DEVELOPMENT AND EXPERIMENTAL ANALYSES OF
MESO AND MICRO SCALE COMBUSTION SYSTEMS

A Thesis in
Mechanical Engineering
by
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The present research was concerned with the development and analysis of meso and micro scale combustion systems for propulsion applications. In a more general sense, the research focused on understanding combustion, heat transfer, and fluid mechanics of chemically reacting flows in small volumes and channels as well as the fabrication and diagnostic aspects of the systems. A series of small scale combustion systems were investigated that operated with gaseous, liquid, and solid reactants. Both steady-state and transient modes of combustion were studied in confinements where the characteristic length scale of the combustion volume approached that of the reaction zone.

Scaling issues related to combustion kinetics as well as fluid and thermal transport were reviewed. The insufficient flow residence time compared to the characteristic chemical time was identified as the critical issue for combustion at the microscale. This challenge was addressed by increasing the flow residence time using vortex flows and decreasing chemical reaction times with oxygen enrichment. Liquid nitromethane combustion, which has a higher volumetric power density than gaseous fuels, was also studied in mesoscale vortex chambers. Pressurization and oxygen enrichment were utilized to achieve high efficiency liquid propellant combustion in miniaturized chambers.

However, combustion with high oxygen concentration in small confinements raises safety concerns. In the present study, deflagration-to-detonation (DDT) was studied to address these concerns and DDT was indeed observed for gaseous flames ignited in capillary tubes with diameters less than 1 mm. Three propagation modes were identified as the size of the tube diameter approached the quenching limit. Propagation of nanoscale Al/MoO$_3$ thermite reactions in channels with dimensions on the order of a hundred microns was also demonstrated. The shorter reaction time of these transient processes can potentially overcome many of the thermal management problems of microscale combustion, since the time scales of the important chemical reactions become much smaller than the thermal diffusion time scales.

Micro counterflow diffusion flame burners were fabricated using low temperature co-fired ceramic (LTCC) tape technology, and were successfully operated with homogeneous gas-phase combustion. Unique to these burners are the incorporation of optical quality windows into
the build process enabling optical diagnostics of the micro diffusion flames stabilized in the burners. A microscopic imaging spectrometer was developed to analyze the flame structure. One-dimensional spatial distributions of CH* and C2* species across the sub-millimeter scale flames were successfully obtained using this technique, and compared with three-dimensional numerical model predictions based on detailed kinetics.

The present research revealed the achievability of many different types of combustion processes at millimeter and sub-millimeter scales. In addition to micro propulsion, the knowledge obtained and techniques developed in this thesis can be applied to many other micro reacting flow applications (e.g., fuel reforming, actuation, fluid pumping, power generation, in situ toxic incineration, etc).
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CHAPTER 1

INTRODUCTION

Motivations

The sizes of combustors providing the majority of energy around the world are usually much larger than the smallest length scale of a self-sustainable flame. However, recent developments of many small scale systems, such as portable electronics devices, unmanned aerial vehicles, and small spacecrafts that present size constraints on power components have driven the research interest in meso- and micro-scale combustors [1-6]. These microcombustors are aimed to address the needs for high energy density power sources for miniature devices. Length scales of the reaction chamber in these microcombustors are often on the same order as the characteristic dimension of the reaction zones.

Utilizing combustion for power generation in micro systems is motivated by the fact that the stored energy densities of hydrocarbon fuels are two orders of magnitude greater than the current battery technology (e.g. ~ 44 MJ/kg for liquid octane versus 0.6 MJ/kg for Lithium-Ion battery). With the large energy densities of hydrocarbon fuels (~ 50 MJ/kg), combustion-based micro power devices remain surpassingly competitive with contemporary lithium batteries (~0.6 MJ/kg), even if the overall efficiency is as low as 10% [2]. Besides, chemically-driven power generation modes may also complement the use of batteries, when high power output or power peaking is desired. As a result, combustion based power generators are considered to be a promising solution to meet the need for a compact high energy density source. Developments in micro-satellite and unmanned aerial vehicles (UAV) require efficient high power-density energy sources, since the power-to-weight ratio is critical to airborne applications. The recent interest in personal power systems further underscores the needs for compact, efficient, human compatible, lightweight power sources [1]. The desired gravimetric energy density for personal power systems is in the range between 1.8 and 18 MJ/kg (500-5000 W-hr/kg), which is more than electrochemical batteries can provide (see Figure 1.1). However, the energy release of
hydrocarbon fuels through combustion can still fulfill the energy density requirements. The gravimetric power density for the desired personal power system is from 10 to 1000 W/kg, which can be obtained by combusting around 0.2 grams of liquid octane per second with an overall efficiency of 10%.

The current research effort is driven by the propulsion applications of micro combustion devices, namely, microthrusters. The size of spacecrafts nowadays can be significantly reduced while giving better performance as well as being more versatile thanks to the recent advancement in micro technologies. Significant progress in the development of small spacecrafts has been demonstrated by the recent successful launch of the XSS-10 experimental microsatellite by the Air Force Research Laboratory (AFRL) [7]. The 31 kg microsatellite was launched as a secondary mission aboard a Delta II launch vehicle and carried an optical camera, a star sensor, a Global Positioning System (GPS) receiver, and a miniature Space-to-Ground Link Systems (SGLS). The mission objectives of the XSS-10 program included the demonstration of autonomous navigation and proximity operation, which are important capabilities of future space-
servicing missions. A follow-on mission called XSS-11, was developed as a year long test of microsatellite technologies instead of the restricted 24-hour mission because of the limited battery power for XSS-10.

There are important advantages for going to small satellites. One benefit is the substantial reduction in the overall life-cycle cost by making satellites less costly to construct, due to fewer components and the potential use of mass production techniques [8]; moreover, smaller launch vehicles can be used. However, the presence of small spacecrafts not only provides a potentially more cost effective solution to the existing mission demands but also owns its unique application areas in satellite inspections and repairs, satellite active protections and decoys, and forming satellite clusters for interferometry research on gravity waves, radar, and communications. These advanced missions, however, all rely on precise maneuvering and agile movement of the microspacecrafts, which require the availability of micropropulsion devices capable of delivering low thrust values at the millinewton level and below as well as low impulse bits of tens of micro newton-seconds and below, while the size and weight of the propulsion systems have to be scaled down to the size comparable to the microspacecrafts.

