catalyst material. These interconnects would extend to the chip’s surface where they could be connected to a current source for the resistive heating.

9.3.2 Hybrid Microcombustors

The catalytic microcombustors were successful in significantly increasing power density and mass flow range for hydrocarbon-fueled devices. However, the exit gas temperatures achieved were significantly lower than that required for the microengine thermodynamic cycle. Attaining these temperatures in a catalytic device of this kind is unlikely because the catalyst wall temperatures required would be high enough to cause significant agglomeration of the catalyst layer and would even approach the softening points of both the catalyst and substrate material. In addition, to accomplish this in a relatively small volume the total pressure loss would be significantly greater than the 5% constraint imposed by the engine cycle. Although the gas-phase devices were capable of achieving high exit gas temperatures and efficiencies with hydrogen-air mixtures, their mass flow rate capability was significantly less than the engine design flow rate of 0.35 g/s and was even worse with hydrocarbon fuels.

As a result, a strategy for achieving both high temperature and high mass flow rate operation in a minimum volume may be to combine the two devices into a “hybrid microcombustor”. This is not a new concept and is commonly used in conventional-
scale catalytic combustors as described and referred to in Section 5.3 (referred to as “staged catalytic combustor”) and references [48,49,50,51,52,53].

For this type of device, the entrance region of the combustion chamber would consist of a porous substrate or micro-channel type geometry coated with a catalyst layer. The first stage would ignite the fuel-air mixture and bring it to some mid-range temperature (~1000 K) with minimal total pressure loss. A second stage of open volume for homogeneous combustion would follow. The exit conditions of the catalytic section would serve as the inlet to the gas-phase section, which would burn the remaining fuel-air mixture. These reactions in the second stage would proceed quickly due to the already very high inlet gas temperature ultimately achieving the 1600 K exit gas temperature in a minimum total volume. In conventional-scale catalytic combustors, this section is often referred to as the “burnout section”. The burnout section geometry may also include additional fuel injection to raise the local equivalence ratio. This may be required as a result of the reduction in mixture ratio due to the upstream catalytic combustion process.

9.3.3 Large Volume External Combustors

Another solution to the problem of achieving high exit gas temperature and efficiency is simply to utilize a large volume external (off-chip) combustor. The advantages of such a system are numerous:

1. Any size volume is possible resulting in a significant increase in residence time.
2. Due to the large volume, catalysis may not be needed.
3. The combustor is thermally isolated from the rest of the engine reducing heat loads to other components.
4. A wide variety of high temperature materials could be used resulting in a more thermally efficient combustor.

This concept was first examined by Protz [3] and rejected for the following reasons:

1. Packaging the combustor to the chip may require significant development.
2. Pressure loss in the ducts required to connect the combustor to the chip would exceed the 5% constraint.
3. Heat loss from the ducts connecting the combustor to the engine chip.
4. Device power density would decrease significantly resulting in a less attractive overall technology.
5. Conventional machining would be used to fabricate these devices eliminating the benefit of batch fabrication.

Although all of these drawbacks still exist, they may be worth re-examining at this time. Advances in packaging technology may mitigate some of these issues.

9.3.4 Liquid Fuels

One final subject of potential future work is to include the use of liquid fuels such as kerosene and JP8 in microcombustor development. These types of fuels are the most commonly used hydrocarbons in gas turbine engines. For potential end users such as the US Armed Services, these are the most practical fuels. A microcombustor, which was capable of burning these fuels, would provide the microengine with a significant advantage over competing micro-scale power technologies that require more exotic fuels. The catalytic microcombustors described in this thesis may be a first step toward achieving this.

The use of these liquid fuels constitutes a significant development challenge. Some issues, which will need to be overcome, include:

1. Liquid fuel injection and droplet atomization.
2. Potential condensation of the fuel upstream of the combustion chamber.
3. Fuel-air mixing after atomization.
4. Diffusion of the much larger hydrocarbon molecules to a catalyst surface.
5. Ignition procedures/methods.
6. Reaction rates of heavy hydrocarbons on catalysts.
Appendix A

Photolithography Mask Set

A.1 Introduction

This appendix shows the photolithography mask set used for the dual-zone microcombustors. However, the differences in the masks for the six-wafer catalytic microcombustors are minimal and noted in the text with each figure. The shield wafer mask used for the catalytic devices is also included in this section. The general die layout on each wafer is shown in Figure A.1. To better present the details of each mask, only one die is shown in the other figures. Each die is 21 mm x 21 mm. A close up of the alignment markers, which are located to the far left and right on each mask, is also presented. Note that all masks were 5-inch soda-lime plates with chrome used to define the features. The figures shown here are the images, which were sent to Advanced Reproduction Corp. for mask fabrication and are photo-negatives of the actual masks. Along with each figure is text explaining which side of the wafer is patterned, as well as the depth and types of each etch associated with the mask.

Figure A.1 General die layout on 4-inch wafer.
A.2 Alignment Mark

Two alignment marks are located along the horizontal centerline of the wafer at a radius of 3.6 cm. These markers are 3.6 mm x 1.6 mm. Only a shallow etch is required to define these features. Typically, they are exposed in the DRIE for approximately 5-10 seconds then covered with photoresist for the remainder of wafer processing. Both sides of every wafer processed require alignment marks.

Figure A. 2 Alignment mark.
A.3 Level 1

Level 1 consists of a 400 μm wafer with a simple through etch using the DRIE to create the hole pattern on the outer surface of the chip. The etch is performed on the top-side of the wafer. These holes feed the device fuel and air and serve as pressure measurement ports. They are sealed to kovar tubes with the glass bead interconnect scheme developed by London, Harrison, and Mehra [23,22,11]. Figure A.3 shows one die on this mask.

![Figure A.3 Top-side mask for level 1.](image-url)
A.4 Level 2

Level 2 is also fabricated from a 400 μm wafer. However, there are three photomasks and 3 etches required. The first etch is a shallow etch of approximately 5-10 μm and is performed on the bottom side of the wafer using the DRIE. This is the clearance etch located above the compressor swirls vanes and is shown in Figure A.4. After this etch is complete, these features are covered with photoresist.

Figure A. 4 Bottom-side shallow clearance etch mask for level 2.
The next etch on this wafer is a 200 μm deep etch using the DRIE on the top-side of the wafer. This defines the fuel and pressure plenums as well as a thermocouple measurement port located in the upper left corner. Figure A.5 shows a die on the mask for this etch.

![Figure A.5 Top-side deep etch mask for level 2.](image-url)
The final etch on this level is also 200 μm deep and performed with the DRIE. These features are defined on the bottom-side of the wafer (same side as the clearance etch shown in Figure A.4) and constitute the fuel injectors. The injectors should line up with the plenums shown in Figure A.5 and can be seen themselves in Figure A.6.

Figure A. 6 Bottom-side mask for level 2.
A.5 Level 3

Level 3 is fabricated from an 800 μm silicon wafer. This includes two deep etches. The first, from the top-side of the wafer is 400 μm deep and creates the upper recirculation jacket and the compressor swirl vanes. This is shown in Figure A.7.

Figure A.7 Top-side mask for level 3.
The second etch on level 3 is also 400 μm deep and is performed with the DRIE on the bottom-side. This etch defines the outer recirculation jacket as well as the dilution holes for the dual-zone combustor and another thermocouple port. There are some variations on this mask for various dilution hole radial locations. For the catalytic combustors, a mask with only the outer recirculation jacket is used and there are no dilution holes.

Figure A. 8 Bottom-side mask for level 3.
A.6 Level 4

Level 4 requires two masks and two DRIE etches. The wafer is 1000 μm thick and is the largest in the stack. Figure A.9 shows the top-side etch which creates half of the combustion chamber itself and more of the outer recirculation jacket. The etch is 500 μm deep.

Figure A.9 Top-side mask for level 4.
The bottom-side of level 4 also consists of a 500 µm etch. This pattern completes the combustion chamber and adds to the outer recirculation jacket. In addition, the combustor exit and the turbine nozzle guide vanes are created. The mask for this pattern and etch is shown in Figure A.10.

Figure A. 10 Bottom-side mask for level 4.
A.7 Level 5

This level is fabricated from an 800 μm wafer and two deep etches. The top-side etch completes the outer recirculation jacket and forms the combustion chamber inlet slots. These features are 400 μm deep. In addition, the igniter port and a pressure measurement port are formed. Figure A.11 shows the photomask used for this etch.

Figure A.11 Top-side mask for level 5.
The second etch on this wafer cuts the remaining 400 μm from the bottom-side forming the bottom of the recirculation jacket, the igniter and pressure ports, and another thermocouple measurement location. Figure A.12 shows the mask for this etch.

Figure A.12  Bottom-side mask for level 5.
A.8 Level 6

The bottom level of the microcombustor consists of a 400 μm wafer and a single deep through etch. This level forms the exhaust gas exit area and the connection locations for the igniter and pressure ports. Figure A.13 shows the photomask for level 6.

Figure A.13 Photomask for level 6 through etch.
A.9 Shield Wafer Photomask

The shield wafer is only used for the catalytic microcombustor. This protective layer is fabricated from a 500 μm wafer with a single deep through etch. The feature created is the same shape as the combustion chamber so that the catalytic foam pieces can be easily passed through into the 4-5-6 stack. This fabrication process is described in detail in Section 6.4.2. Below is the photomask.

Figure A. 14 Shield wafer mask.
Appendix B

Chemical Mechanisms

B.1 Hydrogen-air Combustion Mechanism

Elementary reactions for the modified Yetter H₂-air combustion mechanism [34].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A ( \text{[m}^3/\text{kmol}]n^{-1}/\text{s} )</th>
<th>( E_a ) ( \text{[J/kmol]} )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+O₂&lt;-&gt;O+OH</td>
<td>1.91e11</td>
<td>6.88e7</td>
<td>0</td>
</tr>
<tr>
<td>O+H₂&lt;-&gt;HO+OH</td>
<td>5.01e1</td>
<td>2.63e7</td>
<td>2.67</td>
</tr>
<tr>
<td>OH+H₂&lt;-&gt;H+H₂O</td>
<td>6.38e3</td>
<td>1.24e7</td>
<td>2</td>
</tr>
<tr>
<td>OH+OH&lt;-&gt;O+H₂O</td>
<td>2.10e5</td>
<td>-1.66e6</td>
<td>1.4</td>
</tr>
<tr>
<td>H₂+M&lt;-&gt;H+H+M</td>
<td>4.57e16</td>
<td>4.367e8</td>
<td>-1.4</td>
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<tr>
<td>O+O+M&lt;-&gt;O₂+M</td>
<td>6.17e9</td>
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<td>-0.5</td>
</tr>
<tr>
<td>H₂/2.5/ H₂O/16/</td>
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<td>0</td>
<td>-0.6</td>
</tr>
<tr>
<td>H+OH+M&lt;-&gt;H₂O+M</td>
<td>6.70e13</td>
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<td>-1.42</td>
</tr>
<tr>
<td>H₂O₂+H&lt;-&gt;H₂+O₂</td>
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<td>8.91e6</td>
<td>0</td>
</tr>
<tr>
<td>H₂O₂+H&lt;-&gt;OH+OH</td>
<td>1.66e11</td>
<td>3.64e6</td>
<td>0</td>
</tr>
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<td>H₂O₂+O&lt;-&gt;OH+O₂</td>
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<td>-1.67e6</td>
<td>0</td>
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<td>H₂O₂+OH&lt;-&gt;H₂O+O₂</td>
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<td>0</td>
<td>-1</td>
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<td>H₂O₂+H₂O&lt;-&gt;H₂O₂+O₂</td>
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<td>5.816e6</td>
<td>0</td>
</tr>
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<td>H₂O₂+M&lt;-&gt;OH+OH+M</td>
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<td>1.90e8</td>
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</tr>
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<td>H₂O₂+H&lt;-&gt;H₂O+OH</td>
<td>1.00e10</td>
<td>1.50e7</td>
<td>0</td>
</tr>
<tr>
<td>H₂O₂+H&lt;-&gt;H₂+H₂O₂</td>
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<td>3.33e7</td>
<td>0</td>
</tr>
<tr>
<td>H₂O₂+O&lt;-&gt;OH+HO₂</td>
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<td>1.66e6</td>
<td>2</td>
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<td>7.08e9</td>
<td>5.98e6</td>
<td>0</td>
</tr>
</tbody>
</table>
B.2 GRI-Mech 3.0

Full hydrocarbon combustion mechanism for fuels methane (CH₄) through propane (C₃H₈) in Chemkin readable format [38]:

```
! GRI-Mech Version 3.0 7/30/99 CHEMKIN-II format
! See README30 file at anonymous FTP site unix.sri.com, directory gri;
! WorldWideWeb home page http://www.me.berkeley.edu/grimech/ or
! through http://www.gri.org, under 'Basic Research',
! for additional information, contacts, and disclaimer
ELEMENTS
O  H  C  N  AR
END
SPECIES
H2  H  O  O2  OH  H2O  HO2  H2O2
C  CH  CH2  CH2(S)  CH3  CH4  CO  CO2
HCO  CH2O  CH2OH  CH3O  CH3OH  C2H  C2H2  C2H3
C2H4  C2H5  C2H6  HCCO  CH2O  CH2OH  CH30  CH3OH  CO2  C2H2  C2H3
NH2  NH3  NH  NO  NO2  N2O  N20  HNO  CN  AR
HCN  H2CN  HCN  NO  N2O  N20  HNO  CN
H2O  H20  H202  HO2  HO2  H2O2  H202  H2O2  H2O2
O+H+M<===>OH+M  5.000E+17  -1.000  .00
O+H2<===>H+OH  3.870E+04  2.700  6260.00
O+H2<===>OH+O2  2.000E+13  .000  .00
O+H2<===>OH+O2  9.630E+06  2.000  4000.00
O+CH<===>H+CO  5.700E+13  .000  .00
O+CH2<===>H+HCO  8.000E+13  .000  .00
O+CH2(S)<===>H+HCO  1.500E+13  .000  .00
O+CH3<===>H+CH2O  5.060E+13  .000  .00
O+CH4<===>OH+CH3  1.020E+09  1.500  8600.00
O+CO(+M)<===>CO2(+M)  1.800E+10  .000  2385.00
LOW/  6.020E+14  .000  3000.00/
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ AR/ .50/
O+HCO<===>OH+CO  3.000E+13  .000  .00
O+HCO<===>H+CO2  3.000E+13  .000  .00
O+CH2O<===>OH+HCO  3.900E+13  .000  3540.00
O+CH2O<===>OH+CH2O  1.000E+13  .000  .00
O+CH3O<===>OH+CH2O  1.000E+13  .000  .00
O+CH3OH<===>OH+CH2OH  3.880E+05  2.500  3100.00
O+CH3OH<===>OH+CH3O  1.300E+05  2.500  5000.00
O+C2H<===>CH+CO  5.000E+13  .000  .00
O+C2H2<===>H+HCCO  1.350E+07  2.000  1900.00
O+C2H2<===>OH+CH2  4.600E+19  -1.410  28950.00
```
\[ \begin{align*}
O + C_2H_2 & \rightleftharpoons CO + CH_2 & 6.940 \times 10^6 & \text{ 2.000} & \text{ 1900.00} \\
O + C_2H_3 & \rightleftharpoons H + CH_2CO & 3.000 \times 10^8 & \text{ 0.000} & \text{ 0.00} \\
O + C_2H_4 & \rightleftharpoons CH_3 + HCO & 1.250 \times 10^7 & \text{ 1.830} & \text{ 220.00} \\
O + C_2H_5 & \rightleftharpoons CH_3 + CH_2O & 2.240 \times 10^8 & \text{ 0.000} & \text{ 0.00} \\
O + C_2H_6 & \rightleftharpoons OH + C_2H_5 & 8.980 \times 10^7 & \text{ 1.920} & \text{ 5690.00} \\
O + HCCO & \rightleftharpoons H + 2CO & 1.000 \times 10^9 & \text{ 0.000} & \text{ 0.00} \\
O + C_2HCO & \rightleftharpoons OH + HCCO & 1.000 \times 10^9 & \text{ 0.000} & \text{ 8000.00} \\
O + C_2HCO & \rightleftharpoons CH_2 + CO_2 & 1.750 \times 10^9 & \text{ 0.000} & \text{ 1350.00} \\
O_2 + C_2H & \rightleftharpoons H + CH_2CO & 2.500 \times 10^9 & \text{ 0.000} & \text{ 47800.00} \\
O_2 + CH_2CO & \rightleftharpoons OH + HCO & 1.000 \times 10^9 & \text{ 0.000} & \text{ 40000.00} \\
H_2 + O_2 & \rightleftharpoons H + O_2 + H & 2.800 \times 10^8 & \text{ -0.860} & 0.000 \\
O_2 & \rightleftharpoons O_2 + O & 6.940 \times 10^6 & \text{ 0.000} & \text{ 0.00} \\
O_2 & \rightleftharpoons O_2 + O_2 & 2.500 \times 10^9 & \text{ 0.000} & \text{ 47800.00} \\
O_2 & \rightleftharpoons O_2 + CH_2O & 1.000 \times 10^9 & \text{ 0.000} & \text{ 8000.00} \\
O_2 & \rightleftharpoons O_2 + CH_2CO & 1.000 \times 10^9 & \text{ 0.000} & \text{ 1350.00} \\
O_2 & \rightleftharpoons O_2 + CH_3CO & 1.000 \times 10^9 & \text{ 0.000} & \text{ 27420.00} \\
O_2 & \rightleftharpoons O_2 + CH_4CO & 1.000 \times 10^9 & \text{ 0.000} & \text{ 50800.00} \\
O_2 & \rightleftharpoons O_2 + CH_5CO & 1.000 \times 10^9 & \text{ 0.000} & \text{ 86.00} \\
O_2 & \rightleftharpoons O_2 + CH_6CO & 1.000 \times 10^9 & \text{ 0.000} & \text{ 100000.00} \\
\end{align*} \]
\[ \begin{align*}
H_2/2.00/ & \quad H_2O/6.00/ \quad CH_4/2.00/ \quad CO/1.50/ \quad CO_2/2.00/ \quad C_2H_6/3.00/ \\
H+CH_2OH & \rightleftharpoons H_2+CH_2O \quad 2.000E+13 \quad .000 \quad .00 \\
H+CH_2OH & \rightleftharpoons OH+CH_3 \quad 1.650E+11 \quad .650 \quad -284.00 \\
H+CH_2OH & \rightleftharpoons CH_2(S)+H_2O \quad 3.280E+13 \quad -.090 \quad 610.00 \\
H+CH_3O(+M) & \rightleftharpoons CH_3OH(+M) \quad 2.430E+12 \quad .515 \quad 50.00 \\
\text{LOW} & \quad 4.660E+41 \quad -7.440 \quad 14080.00 \\
\text{TROE} & \quad .700 \quad 100.00 \quad 90000.00 \quad 10000.00 / \\
H+CH_2OH & \rightleftharpoons OH+CH_3 \quad 1.500E+12 \quad .500 \quad -110.00 \\
H+CH_2OH & \rightleftharpoons CH_2(S)+H_2O \quad 3.280E+13 \quad -.090 \quad 610.00 \\
H+CH_3O(+M) & \rightleftharpoons CH_3OH(+M) \quad 2.430E+12 \quad .515 \quad 50.00 \\
\text{LOW} & \quad 4.660E+41 \quad -7.440 \quad 14080.00 \\
\text{TROE} & \quad .700 \quad 100.00 \quad 90000.00 \quad 10000.00 / \\
H+CH_2OH & \rightleftharpoons OH+CH_3 \quad 1.500E+12 \quad .500 \quad -110.00 \\
H+CH_2OH & \rightleftharpoons CH_2(S)+H_2O \quad 3.280E+13 \quad -.090 \quad 610.00 \\
H+CH_3O(+M) & \rightleftharpoons CH_3OH(+M) \quad 2.430E+12 \quad .515 \quad 50.00 \\
\text{LOW} & \quad 4.660E+41 \quad -7.440 \quad 14080.00 \\
\text{TROE} & \quad .700 \quad 100.00 \quad 90000.00 \quad 10000.00 / \\
H+CH_2OH & \rightleftharpoons OH+CH_3 \quad 1.500E+12 \quad .500 \quad -110.00 \\
H+CH_2OH & \rightleftharpoons CH_2(S)+H_2O \quad 3.280E+13 \quad -.090 \quad 610.00 \\
H+CH_3O(+M) & \rightleftharpoons CH_3OH(+M) \quad 2.430E+12 \quad .515 \quad 50.00 \\
\text{LOW} & \quad 4.660E+41 \quad -7.440 \quad 14080.00 \\
\text{TROE} & \quad .700 \quad 100.00 \quad 90000.00 \quad 10000.00 / \\
H+CH_2OH & \rightleftharpoons OH+CH_3 \quad 1.500E+12 \quad .500 \quad -110.00 \\
H+CH_2OH & \rightleftharpoons CH_2(S)+H_2O \quad 3.280E+13 \quad -.090 \quad 610.00 \\
H+CH_3O(+M) & \rightleftharpoons CH_3OH(+M) \quad 2.430E+12 \quad .515 \quad 50.00 \\
\text{LOW} & \quad 4.660E+41 \quad -7.440 \quad 14080.00 \\
\text{TROE} & \quad .700 \quad 100.00 \quad 90000.00 \quad 10000.00 / \\
H+CH_2OH & \rightleftharpoons OH+CH_3 \quad 1.500E+12 \quad .500 \quad -110.00 \\
H+CH_2OH & \rightleftharpoons CH_2(S)+H_2O \quad 3.280E+13 \quad -.090 \quad 610.00 \\
H+CH_3O(+M) & \rightleftharpoons CH_3OH(+M) \quad 2.430E+12 \quad .515 \quad 50.00 \\
\text{LOW} & \quad 4.660E+41 \quad -7.440 \quad 14080.00 \\
\text{TROE} & \quad .700 \quad 100.00 \quad 90000.00 \quad 10000.00 / \\ 
\end{align*} \]


**DUPLICATE**

- $\text{OH} + C \leftrightarrow H + CO$
  - $5.000 \times 10^{13}$  .000  .00
- $\text{OH} + CH \leftrightarrow H + HCO$
  - $3.000 \times 10^{13}$  .000  .00
- $\text{OH} + CH_2 \leftrightarrow H + CH_2O$
  - $2.000 \times 10^{13}$  .000  .00
- $\text{OH} + CH_2 \leftrightarrow CH + H_2O$
  - $1.130 \times 10^{07}$  2.000  3000.00
- $\text{OH} + CH_2 (S) \leftrightarrow H + CH_2O$
  - $3.000 \times 10^{13}$  .000  .00
- $\text{OH} + CH_3 (\pm M) \leftrightarrow CH_3OH (\pm M)$
  - $2.790 \times 10^{18}$  -1.430  1330.00

  **LOW** / $4.000 \times 36$  -5.920  3140.00 /

  **TROE**/  .4120  195.0  5900.00  6394.00 /

- $H_2 / 2.00 / H_2O / 6.00 / CH_4 / 2.00 / CO / 1.50 / CO_2 / 2.00 / C_2H_6 / 3.00 /
- $\text{OH} + CH_3 \leftrightarrow H + CH_3O$
  - $3.430 \times 10^{13}$  .000  .00
- $\text{OH} + CH_3O \leftrightarrow H + CH_3O$
  - $3.000 \times 10^{12}$  .000  .00
- $\text{OH} + CH_3OH \leftrightarrow CH_2OH + H_2O$
  - $1.440 \times 10^{06}$  2.000  2000.00
- $\text{OH} + CH_3OH \leftrightarrow CH_3O + H_2O$
  - $6.300 \times 10^{06}$  2.000  1500.00
- $\text{OH} + C_2H \leftrightarrow H + HCCO$
  - $2.000 \times 10^{13}$  .000  .00
- $\text{OH} + C_2H_2 \leftrightarrow H + CH_2CO$
  - $2.180 \times 10^{04}$  4.500  -1000.00
- $\text{OH} + C_2H_2 \leftrightarrow H + HCCOH$
  - $5.040 \times 10^{05}$  2.300  13500.00
- $\text{OH} + C_2H_2 \leftrightarrow C_2H + H_2O$
  - $3.700 \times 10^{07}$  2.000  14000.00
- $\text{OH} + C_2H_2 \leftrightarrow CH_3 + CO$
  - $4.830 \times 10^{04}$  4.000  -2000.00
- $\text{OH} + C_2H_3 \leftrightarrow H + C_2H_2$
  - $5.000 \times 12$  .000  .00
- $\text{OH} + C_2H_4 \leftrightarrow C_2H_3 + H_2O$
  - $3.600 \times 10^{06}$  2.000  2500.00
- $\text{OH} + C_2H_6 \leftrightarrow C_2H_5 + H_2O$
  - $3.540 \times 10^{06}$  2.120  870.00
- $\text{OH} + CH_2CO \leftrightarrow HCCO + H_2O$
  - $7.500 \times 10^{12}$  .000  2000.00
- $2\text{HO}_2 \leftrightarrow O_2 + H_2O$
  - $1.300 \times 10^{11}$  .000  -1630.00

  **DUPLICATE**

- $2\text{HO}_2 \leftrightarrow O_2 + 2H_2O$
  - $4.200 \times 10^{14}$  .000  12000.00

  **DUPLICATE**

- $H_2O_2 + CH_2 \leftrightarrow OH + CH_2O$
  - $2.000 \times 10^{13}$  .000  .00
- $H_2O_2 + CH_3 \leftrightarrow H_2O + CH_4$
  - $1.000 \times 10^{12}$  .000  .00
- $H_2O_2 + CH_3 \leftrightarrow OH + CH_3O$
  - $3.700 \times 10^{13}$  .000  .00
- $H_2O_2 + CO \leftrightarrow OH + CO_2$
  - $1.500 \times 10^{14}$  .000  23600.00
- $H_2O_2 + CH_2O \leftrightarrow HCO + H_2O$
  - $5.600 \times 10^{06}$  2.000  12000.00
- $C + O_2 \leftrightarrow O + CO$
  - $5.000 \times 13$  .000  576.00
- $C + CH_2 \leftrightarrow H + C_2H$
  - $5.000 \times 13$  .000  .00
- $C + CH_3 \leftrightarrow H + C_2H_2$
  - $5.000 \times 13$  .000  .00
- $CH + O_2 \leftrightarrow O + HCO$
  - $6.710 \times 13$  .000  .00
- $CH + H_2 \leftrightarrow H + CH_2$
  - $1.080 \times 14$  .000  3110.00
- $CH + H_2O \leftrightarrow H + CH_2O$
  - $5.710 \times 12$  .000  -755.00
- $CH + C_2H_2 \leftrightarrow H + C_2H_2$
  - $4.000 \times 13$  .000  .00
- $CH + C_2H_3 \leftrightarrow H + C_2H_3$
  - $3.000 \times 13$  .000  .00
- $CH + CH_4 \leftrightarrow H + C_2H_4$
  - $6.000 \times 13$  .000  .00
- $CH CO (\pm M) \leftrightarrow HCOO (\pm M)$
  - $5.000 \times 13$  .000  .00

  **LOW** / $2.609 \times 28$  -3.740  1936.00 /

  **TROE**/  .5757  237.00  1652.00  5069.00 /

- $H_2 / 2.00 / H_2O / 6.00 / CH_4 / 2.00 / CO / 1.50 / CO_2 / 2.00 / C_2H_6 / 3.00 / AR / .70 /
- $CH + CO_2 \leftrightarrow HCO + CO$
  - $1.900 \times 14$  .000  15792.00
- $CH + CH_2O \leftrightarrow H + CH_2CO$
  - $9.460 \times 13$  .000  -515.00
- $CH + HCOO \leftrightarrow CO + C_2H_2$
  - $5.000 \times 13$  .000  .00
- $CH_2 + O_2 \leftrightarrow OH + HCO$
  - $5.000 \times 12$  .000  1500.00
- $CH_2 + H_2 \leftrightarrow H + CH_3$
  - $5.000 \times 05$  2.000  7230.00
- $2CH_2 \leftrightarrow H_2 + C_2H_2$
  - $1.600 \times 15$  .000  11944.00

217
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<th>Reaction</th>
<th>A</th>
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N20+H <=> N2+OH 3.870E+14 .000 18880.00
N20+OH <=> N2+H2O 2.000E+12 .000 21060.00
N20 (+M) <=> N2+O (+M) 7.910E+10 .000 56020.00

LOW / 6.370E+14 .000 56640.00/
H2/2.00/ H2O/2.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .625/
H2O+NO <=> NO2+OH 2.110E+12 .000 -480.00
NO+O+M <=> NO2+M 1.060E+20 -1.410 .00

H2/2.00/ H2O/2.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
NO2+O <=> NO+O2 3.900E+12 .000 -240.00
NO2+H <=> NO+OH 3.130E+14 .000 360.00
NH+OH <=> NH2+H 2.000E+13 .000 .00
NH+O+M <=> NH2+M 4.300E+13 1.200 .00

NH+O2 <=> HNO+O 4.610E+05 2.000 6500.00
NH+O2 <=> NO+OH 1.280E+06 1.500 100.00
NH+N <=> N2+H 1.500E+13 .000 .00
NH+N2O <=> NH+H2 2.000E+13 .000 13850.00
NH+NO <=> N2+OH 2.160E+13 -1.230 .00
NH+NO <=> N2O+H 3.650E+14 -1.450 .00
NH2+O <=> OH+NH 3.000E+12 .000 .00
NH2+O2 <=> H+HNO 3.900E+13 .000 .00

NH2+H+H2 4.000E+13 .000 3650.00
NH2+OH <=> NH+H2O 9.000E+07 1.500 -460.00
NNH+M <=> N2+H+M 1.300E+14 -1.100 4980.00

H2/2.00/ H2O/2.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

H2/2.00/ H2O/2.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

H2/2.00/ H2O/2.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

H2/2.00/ H2O/2.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

H2/2.00/ H2O/2.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

H2/2.00/ H2O/2.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

HCN+O <=> NCO+H 2.030E+04 2.640 4980.00

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<tr>
<td>NO+O2&lt;&gt;+N2+CO2</td>
<td>3.250E+12</td>
<td>0.000</td>
<td>-705.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ N + \text{CO}_2 \leftrightarrow \text{NO} + \text{CO} \]
\[ O + \text{CH}_3 \rightarrow \text{H} + \text{H}_2 + \text{CO} \]
\[ O + \text{C}_2\text{H}_4 \rightarrow \text{H} + \text{CH}_2\text{CHO} \]
\[ O + \text{C}_2\text{H}_5 \rightarrow \text{H} + \text{CH}_3\text{CHO} \]
\[ \text{OH} + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} \]
\[ \text{OH} + \text{CH}_3 \rightarrow \text{H}_2 + \text{CH}_2\text{O} \]
\[ \text{CH} + \text{H}_2 + \text{M} \leftrightarrow \text{CH}_3 + \text{M} \]

Low:
\[ 11300.00 \]
\[ 220.00 \]
\[ 17330.00 \]
\[ -370.00 \]

Troe:
\[ 122.0 \]
\[ 9365.0 \]
\[ 590.0 \]

H_2: 2.00 / H_2O: 6.00 / CH_4: 2.00 / CO: 1.50 / CO_2: 2.00 / C_2H_6: 3.00 / AR: 0.500 / 

\[ \text{O} + \text{C}_3\text{H}_7 \leftrightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O} \rightarrow 9.64 \times 10^{13} \]
\[ \text{H} + \text{C}_3\text{H}_7(+) \leftrightarrow \text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow 4.06 \times 10^6 \]

Low:
\[ 3716.00 \]
\[ 6756.00 \]
\[ 934.00 \]
\[ 1500.00 \]

Troe:
\[ 277.0 \]
\[ 8748.0 \]
\[ 7891.0 \]

H_2: 2.00 / H_2O: 6.00 / CH_4: 2.00 / CO: 1.50 / CO_2: 2.00 / C_2H_6: 3.00 / AR: 0.70 / 

\[ \text{O} + \text{C}_3\text{H}_8 \rightarrow \text{CH}_3 + \text{C}_3\text{H}_7 \rightarrow 3.00 \times 10^6 \]
\[ \text{H} + \text{C}_3\text{H}_7 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow 2.55 \times 10^6 \]

Low:
\[ 3716.00 \]
\[ 6756.00 \]
\[ 934.00 \]
\[ 1500.00 \]

Troe:
\[ 277.0 \]
\[ 8748.0 \]
\[ 7891.0 \]

H_2: 2.00 / H_2O: 6.00 / CH_4: 2.00 / CO: 1.50 / CO_2: 2.00 / C_2H_6: 3.00 / AR: 0.70 / 

\[ \text{O} + \text{C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O} \rightarrow 9.64 \times 10^6 \]
\[ \text{H} + \text{C}_3\text{H}_7(+) \leftrightarrow \text{C}_3\text{H}_8(+) \rightarrow 3.61 \times 10^6 \]

Low:
\[ 3716.00 \]
\[ 6756.00 \]
\[ 934.00 \]
\[ 1500.00 \]

Troe:
\[ 277.0 \]
\[ 8748.0 \]
\[ 7891.0 \]

H_2: 2.00 / H_2O: 6.00 / CH_4: 2.00 / CO: 1.50 / CO_2: 2.00 / C_2H_6: 3.00 / AR: 0.70 / 

\[ \text{OH} + \text{C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O} \rightarrow 2.41 \times 10^6 \]
\[ \text{HO}_2 + \text{C}_3\text{H}_7 \rightarrow \text{O}_2 + \text{C}_3\text{H}_7 + \text{H}_2\text{O} \rightarrow 2.55 \times 10^6 \]

Low:
\[ 3716.00 \]
\[ 6756.00 \]
\[ 934.00 \]

Troe:
\[ 277.0 \]
\[ 8748.0 \]
\[ 7891.0 \]

H_2: 2.00 / H_2O: 6.00 / CH_4: 2.00 / CO: 1.50 / CO_2: 2.00 / C_2H_6: 3.00 / AR: 0.70 / 

\[ \text{OH} + \text{C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O} \rightarrow 2.41 \times 10^6 \]
\[ \text{HO}_2 + \text{C}_3\text{H}_7 \rightarrow \text{O}_2 + \text{C}_3\text{H}_7 + \text{H}_2\text{O} \rightarrow 2.55 \times 10^6 \]

Low:
\[ 3716.00 \]
\[ 6756.00 \]
\[ 934.00 \]

Troe:
\[ 277.0 \]
\[ 8748.0 \]
\[ 7891.0 \]

H_2: 2.00 / H_2O: 6.00 / CH_4: 2.00 / CO: 1.50 / CO_2: 2.00 / C_2H_6: 3.00 / AR: 0.70 / 

\[ \text{OH} + \text{C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O} \rightarrow 2.41 \times 10^6 \]
\[ \text{HO}_2 + \text{C}_3\text{H}_7 \rightarrow \text{O}_2 + \text{C}_3\text{H}_7 + \text{H}_2\text{O} \rightarrow 2.55 \times 10^6 \]

Low:
\[ 3716.00 \]
\[ 6756.00 \]
\[ 934.00 \]

Troe:
\[ 277.0 \]
\[ 8748.0 \]
\[ 7891.0 \]

H_2: 2.00 / H_2O: 6.00 / CH_4: 2.00 / CO: 1.50 / CO_2: 2.00 / C_2H_6: 3.00 / AR: 0.70 / 

\[ \text{OH} + \text{C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O} \rightarrow 2.41 \times 10^6 \]
\[ \text{HO}_2 + \text{C}_3\text{H}_7 \rightarrow \text{O}_2 + \text{C}_3\text{H}_7 + \text{H}_2\text{O} \rightarrow 2.55 \times 10^6 \]
### B.3 Hydrocarbon-air over Pt Mechanisms

Table B.2 below lists additional chemical mechanisms for hydrocarbon-air reactions over platinum catalysts, which were found in the literature. The table indicates the type of mechanism, the reactions involved or the rate equation, the relevant constants, and the reference in which it was found.