### Table 1.1: Microspacecraft classification [9].

<table>
<thead>
<tr>
<th>Designation</th>
<th>Mass</th>
<th>Impulse bit (Ns)/Thrust (mN)</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>Microsatellite</td>
<td>10-100kg</td>
<td>$1.3 \times 10^{-5}$ / 4.65</td>
<td>“Class I Microsatellite” – 5-20kg</td>
</tr>
<tr>
<td>Nanosatellite</td>
<td>1-10kg</td>
<td>$5 \times 10^{-6}$ / 1.75</td>
<td>“Class II Microsatellite” – 1-5kg</td>
</tr>
<tr>
<td>Picosatellite</td>
<td>0.1-1kg</td>
<td>$7 \times 10^{-7}$ / 0.06</td>
<td>“Class III Microsatellite” - &lt;1kg</td>
</tr>
<tr>
<td>Femtosatellite</td>
<td>10-100g</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Attosatellite</td>
<td>1-10g</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zeptosatellite</td>
<td>0.1-1g</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

For research purposes, small spacecrafts are usually classified according to their weight into several classes as shown in Table 1.1 [8]. It is now accepted that satellites with mass less than 100 kg are categorized as microsatellites. Miniaturization of propulsion components, although not necessary, would clearly benefit the design for satellites in this class. The propulsion hardware of the spacecraft in the Class I category (5-20 kg) is the smallest of any propulsion device available today or currently under substantial development. These technologies may
include conventional hydrazine attitude control thrusters to be used for primary propulsion as well as cold gas thrusters. For example, the XSS-10 utilized cold gas thrusters as the propulsion source. However, no current hydrazine thruster exists that can be used for attitude control of microspacecrafts while fulfilling the mass and volume limitations. Although miniaturized cold gas thrusters do exist, their use may lead to propellant leakage concerns and heavy, high-pressure propellant storage tanks. As a result, the development of new propulsion devices is required for spacecrafts smaller than 10kg. The miniaturization of the propulsion system can take advantage of the currently flourishing microfabrication technologies to achieve a higher degree of integration of the propulsion system.

The interest in developing micro chemical propulsion systems is not only inspired by their smaller sizes to integrate onto microsatellites, but also the potential performance advantages. The thrust-to-weight ratio of a micro thruster or an actuator scales with $L^{-1}$ according to the square-cube law [10-13]. However, the scaling analyses are made under the assumption that the power generated from per unit of fuel stays constant as the size of the combustion system is decreased, which might not be valid. The shortened flow residence time and the enhanced surface-to-volume ratio for a miniature combustion vessel can significantly reduce the combustion efficiency. More details on the scaling analyses will be discussed in Chapter 2.

**Applications of Micro Combustion Systems**

The interest in studying small scale combustion systems owes largely to the wide variety of their potential applications. In this section, a brief review of some of these applications, including propulsion, actuation, power generation, and fuel reforming is given. The review is focused on applications that apply to homogeneous combustion and use gaseous, liquid, and solid phase reactants. Devices using catalytic reactions, although widely studied for small scale reacting flow devices, are briefly mentioned, but not discussed in detail since the focus of the present effort was on non-catalytic microcombustors.
**Micro Thrusters**

A number of research efforts have been made for developing micro thrusters in the aerospace community [8, 14-30]. Table 1.2 is a summary of types of microthrusters under development in academia, government and industry as well as their design performances. These small thrusters, like their macro scale counterparts, are classified by the energy source of the propulsion power into two major categories, chemical and electric.

### Table 1.2: A summary of types of micropropulsion devices under development and their design performances [8].

<table>
<thead>
<tr>
<th>Thruster type</th>
<th>$I_{sp}$, sec</th>
<th>Thrust, mN</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$ monopropellant</td>
<td>160</td>
<td>1-1000</td>
</tr>
<tr>
<td>Cold gas</td>
<td>40-80</td>
<td>50-50000</td>
</tr>
<tr>
<td>Digital solid</td>
<td>200</td>
<td>10-100000</td>
</tr>
<tr>
<td>Turbopump</td>
<td>300</td>
<td>15000000</td>
</tr>
<tr>
<td>Bipropellant</td>
<td>200</td>
<td>3-50</td>
</tr>
<tr>
<td>Digital bipropellant</td>
<td>45-100</td>
<td>100-1000</td>
</tr>
<tr>
<td>Resistojet</td>
<td>75-125</td>
<td>1-100</td>
</tr>
<tr>
<td>Vaporizing liquid</td>
<td>17000</td>
<td>10-200</td>
</tr>
<tr>
<td>FEEP</td>
<td>450-1350</td>
<td>20-100</td>
</tr>
<tr>
<td>Microcolloidal</td>
<td>800-1000</td>
<td>0.1-10</td>
</tr>
<tr>
<td>Micro-PPT</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Chemical thrusters can be further classified into solid, bipropellant, liquid, cold gas, warm gas, and hybrid thrusters depending on the propellant used. Similarly, electric propulsion devices refer to a general class of thrusters that may include ion engines, hall thrusters, field emission electric propulsion devices, colloid thrusters, pulsed plasma thrusters, and resistojets. Cold gas thrusters have already been used in the attitude and position control propulsion unit of small satellites. Nitrous oxide has recently been proposed to be used in cold gas microthrusters [31]. Although nitrous oxide provides relatively low specific impulse compared to other propellants used for cold gas thrusters, its storage density is among the highest when stored in liquefied form at 21 °C. Nitrous oxide microthrusters also have the potential of operating in a
resistojet mode and a monopropellant mode. In resistojet mode, nitrous oxide decomposes into nitrogen and oxygen gases with externally applied heat. Interestingly, the decomposition is exothermic and the reaction becomes self-sustained after the external heat input exceeds a certain value. Studies have also been made on using the heat generated by fuel rich hydrogen/oxygen catalytic reaction as a mean of ignition in microthrusters [32-34].

A solid microthruster is called a “digital microthruster” [29, 30] when an array of single-shot sub-millimeter scale solid thrusters cells are integrated on a single chip. The digital thruster has received a significant amount of attention and is largely responsible for the research interest in micropropulsion. These devices are often fabricated with micro-electro-mechanical technologies (MEMS). Advantages of digital thruster arrays are their relative simplicity and the absence of micro-machined valves or complex feed systems. Each element in the array by itself is a complete propulsion module, including the propellant tank. The impulse bit and thrust from each thruster cell can be quite small. Larger impulse and thrust have to be generated through programmed firing of cell clusters, and the increments of the impulse and thrust levels are limited by the smallest impulse and thrust that each cell provides. The inherent single-shot nature of most solid thrusters makes the cell an obsolete component on the system after firing. Unfortunately, the large area on the surface of a satellite that the digital microthruster array occupies is also valuable for other subsystems such as solar cells, antennas, and surveillance instruments. Further increasing the element density of digital microthrusters is challenging because thermal interactions between thruster elements might accidentally ignite neighboring thrusters, making the output of the thruster unpredictable.