<table>
<thead>
<tr>
<th>TYPE</th>
<th>REACTIONS</th>
<th>CONSTANTS</th>
<th>SOURCE</th>
</tr>
</thead>
</table>
| Langmuir-Hinshelwood, 3-step | HC + S ↔ HC-S  
O2 + S ↔ O2-S  
HC-S + O2-S ↔ 2S + prods | see source for $E_a$ and A for each reaction | Veser & Schmidt, 1996 |
| Arrhenius, 1-step | $C_3H_8 + 5O_2 ↔ 3CO_2 + 4H_2O$ | $E_a = 17$ kcal/mole  
$A = 1.1 \times 10^9$ cm/sec | Hiam, Wise, & Chaikin, 1968 |
| Arrhenius, 1-step (alumina support) | $C_3H_8 + 5O_2 ↔ 3CO_2 + 4H_2O$ | $E_a = 22.1$ kcal/mole  
A varies with loading | Otto, Andino, & Parks, 1991 |
| Arrhenius, 1-step (zirconia support) | $C_3H_8 + 5O_2 ↔ 3CO_2 + 4H_2O$ | $E_a = 17.8$ kcal/mole  
A varies with loading | Hubbard, Otto, et al., 1993 |
| Arrhenius, 1-step | $R = kP_a^{HCP}P_o^{b}$ | $a = 1.2$  
b = -0.2  
$E_a = 23.3$ kcal/mole  
$A = 540000$ s$^{-1}$ cm$^{-2}$ | Aryafar & Zaera, 1997 |
Appendix C

Gas-phase Microcombustor Emissions Predictions

C.1 Introduction and Objective

A high temperature, hydrocarbon-fueled gas-phase microcombustion system may produce significant levels of undesirable exhaust gas emissions such as nitrous oxides (NO, NO₂, NOₓ) and unburned hydrocarbons. It is the objective of this study to analytically predict the emissions levels for micro-scale combustion systems. For this parametric study, various thermal boundary conditions and a range of combustor volumes for given flow conditions will be examined with respect to their relative emissions levels. The following sections will provide some background of how these exhaust gas species are formed, define the specific problem and parameters to be reviewed, present the models and tools used for the analysis, and discuss the results.

C.2 Background

C.2.1 Unburned Hydrocarbon Emissions

For the gas-phase microcombustor, hydrocarbon emissions are unburned fuel being exhausted from the device. In this case, it will likely be due to a lack of residence time (small volume and relatively large mass flow rate) and incomplete combustion. While the fluid dynamic time-scales vary with geometry, chemical time-scales do not. For a large enough residence time, the fuel should be completely consumed and emissions negligible. However, at the volumes and flow rates required by the combustor for the microengine, this is not the case. A detailed review of the trade-off between these competing time-scales can be found in Section 2.1 of this thesis.

For this study, and the gas-phase microcombustor in general, we are most interested in using propane (C₃H₈) as the fuel. Unburned hydrocarbon emissions can take several forms. First, they can consist of unburned propane itself. However, it is unlikely that much of this will be present in the exhaust gas as the initial steps of the combustion
process involve breaking this molecule into smaller hydrocarbon species. The hydrocarbon species, which will most likely be present in the exhaust, are acetylene (C$_2$H$_2$) and ethylene (C$_2$H$_4$). For the purposes of this analysis, all hydrocarbons predicted in the exhaust stream will be summed to yield one value (presented here in terms of mole fraction) of unburned hydrocarbons (UHC) as shown below.

$$[UHC] = \sum [C_{x}H_{y}]$$  \hspace{1cm} (C.1)

UHCs are expected to be higher for lower residence time conditions (smaller volumes) for a given mass flow rate. At some point the residence time will be too small to sustain any combustion and flame blowout will occur resulting in all of the fuel being exhausted from the device. A notional plot of this phenomenon is shown in Figure C.1 for UHC mole fraction versus volume. For conditions of constant residence time and varying mass flow rate, UHC emissions are expected to remain constant with volume as indicated in Figure C.1. As temperature increases for constant residence time conditions, UHC emissions will decrease due to increased reaction rates. This is shown notionally in Figure C.2.

![Figure C.1 Notional plot of UHC emissions versus volume.](image-url)
C.2.2 NO\textsubscript{x} Emissions

NO and NO\textsubscript{2} are the most common forms of NO\textsubscript{x} and their respective mole fractions are summed to give the overall concentration. For NO\textsubscript{x} emissions, the same general concepts used to assess UHCs apply, however NO\textsubscript{x} is formed rather than consumed. This should result in the opposite trends as those expected for UHCs. As volume decreases (residence time decreases) for a constant mass flow rate, NO\textsubscript{x} formation should decrease. For constant residence time conditions, NO\textsubscript{x} will remain constant with varying volume. These trends are illustrated in Figure C.3. NO\textsubscript{x} formation is slow at lower temperatures (<1000 K) and increases dramatically with temperature until reaching its equilibrium value. This is indicated in the notional plot shown in Figure C.4. As a result, it is also expected that NO\textsubscript{x} formation will be a maximum at an equivalence ratio of unity as this is the mixture ratio, which will result in the largest heat release and highest temperatures. The richer or leaner a mixture gets, the less NO\textsubscript{x} is created.
Figure C. 3 Notional plot of NOx emissions versus volume.

Figure C. 4 Notional plot of NOx emissions versus temperature.
There are four chemical mechanisms for NO\textsubscript{x} formation. These include thermal NO\textsubscript{x}, prompt NO, N\textsubscript{2}O mechanisms, and fuel-bound mechanisms. Thermal NO\textsubscript{x} (also known as the Zeldovich mechanism) is the most common method of formation and occurs readily at higher temperatures. Some reactions are shown below [72,73].

\begin{align*}
N_2 + O_2 & \Leftrightarrow 2NO \quad (C.2) \\
O + N_2 & \Leftrightarrow NO + N \quad (C.3) \\
N + O_2 & \Leftrightarrow NO + O \quad (C.4)
\end{align*}

Prompt NO formation occurs near the flame itself and its reactions include

\begin{align*}
CH + N_2 & \Leftrightarrow HCN + N \quad (C.5) \\
C_2 + N_2 & \Leftrightarrow 2CN \quad (C.6)
\end{align*}

followed by subsequent oxidation of N and NH to form NO species [72,73]. N\textsubscript{2}O mechanisms are common in lean premixed systems such as the microcombustor. These reactions tend to form NO\textsubscript{x} at a slower rate and at lower temperatures. Possible reactions are shown below [72,73].

\begin{align*}
N_2O + O + M & \Leftrightarrow N_2O + M \quad (C.7) \\
N_2O + O & \Leftrightarrow 2NO \quad (C.8)
\end{align*}

Finally, fuel-bound NO\textsubscript{x} formation is unlikely for the microcombustor. This mechanism of NO\textsubscript{x} formation relies on N\textsubscript{2} already being present in the fuel itself, such as in coal [73]. For a propane-air mixture, the N\textsubscript{2} species are from the air only and are not present in the fuel.
C.3 Parameter Definition

This section will briefly describe the flow conditions, thermal boundary conditions, and volume variations, which will be studied in this parametric investigation. The flow conditions will be held constant for all analyses while results for various thermal boundary conditions are shown with respect to a varying combustor volume. All cases will be run for both a constant mass flow rate and constant residence time.

UHC and NOx emissions will be evaluated for the flow conditions, which are shown in Table C.1. These conditions are typical of a combustor for the microengine.

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel species</td>
<td>Propane (C(_3)H(_8))</td>
</tr>
<tr>
<td>Equivalence ratio</td>
<td>0.8</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>500 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>2 atm</td>
</tr>
<tr>
<td>Mass flow rate (for constant mass flow cases)</td>
<td>0.2 g/s</td>
</tr>
<tr>
<td>Residence time (for constant residence time cases)</td>
<td>0.4 ms</td>
</tr>
</tbody>
</table>

The emissions predictions will be performed for combustor volumes of 1/10, 1/100, and 1/1000 of a baseline volume. The actual microcombustor volume will be taken as this baseline and is 191 mm\(^3\). The thermal boundary conditions, which will be considered in this analysis, are:

1. Adiabatic conditions.
2. Constant wall temperature conditions (850 K will be used).
3. Constant heat flux (to the wall) per unit volume (10% heat loss from the baseline combustor will be used, corresponding to \(Q/V = 1.0 \times 10^8 \) W/m\(^3\)).
C.4 Models

C.4.1 Fluid/Chemical

The chemical model, which will be used for this analysis, is GRIMech 3.0 [38]. This mechanism contains approximately 300 reactions and 50 different species. This is the most well developed mechanism for hydrocarbon-air reactions available and is capable of accounting for all hydrocarbon species smaller than and including propane (C₃H₈). The species and reactions of GRIMech 3.0 are listed in Appendix 3.2.

The fluid model selected for this analysis is that of a perfectly stirred reactor (PSR). This assumes that the fuel-air mixture is already well mixed and the reactor is isothermal and isobaric. Chemkin III’s *Aurora* subroutine is able to perform calculations for a PSR’s exit conditions (temperature, species concentrations, etc.) given an inlet gas mixture, inlet temperature, reactor pressure, and thermal boundary condition (adiabatic condition or heat loss in Watts can be specified).

C.4.2 Estimating Heat Loss for Constant Wall Temperature Cases

For the constant wall temperature boundary condition, some additional calculations must be performed. In order to utilize *Aurora*’s non-adiabatic mode of operation, the heat loss from the reactor must be specified in Watts. In order to obtain this value and subsequently the exhaust gas species concentrations, an iterative process is required.

The wall temperature will be held constant at 850 K for all cases. This value was selected as a reasonable approximation of the actual microcombustor wall temperature. The next step in the process is to guess the reactor temperature. Using this temperature, a heat transfer coefficient is then computed using a Nusselt number correlation [35].

\[
Nu = 0.332 \, Pr^{0.3} \, Re^{0.2} \tag{C.9}
\]

Prandtl number and Reynolds number are defined as
\[ Pr = \frac{\mu C_p}{k} \] (C.10)

\[ Re = \frac{\rho v L}{\mu} = \frac{\dot{m}L}{A\mu}. \] (C.11)

Correlations for viscosity and thermal conductivity of the gas are shown below and are in units of Ns/m² and W/mK respectively [36].

\[ \mu = 1.716 \times 10^{-5} \left( \frac{T}{273} \right)^{\frac{1}{2}} \left( \frac{273+111}{T+111} \right) \] (C.12)

\[ k = 0.241 \left( \frac{T}{273} \right)^{\frac{1}{2}} \left( \frac{273+194}{T+194} \right) \] (C.13)

An estimate of the heat transfer coefficient can then be found from

\[ h = \frac{NuL}{k}. \] (C.14)

Next, the heat lost from the reactor can be estimated using the heat transfer coefficient and the wall and reactor temperatures.

\[ Q_{out} = hA(T_{reactor} - T_{wall}) \] (C.15)

This heat loss estimate is then input into Aurora and the resulting exhaust species and outlet temperature are obtained. This temperature is then checked with the initial guess. If it is reasonably close (within 1 K) then the Aurora output is considered a reasonable estimate of the outlet gas species concentrations. If the temperatures do not converge, then a new reactor temperature is selected based on the Aurora output. The procedure is
repeated until this convergence is obtained. A flow chart representation of this process is shown in Figure C.5.

![Flow chart for constant wall temperature cases.](image)

**Figure C.5** Flow chart for constant wall temperature cases.
C.5 Results

C.5.1 Constant Mass Flow Rate

The results obtained for the constant mass flow rate cases follow the trends, which were described in Section C.2. For UHCs, as volume decreases (causing a corresponding decrease in residence time) emissions of these species increases due to incomplete reactions as shown in Figure C.6. Eventually, there is no reaction at all and the final mole fraction of hydrocarbons equals the initial for the cases of $1/100$ and $1/1000$ of the baseline volume. The varying thermal boundary conditions have little effect on the results indicating that the time-scale constraint is the dominant factor. In the case of NO\textsubscript{x} emissions, there is some variation with the different thermal boundary conditions. At the baseline volume, there is more NO\textsubscript{x} formed in the adiabatic case. This is a result of it being the highest temperature case. The results in Figure C.7 also indicate that NO\textsubscript{x} emissions trend as expected with volume for constant mass flow rate.

![Figure C. 6 UHC emissions predictions for constant mass flow rate.](image)
Figure C.7 NOx emissions predictions for constant mass flow rate.

C.5.2 Constant Residence Time

For the constant residence time cases, the thermal boundary conditions become more important. Figure C.8 shows the UHC emissions versus volume for a residence time of 0.4 ms. For the adiabatic and constant heat loss cases, the UHC emissions are negligible. This is primarily due to the high temperatures associated with these cases resulting in fast reaction rates and consumption of all of the fuel. In the constant wall temperature case, as the volume gets smaller heat loss per unit volume from the reactor increases to a level where it significantly impacts the reaction time-scale. Eventually, there is no reaction and the initial hydrocarbon concentration equals that in the exhaust. NOx emissions are shown in Figure C.9. For adiabatic and constant heat loss per unit volume conditions, NOx emissions are constant with volume as expected. More NOx is formed in the adiabatic case due to the higher temperatures involved. For the constant wall temperature case, NOx emissions rise with volume. As the volume increases, the heat loss per unit volume decreases and the emissions levels will approach that of the adiabatic case.
Figure C. 8 UHC emissions predictions for constant residence time.

Figure C. 9 NOx emissions predictions for constant residence time.
C.6 Summary and Conclusions

The gas-phase microcombustor emissions predictions revealed that the most likely emissions are unburned hydrocarbons resulting from inadequate residence time. NO$_x$ emissions should be very low for similar reasons. The high mass flow rates and small volumes do not provide enough time for significant quantities of NO$_x$ to form. As volume decreases below the baseline, reactions in general cease and the exhaust gas concentrations are the same as at the inlet. For varying thermal boundary conditions and constant residence time it was found that NO$_x$ emissions scale with heat loss per unit volume. The adiabatic case results in the highest NO$_x$ levels, while the constant wall temperature case approaches the adiabatic limit as volume increases and heat loss per unit volume decreases.
Appendix D

Thermo-Acoustic Stability Analysis

D.1 Introduction and Objective

The gas-phase combustion system for the demonstration micro gas turbine engine is designed for lean premixed operation. Unfortunately, such lean premixed combustion systems have been known to exhibit combustion instabilities. As the combustion process becomes leaner, flame thickness, flame speed, and reaction rates become more sensitive. Self-excited oscillations occur when unsteady heat release interacts detrimentally with the systems dynamics via some feedback mechanism. Rayleigh’s criterion states that for a self-excited oscillation to occur the unsteady heat release process must be in phase with the fluctuating acoustic pressure and the rate of energy addition must be greater than the rate of dissipation.

One possible feedback mechanism is the generation of heat release oscillations by periodic variations in equivalence ratio. A time varying mixture ratio can be convected downstream from the fuel injection point to the flame zone. As a result, an oscillatory heat release process will occur. This process can then cause acoustic pressure waves to propagate back upstream resulting in the equivalence ratio oscillations at the fuel injectors. It is the objective of this study to evaluate the potential for this type of instability in the combustor for the microengine.

D.2 Model

This phenomenon can be modeled by representing a typical lean premixed combustion system as a series of ducts with fuel injectors and a flame zone \([74,75]\). Figure D.1 shows a schematic of this representation. The inlet duct includes the fuel injectors and the entrance to the flame zone. The combustion chamber itself consists of the flame zone and a downstream section. The boundary condition at the inlet is that of an open duct with \(p'(0,t) = 0\) and at the combustion chamber exit, it is a choked nozzle.
The flow in the system is assumed to be one-dimensional, unsteady, compressible, and inviscid. All perturbations are small so that a linear analysis can be conducted (e.g. \( p(x,t) = \bar{p} + p'(x,t) \)). Entropy waves in the inlet duct are neglected and small changes in density and pressure are assumed to be isentropic. Mixing occurs instantaneously at the fuel injectors and non-uniformities in the mixture are convected downstream with the mean flow as oscillations in equivalence ratio. All periodic disturbances are of the form \( e^{i\omega t} \).

![Figure D. 1 Schematic of lean premixed combustion system.](image)

The linearized continuity and momentum equations are

\[
\frac{\partial \rho'}{\partial t} + \bar{u} \frac{\partial \rho'}{\partial x} + \bar{\rho} \frac{\partial u'}{\partial x} = 0 \tag{D.1}
\]

\[
\frac{\partial u'}{\partial t} + \bar{u} \frac{\partial u'}{\partial x} + \left( \frac{1}{\bar{\rho}} \right) \frac{\partial p'}{\partial x} = 0 \tag{D.2}
\]

respectively. The linearized isentropic relation is

\[
\frac{p'}{\bar{p}} = \frac{\gamma \rho'}{\bar{\rho}}. \tag{D.3}
\]

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Combining these yields equations for the pressure and velocity fluctuations as a function of time and space.

\[
\left( \frac{1}{\bar{a}} \frac{\partial}{\partial t} + \bar{M} \frac{\partial}{\partial x} \right) \begin{bmatrix} u' \n p' \end{bmatrix} - \frac{\partial^2}{\partial x^2} \begin{bmatrix} u' \n p' \end{bmatrix} = 0 \quad (D.4)
\]

For periodic disturbances of the form \( e^{j\omega t} \), the solutions to the above system of equations are

\[
u' = A e^{j(\omega t - k_1 x)} + B e^{j(\omega t - k_2 x)} \quad (D.5)
\]

\[
p' = A \bar{\rho} \bar{a} e^{j(\omega t - k_1 x)} - B \bar{\rho} \bar{a} e^{j(\omega t + k_2 x)} \quad (D.6)
\]

where the wave numbers \( k_1 \) and \( k_2 \) are given by

\[
k_1 = \left( \frac{\omega}{\bar{a}} \right) \frac{1}{1 + \bar{M}} \quad (D.7)
\]

\[
k_2 = \left( \frac{\omega}{\bar{a}} \right) \frac{1}{1 - \bar{M}} \quad (D.8)
\]

The wave number is proportional to the inverse of wavelength \((1/\lambda)\) and \( k_1 \) and \( k_2 \) represent forward and backward traveling waves respectively.

To couple these solutions to the wave equation between various fluid components, transmission matrices may be used. For any fluid component, the pressure and velocity perturbation at the exit can be written in terms of the inlet pressure and velocity perturbation. This can be expressed generally as

\[
\begin{bmatrix} p' \\ \frac{\partial p'}{\partial u'} \end{bmatrix}_{\text{EXIT}} = \begin{bmatrix} 2 \times 2 \text{ MATRIX} \end{bmatrix} \begin{bmatrix} p' \\ \frac{\partial p'}{\partial u'} \end{bmatrix}_{\text{INLET}} . \quad (D.9)
\]

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This formulation will be used to determine the unstable frequencies and to explore the effect of fuel injector location on system stability. A transfer matrix will represent each segment of the system. These matrices will be combined to relate the upstream end of the system to the downstream end. This will result in an eigenvalue problem, which can be solved for the eigenfrequencies and the system stability.