Figure 1.2 shows the design of the digital thruster developed by the Aerospace Corp., TRW, and CalTech [29]. The design consists of three dies; the top and the bottom dies are made from silicon and the center die from glass. In the top die, a matrix of nozzles is anisotropically etched on a <100> silicon wafer, each with an exit cross sectional area of 1 mm × 1 mm. At the base of the top die is a 0.5 μm thick silicon nitride diaphragm used to seal the propellant in the cylindrical combustion chambers of the center die. Each combustion chamber has a volume of ~0.5 mm³ and is filled with lead styphnate, which is typically used as primer in explosives, as the solid propellant. On the bottom die, polysilicon resistors are deposited, which is resistively heated to ignite the propellant. Fifty watts has to be applied to the resistor for ignition. After the propellant decomposes and gasifies, the chamber pressure raises to ~10 atm, which is the burst
pressure of the diaphragm. The expelling gas produces an impulse bit of $10^{-4}$ N·s and thrust of 0.1 N. In the design, the combustion efficiency is poor largely due to the fact that the propellant is ignited from below and significant unburnt propellant escapes prior to its decomposition.

The expansion angle of the nozzle is 35.3° (from centerline to one side wall) resulting from the nature of KOH selective etching along the <100> planes, which is larger than the typical optimized angles for macroscale rocket nozzles, which are between 15° to 20°. The overexpanded nozzles may cause significant thrust lost, although the optimal expansion angles for micro scale nozzles might not be the same as the macroscale nozzles considering the relatively larger boundary effects. Underexpanded micro nozzles on the digital micro thruster array have also been demonstrated using the Bosch patented deep reactive ion etch (DRIE) technique [30].

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Probably the most sophisticated design, from an engineering perspective, is the liquid bi-propellant thruster being developed at MIT (see Figure 1.3) [27, 28]. This high pressure bipropellant rocket engine is fabricated by fusion bonding a stack of six individually etched single crystal silicon wafers. The 18 mm long, 13.5 mm wide, and 2.9 mm thick micro rocket engine weighs 1.2 g, and the volume of the combustion chamber is about 100 mm³. A rectangular converging diverging nozzle with throat cross section dimensions of 0.5 mm × 1.4 mm was integrated in the rocket engine with the thrust chamber. Preliminary firing tests were carried out using methane and oxygen as the fuel and the oxidizer, respectively, while water was used as the coolant. Thrust up to 1 N was obtained at chamber pressures above 12 atm. The specific impulse
measured is ~ 150 sec. Successful liquid propellant operations, however, haven't been reported in the micro bipropellant thruster so far.

Chen et al. [35] studied the feasibility of using homogeneous catalytic decomposition of hydrogen peroxide (H$_2$O$_2$) to generate thrust in a microthruster. The water solution of ferrous chloride (FeCl$_2$) was chosen as the homogeneous catalyst. The selection of FeCl$_2$ was due to its ability to produce short ignition delays and its solubility in water. Conventional H$_2$O$_2$ catalysts in large rockets (such as hypermanganate) form oxide depositions that clog the microthruster nozzle despite their high decomposition efficiencies. The micro electro-discharge machined thruster chamber of the prototype microthruster has an overall size of 7 mm in diameter and 12 mm long. The prototype thruster can provide ~ 20 mN of thrust at 5 atm chamber pressure. However, the dead volume in this miniaturized chamber is too large such that the long delay time of the thrust force makes the thruster incompatible for station-keeping and orbit maneuvering operations. Research on fabricating a smaller silicon thruster with deep reactive ion etching (DRIE) techniques to realize the concept is underway. Table 1.3 is a summary of chemical thrusters that have appeared in the literature. Most efforts have adopted solid propellants in their microthruster designs.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Propellant</th>
<th>Thrust/Impulse</th>
<th>Material and Fabrication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zakirov et al.[31]</td>
<td>N$_2$O</td>
<td></td>
<td>Quartz tube, catalytic combustion.</td>
</tr>
<tr>
<td>Chen et al.[36]</td>
<td>H$_2$</td>
<td>7 mN</td>
<td>Polymer/Si/Glass three layers, low ignition energy input, fluid plug.</td>
</tr>
<tr>
<td>Kang et al.[37]</td>
<td>Perfluoro normal hexane (FC72, C$_6$F$_6$)</td>
<td>2 - 6 * 10$^{-8}$ Ns</td>
<td>Silicon, layer Si, DRIE, ethanol and water as coolants.</td>
</tr>
<tr>
<td>London et al.[27, 28]</td>
<td>Methane/oxygen</td>
<td>1 N</td>
<td>6 layer Si, DRIE, ethanol and water as coolants.</td>
</tr>
<tr>
<td></td>
<td><strong>Gas</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chen et al.[35]</td>
<td>H$_2$O$_2$/FeCl$_2$</td>
<td>80 μNs (rmin)</td>
<td>SS /w EDM, Si /w DRIE, homogeneous catalysis</td>
</tr>
<tr>
<td></td>
<td><strong>Liquid</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>London et al.[27, 28]</td>
<td>Ethanol/O$_2$ (est.)</td>
<td></td>
<td>No successful liquid fuel firing reported yet.</td>
</tr>
<tr>
<td>Schneidel et al.[32]</td>
<td>H$_2$/CH$_4$/O$_2$</td>
<td>1-10 mN</td>
<td>Use catalytic combustion of rich H$_2$/O$_2$ for ignition.</td>
</tr>
<tr>
<td>Cheung &amp; Tilston[26]</td>
<td>H$_2$O$_2$/Hydrocarbons</td>
<td></td>
<td>SS, traditional machining, various fuel nozzles, catalyst and fuel.</td>
</tr>
<tr>
<td></td>
<td><strong>Bi-propellant</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rossi et al.[16, 19, 38-47]</td>
<td>GAP/AP/Zr</td>
<td>36 mN</td>
<td>Si/Foturan glass.</td>
</tr>
<tr>
<td>Lewis et al. [29]</td>
<td>Lead styphnate</td>
<td>0.1 mN s</td>
<td></td>
</tr>
<tr>
<td>Teasdale et al.[30]</td>
<td>HTPB/AP</td>
<td>10-15 mN</td>
<td>Si nozzle/ceramic body</td>
</tr>
<tr>
<td>Tanaka et al.[43]</td>
<td>NAB w/wo RK ignition aid</td>
<td>2.10$^{-5}$ - 3 * 10$^{-4}$ Ns</td>
<td>Si, bulk and surface micromachining.</td>
</tr>
<tr>
<td>Zhang et al.[23, 24, 44]</td>
<td>HTPB/AP/Al</td>
<td>0.76 - 4.38 mN, 1.16 * 10$^{-4}$ - 4.37 * 10$^{-4}$ Ns</td>
<td>Si/Pyrex, bulk.</td>
</tr>
<tr>
<td>Zhang et al.[45]</td>
<td>Gun powder/AP/Al/Fe$_2$O$_3$</td>
<td>0.4 N</td>
<td>Ceramic, LTCC.</td>
</tr>
<tr>
<td>Ali et al.[46]</td>
<td>BTAZz/DAATO3.5</td>
<td>0.1 N est.</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.3:** Summary of microthruster technologies.
Micro Actuators

Energetic material (EM) combustion is an attractive approach for mechanical actuation due to the high actuation pressure (see Table 1.4 [47]) and the large actuation displacement the EM based actuators can potentially provide. Electromagnetics are the traditional approach for mechanical actuation, but they are hard to integrate into micro devices. Piezoelectrics can be inherently integrated into micro systems using silicon based MEMS fabrication process, but they typically require high electric power to operate. Thermomechanic and shape memory alloys can only provide relatively small mechanical displacement. Electrostatics are also easy to integrate into micro systems, but their actuation pressures are low. EM based actuation is able to provide both high pressure and large displacement.

Table 1.4: Comparison of the actuation pressure for various types of actuation methods [47].

<table>
<thead>
<tr>
<th>Type of actuation</th>
<th>Actuation pressure (N/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piezoelectric (PZT)</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Electromagnetic</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Thermomechanic</td>
<td>~$10^5$</td>
</tr>
<tr>
<td>Thermopneumatic</td>
<td>$10^6$</td>
</tr>
<tr>
<td>Shape memory alloy (SMA)</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Solid-liquid phase change</td>
<td>$10^6$ (acetimine) to $10^7$ (paraffin)</td>
</tr>
<tr>
<td>Energetic material combustion</td>
<td>$10^7$ to $10^8$</td>
</tr>
</tbody>
</table>

An interesting application of EM combustion actuation has been investigated by Hong et al.[48], who integrated combustion based actuators in a micro fluidic chip to drive the micro flow network on the chip (see Figure 1.4). The chip is made of cyclic olefin copolymer (COC) to reduce the power consumption due to its low thermal conductivity. A gold (Au) microheater was patterned on the substrate to ignite the propellant. In the on-chip pressure generator, azobisisobutyronitrile (AIBN), which has been widely used as an initiator in various polymerization reactions to produce different polymers, is used as the solid chemical propellant. The propellant was deposited on the microheater using a screen-printing technique as shown in the figure. The screen-printing technique has been considered as an effective approach for depositing materials with feature sizes on the order of tens of microns. Nitrogen gas was produced by heating the
propellant above 70 °C with the electric microheater. The output pressure determined by the decomposing rate of the solid propellant into gaseous nitrogen is adjustable by controlling the input power of the heater. De-ionized water was successfully pumped through a 70 mm long, 100 μm wide and 50 μm high microfluidic channel at a flow rate of 17 ml/min as shown in the figure while consuming only 189 mJ of electric power. This power consumption is extremely low compared to traditional electric syringes.

![Figure 1.4: The on-chip micro actuator using AIBN as solid propellant to generate nitrogen gas that act as the pressure source to pump liquid in the microchannel.](image)

Air bag type one-shot micro actuators, which use elastomer membranes to confine the generated gas, have also been proposed. The design has even been considered for drug delivery. Isolation between the drug and the EM material is an important issue for this kind of application. Diaphragms and membranes are therefore preferred over piston types of design not only due to considerations on sealing but also the increased friction force per unit volume. The pressure in earlier designs is fixed as a function of the ratio between the initial EM volume and the initial chamber volume. This approach is still commonly seen in one-shot microvalves, which use EM to break the thin membrane that isolate the pressure head. The pressure regulation in recent
microactuator designs, like the above mentioned study by Hong et al. [48], is achieved by controlling the heating temperature because the decomposition of an EM is usually temperature dependent. A novel solid-phase conductive fuel allows ignition to occur by passing current directly through the fuel sample as opposed to relying on the transfer of heat from external or imbedded ignitor [49].

Meso scale actuators based on gaseous combustion have also been studied. Funk et al. [50] designed a combustion-driven fluidic actuator array to control the flow attachment over an airfoil at high angle of attack. The actuator produces a high momentum, impulsive jet by combusting a premixed fuel/air mixture in a 1 cm³ chamber before exhausting it through a small orifice. The actuator is able to work in a pulsating mode up to 150 Hz with repetitive spark ignition of hydrogen/air mixtures.

**Micro Engines**

Much effort has been invested in developing combustion based micro power generators during the relative short history of the field. The goal is to develop a microscale engine that converts the chemical energy of the fuel into kinetic energy. With the evolution of micromachining technologies, a great proportion of research has been devoted to the scaling down the existing macro scale engine concepts. For example, Waitz et al. [51-53] reported on a sophisticated silicon-based micro gas turbine engine that if successful could produce 10-50W of power in a volume less than 1 cm³. Figure 1.5 shows the schematic illustration of the micro gas turbine. The combustor was micro-machined from silicon using DRIE and aligned fusion wafer bonding. A total of six layers of silicon wafers are bonded. Hydrogen/air and hydrocarbon/air combustion was successfully stabilized in the 191 mm³ combustion chamber. Combustion efficiencies over 90 % for hydrogen/air and 60 % for hydrocarbon/air are reached in the miniaturized combustor.
Designs such as micro Stirling engines [10, 54], micro-rotary engines [55-57], micro internal combustion swing engines [58, 59], micro reciprocating engines [60, 61], micro homogeneous charge compression engines [62-64] and micro-free piston knock engines [65] have also being reported. Kinetic energy generated through these designs can be further transformed into electricity by electrical generators using electromagnetic induction.

Micro Electrical Power Generators

Many studies have been focused on developing micro combustion systems that directly convert the chemical energy from the fuel into electrical energy using thermal-photovoltaic [66-69], thermoelectric [70-74], or piezoelectric elements [75]. So far, the performance of these devices is very low due to the low efficiencies of the thermal/photo-electric converting elements. However, these designs are still attractive solutions for micro power generation because they do not involve any moving parts and are relatively simple in construction.