D.3 Section #1 – Open Duct to Fuel Injector

Equations for pressure and velocity perturbations in the duct section from the opening to the fuel injectors can be developed. Knowing the boundary condition at the opening \( p'(0, t) = 0 \), the equations for pressure and velocity at \( x = 0 \) are

\[
\begin{align*}
\begin{bmatrix} p' \\ \rho a u' \end{bmatrix}_0 &= \begin{bmatrix} \rho_a - \rho_a \\ \rho a \\ \rho a \end{bmatrix} A \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{j\omega t}.
\end{align*}
\]

We can then write the equations for the fuel injector location in terms of those at \( x = 0 \) and a transmission matrix.

\[
\begin{align*}
\begin{bmatrix} p' \\ \rho a u' \end{bmatrix}_{\text{INJ}} &= \begin{bmatrix} \frac{1}{2} \left( e^{-jkL_{\text{INJ}}} + e^{jkL_{\text{INJ}}} \right) & \frac{1}{2} \left( e^{-jkL_{\text{INJ}}} - e^{jkL_{\text{INJ}}} \right) \\
\frac{1}{2} \left( e^{-jkL_{\text{INJ}}} - e^{jkL_{\text{INJ}}} \right) & \frac{1}{2} \left( e^{-jkL_{\text{INJ}}} + e^{jkL_{\text{INJ}}} \right) \end{bmatrix} \begin{bmatrix} p' \\ \rho a u' \end{bmatrix}_0.
\end{align*}
\]

For later use we will define these transmission matrices as \( \beta_0 \) and \( \beta_{\text{INJ}} \) respectively.

D.4 Section #2 – Combustion Chamber Inlet

The equations describing the flow perturbations at the combustion chamber inlet (\( x=L \)) can be written in terms of those at the fuel injector and a transmission matrix.
\[
\left[ \frac{p'}{\bar{\rho} \bar{u}'} \right]_1 = \left[ \frac{1}{2} \left( e^{-j \lambda_1 (L-u_1)} + e^{j \lambda_2 (L-u_1)} \right) \right] \frac{1}{2} \left( e^{-j \lambda_3 (L-u_2)} - e^{j \lambda_2 (L-u_2)} \right) \left[ \frac{1}{2} \left( e^{j \lambda_1 (L-u_1)} - e^{-j \lambda_2 (L-u_1)} \right) \right] \left[ \frac{1}{2} \left( e^{-j \lambda_3 (L-u_2)} + e^{j \lambda_2 (L-u_2)} \right) \right] \left[ \frac{p'}{\bar{\rho} \bar{u}'} \right]_{NJ}
\]

This transmission matrix will be defined as \( \beta_1 \).

**D.5 Section #3 – Flame Zone**

The equations describing the perturbations in the flame zone can also be written as a function of upstream components and a transmission matrix, however simple duct relations cannot be used. It is first assumed that this section of the system is acoustically compact (i.e. \( \rho'_1 = \rho'_2 \)). This gives the first row of the matrix. The second row of the matrix can be obtained from a control volume analysis across the flame zone.

**D.5.1 Control Volume Analysis**

An unsteady energy balance across the flame zone yields the following equation.

\[
\frac{\partial E_{CV}}{\partial t} = \dot{m}_1 h_{r_1} - \dot{m}_2 h_{r_2} + \dot{Q}
\]  \( \text{(D.13)} \)

Using the definition of total energy in the control volume and the equation of state

\[
E_{CV} = e \cdot m = c_T \rho V
\]  \( \text{(D.14)} \)

\[
p = \rho RT
\]  \( \text{(D.15)} \)

the energy balance can be re-written as

\[
\frac{c_p V}{R} \frac{\partial (p)}{\partial t} = \rho_1 u_1 A_1 c_p T_{r_1} - \rho_2 u_2 A_2 c_p T_{r_2} + \dot{Q}.
\]  \( \text{(D.16)} \)
By assuming low Mach number in the flame zone, stagnation quantities are approximately equal to static properties (e.g. $T_t \approx T$) and the equation becomes

$$
\frac{c_v V}{R} \frac{\partial (p)}{\partial t} = \rho_1 u_1 A_1 c_p T_1 - \rho_2 u_2 A_2 c_p T_2 + \dot{Q}.
$$

(A.17)

Again applying the equation of state,

$$
\frac{c_v V}{R} \frac{\partial (p)}{\partial t} = \frac{p_1}{R} u_1 A_1 c_p - \frac{p_2}{R} u_2 A_2 c_p + \dot{Q}.
$$

(A.18)

Next, the unsteady energy balance is linearized and Laplace transformed. Higher order terms are eliminated resulting in

$$
\frac{c_v V}{R} s p' = \frac{A_1 c_v}{p_1} u_1' + \frac{A_2 c_v}{p_2} \bar{u}_1 - \frac{A_1 c_v}{p_2} u_2' + \frac{A_2 c_v}{p_2} \bar{u}_2 + \dot{Q}'
$$

(A.19)

where $s = j \omega$. Finally, solving for $u_2'$, collecting terms, and recalling that $p_1' = p_2'$ we can write

$$
u_2' = \left[ \frac{A_1 \bar{p}_1}{A_2 \bar{p}_2} \right] u_1' + \left[ \frac{A_1 \bar{u}_1 - \bar{u}_2 - \frac{V_s}{\gamma A_2 \bar{p}_2}}{A_2 \bar{p}_2} \right] p_1' + \frac{\dot{Q}'}{\bar{p}_1} \left( \frac{\gamma - 1}{\gamma} \right).
$$

(A.20)

The expression can be further simplified after noting that the mean pressure is constant.

$$
u_2' = \left[ \frac{A_1}{A_2} \right] u_1' + \left[ \frac{A_1 \bar{u}_1 - \bar{u}_2 - \frac{V_s}{\gamma A_2 \bar{p}}}{A_2 \bar{p}} \right] p_1' + \frac{\dot{Q}'}{\bar{p}} \left( \frac{\gamma - 1}{\gamma} \right)
$$

(A.21)
D.5.2 Equivalence Ratio Fluctuations

Perturbations in equivalence ratio will occur in the upstream duct between the fuel injectors and the flame zone. They propagate with the mean flow and are of the form

$$\frac{\phi'}{\phi} = Ce^{i\omega t - \frac{\gamma x}{a}}$$  \hspace{1cm} (D.22)

Assuming that the fuel injectors are choked, the following linearized form of the definition of equivalence ratio holds at the injector location $x = L_{INJ}$.

$$\frac{\phi'}{\phi} = -\frac{\rho'}{\rho} - \frac{1}{M} \frac{u'}{a}$$  \hspace{1cm} (D.23)

Therefore, we can solve for the coefficient $C$ by equating these two relations at the fuel injector location.

$$Ce^{i\omega \left(\frac{t - L_{INJ}}{u_{INJ}}\right)} = -\frac{\rho'_{INJ}}{\rho_{INJ}} - \frac{1}{M_{INJ}} \frac{u'_{INJ}}{a_{INJ}}$$  \hspace{1cm} (D.24)

Combining this with the linearized isentropic relation, $C$ can be written as

$$C = \left[-\frac{p'_{INJ}}{\rho_{INJ}} - \frac{1}{M_{INJ}} \frac{u'_{INJ}}{a_{INJ}}\right] e^{-i\omega \left(\frac{t - L_{INJ}}{u_{INJ}}\right)}.$$  \hspace{1cm} (D.25)

An expression for the perturbation in equivalence ratio at the entrance to the flame zone will be required for later analysis. Using the expression derived for the coefficient $C$ and knowing that $\bar{u}_{INJ} = \bar{u}_1$, the oscillation in mixture ratio at $x = L$ can be written as

$$\phi' = \phi \left[-\frac{p'_{INJ}}{\rho_{INJ}} - \frac{1}{M_{INJ}} \frac{u'_{INJ}}{a_{INJ}}\right] e^{i\omega \left(\frac{L_{INJ}}{\bar{u}_1}\right)}.$$  \hspace{1cm} (D.26)
D.5.3 Unsteady Heat Release

The heat release process in the combustion chamber is very complex. The reactive mixture will not be consumed instantly when it reaches the flame base. Different parts of the flow entering the flame zone will be consumed at different locations and will not be completely consumed until it reaches the end of this region. The heat release will then lag the oscillations in equivalence ratio at the base of the flame structure. For this analysis it will be assumed that heat release is a function of equivalence ratio such that $\dot{Q} = f(\phi)$. Including a first order lag term, the quasi-steady heat release $\dot{Q}_{qs} = \dot{Q}_{qs}(\phi)$ can be written as

$$\frac{d\dot{Q}'}{dt} = \frac{\dot{Q}_{qs} - \dot{Q}'}{\tau_{flame}}. \quad (D.27)$$

Linearizing this relation and assuming periodic fluctuations of the form $e^{j\omega t}$ one can write

$$\dot{Q}' = \frac{K}{\tau_{flame} (s + 1)} \phi'_i \quad (D.28)$$

where $s = j\omega$ and

$$K = \frac{\partial \dot{Q}_{qs}}{\partial \phi} \bigg|_{\dot{\phi}}. \quad (D.29)$$

The constant K depends on the choice of fuel and oxidizer. For this analysis, the quasi-steady sensitivity of heat release to equivalence ratio is shown in Figure D.2 for a well-stirred reactor burning propane-air at a residence time of 0.1 ms [75]. The time lag of heat release with respect to the flame base $\tau_{flame}$ will be modeled as

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where $\alpha = \frac{L_{eq}}{L_{flame}}$ is a flame length correction coefficient which represents the fractional location of a theoretical flame sheet that consumes the entire mixture at one location. This coefficient is a function of flame Strouhal Number $St = \frac{f L_{flame}}{\bar{u}}$ and can be obtained from Figure D.3 [74]. Initially, a Strouhal number must be estimated and checked after the analysis is complete. If it does not approximately match, the Strouhal number must be corrected and the analysis becomes iterative.

![Figure D. 2 Quasi-steady sensitivity of heat release to equivalence ratio [75].](image)
D.5.4 Assembling the Transmission Matrix

The perturbation in equivalence ratio at the entrance to the flame zone, which was derived in section 5.2, can be substituted into the expression for unsteady heat release.

\[
\dot{Q}' = \frac{K}{\tau_{\text{flame}}(s+1)} \phi \left[ \frac{p'_{\text{INJ}}}{\overline{p}_{\text{INJ}}} - \frac{1}{M_{\text{INJ}} \overline{a}_{\text{INJ}}} \right] e^{j \omega \left( \frac{t_{\text{INJ}} - t}{\overline{u}_i} \right)}
\]  \hspace{1cm} (D.31)

\(p'_{\text{INJ}}\) and \(u'_{\text{INJ}}\) can be written in terms of \(p'_i\) and \(u'_i\)
\[ u'_{\text{INJ}} = -\frac{1}{2\rho a} \left( p'e^{jk(t_{\text{INJ}}-L)} - p'e^{-jk(t_{\text{INJ}}-L)} - \overline{\rho a'u'}e^{jk(t_{\text{INJ}}-L)} \right) \]

\[ -\overline{\rho a'u'}e^{-jk(t_{\text{INJ}}-L)} \right) e^{-jk(t_{\text{INJ}}-L)+j\beta(t_{\text{INJ}}-L))} \]

\[ p'_{\text{INJ}} = \frac{1}{2} \left( p'e^{jk(t_{\text{INJ}}-L)} + p'e^{-jk(t_{\text{INJ}}-L)} - \overline{\rho a'u'}e^{jk(t_{\text{INJ}}-L)} \right) \]

\[ + \overline{\rho a'u'}e^{-jk(t_{\text{INJ}}-L)} \right) e^{-jk(t_{\text{INJ}}-L)+j\beta(t_{\text{INJ}}-L))} \]

Maple 6, a symbolic math program was used to substitute these expressions back into the equation for unsteady heat release and to collect terms, resulting in

\[ \dot{Q}' = u' \frac{\phi K_{\text{flame}}}{\tau_{\text{flame}}(s+1)} \left( \frac{1}{2\rho a} \left( e^{jk(t_{\text{INJ}}-L)} - e^{-jk(t_{\text{INJ}}-L)} \right) e^{jk(t_{\text{INJ}}-L)+j\beta(t_{\text{INJ}}-L)} \right) \]

\[ - \frac{1}{2\rho a} \left( e^{jk(t_{\text{INJ}}-L)} + e^{-jk(t_{\text{INJ}}-L)} \right) e^{jk(t_{\text{INJ}}-L)+j\beta(t_{\text{INJ}}-L)} \]

\[ + p' \frac{\phi K_{\text{flame}}}{\tau_{\text{flame}}(s+1)} \left( e^{jk(t_{\text{INJ}}-L)} \right) \]

\[ + \left( \frac{1}{2\rho a} \left( e^{jk(t_{\text{INJ}}-L)} + e^{-jk(t_{\text{INJ}}-L)} \right) e^{jk(t_{\text{INJ}}-L)+j\beta(t_{\text{INJ}}-L)} \right) \]

\[ \frac{1}{2\rho a^2 M} \]

This expression for \( \dot{Q}' \) can then be substituted back into equation D.21 for \( u'_2 \). Again using Maple 6, this can be simplified and terms can be collected. The resulting relation expresses \( u'_2 \) as a function of \( u'_1 \), \( p'_1 \), and known parameters. This can then be put into transmission matrix form. The resulting matrix formulation is

\[
\begin{bmatrix}
   p' \\
   \overline{\rho a'u'}
\end{bmatrix}_2 = \begin{bmatrix}
   1 & 0 \\
   \Omega & \Psi
\end{bmatrix} \begin{bmatrix}
   p' \\
   \overline{\rho a'u'}
\end{bmatrix}
\]

where

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This transmission matrix will be designated $\beta_{2,4}$.

### D.6 Flame Zone Exit

Relations similar to those used in upstream sections can characterize the duct occupying the space between the flame zone exit and the choked nozzle. The velocity and pressure perturbations in this section can generally be written as

\[
\begin{align*}
    u' &= D e^{j(\omega t - k_3 x)} + E e^{j(\omega t + k_4 x)} \quad (D.38) \\
    p' &= D \rho \bar{a} e^{j(\omega t - k_3 x)} - E \rho \bar{a} e^{j(\omega t + k_4 x)} \quad (D.39)
\end{align*}
\]

where $k_3$ and $k_4$ are wave numbers. $D$ and $E$ are amplitudes and are different than $A$ and $B$ in the upstream duct. At the exit of the flame zone we can write this in matrix form as

\[
\begin{bmatrix}
    p' \\
    \rho \bar{a} u'
\end{bmatrix}
= \begin{bmatrix}
    \rho \bar{a} e^{-j k_3 l_2} & - \rho \bar{a} e^{j k_4 l_2} \\
    \rho \bar{a} e^{-j k_3 l_2} & \rho \bar{a} e^{j k_4 l_2}
\end{bmatrix}
\begin{bmatrix}
    D \\
    E
\end{bmatrix}
e^{j \lambda x}.
\]
These relations can then be equated to those derived in previous sections for the same location. Defining the above $2 \times 2$ matrix as $\beta_{2B}$, we can then find coefficients D and E as a function of A and B from

$$
\begin{bmatrix}
D \\
E
\end{bmatrix} = [\beta_{2B}]^{-1} \begin{bmatrix} \beta_{A} & \beta_{INJ} & \beta_{0} \\
A \\
B
\end{bmatrix}.
$$

(D.41)

### D.7 Choked Nozzle

The flow through the exit nozzle at the end of the system is assumed to be isentropic and choked, thus no knowledge of the flow downstream is required. Linearizing the modified definition of corrected mass flow for choked conditions

$$
\frac{\dot{m}\sqrt{T}}{P} = f(M)
$$

where $M = 1$, and using continuity, the following relation between perturbations holds at the location of the choked nozzle.

$$
\frac{u_1'}{u_3} = \frac{1}{2} \frac{T_1'}{T_3}
$$

(D.43)

Combining this expression with the linearized isentropic flow relation and the linearized equation of state, an equation relating $u_1'$ and $p_3'$ can be found.

$$
\frac{u_3'}{u_3} - \frac{1}{2} \frac{p_3'}{\bar{p}_3} \left( \frac{\gamma - 1}{\gamma} \right) = 0
$$

(D.44)

This boundary condition can be written in matrix form as
\[
\begin{bmatrix}
-\frac{1}{2\bar{p}_3} \left( \frac{\gamma-1}{\gamma} \right) & \frac{1}{\bar{\rho}u'_3} \\
\end{bmatrix}
\begin{bmatrix}
p' \\
\end{bmatrix}
= 0.
\] (D.45)

\(u'_3\) and \(p'_3\) can be written in terms of \(u'_2\) and \(p'_2\) and a transmission matrix

\[
\begin{bmatrix}
p' \\
\end{bmatrix}
\begin{bmatrix}
\frac{1}{2} (e^{-jk_3(u_3-L_2)} + e^{jk_4(u_3-L_2)}) & \frac{1}{2} (e^{-jk_3(u_3-L_2)} - e^{jk_4(u_3-L_2)}) \\
\end{bmatrix}
\begin{bmatrix}
\rho u'_3 \\
\end{bmatrix}
= \begin{bmatrix}
p' \\
\end{bmatrix}
\begin{bmatrix}
\frac{1}{2} (e^{-jk_3(u_3-L_2)} - e^{jk_4(u_3-L_2)}) & \frac{1}{2} (e^{-jk_3(u_3-L_2)} + e^{jk_4(u_3-L_2)}) \\
\end{bmatrix}
\begin{bmatrix}
\rho u'_3 \\
\end{bmatrix}
\] (D.46)

where the transmission matrix is designated \(\beta_3\). Combining these matrix expressions with the other transfer matrices yields

\[
\begin{bmatrix}
p' \\
\end{bmatrix}
\begin{bmatrix}
\frac{1}{2} (e^{-jk_3(u_3-L_2)} + e^{jk_4(u_3-L_2)}) & \frac{1}{2} (e^{-jk_3(u_3-L_2)} - e^{jk_4(u_3-L_2)}) \\
\end{bmatrix}
\begin{bmatrix}
\rho u'_3 \\
\end{bmatrix}
= \begin{bmatrix}
\rho u'_3 \\
\end{bmatrix}
\begin{bmatrix}
\frac{1}{2} (e^{-jk_3(u_3-L_2)} - e^{jk_4(u_3-L_2)}) & \frac{1}{2} (e^{-jk_3(u_3-L_2)} + e^{jk_4(u_3-L_2)}) \\
\end{bmatrix}
\begin{bmatrix}
\rho u'_3 \\
\end{bmatrix}
\] (D.47)

an expression for the pressure and velocity perturbations at the nozzle as a function of \(A\) and \(B\), the upstream amplitudes. This relation can then be substituted into the nozzle boundary condition to give

\[
\begin{bmatrix}
-\frac{1}{2\bar{p}_3} \left( \frac{\gamma-1}{\gamma} \right) & \frac{1}{\bar{\rho}u'_3} \\
\end{bmatrix}
\begin{bmatrix}
\beta_3 \begin{bmatrix}
\beta_{2,8} & \beta_{2,9} \\
\end{bmatrix} \begin{bmatrix}
\beta_{2,8} & \beta_{2,9} \\
\end{bmatrix}^\dagger \begin{bmatrix}
\beta_2 & \beta_{1,8} & \beta_{1,9} \\
\end{bmatrix} \begin{bmatrix}
\beta_2 & \beta_{1,8} & \beta_{1,9} \\
\end{bmatrix}^\dagger \\
\end{bmatrix}
\begin{bmatrix}
A \\
B \\
\end{bmatrix}
= 0.
\] (D.48)

### D.8 Eigenvalue Problem

From the boundary conditions and the transmission matrices, we now have two relations with only coefficients \(A\) and \(B\) and \(s = \sigma - j\omega\). This can be posed as an eigenvalue problem of the form

\[
\begin{bmatrix}
2 \times 2 \\
\text{matrix} \\
\end{bmatrix}
\begin{bmatrix}
A \\
B \\
\end{bmatrix}
= 0.
\] (D.49)
The open duct boundary condition of \( p'(0,t) = 0 \) results in the first row of the matrix while the second row comes from the choked nozzle boundary condition written as a function of \( A \) and \( B \) by assembling all of the transmission matrices as shown above in equation D.48. The eigenvalue problem can be written as

\[
\begin{bmatrix}
1 & -1 \\
X & Y
\end{bmatrix}
\begin{bmatrix}
A \\
B
\end{bmatrix} = 0
\]

where \( X \) and \( Y \) are derived from equation D.48 and are too cumbersome to write in symbolic form here.