The foundation of thermoelectric power generation is the electric potential produced by a temperature difference across a material, known as Seebeck effect. For a thermoelectric generator, the efficiency is proportional to the temperature difference between the hot and cold fluids. For example, a commercial thermoelectric generator yields an efficiency of about 3% with a 70°C difference. Thermoelectric power generation is constrained by the upper limit of
operational temperature of the thermoelectric material. These materials can hardly sustain temperatures above 1200 K [76], while the adiabatic flame temperatures of most combustion reactions exceed 2000 K. Combustors of thermoelectric generators must run at extremely lean conditions to keep the temperature low. However, flame quenching becomes an issue for small combustors under these conditions. This is the reason why most combustion based thermoelectric generators either utilize catalytic combustion or apply heat recirculation combustion techniques to sustain the flame [71, 74, 77].

Micro thermal-photovoltaic (TPV) generators [66, 68, 69, 78-82] convert collected photons emitted from the flame into electricity. Photons emitted from heat sources at 1200-1700 K in most meso scale combustors are distributed at much lower energy regions with longer wavelengths compared to solar radiation. Silicon is therefore not a suitable choice for non-wavelength-selective thermophotovoltaic radiators operating at temperatures below 1400 °C due to its high bandgap [83], hence, unconventional low band gap semiconductor diodes have to be used for energy conversion in TPV. Yang et al. [66, 68, 69, 81] have designed a TPV system predicted to generate 4.5 W of electrical power in a 100 mm³ micro combustor. Nielsen et al. [82] were able to obtain 1.0 mW electrical output using stoichiometric propane/air combustion with a system efficiency of 0.08%. Both designs used Gallium-Antimony alloy (GaSb), which has a bandgap of 0.72 eV, as material of photocells for energy conversion. The 0.72 eV bandgap is equivalent to the energy of photons radiated at 1723 nm.

The design of the piezoelectric power generator is based on the kinetic-electric conversion during the vibration of piezoelectric membranes. In the design of Whalen et al. [75], a saturated two-phase working fluid in a cavity bounded on the top and bottom by thin membranes expands and contracts with the addition and rejection of heat from a heat source underneath the lower membrane. The top membrane is a piezoelectric membrane generator that converts this cyclic motion into electricity. A micro combustion device with an external heat source is proposed. The resonant frequency of the piezoelectric membrane is usually at several hundred hertz, which is fast for thermal diffusion. However, with the smaller thermal mass in a miniaturized system, the reduced Fourier number can be an advantage for piezoelectric power generator to operate at optimum resonant frequency.
**Micro Fuel Reformers**

A micro combustor is essentially a type of micro reactor that can sustain fast exothermic reactions. With the recent surge in hydrogen energy research, many studies on micro combustors have been focusing on incorporating combustors into hydrogen production systems for fuel cells [84-90]. Combustors in this case act as fuel reformers that produce hydrogen from hydrocarbon fuels, such as methanol. This type of application usually involves catalytic combustion. For example, methanol is reformed into hydrogen using metal oxide with the following reactions.

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + 3\text{H}_2 \\
\text{CH}_3\text{OH} & \leftrightarrow \text{CO} + 2\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

The heat generated by combustion can also be used to provide heat for vaporization and endothermic reforming reactions such as CO\textsubscript{2} and steam reforming in a micro power system [86, 91]. Alternatively, hydrogen can be produced via partial oxidation of methane and other hydrocarbons.

\[
\text{CH}_3\text{O} + 1/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H = -247 \text{ kJ/mol}
\]

The reaction has to be carried out at 1200-1500 °C without a catalyst. A miniaturized reactor has the potential benefit of being able to more precisely control the reaction temperatures due to the smaller thermal mass [89, 92].

**Objectives**

In general, catalytic combustion [74, 77, 87, 93-99] and excess enthalpy burners [74, 94, 100-103] have been widely studied to address the issues of microcombustion in the applications discussed in the previous section. These approaches somewhat resolve the limitations on the combustor designs due to the thermal and radical quenchings in small confinements. Although the performance and operating characteristics of Swiss-roll burners are extensively studied [70, 74, 101, 103-105], degradation of the catalyst in excess enthalpy burners restricts the development of
these combustor designs into practical systems. Both catalytic and excess enthalpy combustion concepts deposit thermal energy into the body structure and can also make thermal management much more difficult.

The objectives of this research are to study the combustion characteristics of systems where the characteristic length scale of the combustion volume approaches that of the reaction zone. Flame stabilization mechanisms in meso/micro scale combustors without the assistance of catalysis for gaseous combustion are investigated for cases where flow residence times approach characteristic chemical time scales. As an alternative to achieving thermal energy at steady-state conditions, transient combustion with fast kinetics can potentially be used to overcome the thermal management problems of microscale combustion systems as the time scales of chemical reactions become smaller than the thermal diffusion time scales. The ability to achieve detonation in microchannels is also investigated. The form of the reactants is also important to microscale combustion systems, e.g., liquids generally have higher energy densities than gases. Therefore, the objective of the present research was also to investigate the use of several gaseous, liquid and solid reactants in microscale systems. Finally, fabrication techniques for the combustion systems and diagnostic methods for microscale flames are to study the fundamental problems associated with meso and micro scale combustion.

Several meso and micro combustion systems are designed, fabricated, and analyzed in the thesis. Both steady state operation and transient reaction propagation in millimeter and sub-millimeter scale confinements are studied. It is worth noting that characteristic dimensions of the combustion systems studied here \( d \) are far greater than the mean free paths \( l \) of the reactant molecules, i.e. Knudsen number, \( Kn \equiv l/d < 0.01 \), so that no-slip conditions and continuum models are appropriate.

**Organization of the Thesis**

In Chapter 2, general scaling laws are discussed and applied to the governing equations for chemically reacting flows to explore the characteristics of a combustion system as its size is reduced. The impact of miniaturization on transport phenomena are discussed through the nondimensionalized governing equations. The shortened flow residence time and the increased
surface-to-volume ratio are identified as the most remarkable challenges for combustion in a small confinement. An analysis on the performance of a chemical micro thruster is presented as an example of a scaling analysis.

Fabrication methods used in this study included electro-discharge machining (EDM), low temperature ceramic tapes (LTCC), and ceramic stereolithography and are presented in Chapter 3. EDM was utilized to build mesoscale vortex combustors that are discussed in Chapter 6 and microchannels for thermite reaction propagation in Chapter 8. Counterflow diffusion flame burners were fabricated with LTCC and discussed in Chapter 5. Ceramic thrusters shown in Appendix A were manufactured using stereolithography. Material considerations for high temperature reacting flow systems are also discussed in this chapter.