**D.9 Solution Method**

To solve the eigenvalue problem for the eigenfrequencies, the complex domain is discretized. A range of values on both the real and imaginary axes are selected, corresponding to \( \sigma \) and \( \omega \). These values are substituted into the transmission matrices along with the fluid and geometric properties of the system. The final matrix for the eigenvalue problem can then be found. Eigenvalues correspond to wherever

\[
\det\begin{bmatrix}
1 & -1 \\
X & Y
\end{bmatrix} = 0.
\]

The determinant of the system is found at every grid-point and a contour plot of where the real and imaginary components are equal to zero is generated in the complex plane. The real and imaginary contours will cross where the determinant equals zero, thus graphically locating an eigenvalue [76]. The imaginary axis value at the crossing indicates the frequency. If the intersection is located in the left-half plane, then the eigenvalue is stable. This is because the real part of the eigenvalue indicates the growth rate. A Negative real part implies a decaying oscillation. If it is in the right-half plane, it is unstable and the positive real part indicates a positive growth rate of the disturbance.
However, there can be numerical problems with this technique. The grid must be sufficiently refined to accurately locate the eigenvalues. If the grid is too coarse, then the location of the eigenvalues may be incorrect, thus falsely indicating stability and frequency. A grid resolution study should be performed to ensure that this is not the case.

The grid refinement may also be computationally expensive requiring a significant amount of processor time and memory. If this is the case, a technique known as the “shotgun method” developed by Spakovszky [76] may also be used. To utilize this method, some a priori information about the location of the eigenvalue is required. This information gives the solution algorithm a starting location. The code then “fires” a random spread of points around this location and the determinant of the eigenvalue problem is solved at each point. A cost function is then minimized and a new firing location is selected. One fewer shots are fired in each successive spread until a preset convergence criterion is met. The last point fired is the eigenvalue.

D.10 Microcombustor Thermo-acoustic Stability

The actual microcombustor geometry is shown in Figure D.4. Table D.1 lists all of the relevant geometric values for use in the stability model. Table D.2 indicates the fluid properties used.

![Microcombustor geometry](image-url)

**Figure D.4 Microcombustor geometry.**
Table D. 1 Geometric values for microcombustor.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{\text{injector}}$</td>
<td>0.003 m</td>
</tr>
<tr>
<td>$L_{\text{duct}}$</td>
<td>0.009 m</td>
</tr>
<tr>
<td>$L_{\text{flame}}$</td>
<td>0.004 m</td>
</tr>
<tr>
<td>$L_{\text{comb}}$</td>
<td>0.006 m</td>
</tr>
<tr>
<td>$A_{\text{duct}}$</td>
<td>1.256e-5 m²</td>
</tr>
<tr>
<td>$A_{\text{comb}}$</td>
<td>2.51e-5 m²</td>
</tr>
</tbody>
</table>

Table D. 2 Fluid properties for microcombustor.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{m}$</td>
<td>0.30 g/s</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.5</td>
</tr>
<tr>
<td>$P$</td>
<td>2 atm</td>
</tr>
<tr>
<td>$T_{\text{inlet}}$</td>
<td>500 K</td>
</tr>
<tr>
<td>$T_{\text{flame}}$</td>
<td>1600 K</td>
</tr>
<tr>
<td>$\gamma_{\text{duct}}$</td>
<td>1.4</td>
</tr>
<tr>
<td>$\gamma_{\text{flame}}$</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Figure D.5 shows the intersection of the real and imaginary contours for the second eigenvalue. The frequency of the eigenvalue is 49.7 kHz and is stable, located in the left-half plane. However, after performing a grid resolution study it was found that the eigenvalues moved significantly along the real axis. A grid density that was computationally impractical was required to converge to the actual solution. As a result, the shotgun method was used. Fortunately, the convergence on the imaginary axis was accurate enough in the discretized domain to use these values as starting points for $\omega$ in the shotgun code. Table D.3 lists the first six eigenfrequencies and their respective stability while Figure D.6 plots the locus of these eigenvalues in the complex domain. Note that the system appears to always be stable.
Figure D. 5 Second eigenvalue for microcombustor.

Table D. 3 First six eigenfrequencies and their stability for the microcombustor.

<table>
<thead>
<tr>
<th>FREQUENCY</th>
<th>STABILITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.9 kHz</td>
<td>stable</td>
</tr>
<tr>
<td>49.7 kHz</td>
<td>stable</td>
</tr>
<tr>
<td>74.6 kHz</td>
<td>stable</td>
</tr>
<tr>
<td>99.5 kHz</td>
<td>stable</td>
</tr>
<tr>
<td>124.3 kHz</td>
<td>stable</td>
</tr>
<tr>
<td>149.2 kHz</td>
<td>stable</td>
</tr>
</tbody>
</table>
As a first order check on the solution, the Helmholtz frequency can be estimated and compared to the frequencies shown above. The first eigenfrequency generated by the model should be on the order of the Helmholtz frequency for the microcombustor geometry. The Helmholtz frequency is given by

$$\omega = \frac{a}{2\pi} \sqrt{\frac{A_c}{VL}}$$  \hspace{1cm} (D.52)

where $a$ is the speed of sound, $V$ is the chamber volume, $L$ is the length of the upstream duct, and $s$ is the cross-sectional area of that duct. For the micro-combustor geometry, the Helmholtz frequency is $\sim 20$ kHz which is on the order of the first eigenfrequency of 24.9 kHz.
D.11 Effect of Fuel Injector Location

A critical parameter in the stability of the micro-combustor is the location of the fuel injectors. As the fuel injectors move farther upstream, the eigenfrequencies of the system become lower. This is apparent from the equation for the Helmholtz frequency where there is a $\frac{1}{\sqrt{L}}$ dependence on upstream duct length for a constant volume and duct cross-sectional area. Figure D.7 shows the lowest two eigenfrequencies as a function of fuel injector location for the microcombustion system. All other parameters are held constant.

![Figure D.7 Eigenfrequencies as a function of fuel injector location.](image)

Although Figure D.7 indicates that the harmonic frequencies are reduced as fuel injector distance from the flame zone increases, it does not indicate stability. To determine system stability as a function of fuel injector location, the real part of the eigenvalue must be considered. Figure D.8 shows the least stable eigenvalue for several fuel injector locations in the complex plane. All other thermo-fluid and geometric
parameters have been kept constant. As fuel injector distance from the flame zone increases, the harmonic frequency decreases (as previously shown in Figure D.7) and the system becomes less stable, approaching neutral stability. Generally, an increase in fuel injector upstream location drives the eigenvalues down and to the right in the complex plane. However, even at very large fuel injector distances, the system does not appear to become unstable. If the system volumes and cross-sectional areas are increased by several orders of magnitude, the model will predict a thermo-acoustic instability.

![Figure D. 8 Eigenvalues for several fuel injector locations.](image)

**D.12 Summary and Conclusions**

The homogeneous gas-phase combustion system for the demonstration microengine has been designed to operate in a lean premixed mode. This operating space has been found to be unstable in several large-scale devices. It has been suggested that this is a result of a thermo-acoustic coupling known as Rayleigh's criterion, which may
result from the propagation of equivalence ratio oscillations from the fuel injectors to the
flame zone [74,75]. This would cause an unsteady heat release process that could feed
back to the fuel injectors via an upstream traveling acoustic wave. This work has sought
to explore the possibility of this phenomenon causing a thermo-acoustic instability in the
microcombustor.

A model utilizing transmission matrices to couple fluid components has been
developed to examine this feedback mechanism in a microcombustion system. The
system is approximated as a series of ducts with fuel injectors and a flame zone with heat
release. The upstream boundary condition is that of an open duct, while downstream is a
choked nozzle. The fuel injectors are assumed to be choked as well. The heat release is
modeled as a quasi-steady process that is a function of equivalence ratio. After coupling
all of these components, an eigenvalue problem presents itself. It can be solved by
finding the determinant of the system matrix. Several methods for this are described in
Section D.9. The result is a series of eigenvalues, which indicate the system’s harmonic
frequencies and their respective stability.

The acoustic portion of this type of model has been shown to be valid in studies of
compressor dynamic system modeling [76]. However, the heat release section of the
model is limited. The quasi-steady sensitivity to heat release shown in Figure D.2 was
generated by Lieuwen et. al. from a single step reaction mechanism for propane air
combustion. This was marginally effective in predicting instability in a larger-scale
combustor [75]. Using GRIMech 3.0 (see Appendix B.2), which represents the full
propane kinetics to generate this sensitivity, would add fidelity to the model. In addition,
modeling the heat release process as occurring at a single location via a flame correction
coefficient may be improved by accounting for a more distributed reaction zone. Also, in
the case of the microcombustor where fuel is injected far upstream, accounting for
diffusion of fuel species would be an improvement.

The current microcombustor geometry was found to be stable over all of the
harmonics that were examined. The third and fourth modes approached neutral stability
but did not cross into the right half plane in the complex domain. The fifth and sixth
eigenvalues began to move away from the y-axis back into more stable space. The first
mode was found to be consistent with the Helmholtz frequency for this geometry.
Fuel injector location (and upstream duct length) was found to be a critical parameter for stability. As the fuel injectors were moved farther upstream, the system became less stable and the mode frequencies became lower. However, even at large upstream distances (on the order of meters) the eigenvalues approached neutral stability but did not become unstable. An increase in combustor volume several orders of magnitude would result in an unstable system.

The model predicts that thermo-acoustic instabilities are unlikely in the microcombustor. Only at large upstream fuel injector distances does the system become neutrally stable. Even in this case, instabilities are unlikely. The model assumes that the species concentrations propagating down the inlet duct are frozen. However, in a practical system this is not the case. Over large distances, diffusion of the fuel species is likely, resulting in little or no variation in equivalence ratio at the flame zone and no unsteady heat release. The convective time scales for the system with a long upstream duct are on the order of 0.1 to 1 second. The diffusive time-scales for propane through air are on the order of tens of milliseconds (this can be computed by estimating the diffusion coefficient from the Fuller correlation [36]). Significant diffusion of the fuel will occur well before reaching the flame zone. Thus, even at large upstream duct lengths where the model predicts neutral stability, a thermo-acoustic harmonic excitation is unlikely.
References


[32] Robert Bosch Gmbh, Patents 4855017 and 4784720 (USA), and 4241045C1 (Germany).


DESIGN AND CHARACTERIZATION OF MICRO-IMPELLERS

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ABSTRACT
A study has been conducted, using steady three-dimensional Reynolds-averaged Navier-Stokes simulations (FLUENT) to investigate dominant performance limiting mechanisms for micro-scale, high-speed compressor impellers with diameter in the range of 5mm to 10mm and peripheral speed ~ 500 m/s. Heat transfer to impeller flow (hence non-adiabatic in contrast to nearly adiabatic macro-scale centrifugal compressors for aircraft engine application), casing drag, and impeller passage boundary layer loss are identified as micro-scale impeller performance limiting mechanisms. Heat transfer could lead to up to 25 efficiency points penalty, casing drag to about 10-15 pts, and passage boundary layer loss to another 10 pts for the investigated micro-impellers. Micro-compressor stage efficiency of up to 75% is achievable (assuming diffuser pressure recovery coefficient $C_p = 0.6$) if design is directed at mitigating these performance limiting mechanisms. The effect of heat addition on impeller performance is detrimental and depends on a single non-dimensional parameter (ratio of added heat to inlet stagnation enthalpy). The performance penalty is associated with the physical fact that compression at high temperatures requires more work. Casing drag associated with impeller rotating relative to stationary casing results in a torque on the flow near the casing and impeller blade tip that can be characterized in terms of rotational Reynolds number and ratio of tip clearance to impeller radius. Channel boundary layer loss can be characterized in terms of Reynolds number, geometry (impeller exit-to-inlet diameter ratio, blade angles, chord-to-inlet diameter ratio, average-to inlet span ratio, inlet diameter-to-inlet span ratio), and exit-to-inlet temperature ratio related to work input (rotor geometry and speed). A physics-based model is developed for quantifying each of these performance-limiting processes, given the key design parameters. The results from the models are in accord with CFD (FLUENT) data. Implications on impeller design are discussed and design guidelines are formulated. The paper proposes the first quantitative investigation of micro-turbomachinery performance limiting mechanisms and offers design guidelines based on physical understanding.

Keywords: micro-scale, compressor, CFD, loss

NOMENCLATURE

- $\alpha$: blade inlet angle measured from radial direction
- $A$: area
- $adb$: adiabatic
- $\beta$: blade back-sweep angle
- $c$: blade chord
- $cor$: corrected
- $Cd$: dissipation coefficient
- $Cm$: moment coefficient
- $Cp$: pressure coefficient
- $D$: impeller diameter
- $e$: exit
- $f$: Darcy friction factor
- $i$: ideal
- $in$: inlet
- $m$: mass flow
- $\mu$: viscosity
- $N$: number of impeller blades
- $\eta$: impeller efficiency
- $\Omega$: rotor angular velocity
- $\pi$: impeller total pressure ratio
experimental data is still extremely limited and available only relative importance of the performance limiting fluid in contrast to macro-scale centrifugal compressors considered here because at MIT compressor manufacturing is based on micro-fabrication as used for microprocessors and chips. As such, the blades are confined to nearly two-dimensional extrusion. This constraint does not lead to intolerable rotor performance penalty as will be shown later.

The objective of the work reported in this paper is first to lay the scientific foundation for the design and development of micro-compressors on a rational basis, to characterize micro-impeller performance on a non-dimensional basis, as well as to provide design guidelines. The paper is arranged as follows: The first section presents the overall technical approach. Results section presenting the identification of dominant performance limiting mechanisms follows. Modeling and characterization of the effects of these mechanisms on impeller performance are presented in the next section. Design guidelines are provided in the following section and the paper ends with Summary and Conclusions section.

INTRODUCTION

The increasing need for compact power sources in industry and the military drives the investigation of various micro-engine concepts. The pioneering concept was the micro-gas-turbine engine invented by Epstein at MIT, which is capable of achieving very high power density compared to batteries [1,2]. This engine operates on a simple Brayton cycle and its primary application is electric power generation. The MIT micro-engine is expected to produce on the order of 10–100 Watts electric power. The compressor rotor is 8 mm in diameter spinning at 1.2 million RPM design speed. Micro-turbomachinery development is essential for the success of MIT micro-engine initiative and this forms the topic of the present paper. The MIT micro engine project was initiated when both understanding of micro-turbomachines and availability of experimental data were non-existent. Presently, experimental data is still extremely limited and available only at low speeds. MIT has spun its compressor (the smallest known to the authors) to 40% of design speed using gas bearings [3].

Micro-turbomachinery for micro-gas turbine application operates in low Reynolds number, high Mach number, non-adiabatic regime and this work identifies for the first time the relative importance of the performance limiting fluid phenomena and the parameters characterizing micro-impeller performance. It was the lack of physical understanding and design guidelines for micro compressors that motivated this work. Initial attempts at MIT to design micro compressors using conventional techniques and philosophy led not only to quite unusually looking geometries but also to compressors with unsatisfactory performance. It was found that the key performance-limiting factor is the non-adiabatic operation of the compressor, in contrast to macro-scale centrifugal compressors for aircraft engine applications.

Useful work on micro-compressors is reported by Kang, et al. [4] on the design and performance of a 12 mm impeller and Isomura, et al. [5,6] on the design of a 10 mm impeller. These designs, however, are somewhat distinct from the micro-compressors considered here because at MIT compressor manufacturing is based on micro-fabrication as used for microprocessors and chips. As such, the blades are confined to nearly two-dimensional extrusion. This constraint does not lead to intolerable rotor performance penalty as will be shown later.

The objective of the work reported in this paper is first to lay the scientific foundation for the design and development of micro-compressors on a rational basis, to characterize micro-impeller performance on a non-dimensional basis, as well as to provide design guidelines. The paper is arranged as follows: The first section presents the overall technical approach. Results section presenting the identification of dominant performance limiting mechanisms follows. Modeling and characterization of the effects of these mechanisms on impeller performance are presented in the next section. Design guidelines are provided in the following section and the paper ends with Summary and Conclusions section.