Chapter 4 presents the diagnostics techniques applied to micro combustion systems in the present study. Species measurements using gas chromatography, Fourier transform infrared spectroscopy, and chemiluminescence imaging spectroscopy were performed. Operation principles of these experimental techniques are briefly outlined and characteristics of the particular systems used as well as the operating parameters are described.

One of the simplest combustion systems is the counterflow stagnation point diffusion flame. This flame has become a standard system at the macroscale to study combustion phenomena such as extinction, ignition, and diffusive controlled combustion. In Chapter 5, microscale counter flow diffusion flame system is developed and analyzed. Imaging spectroscopy is applied to study the flame structure via chemiluminescence of CH* and C2* species in the visible range. Spatial distributions of the luminescence from each species are resolved along a spatial line from the fuel exit plane to the oxidizer exit plane. Experimental results are compared with three dimensional simulations using FLUENT by incorporating chemiluminescence reactions into a well studied reaction mechanism for methane combustion.

As a means to extend the stability limits of micro diffusion flames, vortex flows were studied at the meso/microscale. In particular, several non-premixed combustors for use in small-scale power and propulsion systems were investigated and are discussed in Chapter 6. Scaling studies were performed with a series of combustors ranging in size from ~10.6 to 124 mm³ (i.e., combustor diameters of 2.4-6.4 mm). Combustor performance was evaluated by analyzing the
stability limits and chemical efficiencies. Both hydrogen and hydrocarbons (methane and propane) were studied with inlet chemical energy varying from 25 to 174 W. Since higher energy densities are achievable with liquid fuels over gaseous fuels, the feasibility of using liquid propellants in the small combustors was also studied. Of particular interest was the possibility of introducing the liquid as a film into the combustor to cover the walls and thereby contribute to thermal management. Both liquid nitromethane/air and high pressure pure liquid nitromethane combustion were studied. In Appendix A, the vortex flow concept is applied to a mesoscale thruster, in which the thruster body was fabricated using ceramic stereolithography.

Chapters 5 and 6 are concerned with steady-state combustion at small scales. Transient combustion is also important and may be used to overcome many of the thermal management problems of microscale combustion. In addition, there are also numerous applications such as impulse-bit generation from microthrusters, micro gas generation for pulsed actuation, circuit destruction, to name a few. In Chapter 7, the topic of transient ignition and flame propagation is studied in capillary tubes with smooth circular cross-sections and diameters as small as 500 μm. Flames are shown to propagate and accelerate to detonation speeds in stoichiometric ethylene and oxygen mixtures initially at room temperature. In contrast to macroscale systems, boundary layer generation is found to play a more significant role because of the increased surface-to-volume ratio of the small dimensions, which accelerates the deflagration-to-detonation transition process.

Another transient system that has significant advantages at the microscale is the reaction between solid nano metallic particles and solid nano metal oxide particles. At the macroscale, these reactions are referred to as thermite reactions. Because nano particles have length scales smaller than the physical length scales of the microscale systems of interest to the present research, the use of nanothermites may be another means to achieve high temperature and pressures for very short durations. In Chapter 8, the combustion of mixtures of nanoscale aluminum with molybdenum trioxide in microscale channels is examined. In particular, the burning rates of the nanothermites in microscale channels and tubes are measured with high speed cinematography. The results infer that high temperature reactions that can produce significant gas pressures may be achieved in dimensions of a few microns. In Appendix B, the fabrication of microchannels from silicon is described. These channels could be of particular interest to nanothermites because silicon could be used to replace the aluminum as the fuel in nanothermite systems.
Finally, in Chapter 9, the collective research is summarized and recommendations are made for future research. It is evident from the present research that many different types of combustion processes are achievable at millimeter and sub-millimeter scales. The knowledge obtained from the effort will provide guidance for developing future meso and micro scale chemical propulsion and power systems.
CHAPTER 2

ISSUES AND CHALLENGES

The wide variety of potential applications discussed in the previous chapter largely rely on the effectiveness of being able to convert the chemical energy in the fuel into thermal energy in a miniaturized combustion chamber. However, numerous issues on flame dynamics emerge as the size of the combustor is reduced [3, 5, 6, 11, 106-109]. For example, there is a minimum gap distance, known as the quenching distance, through which a gaseous flame will propagate without the aid of heterogeneous catalytic combustion. In this chapter, the issues that affect flame dynamics will be discussed. General scaling laws are applied to properties that affect the flame. Scaling of the governing equations for reacting flows is also presented. The shortened flow residence time and the increased surface-to-volume ratio are the two important challenges for combustion in a small confinement. They lead to incomplete combustion and quenching, i.e., low efficiency and flame extinction. An analysis on the performance of a chemical micro thruster is also included in this chapter as an example.

Scaling Laws

Many characteristics of systems can be explored using simple scaling laws. Consider a linear characteristic dimension of a system $L$; the areas of the system $S$ vary with $L^2$

$$S \sim L^2$$

(2.1)

and the volumes $V$ is proportional to $L^3$

$$V \sim L^3$$

(2.2)

Thus, the surface-to-volume ratio scales with $1/L$

$$S/V = L^2/L^3 = 1/L.$$  

(2.3)
For the case that density does not change, the mass also scales with $L^3$

$$m \sim L^3. \quad (2.4)$$

As a result, the gravitational force $F_g = mg$, where $g$ is the gravitational acceleration, scales with $L^3$

$$F_g \sim L^3. \quad (2.5)$$

The pressure force exerted by the gravitational force $P_g = F_g/S$ is then scaled to $L$

$$P_g = F_g/S \sim L^3/L^2 = L. \quad (2.6)$$

For a force that is exerted by a certain pressure $F_p = PS$, the force varies with $L^2$

$$F_p = PS \sim L^2. \quad (2.7)$$

Table 2.1 provides the results of how parameters scale using this simple scaling procedure. The table has been modified and expanded from the earlier work of Nakajima et al. [10]. For this type of analysis, it is important to identify beforehand which controlling parameters are going to be scaled with length. For example, the centrifugal force scales with $L^4$ when the rotating object as well as the radius of the rotation scale, but if one is interested only in scaling the object while keeping the rotating arm length fixed, the centrifugal force scales with $L^3$ instead.