APPROACH

The approach consists of implementing a set of numerical experiments to identify dominant performance-limiting mechanisms in micro-impellers and quantify and characterize their effect on performance. Steady, Reynolds-averaged, Navier-Stokes simulations are carried out with Fluent CFD code to study performance-limiting mechanisms. One of MIT micro-impeller designs is selected as baseline geometry and boundary conditions are varied to isolate effects of different mechanisms. The selected design has 20 impeller blades, 8mm rotor diameter with blades running from 2 to 4 mm radius (impeller diameter ratio = 2). Blade span varies linearly from 400 microns at inlet to 200 microns at exit that is made possible by a pioneering micro-fabrication technology developed at the University of Maryland [7,8]. Tip clearance gap is 20 microns, 5 to 10 % of blade height depending on location. Impeller blade inlet angle is 55 degrees and exit back-sweep angle is 45 degrees. The impeller tip speed is 500 m/s, rotating at 1.2 million RPM.

Effect of heat transfer was studied by running an adiabatic wall case and comparing it to cases with given wall temperature. The temperature in one case was fixed to 950K representative of the wall temperature of MIT compressor without isolation between the hot sections of the engine and the impeller allowing heat flow to the compressor. Another case was studied with wall temperature fixed to 600K assuming some thermal isolation of the impeller. The casing effects associated with casing drag and tip clearance flow were studied by shrouding the impeller and comparing it to an un-shrouded one with the same geometry. The effect of the flow turning through a right angle in the inlet from axial to radial direction (characteristic of the 2-D micro-fabrication constraints imposed on the MIT design) is studied by prescribing inlet condition of flow that is already in the plane.
of the impeller and does not turn. Finally, the loss associated with a shrouded, adiabatic impeller without any turn at inlet is attributed to blade passage boundary layers.

Once the dominant performance limiting mechanisms are identified, simple models are developed to provide insight to the non-dimensional parameters controlling impeller performance. Characterization of micro-impeller performance based on the developed models allows formulation of general design guidelines.

**NUMERICAL TOOLS**

The Computational Fluid Dynamics code selected for this investigation is FLUENT [9]. It is a commercial code capable of running structured and unstructured grids for numerous applications. It offers a selection of solvers, boundary and initial conditions, fluid specification, turbulence models, etc. For this work unstructured grids were prepared using GAMBIT [10] and exported to FLUENT. The baseline computational grid has 237,379 nodes. The steady coupled explicit solver was used to obtain solution for the flow-field within the impeller passage. Since the flow in the impeller is taken to be turbulent the $\kappa$-$\varepsilon$ turbulence model was selected. The Reynolds number within the impeller passage based on passage exit blade span and peripheral speed at design condition is $\sim 7000$. The enhanced wall treatment option was used to solve for the flow near walls. This option combines a two-layer model with wall functions. If the near-wall grid were fine enough to resolve the laminar sub-layer, then the enhanced wall treatment would use the two-layer zonal model. Three levels of multi-grid were used and the code was run in parallel for faster convergence.

**RESULTS**

The results for the baseline impeller investigation are summarized in Fig. 1. The dominant performance limiting mechanisms are identified with the following set of computational cases:

1) 900K wall temperature, unshrouded impeller with right-angle turn at inlet
2) 600K wall temperature, unshrouded impeller with right-angle turn at inlet
3) adiabatic wall, unshrouded impeller with right-angle turn at inlet
4) shrouded, adiabatic impeller with right-angle turn at inlet
5) no turn at inlet, shrouded, adiabatic impeller

By comparing case 1 to 3 the penalty in impeller efficiency associated with heat addition is up to 25 pts. For case 1 the heat transfer to the impeller flow is on the order of the work input to the impeller rotor. Heat addition is the dominant performance limiting mechanism. By comparing case 3 to 4, another important loss source is quantified. It is associated with casing effects including casing drag, tip clearance flow, and secondary flows of which casing drag dominates. Shrouding the impeller leads to about 17 pts improvement in efficiency of which 13 pts are directly linked to casing drag.

(1) (2) (3) (4) (5)

Fig. 1 Peak isentropic impeller efficiency for cases of interest. Identification of performance limiting mechanisms for MIT micro impeller.

(The practical benefit from shrouding will be reduced due to friction between the rotating shroud disc and the stationary casing. Preliminary estimates show that friction can be significant only in the shroud seal gap and depends on the seal geometry. It consumes about 30% of the observed benefit due to shrouding). The remaining 4 pts may be attributed to tip clearance flow in accord with the estimates by Kang at Stanford for a 10% tip-clearance-to blade height ratio [4]. Comparing case 4 to 5 the effect of flow turning in the inlet is isolated. The loss associated with the flow turning in the right angle inlet is about 5 efficiency points. Comparing impeller performance in case 5 to an ideal 100% efficient impeller the passage boundary layer loss is estimated to be about 10 pts. Dissipation in the passage boundary layers is significant because of the low Reynolds number and it is the third dominant performance limiting mechanism. It can be inferred that heat addition to impeller, casing drag and boundary layer loss are the major mechanisms that control micro-impeller performance.

The effect of heat addition was also investigated by Isonumra, Murayama, and Kawakubo at IHI [5]. They calculated a 40 pts efficiency drop at 1000 K wall temperature for their micro-impeller design, which supports the conclusion that heat addition may have devastating effects on impeller performance and is the dominant performance limiting mechanism. Casey [11] experimentally investigated the effect of Reynolds number (based on exit span) on shrouded compressor stage efficiency. He measured about 10 pts stage efficiency drop from large Reynolds numbers (70,000-120,000) typical for conventional impellers to low Reynolds numbers (about 20,000) representative of micro-impellers. This supports the idea that dissipation in the passage boundary layers is also a dominant performance limiting mechanism for micro-impellers. If the dissipation was evenly distributed between the impeller and diffuser in Casey’s experiments the additional impeller boundary layer loss due to low Re would be responsible for about 5 efficiency points drop which agrees with the 5-6 points efficiency drop that would be estimated.
between a large scale 90-95% efficient impeller and the 85-90% efficient adiabatic shrouded MIT micro-impellers. The combined effect of boundary layer loss and casing drag can be compared to the experimental studies at Stanford by Kang et al. [4]. The impeller tested at Stanford was unshrouded and its performance can be compared to a corresponding case for the MIT impeller. The peak polytropic efficiency measured at Stanford was 73% and computed with CFD was 76% compared to the 73% polytropic efficiency computed with FLUENT for the MIT impeller. The overall agreement between the results presented in this paper and available calculations and experiments provides additional confidence in the conclusions drawn.

MICRO-IMPELLER MODELING
In this section models are presented to describe the important physics of the identified dominant performance limiting mechanisms. The three mechanisms that will be addressed are heat addition, casing drag, and passage boundary layer loss because they are responsible for most of the performance penalty.

Heat Addition
A model for the effect of heat addition on impeller performance is developed by Gong [12] and will be briefly described here for completeness. The main idea is that impeller with heat addition has similar performance to adiabatic impeller whose inlet flow is preheated with the same amount of heat addition. The effect can be described by thermodynamics and is explained by the physical fact that compression of air to a certain pressure at higher temperature requires more work. The results from the model are compared to CFD calculations for different impellers and heat addition levels and there is very good agreement [12]. Gong describes the effect of heat addition on efficiency in the following manner (the effects on pressure ratio and mass flow can be described in a similar fashion):

\[ \eta = \eta_{ad} \frac{1}{1 + QH} \]  
\[ \frac{1}{1 + QH} = \frac{T_{T1}}{T_{T1.5}} \]  
\[ \pi = \left[ \left( \frac{1}{1 + QH} \right) \pi_{ad}^{y-1} - 1 \right]^{y-1} + 1 \]  
\[ m = m_{ad} \frac{1}{1 + QH} \]

The model states that impeller non-adiabatic performance can be estimated from knowledge of impeller adiabatic performance, heat addition parameter, and equations 1-4. For example, if impeller adiabatic efficiency is known, eqn (1) provides an estimate for impeller non-adiabatic efficiency for any level of heat addition represented by QH. QH is heat addition parameter defined as the ratio of total heat added to inlet stagnation enthalpy. \( T_{T1} \) is the inlet stagnation temperature and \( T_{T1.5} \) is the inlet stagnation temperature that would be achieved after the flow at inlet has been pre-heated with the specified amount of heat addition. Thermodynamics tells us that if the air to impeller inlet were preheated, for given work input the achieved pressure ratio would be lower compared to a case without preheating (hence the pressure ratio penalty - Eq 3). At the same time efficiency is lower for the preheated case consistent with the lower pressure ratio for the same given work input (Eq 1). Mass flow is also affected simply due to the change in density of the flow entering the impeller after preheating (Eq 4). As mentioned earlier, the effect of heat addition on impeller performance can be described with a single non-dimensional parameter QH. The local effects of heat addition on impeller aerodynamics can be ignored compared to the much stronger thermodynamic penalty on impeller performance due to pre-heating the flow. Therefore, the effect of heat addition can be treated separately from the aerodynamic effects and QH can be adjusted independently. This assumption is verified by CFD. QH will depend on the boundary conditions imposed on the impeller by the rest of the system. The performance of a micro-impeller would therefore be greatly affected by the rest of the system and a designer must take this into account.

The added heat is proportional to the wetted area in the impeller while the inlet enthalpy is proportional to impeller mass flow. To decrease the detrimental effect of heat addition (for given wall boundary conditions) on impeller performance a decrease in QH is required. One way of achieving this is to design for lower wetted area per unit mass flow. For the MIT impeller this can be achieved by etching taller blades (increasing blade span and mass flow).

Casing Drag
Unshrouded impellers suffer additional performance penalty due to casing drag. The work of the viscous shear between the flow rotating with the blades within the blade passages and the stationary flow on the casing is dissipated. To counteract the effect of casing drag on the flow additional power must be supplied to the impeller. To estimate this additional power the flow within the micro-impeller can be viewed in the following manner: The flow within the blade passage is approximated to be in solid body rotation with a characteristic angular velocity. Because the blades in micro-impellers have back-sweep and experience slip velocity at exit, the characteristic angular velocity is obtained by correcting the actual rotor angular velocity for these two effects. The correction is performed at the exit radius. Next, the flow in the casing region (between the casing and the plane of the blade tips) is approximated as flow for an enclosed rotating disc with superposed radial outflow. For the investigated impellers the regime is turbulent with small clearance gap. To obtain an estimate for the torque on the disc (or the casing) an expression developed by Dorfman for this
regime is used [13]. When the casing torque is multiplied by the actual angular velocity of the impeller an estimate for the lost power due to casing drag is obtained.

\[
Re_{rot} = \frac{\rho \Omega r^2}{\mu}
\]

\[
TR = \frac{t}{r}
\]

\[
C_m \sim Re_{rot}^{-4} TR^{-4}
\]

\[
\frac{W_{\text{lost}}}{\rho \Omega^2 r^5} \sim Re_{rot}^{-4} TR^{-4}
\]

The rotational Reynolds number is based on rotor exit radius and gas properties at the exit radius and the clearance ratio TR is the ratio of tip clearance to rotor radius. From Dorfman’s expression it follows that the moment coefficient of the rotor (and thus the torque and the lost power due to casing drag) is a function of Reynolds number and clearance ratio (geometry). The lost power scales with angular velocity to the third power and radius to the fifth power. Therefore, the contributions to the lost power from near the outer radius will be much more significant compared to the ones from near the inlet radius. This justifies the correction of angular velocity at the exit radius, and the use of gas properties in the model based on exit radius. The estimate from the model is compared to CFD results for different impeller speeds and there is good agreement (Fig. 2). The inputs to the model are extracted from the CFD solutions, lost power is estimated with the model, and compared to the lost power calculated from casing torque and rotor angular velocity. The casing is stationary so the torque on the casing multiplied by angular velocity does not give power. However, the torque on the casing can be linked to the torque on the flow at the plane of the blade tips with a simple control volume analysis and this provides an estimate for the lost power.

**Impeller Passage Boundary Layer Loss**

The loss in the impeller passage (for shrouded impellers) is predominantly boundary layer dissipation. Intuitively, one might link flow separation to large mixing losses downstream of the trailing edges and such thinking led to the initial MIT designs with extremely high back-sweep angle (70 degrees) and very long passages to control diffusion. These designs resulted in impellers with very low efficiency because the boundary layer dissipation was increased due to the increased passage length and the work input to the flow was decreased due to the high back-sweep. Interestingly, the mixing loss behind the rotor is negligible, based on CFD. The reason is the very high swirl at exit and Cumpsty explains this point in his book [14] in the following manner: in the absolute frame at rotor exit the wake fluid and the mainstream fluid have similar large swirl velocity components and very small radial velocity components. The mixing loss is caused by the difference in the radial components and since they are very small, the mixing loss is negligible. It is very difficult to avoid separation in impellers (most impellers have very high area-density ratios) but fortunately its impact on rotor efficiency is not dramatic for impellers with strong exit swirl as explained above.

To estimate impeller passage loss it is useful to model impeller passages as channels of given hydraulic diameter or critical dimension. Simple channel flow ideas like Darcy friction factor provide useful loss estimates. Eight different impeller designs were investigated at MIT to study impeller passage loss. The Reynolds number in the impellers is high enough so that the flow is turbulent. The geometric parameters that were varied from design to design were blade back-sweep angle (25, 45 and 70 degrees), inlet angle (45, 55, and 65 degrees) and blade inlet-to-exit span ratio (1:1, 2:1, and 3.3:1). The results are presented in Fig. 3.

![Fig. 3 Impeller passage loss as a function of inlet flow power.](image)

It can be inferred from Fig. 3 that passage loss in all eight impellers when appropriately scaled and non-dimensionalized (lost power as fraction of inlet flow power) is only a function of Darcy friction factor (Reynolds number). The effects of
relative wall roughness on friction factor were not included. Boundary layers are relatively thick due to the low Re and typical wall roughness on the order of several microns has little effect on the flow. The actual lost power scales with friction factor, wetted area, inlet velocity cubed and impeller temperature ratio. The dependence on inlet velocity cubed is not surprising if one is familiar with boundary layer dissipation coefficient. The dependence on impeller temperature ratio (or work input) is related to the rotation of the impeller.

The lost power in the eight impellers is calculated from CFD calculations. Power input is calculated from torque and rotor angular velocity and efficiency is calculated from impeller total pressure ratio, mass flow, and power input. The lost power is obtained from efficiency and actual power input. The same loss mechanism would produce different power loss in the same stationary and rotating channels. This is the reason why the lost impeller power is scaled down to stationary conditions with the impeller temperature ratio. This will be explained in the next paragraph. The lost power per unit wetted area is calculated from geometry. At the same time, the inlet flow power per unit inlet area is calculated from inlet velocity and density. The ratio of the two is proportional to Darcy friction factor, which is also the slope of the lines on Fig 3. Dissipation coefficient can also be used instead of friction factor. Both, friction factor and dissipation coefficient are functions of Reynolds number and the parametric dependence of lost power can be expressed in the following manner:

\[
Re = \frac{\rho \omega r s_{exit}}{\mu}
\]

\[
C_d \sim Re^{-1}
\]

\[
W_{lost} \sim \frac{A_{wet}}{\rho_{in} V_{in}^3} \left( \frac{T_{in}}{T_{Te}} \right) \sim C_d \sim Re^{-1} \sim f \frac{1}{8}
\]

Reynolds number is based on hydraulic diameter or exit span (which is the limiting dimension) for friction factor estimate and on boundary layer momentum thickness for dissipation coefficient estimate. Friction factor (slope of lines on Fig 3) is calculated for the highest and lowest Reynolds numbers for the eight impellers at different conditions and the two lines bound all the data points confirming the above expressions for impeller passage lost power. Therefore, shrouded impeller passage loss is predominantly generated in the boundary layers and can be estimated with simple channel flow model. The difference between lost power in rotating and stationary passages can be explained with the help of Fig 4. For a micro impeller it was shown that loss scales as velocity cubed. Therefore, the highest losses will be generated near impeller inlet. At the same time, most of the compression happens near impeller exit, where the rotational speed is the highest. Conceptually, the flow processes within the impeller channel can be divided into loss generation first followed by compression. Let’s assume that the compression part is isentropic and ignore the differences between static and stagnation temperatures. The lost power, as shown in Fig. 4 due to compression at higher entropy (after the boundary layer loss is generated in the channel) is \(\Delta S_{Te}\). If the impeller passage were stationary, the lost power in the channel boundary layers would simply be \(\Delta S_{Tin}\). Therefore, the same increase in entropy due to the same boundary layer dissipation process will lead to different power loss depending on the amount of work the impeller is transferring to the flow.

![Fig. 4 Power loss due to boundary layer dissipation for stationary and rotating passages.](image)

\[
W_{lost\_channel} = W_{lost\_imp\_channel} \frac{T_{in}}{T_{Te}}
\]

The higher the impeller rotating speed, the larger the temperature ratio and the lost power become. Consequently, to compare loss in impeller channels the effect of rotation and work input should be removed by scaling with impeller temperature ratio. In the above description it is assumed that effect of rotation on boundary layer level is small because Rossby number at inlet where most of the loss occurs is higher than one. At inlet relative velocity is highest and rotation velocity is lowest.

Based on the expressions for impeller passage loss (Eq. 11) and adiabatic efficiency, the impeller adiabatic efficiency can be expressed in the following manner:

\[
\eta = 1 - \frac{f}{8} \left( \frac{2N \cdot c \cdot s_{exit} + 4N \cdot D_{n} \cdot \left( \frac{D_{r}}{D_{n}} \right)^{2}}{D_{r}} \right)^{\frac{1}{2}} \sin(\alpha) \cos(\alpha) \left( 1 + \frac{\Delta \omega^{2}}{\omega^{2}} \right)
\]

In the above expression efficiency is linked to friction factor, geometric factors, and work input factor. Wetted area is approximated in terms of rotor geometry, and work input factor (giving temperature ratio) is approximated from exit radius and rotor angular velocity. Passage Reynolds number is used to calculated Darcy friction factor. For simplicity the expression given is for adiabatic impellers without back-sweep and slip velocity. N is number of blades, c is blade chord, s is blade span, \(\alpha\) is blade angle, and D is rotor diameter.
similar, although more complicated, expression can be
developed to account for back-sweep, slip, and effects of heat
addition and casing drag on impeller efficiency. Such an
expression will be interrogated to provide insight to impeller
design in the next section.