Similarly, for the pressure loss per unit length in a duct assuming laminar Poiseuille flow,

$$\frac{dP}{dx} = \mu \frac{V^2}{L} \hat{u}. \quad (2.8)$$

The scaling factor depends on how the flow rates are scaled. The pressure loss increases quartically when the volumetric flow is kept constant while the size of the duct goes down. For the case where the flow velocity is fixed, the pressure loss scales with $L^{-2}$. However, the pressure loss increases proportional to the characteristic length if the volumetric flow rate scales down at the same rate as the characteristic dimension of the duct. This is important for micro chemical power devices because the flow rate is often related to the chemical power input and the velocity of the flow will affect the flame dynamics. Furthermore, the dimension of the combustion chamber is constrained by factors such as the quenching distance and temperature limits of the materials.
For microthruster scaling analyses, the thrust force is usually given by the following definition:

\[ F = \dot{m}V_e + A_e(p_e - p_a) \]  \hspace{1cm} (2.9)

where \( \dot{m} \) is the mass flow rate, \( V_e \) the flow velocity at the nozzle exit, \( A_e \) the cross-sectional area of the nozzle exit, \( p_e \) the exit pressure, and \( p_a \) the ambient pressure. The expression shows that the total thrust actually consists of two parts: the momentum thrust, which is the first term in the right hand side, and the pressure thrust that appears on the second term. When the nozzle is properly designed and the optimum expansion ratio is attained, the pressure thrust becomes zero and the total thrust is maximized. The expression for thrust is then reduced to

\[ F = \dot{m}V_e. \]  \hspace{1cm} (2.10)

For ideal gas flow through an isentropic nozzle, the exit velocity take the following form [110].

\[ V_e = \sqrt{\frac{2\gamma}{\gamma - 1} \frac{RT_e}{P_e}} \left[ 1 - \left( \frac{P_e}{P_c} \right)^{\frac{\gamma - 1}{\gamma}} \right], \]  \hspace{1cm} (2.11)

where \( \gamma \) is the specific heat, \( R \) the gas constant, \( T_e \) the chamber temperature, and \( P_e \) the chamber pressure. The mass flow rate through a “choked” nozzle is

\[
\dot{m} = \frac{AP_e}{\sqrt{T_e}} \sqrt{\frac{2}{\gamma + 1}} \left( \frac{P_e}{P_c} \right)^{\frac{\gamma + 1}{\gamma - 1}} \frac{\gamma}{R} \left( \frac{\gamma}{\gamma + 1} \right)^{\frac{\gamma + 1}{\gamma - 1}} \frac{\gamma}{R},
\]  \hspace{1cm} (2.12)

where \( d_t \) is the throat diameter. The mass flow rate therefore scales with \( L^2 \) when pressure, temperature and the composition of the gas are unaffected.

By substituting Equation 2.11 and 2.12 into Equation 2.10, an expression for thrust in terms of fluid properties can be derived in the following form

\[ F = \frac{\pi d_t^2}{4} V_e \left( \frac{2}{\gamma - 1} \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma + 1}{\gamma - 1}} \left( 1 - \frac{P_e}{P_c} \right)^{\frac{\gamma - 1}{\gamma}} \right). \]  \hspace{1cm} (2.13)
This equation shows that for a micro-thruster that has been scaled down to 1/10 to provide the same thrust, the chamber pressure has to be increased 100 times without considering the effects of combustion (scaling factor of $L^2$). This high pressure is putting a demanding requirement on the combustion chamber design and material selection even though the state-of-the-art MEMS bonding technique can survive up to the order of hundred atmospheres [111]. However, the thrust to weight ratio ($F/mg$) of a microthruster goes up with $L^{-1}$ if the weight of the propellant contributes to the majority of the total weight of the system.

The purpose of miniaturizing a thruster is usually not only to have a propulsion source with a smaller dimension, but also a smaller thrust and a finer impulse bit. The minimum impulse bit,

$$I_{bit} = \int_{0}^{t_p} F dt,$$  \hspace{1cm} (2.14)

where the pulse duration $t_p$ depends on response time of the thruster feeding valve and thruster chamber design. The expression shows that the minimum impulse bit can be reduced by a factor of 100 shrinking the nozzle throat diameter by a factor of 10 ($L^2$ dependence).

Another important issue to be considered in micro thruster design is the impact of the more pronounced friction loss of the fluid flow through the thruster. Laminar flows are expected in the micro thruster except in some local regions near nozzle throat and propellant injection ports. The effect is caused by the decreased Reynolds number that leads to an increase in boundary layer thickness growth in the nozzle. With the friction in the nozzle non-negligible, isentropic relations above will no longer be appropriate. A theoretical analysis of the scaling effect will be very complicated if not impossible. Several numerical and experimental studies have been performed on this subject [38, 112-115]. These studies indicate that the thrust efficiency deteriorates as the dimension of the nozzle is decreased, nevertheless, smaller impulse bit can be achieved.

The specific impulse, $I_{sp}$, is given by the relationship

$$I_{sp} = \frac{F}{\dot{m}g} = \frac{V_s}{g}.$$  \hspace{1cm} (2.15)
The specific impulse, which measures the overall performance of the thruster by how long (in sec) of unit thrust a unit weight of propellant can provide is found to be a direct function of the exit velocity of the flow at the nozzle if the flow is perfectly expanded in the diffuser. No direct influence of dimension on the specific impulse is obtained by inspecting Equation 2.11, but suggests that the specific impulse is a function of chamber temperature, the gas constant, chamber pressure, and the specific heat ratio, which indicates the energy storing capability of the gas molecules in an isentropic nozzle. In summary, scaling of the various thruster performance indicators can be derived by applying the scaling laws on the mathematical relations shown in this section.