**CHARACTERIZATION**

Based on the models for the effects of heat addition, casing
drag and passage boundary layer loss, the impeller
performance can be characterized as follows:

\[ \eta = f(m_c, N_c, \text{Re}, \text{geometry}, QH) \]  \hspace{1cm} (13)
\[ \alpha = g(m_c, N_c, \text{Re}, \text{geometry}, QH) \]  \hspace{1cm} (14)

These expressions lead to the statement that the only new
parameter entering the performance characterization of micro-
impellers compared to large conventional impellers is heat
addition parameter, QH. The other parameters characterizing
micro-impeller performance are corrected speed, corrected
mass flow, geometry, and Reynolds number. For large
compressors operating at large enough Reynolds numbers,
dependence on Reynolds number is often omitted. This is
because for large Reynolds numbers boundary layer
dissipation coefficient is nearly constant. This is not the case
for micro-impellers, as the models suggest, and the
dependence on Reynolds number is included.

**PERFORMANCE TRENDS FROM MODELS AND
DESIGN GUIDELINES**

The results from the expression developed for shrouded
impeller efficiency (similar to Eqn. 12) including effects of
back-sweep, slip, and heat addition are compared to CFD
results in Figures 5-8 and design guidelines are formulated.
The trends from the model are referenced to a baseline
impeller of 8mm diameter rotating at design speed of 1.2
million RPM. All impellers have the same inlet blade span
(400 um) and diameter ratio (2:1). The variation between inlet
and exit blade span is linear with radius. Both model and CFD
simulation include the right angle inlet losses.

The results from the model suggest an optimum inlet
angle for micro-impeller blades at about 55 degrees for the
selected design rotational speed and size (Fig 5). This
optimum is confirmed with CFD data. The existence of an
optimum inlet angle is expected because at very low inlet
angles the inlet velocity triangles for fixed design rotational
speed dictate very high inlet velocity. It was shown that
passage loss scales with velocity cubed. For very high inlet
angles velocity decreases, but mass flow, work input and
efficiency tend to zero.

The effect of blade back-sweep on impeller performance is
presented on Fig. 6. The trend from the model shows
deterioration in impeller performance for back-sweep angles
higher than 45 degrees. This is due to the elongated passages
and to the reduced work input and is confirmed by CFD.

![Fig 5. Shrouded impeller adiabatic efficiency as a function of
blade inlet angle showing optimum $\alpha = 55$. QH = 0.](image)

![Fig 6. Shrouded impeller adiabatic efficiency as a function of
blade back-sweep angle showing performance degradation for
angles higher than $\beta = 45$. QH = 0.](image)

![Fig 7. Shrouded impeller efficiency as a function of impeller
radial scaling. Friction loss between rotating shroud and
stationary casing is not included.](image)
It is useful to know the optimum radial dimension for a micro-impeller of fixed tip speed and fixed blade span (these are real practical constraints for the MIT impeller because they are related to the material strength and to the ability to etch silicon). Is it more advantageous to design larger diameter impellers rotating at lower RPM or the opposite? It can be observed on Fig. 7 that there is optimum radial size and this optimum moves towards smaller scales with heat addition. The physical reason why efficiency increases as radial scale is reduced is that wetted area decreases faster than mass-flow. This can be seen directly from Eqn. 12. If we scale down the impeller the only geometry term that changes is the ratio of inlet diameter to inlet span and it decreases. Therefore, efficiency increases. Since heat addition scales also with wetted area, for cases with heat addition the benefit would be larger. Of course, this trend cannot be monotous because at some point Reynolds number will decrease and viscous losses increase and also inlet effects will become important. Therefore the radial size should be kept as small as possible without affecting passage critical dimension, which sets Re and inlet area. Noting that the critical dimension in the rotor is the blade span can form useful guideline. Radial size therefore can be reduced until inlet diameter or inlet blade pitch becomes critical dimension without affecting Reynolds number significantly although heat addition is also a factor. CFD results confirm the general trends from the model and the existence of an optimum. For all cases the flow remained turbulent.

Model trends in Fig. 8 suggest an optimum number of blades but this is not confirmed by CFD. It is reasonable though because it is not hard to identify the two competing effects. If we decrease the number of blades, the wetted area is reduced but the slip velocity is increased. At adiabatic conditions, however, both model and CFD suggest that the two effects are balanced for large range of blade numbers and efficiency is nearly independent from blade number.

The effect of variable blade span geometry on impeller performance is also investigated. The ability to etch variable height blades is being developed by a team at the University of Maryland working in collaboration with MIT on the micro-engine project [7,8]. The effects of blade variable span are summarized on Fig. 9.

\[ \eta = 1 - \frac{W_{\text{out}}}{W_{\text{in}}} = 1 - \frac{\frac{V_{\text{in}}^2 \Omega^2 R^2}{V_{\text{in}}}}{\frac{V_{\text{in}}^2 \Omega^2 R^2}{V_{\text{in}}}} = 1 - \left( \frac{V_{\text{in}}}{\Omega R^2} \right)^2 \]

A quadratic relation between velocity (mass-flow) and efficiency follows which is the similarity curve on Fig. 9. Therefore it is beneficial to increase span ratio. However, at a certain ratio, any diffusion within the impeller passage will be eliminated and performance will level off as seen on the curve. Consequently, for the impellers of interest it is advantageous to fabricate span ratios of 2 but the benefit is negligible if the ratio is increased to 3 as can be seen on Fig. 9. Another way to think about the effect of variable span is noting that increasing the inlet-to-exit span ratio squeezes the flow at exit and forces the flow to follow the blade geometry and angles. This reduces the effect of slip and improves performance. Obviously, at a given ratio the flow will follow the blades exactly and increasing further the ratio will have little effect. In fact it can lead to detrimental effects like blockage and exit velocity increase. The beneficial effects from increasing the span ratio decrease with heat addition as dictated by the heat addition model scaling.

Based on the insight gained from the flow models and CFD solutions the following general guidelines can be formulated:

1. Micro-impellers should be thermally isolated as much as possible to avoid large performance
penalties associated with heat addition. The design of micro-impellers should be such to maximize mass-flow per unit wetted area (minimize QH) to reduce detrimental effect of heat addition on impeller performance.

2. Impeller radial size should be minimized for given tip speed and inlet critical dimension to reduce effects of heat addition and boundary layer loss.

3. Micro-impellers should be shrouded if possible to avoid significant penalty associated with casing drag.

4. There exists an optimum inlet blade angle and for the MIT impeller it is about \(-55^\circ\) degrees.

5. The blade back-sweep angle should be low to moderate not exceeding 45 degrees to avoid performance deterioration.


7. As low a blade count as possible should be used to reduce wetted area (~8-10 blades) without significant reduction in turning.

The current MIT micro-impeller geometry designed with the above guidance in mind is shown on Fig. 10. A shroud will be added to the impeller in the future builds.

Fig 10. MIT variable span micro-impeller [7,8]

<table>
<thead>
<tr>
<th>Blade count, N</th>
<th>Mach in rel</th>
<th>0.83</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter ratio, De/Din</td>
<td>2</td>
<td>Mach e rel</td>
</tr>
<tr>
<td>Blade span ratio in/e</td>
<td>2</td>
<td>Mach e abs</td>
</tr>
<tr>
<td>Blade inlet angle [deg]</td>
<td>-55</td>
<td>V rel e / V rel in</td>
</tr>
<tr>
<td>Blade exit angle [deg]</td>
<td>-45</td>
<td>exit angle rel [deg]</td>
</tr>
<tr>
<td>Rotational speed [rad/s]</td>
<td>125000</td>
<td>exit angle abs [deg]</td>
</tr>
<tr>
<td>Peripheral speed [m/s]</td>
<td>500</td>
<td>exit slip, Vθ/Vθi abs</td>
</tr>
<tr>
<td>Re (from Eq. 9)</td>
<td>7160</td>
<td>exit swirl, Vθ/Vr abs</td>
</tr>
<tr>
<td>Heat parameter, QH</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. MIT impeller design information

SUMMARY AND CONCLUSIONS

This study investigated performance-limiting mechanisms in micro-impellers. Dominant performance limiting mechanisms are identified and models describing their effects on impeller performance presented. The insight gained from modeling and CFD allows for performance characterization of micro-impellers and design guidelines formulation. The findings can be summarized as follows:

1. Relative importance of micro-impeller performance-limiting mechanisms is investigated and quantified and three mechanisms are identified as dominant. These are heat addition, casing drag, and passage boundary layer loss responsible for up to 25 pts, 13 pts, and 10 pts efficiency penalty respectively.

2. The effect of heat addition on impeller performance can be described by thermodynamics and is summarized as follows: The performance of micro-impeller with heat addition is similar to the performance of the same adiabatic impeller if its inlet flow is pre-heated with the same amount of heat addition.

3. The effect of casing drag is caused by the shear between the flow rotating with the blades and the stationary flow on the casing. An approximate model is developed for estimation of power loss using expression for torque on enclosed rotating disc with superposed radial outflow.

4. The effect of passage boundary layers on impeller performance can be successfully described by simple channel flow ideas and friction factor.

5. There is one additional parameter appearing in the characterization of micro-impellers and it is heat addition parameter, QH. Reynolds number should also be included in characterization.

6. Micro-impeller design guidelines are formulated based on insight gained from the flow models and CFD solutions.

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[9] FLUENT CFD code by FLUENT Inc.
www.fluent.com


Large deflection analysis of a pre-stressed annular plate with a rigid boss under axisymmetric loading

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Abstract

The large deflection analysis of a pre-stressed annular plate with a central rigid boss subjected to axisymmetric loading is presented. The factors affecting the transition from plate behaviour to membrane behaviour (e.g. thickness, in-plane tension and material properties) are studied. The effect of boss size and pre-tension on the effective stiffness of the plate are investigated. The extent of the bending boundary layers at the edges of the plate are quantified. All results are presented in non-dimensional form. The design implications for microelectromechanical system components are assessed.

1. Introduction

Over the past decade, the development of precision micromachining technology has led to the realization of complex miniature mechanical devices which are integrated with microelectronics at the 'chip' level. Such microelectromechanical systems (MEMS) offer great potential for compact, low-cost sensors, actuators and power sources. One structure common to numerous MEMS devices is that of a thin circular plate or membrane with a central circular boss or proof mass. Structures of this type can be found in pressure sensors, accelerometers, microvalves [1], and micro hydraulic transducers [2]. Often during operation, such structures are loaded into the large deflection regime where linear deformation theory no longer applies. In addition, these structures are often created by wafer-bonding operations [3], which may introduce in-plane residual stress due to thermal expansion, mismatch between adjacent wafers, or due to other process related effects. In extreme cases thermal-induced buckling may occur.

This paper presents a mechanical analysis of these issues, and builds upon previous work by others, notably [4–8]. In particular, this paper extends the work of [8] to study the large deflection of a pre-tensioned annular plate bonded with a rigid boss under axisymmetric pressure and in-plane loading. A comprehensive review of the literature can be found in [8]. The structure of this paper is as follows. In section 2, the derivation of the nonlinear governing equations is detailed. The numerical algorithm used to solve the problem is introduced in section 3. The membrane response and the plate response are compared in section 4. In section 5, nonlinear effects due to large deformations are compared with the results obtained from linear theory. The effects of boss size, pre-tension, and compliance of the boss are also addressed in this section. In section 6, several assumptions made in section 2 are justified a posteriori. The important conclusions of this work are summarized in section 7.

2. Formulation

We consider an annular plate with inner radius $r_b$, outer radius $r_a$ and thickness $h$ bonded with a rigid boss and pre-stressed by an uniform in-plane loading $N_r = N_0$ along its outer circumference. Then a uniform pressure $p_0$ is applied under the plate as shown in figure 1.
where \( N_r \) is the radial force per unit length along the circumference (its direction is always tangential to the deformed neutral surface), \( N_\theta \) is the circumferential force per unit length, and \( Q_r \) is the shearing force per unit length and is normal to the deformed middle surface.

Moment equilibrium gives

\[
M_r = D(K_r + \kappa_r), \quad M_\theta = D(\kappa_\theta + \nu \kappa_r)
\]

where

\[
D = \frac{Eh^3}{12(1-\nu^2)}.
\]

Kinematic considerations give

\[
\kappa_r = -\frac{d^2 w}{dr^2}, \quad \kappa_\theta = -\frac{1}{r} \frac{dw}{dr}.
\]

With simple algebra, we obtain

\[
\frac{d^3 w}{dr^3} + \frac{1}{r} \frac{d^2 w}{dr^2} + \frac{1}{r^2} \frac{dw}{dr} = \frac{N_r}{D} \frac{dw}{dr} - \frac{p_0 r}{2D}.
\]

The strain–displacement relationship can be written as follows

\[
\epsilon_r = \frac{du}{dr} + \frac{1}{2} \left( \frac{dw}{dr} \right)^2, \quad \epsilon_\theta = \frac{u}{r}.
\]

In order to eliminate \( u \), we rewrite the strain–displacement relationship as follows

\[
r \frac{d\epsilon_\theta}{dr} + \epsilon_\theta - \epsilon_r + \frac{1}{2} \left( \frac{dw}{dr} \right)^2 = 0.
\]

The material is assumed to follow Hooke's law, i.e. for a material with Young's modulus \( E \) and Poisson's ratio \( v \),

\[
\epsilon_r = \frac{1}{E} \left( \frac{N_r}{h} - \nu \frac{N_\theta}{h} \right), \quad \epsilon_\theta = \frac{1}{E} \left( \frac{N_\theta}{h} - \nu \frac{N_r}{h} \right).
\]

Substituting equation (9) into (8) gives

\[
\frac{dN_\theta}{dr} - \frac{N_r - N_\theta}{r} + \frac{Eh}{2r} \left( \frac{dw}{dr} \right)^2 = 0.
\]

Equations (1), (6) and (10) form three nonlinear differential equations with three unknowns \( N_r, N_\theta \) and \( w \).

The boundary conditions that must be satisfied are

\[
\frac{dw}{dr} = 0, \quad u = r \phi = 0 \quad \text{at} \quad r = r_b
\]

1 Note that the assumption of plane sections remaining plane is applied here; shearing deformation is not taken into account.

2 Note that plane stress is assumed here.
Large deflection analysis of a pre-stressed annular plate


and

\[
\frac{dw}{dr} = 0, \quad u = r\epsilon_0 = 0 \quad \text{at} \quad r = r_a. \tag{12}
\]

The linear solution of the initial in-plane pre-stress resulting from a uniform tension load \( N_r = N_0 \) applied at \( r = r_a \) and zero displacement \( u = 0 \) at \( r = r_s \) can be shown to be

\[
N_{n0} = C \left[ 1 + \beta^2 \left( \frac{r_a}{r} \right)^2 \right] \tag{13}
\]

\[
N_{\theta 0} = C \left[ 1 - \beta^2 \left( \frac{r_a}{r} \right)^2 \right] \tag{14}
\]

where

\[
\beta = \sqrt{\frac{1 - v}{1 + v} \xi_b} \tag{15}
\]

\[
C = \frac{N_0}{1 + \beta^2} \tag{16}
\]

and

\[
\xi_b = \frac{r_b}{r_a}. \tag{17}
\]

This was obtained from equations (1)–(7) by setting \( w = 0 \) and \( p_0 = 0 \). Note that the stresses vary with \( r \), instead of being constant as in the case of a uniform circular plate without a central boss.

After the pre-stress is applied, the plate is subjected to a transverse pressure \( p_0 \). The lateral loads are then decomposed as follows

\[
N_r = N_{n0} + \tilde{N}_r \quad \text{and} \quad \theta = N_{\theta 0} + \tilde{\theta}. \tag{18}
\]

The three nonlinear governing equations can then be rewritten as

\[
\frac{d\tilde{N}_r}{dr} + \frac{\tilde{N}_r - \tilde{\theta}}{r} = 0 \tag{19}
\]

\[
d^3w \over dr^3 + \frac{1 d^2w}{dr^2} \over r^2 - \left( \frac{\beta^2 d^2 C}{D} + 1 \frac{d w}{dr} \right) \frac{\tilde{N}_r + C \frac{d w}{dr}}{D} = \frac{p r}{2 D} \tag{20}
\]

\[
\frac{d\tilde{\theta}}{d\xi} - \left( \frac{\tilde{\theta}}{\xi} \right) - \frac{\tilde{\theta}}{\xi} + \frac{\tilde{\theta}^2}{\xi^2} + \frac{E h}{2r} \left( \frac{d w}{dr} \right)^2 = 0. \tag{21}
\]

2.1. Non-dimensionalization

After Sheplak [8], the following characteristic quantities are introduced to non-dimensionalize equations (19)–(21)

\[
\xi = \frac{r}{r_a}, \quad (\xi') = \frac{r}{h} \frac{d w}{h}, \quad U = \frac{u}{h}
\]

\[
\theta = \frac{d W}{d \xi} = \frac{r_a}{h} \frac{d w}{h}, \quad \Psi = \frac{d \theta}{d \xi} = \frac{r_a^2}{h} \frac{d w}{d r^2}, \quad S_r = \frac{\tilde{N}_r r_a^2}{E h^3}, \quad S_\theta = \frac{\tilde{\theta} r_a^2}{E h^3}. \tag{22}
\]

The dimensionless forms of equations (19)–(21) are thus

\[
\theta'' + \frac{\theta' \theta}{\xi} - \left( k^2 + \frac{s^2 + 1}{\xi^2} \right) \theta - 12(1 - v^2) S_r \theta = 6(1 - v^2) P \xi \tag{23}
\]

\[
S_r + \frac{S_r - S_\theta}{\xi} = 0 \tag{24}
\]

and

\[
S_\theta - \frac{S_r - S_\theta}{\xi} = -\frac{1}{2\xi} \theta^2 \tag{25}
\]

where \( k \) and \( s \) are dimensionless pre-tension parameters, and \( P \) is a loading parameter, which are defined as follows

\[
k = r_a \sqrt{\frac{12(1 - v^2) N_0}{1 + \beta^2 E h^3}}, \quad s = \beta k \tag{26}
\]

and

\[
p = \frac{p r_a^4}{E h^3}. \tag{27}
\]

The corresponding dimensionless boundary conditions can be expressed as

\[
\theta = 0, \quad S_\theta = 0 \quad \text{at} \quad \xi = \xi_b = \frac{r_b}{r_a} \tag{27}
\]

and

\[
\theta = 0, \quad S_\theta = 0 \quad \text{at} \quad \xi = \xi_s = 1. \tag{28}
\]

Here, equations (1) and (9) are used to simplify equations (11) and (12).

In order to solve equations (23)–(25), we first substitute equation (24) into (25) to eliminate \( S_\theta \)

\[
\xi^2 S_r'' + 3 \xi S_r' = -\frac{\theta^2}{2}. \tag{29}
\]

Equation (23) can be rewritten as follows

\[
\xi^2 \theta'' + \xi \theta' - \left( k^2 + 1 + \xi^2 \frac{6(1 - v^2)}{2} S_r \right) \theta = 6(1 - v^2) P \xi^3. \tag{30}
\]

The boundary conditions which must be satisfied are

\[
\theta = 0, \quad \xi S_r' + (1 - v) S_r = 0 \quad \text{at} \quad \xi = \xi_b \tag{31}
\]

and

\[
\theta = 0, \quad \xi S_r' + (1 - v) S_r = 0 \quad \text{at} \quad \xi = \xi_s. \tag{32}
\]

A careful examination of the dimensionless equations reveals that for a given material (more specifically, \( v \)) the problem is characterized by three dimensionless parameters: the modified boss size \( \beta \), the pre-tension \( k \), and the loading \( P \). Note that the modified boss size \( \beta \) plays roles only in defining the boundary conditions and in determining \( k \). However, the effect of \( \beta \) on \( k \) is very limited. More interestingly, the thickness \( h \) plays no explicit role in the problem.

2.2. Stress calculation

After solving equations (29)–(32), we obtain the distributions of \( S_r \) and \( \theta \). To calculate the stress fields, we define the dimensionless parameters of the in-plane pre-stress, \( S_{n0} \) and \( S_{\theta 0} \), as follows

\[
S_{n0} = \frac{N_{n0} r_a^2}{E h^3} = \frac{k^2}{12(1 - v^2)} \left[ 1 + \beta^2 \left( \frac{r_a}{r} \right)^2 \right] \tag{33}
\]

\[
S_{\theta 0} = \frac{N_{\theta 0} r_a^2}{E h^3} = \frac{k^2}{12(1 - v^2)} \left[ 1 - \beta^2 \left( \frac{r_a}{r} \right)^2 \right]. \tag{34}
\]
Then the corresponding dimensionless radial stress can be expressed as
\[ \sigma_r = S_0 + S_r - \frac{z}{(1 - \nu^2)h} \left( \Psi + \frac{\theta}{\xi} \right) \]  
(35)

and the corresponding dimensionless circumferential stress can be written as
\[ \sigma_\theta = S_0 + S_\theta - \frac{z}{(1 - \nu^2)h} \left( \nu \Psi + \frac{\theta}{\xi} \right) . \]  
(36)

\( S_\theta \) can be evaluated through equation (24) as follows
\[ S_\theta = \xi S^* \xi + S_\theta . \]  
(37)

### 3. Numerical Integration

Finite difference methods provide an efficient means of solving the governing equations derived above. Previous work [8] on a similar configuration has identified the importance of thin boundary layers near clamped edges. In order to resolve the boundary layers for the present case using numerical integration, two coordinate transformations, similar to those used in [8], were introduced to achieve better resolution near the boundary layer regions as follows.

For \( \xi_a \leq \xi \leq 0.5(\xi_a + \xi_b) \),
\[ \xi = \xi_a + (\alpha - 1)(\xi_b - \xi_a) \frac{r - r_b}{1 + r_b} , \quad 0 \leq \xi \leq 1 \]  
(38)

where \( \alpha \) can be thought of as the coordinate stretching parameter and
\[ r \equiv \frac{\alpha + 1}{\alpha - 1} . \]

For \( 0.5(\xi_a + \xi_b) \leq \xi \leq \xi_a \),
\[ \xi = \xi_a + (\alpha - 1)(\xi_b - \xi_a) \frac{r - r^b}{1 + r^b} , \quad 0 \leq \xi \leq 1 \]  
(39)

For \( 0 \leq \eta \leq 0.5 \),
\[ \eta = 0.5 - 0.5 \xi . \]

and for \( 0.5 \leq \eta \leq 1 \),
\[ \eta = 0.5 + 0.5 \xi . \]

Conversely, for \( 0.5(\xi_a + \xi_b) \leq \xi \leq \xi_a \) we have
\[ \xi = \frac{1}{\ln(r)} \frac{r(\alpha - 1)(\xi_a - \xi_b) - (\xi_b - \xi_a)}{\alpha - 1} . \]

Setting \( m \equiv (\alpha - 1)(\xi_a - \xi_b) \) for convenience gives
\[ \xi = \frac{1}{\ln(r)} \ln \left[ \frac{m r - (\xi - \xi_b)}{m + (\xi_a - \xi_b)} \right] . \]

For the derivatives, we have
\[ \frac{d \xi}{d \xi} = \frac{1}{\ln(r)} \frac{m(1 + r)}{m r - (\xi - \xi_b)} \]  
(40)

This will be explained later in section 4.

### Table 1. Comparison of finite element and finite difference solutions.

<table>
<thead>
<tr>
<th>( r_0 (\text{mm}) )</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finite element (( \mu \text{m} ))</td>
<td>38.7</td>
<td>32.8</td>
<td>22.3</td>
<td>9.00</td>
<td>1.89</td>
</tr>
<tr>
<td>Finite difference (( \mu \text{m} ))</td>
<td>38.67</td>
<td>32.76</td>
<td>22.27</td>
<td>8.95</td>
<td>1.83</td>
</tr>
</tbody>
</table>

\[ \frac{d^2 \xi}{d \xi^2} = \frac{1}{\ln(r)} \frac{m(1 + r)(m_2 - 2 \xi)}{\ln(r) \left[ (m r - (\xi - \xi_a))^2 + (m + (\xi - \xi_a))^2 \right]} \]  
(41)

where
\[ m_1 = (m r + \xi_a)(m - \xi) \quad \text{and} \quad m_2 = (m r - m + 2 \xi) \] .

For \( \xi_a \leq \xi \leq 0.5(\xi_a + \xi_b) \), \( r_b \) is replaced with \( r_0 \) in the previous equations (40) and (41). In the present case, the stretching parameter \( \alpha = 1.05 \) is used.

The governing equation in the transformed coordinate system can be written as follows
\[ \xi^2 (\xi) \left( \frac{d \xi}{d \xi} \right)^2 + \xi^2 (\xi) \left( \frac{d}{d \xi} \right)^2 \xi + \xi^2 (\xi) \left( \frac{d^2 \xi}{d \xi^2} \right) \]  
(42)

and
\[ \xi^2 (\xi) \left( \frac{d \xi}{d \xi} \right)^2 + \xi^2 (\xi) \left[ 2 \xi + 2 \xi (\xi + 2) (1 - \nu) \right] \]  
(43)

The boundary conditions to be satisfied are
\[ \theta = 0 , \quad \xi_a = \frac{d \eta}{d \xi} \xi_S + (1 - \nu) \xi_S = 0 \quad \text{at} \ \eta = 0 \]  
(44)

\[ \theta = 0 , \quad \xi_a = \frac{d \eta}{d \xi} \xi_S + (1 - \nu) \xi_S = 0 \quad \text{at} \ \eta = 1 . \]  
(45)

The governing equations were implemented using a second-order central-difference scheme, while the boundary conditions were implemented by using second-order forward and backward differencing schemes, respectively. The under-relaxation technique was used to accelerate convergence. In the present case, the under-relaxation parameter \( \omega = 0.25 \) is used.

In order to assess the accuracy of the finite difference schemes, a finite element model (FEM) was created (using the commercial FEM program ANSYS\textsuperscript{TM} version 5.6, 400 three-dimensional (3D) axisymmetric solid elements with nonlinear analysis are used). The following material and geometrical parameters were used: \( E = 165 \text{ GPa} ; \nu = 0.22 ; r_a = 0.8 \text{ mm} ; \) \( h = 10 \mu \text{m} ; \) \( r_0 = 1 \text{ MPa} ; \) \( N_0 = 0 \) and \( r_0 = 0.0, 0.2, 0.4, 0.6 \) and 0.75 mm, respectively. These parameters are representative of the micro-hydraulic transducer element made of silicon described in [2]. Table 1 shows the comparison between the centre deflections obtained from FEM and those

\[ \text{Here silicon, an anisotropic material, is modelled as an isotropic material for simplicity. For the particular case of a (100) silicon wafer loaded axysymmetrically this is a valid assumption due to the invariance of the effective modulus } E/(1 - \nu). \]  

For other orientations and non-axisymmetric loading this assumption only allows for an approximate solution [10, 11].
obtained from the present method. The two results agree with each other very well. Note that the largest discrepancy between the two analyses occurs when \( r_b \) approaches \( r_a \). This is due to the neglect of the shear deformation in the derivation of the governing equations.

4. Differences between membrane and thin plate behaviours

By definition, membranes can sustain only tensile stress, but no bending moment. In MEMS applications, unsupported thin films are typical examples. In contrast, plates can sustain both tensile stress and bending moments. In the limiting case of a very thin plate, the bending stress becomes insignificant compared to the tensile stress, and the membrane behaviour is recovered. In the context of designing MEMS, it is important to identify the transition from plate to membrane-dominated behaviour. When the thickness of the plate becomes very thin, the bending stress becomes insignificant compared to the tensile stress and the difference between a membrane and a thin plate diminishes. It is therefore interesting to compare the two results under this limit.

4.1. Membrane response

The governing equations describing the response of the structure shown in figure 1, if it acts as a pure membrane, can be obtained by neglecting the shear \( Q_x \) and bending moments \( M_x \) and \( M_y \) in the derivation given in section 2. The resulting dimensionless equations can be written as follows

\[
S_x + \frac{k^2 + (s/\xi)^2}{12(1-v^2)} \theta = -\frac{1}{2} \rho \xi, \quad \xi_b \leq \xi \leq \xi_a \quad (46)
\]

and

\[
\xi^2 S_x'' + 3\xi S_x' = -\frac{\theta^2}{2} \quad (47)
\]

where \( k \) and \( s \) are defined in equation (26).

The boundary conditions to be satisfied are

\[
\xi S_x' + (1-v)S_y = 0 \quad \text{at} \quad \xi = \xi_b \quad (48)
\]

and

\[
\xi S_x' + (1-v)S_y = 0 \quad \text{at} \quad \xi = \xi_a. \quad (49)
\]

Note that the boundary conditions \( \theta = 0 \) at \( \xi = \xi_b \) and \( \xi_a \), assumed in the plate case, no longer apply, since the membrane cannot sustain bending moments. The same solution algorithm used for the plate case can be applied to the membrane case.

Linearization of equation (46) indicates that a membrane without pre-tension \( (k, s = 0) \) cannot sustain any lateral loading \( \rho \) under linearized theory.

For the purpose of illustration, a thin silicon plate \( (E = 165 \text{ GPa}, r_s = 0.8 \text{ mm}, t = 5 \mu\text{m}) \) without a rigid boss is chosen, i.e. \( r_b = 0 \), and a uniform transverse pressure \( p_0 = 2 \text{ MPa} \) is applied. (The corresponding dimensionless parameters are \( P = 7934, \beta = 0 \) and \( k = 0 \).) The problems shown in figure 3 are analysed. The balloon case is shown only for the demonstration of the constant curvature phenomenon. The deflection curves for both cases are plotted in figure 4. Away from the boundaries, the membrane under constant pressure acts very similarly to the equivalent segment of a balloon with constant internal pressure. Furthermore, the extremely thin plate also behaves essentially as a membrane.

The effect of the boundary condition is seen more clearly in the slope and curvature of the structures shown in figure 3. A boundary layer exists near \( \xi = \xi_a \) as indicated in figure 5(a). This implies that the bending stress of the plate is significant only within the thin boundary layer where the two results differ. This effect is shown explicitly in figure 5(b). Note that in both cases the curvature is nearly constant everywhere away from the wall.

The in-plane stresses for the membrane and plate cases are shown in figure 6. Note that in both cases there is no in-plane pre-stress applied. Clearly the in-plane stresses

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**Figure 3.** Comparison between balloon, membrane and plate cases.

**Figure 4.** Comparison of the deflection curves between the membrane and plate cases.

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behave similarly to each other. This indicates that the in-plane stress dominates in the plate case. Interestingly, the in-plane stresses decrease with the increasing radial coordinate. The stresses become singular near the centre in both cases since the tangential slopes are horizontal at the centre.

5. Linear versus nonlinear analysis

As discussed in the introduction thin plate structures are often used in the large deflection regime. It is therefore important to understand the limitations of using linear solutions to predict their behaviour. It is very tempting to approximate this nonlinear deflection by superposing the linear bending deflection with the deflection caused by the in-plane pre-stress. Unfortunately, the deflection due to bending is very often overestimated by several orders of magnitude and the deflection due to in-plane pre-stress is always zero because of the lack of coupling between in-plane pre-stress and bending stress. Another possible way to approximate the nonlinear deflection is to make use of the linearized systems of equations (19)–(21). Unfortunately, this leads to the same difficulty mentioned above. The significant difference between the linear and nonlinear cases will be illustrated in the following discussion.

5.1. Effect of boss size

Results of the linear calculations of the centre deflection \( W_0 \) for various boss sizes \( \xi_b \) are given in figure 7. The results based on nonlinear theory for \( P = 1 \) are also plotted on the same diagram. The two curves are essentially the same, since the deflection under this pressure level is still much smaller than the plate thickness.

The centre deflections calculated using nonlinear theory versus boss size under various pressure levels are presented in figure 8. The corresponding results based on linear theory can be obtained by multiplying the deflection curve in figure 7 by \( P \). As can be seen from figure 8, there are large differences corresponding to several orders of magnitude between the linear and nonlinear results. Obviously, the linear theory is not appropriate for predicting the behaviour of MEMS structures with large deflections.

Figure 9 shows the distribution of the normalized slope in a plate with \( \xi_b = 0.4 \) under various pressure levels \( (P = 10^{-3}, 10^{-4}, 10^{-5}) \).
As shown in the diagram, the importance of the bending stress compared with the membrane stress decreases with the increasing pressure level. Bending effects are thus confined within a very thin boundary region when $P \gg 1$. Away from the boundary layers, the curve is almost straight which signifies a constant curvature behaviour. This indicates that the membrane stress dominates over this region.

The distributions of the deflection, slope, and curvature in the plates with various boss sizes under pressure $P = 10^4$ are shown in figures 10–12. As indicated in figure 11, boundary layers form at each of the two edges as expected. The nearly constant curvature behaviour away from the boundary layers is illustrated in figure 12.

5.2. Effect of pre-tension

Pre-tension tends to stiffen the plate both in linear and nonlinear theory. This plays an important role in determining the plate behaviour. This is best illustrated in figure 13. When the pre-tension $k$ is small, the pre-tension has little effect on the plate stiffness. This is shown by the flat regions in figure 13. When the pre-tension $k$ is very large, the stiffness of the plate is increased significantly which in turn determines the deflection. This is confirmed by the significant reduction in the deflection in figure 13. Interestingly, the linear and nonlinear solutions coincide with each other in this limit. This indicates
that the pre-tension dominates over the plate behaviour and effectively causes the structure to behave more as a membrane, except in the boundary regime. This is demonstrated further in figures 14–16. Figure 14 shows the distribution of deflection of a thin plate with a rigid boss of size $b = 0.4$ subjected to pressure $P = 1000$ and pre-tension $k = 100$. Also shown in the same diagram is the deflection curve obtained by treating the plate as a hinged membrane (thick curve). Figures 15 and 16 show excellent agreement between the two models in the regions away from the boundary layers.

Another interesting observation, originally made by Sheplak and Dugundji [8], is that the centre deflection $W_0$ of a thin plate without a rigid boss varies linearly with loading $P$ when $P$ is small and $W_0 \sim P^{1/3}$ when $P$ is large. For a large pre-tension $k$, the linear region grows reflecting the increased dominance of the membrane response. The same phenomenon is also observed in the cases of a plate with a rigid boss, as shown in figure 17.

**Figure 13.** Centre deflection as a function of in-plane pre-tension $k$ for different boss sizes $b = 0, 0.2, 0.4, 0.6$ and $0.8$. Both the linear (dashed) and nonlinear (solid) cases are shown.

**Figure 15.** Comparison between the slopes of the plate case and the membrane case.

**Figure 14.** Comparison between the deflected shapes of the plate case and the membrane case.

**Figure 16.** Comparison between the curvatures of the plate case and the membrane case.

**Figure 17.** Centre deflection as a function of loading for in-plane pre-tension $k = 0, 5, 10, 20, 50$ and $100$ ($b = 0.4$).
Large deflection analysis of a pre-stressed annular plate

Figure 18. Displacement and strain fields for an annular plate with \( r_b = 0.31 \) mm, \( r_a = 0.8 \) mm, \( h = 10 \) \( \mu \)m, under pressure \( P = 1 \) MPa.

6. Justification a posteriori

Several assumptions have been made in the previous analysis. Before concluding it is appropriate to evaluate these assumptions. In particular, the assumptions of \( u \ll w \) and the applicability of Hooke's law lie at the heart of this analysis. In order to investigate further, let us take the following examples: \( E = 165 \) GPa, \( v = 0.22 \), and a failure stress \( \sigma_u = 1.0 \) GPa (typical for a Si wafer), \( r_b = 0.31 \) mm, \( r_a = 0.8 \) mm, \( h = 10 \) \( \mu \)m, \( P = 1.0 \) MPa. Figure 18 shows the displacement and strain fields of the corresponding structure. The maximum radial displacement \( u \) is 0.232 \( \mu \)m and the maximum vertical deflection \( w \) is 27.4 \( \mu \)m. Clearly, \( u \ll w \) is a valid assumption. It is also seen from the diagram that the maximum radial strain \( \varepsilon_r = 2.5 \times 10^{-3} \) which is smaller than the ultimate strain \( \sigma_u/E = 6 \times 10^{-3} \). Since silicon is a brittle material, this implies that Hooke’s law is still valid. More specifically, this is a typical example of the large deformation but small strain problem.

7. Conclusion

The deflection of pre-tensioned annular plates containing rigid bosses has been examined. The conditions for the transition from plate behaviour under low loads to membrane behaviour under higher pressure and pre-tension have been identified. The presentation of the results in dimensionless form allows them to be readily applied to the design and analysis of structures of this configuration. The effect of large deflection and the influence of radial pre-stress are important factors that must be accounted for in the design of MEMS elements. The semi-analytical solutions presented herein have been shown to be accurate to within 3% for typical MEMS structures and materials given the assumptions on boundary conditions and material properties. Future work (currently undergoing) will provide experimental evidence to test these assumptions. The use of semi-analytical methods to derive these solutions allows parametric studies to be conducted more efficiently than if finite element methods were used. Furthermore, the solutions can be incorporated directly into the dynamic simulations required to validate the operation of MEMS devices.

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