Scaling of characteristic times in a fluidic system is also important when considering a combustion system. The interplay of flow residence time, characteristic chemical reaction time, and characteristic diffusion time are crucial not only on deciding the efficiency of the combustion process, but also the sustainability of reactions in microscale combustion devices. Table 2.2 shows the results of scaling analyses on several characteristic times related to combustion. For the case of a constant mass flow rate, the residence time scales with the combustor volume (~$L^3$). Although the scaling factor for flow mixing time, $L^2$, implies that diffusive mixing might be enhanced in small combustors, the residence time still might not be long enough for complete mixing because as the length scale decreases, so does the Reynolds number. The flow becomes more laminar and therefore has an inverse effect on mixing. Proper selection of flow conditions and flow ports orientation is thus important in designing a micro scale non-premixed flame combustor [116, 117]. Damköler number $Da(\tau_r/\tau_c)$ where $\tau_r$ is the flow residence time, and $\tau_c$ is the characteristic chemical kinetic time scale is an important nondimensionalized number for flame stabilization. If the $Da$ is close to or less than one, which is often the case for microcombustors, the flame will not be stabilized inside the combustor.
Table 2.1: Scaling factors of various properties.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
<th>Scale factor</th>
<th>Scale factor (1/volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$m = \rho V$</td>
<td>$L^2$</td>
<td>1</td>
</tr>
<tr>
<td>Force due to pressure</td>
<td>$F_p = pS$</td>
<td>$L^2$</td>
<td>$L^1$</td>
</tr>
<tr>
<td>Force due to gravity</td>
<td>$F_g = mg$</td>
<td>$L^3$</td>
<td>1</td>
</tr>
<tr>
<td>Force due to inertia</td>
<td>$F_i = ma$</td>
<td>$L^3$</td>
<td>1</td>
</tr>
<tr>
<td>Force due to constant pressure thermal expansion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centrifugal force</td>
<td>$F_c = m \omega^2 r$</td>
<td>$L^4$</td>
<td>$L$</td>
</tr>
<tr>
<td>Buoyancy force</td>
<td>$F_b = \Delta \rho g V$</td>
<td>$L^3$</td>
<td>1</td>
</tr>
<tr>
<td>Drag force</td>
<td>$F_D = C \mu U a$</td>
<td>$L$</td>
<td>$L^2$</td>
</tr>
<tr>
<td>Spring force</td>
<td>$F_s = k x$</td>
<td>$L$</td>
<td>$L^2$</td>
</tr>
<tr>
<td>Force due to pressure</td>
<td>$F_p = \mu F_p$</td>
<td>$L^2$</td>
<td>$L^1$</td>
</tr>
<tr>
<td>Force due to gravity</td>
<td>$F_g = \mu F_g$</td>
<td>$L^2$</td>
<td>1</td>
</tr>
<tr>
<td>Force due to inertia</td>
<td>$F_i = \mu F_i$</td>
<td>$L^3$</td>
<td>1</td>
</tr>
<tr>
<td>Force due to flow viscosity</td>
<td>$F_v = \mu S du/dy$</td>
<td>$L$</td>
<td>$L^2$</td>
</tr>
<tr>
<td>Stress due to pressure force</td>
<td>$\sigma_p = F_p / S$</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Stress due to gravity force</td>
<td>$\sigma_g = F_g / S$</td>
<td>$L$</td>
<td>-</td>
</tr>
<tr>
<td>Stress due to inertia force</td>
<td>$\sigma_i = F_i / S$</td>
<td>$L$</td>
<td>-</td>
</tr>
<tr>
<td>Stress due to thermal expansion force</td>
<td>$\sigma_t = F_t / S$</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Stress due to centrifugal force</td>
<td>$\sigma_c = F_c / S$</td>
<td>$L$</td>
<td>-</td>
</tr>
<tr>
<td>Moment of inertia</td>
<td>$I = m r^2$</td>
<td>$L^5$</td>
<td>$L^3$</td>
</tr>
<tr>
<td>Heat conduction</td>
<td>$H_c = k S dT / dx$</td>
<td>$L$</td>
<td>$L^2$</td>
</tr>
<tr>
<td>Heat convection with constant heat transfer coefficient</td>
<td>$H_v = h S \Delta T$</td>
<td>$L^2$</td>
<td>$L^4$</td>
</tr>
<tr>
<td>Heat radiation</td>
<td>$H_r = \alpha S (T_1^4 - T_2^4)$</td>
<td>$L^2$</td>
<td>$L^4$</td>
</tr>
<tr>
<td>Pressure loss per unit length for laminar</td>
<td>$dP / dX = C \mu u / r^2$</td>
<td>$L^{-2}$</td>
<td>-</td>
</tr>
<tr>
<td>Poiseuille flow</td>
<td>$dP / dX = C Q \mu r^4$</td>
<td>$L^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>Pressure loss per unit length for laminar flow in a duct</td>
<td>$dP / dX = C Q \mu r^4$</td>
<td>$L^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>Pressure loss per unit length for laminar flow in a duct</td>
<td>$dP / dX = C Q \mu r^4$</td>
<td>$L^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>Natural frequency</td>
<td>$W = (k / m)^{1/2}$</td>
<td>$L^{-3/2}$</td>
<td>$L^{-9/2}$</td>
</tr>
</tbody>
</table>
Impacts on Transport Phenomena

For premixed combustion, flow residence time in a combustor has to be at least longer than the chemical reaction time scale in order to have complete combustion while containing the reaction zone in the combustion vessel. For non-premixed combustion, which is more common in industrial applications because the combustor is safer and easier to build and operate, the flow residence time has to be larger than the combination of the mixing time scale and the chemical reaction time scale. The flow residence time is usually defined as

$$ t_r = \frac{\rho V}{m} \sim \frac{L}{u_c} $$  \hspace{1cm} (2.16)

It can sometimes be simplified as the ratio between the characteristic length and the characteristic velocity scale in the flow system as shown in Equation 2.16.

Some of the scaling issues involved in microcombustors can be understood by normalizing the conservation equations of momentum, energy, and species[106]. The one dimensional normalized form of the governing equations in the gas phase can be written as

<table>
<thead>
<tr>
<th>Time scale</th>
<th>Governing equation</th>
<th>Scale factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residence time when inlet velocity is fixed</td>
<td>$\tau = \frac{\rho V}{m} \sim \frac{V}{ud^2}$</td>
<td>$L$</td>
</tr>
<tr>
<td>Residence time when inlet mass flow rate scales with volume</td>
<td>$\tau = \frac{\rho V}{m}$</td>
<td>$l$</td>
</tr>
<tr>
<td>Residence time when inlet mass flow rate is fixed</td>
<td>$\tau = \frac{\rho V}{m}$</td>
<td>$L^3$</td>
</tr>
<tr>
<td>Transient time for tracking particles (Stokes flow)</td>
<td>$\tau = \frac{d^2 \rho_p}{18 \mu}$</td>
<td>$L^2$</td>
</tr>
<tr>
<td>Diffusion time</td>
<td>$\tau_{diff} = \frac{L^2}{\alpha D}$</td>
<td>$L^2$</td>
</tr>
</tbody>
</table>
The non-dimensionalized heat transfer equation on the solid wall can be represented in the following form:

\[
\frac{L}{t_c u_c} \frac{\partial u^*}{\partial t^*} + u^* \frac{\partial u^*}{\partial x^*} = - \frac{p_c}{\rho_c u_c^2} \frac{\partial p^*}{\partial x^*} + \frac{1}{\text{Re}} \nu^* \frac{\partial^2 u^*}{\partial x'^2} + \frac{gL}{u_c^2},
\]

(2.17)

\[
\frac{L}{t_c u_c} \frac{\partial T^*}{\partial t^*} + u^* \frac{\partial T^*}{\partial x^*} = \frac{1}{\text{Pe}} \alpha^* \frac{\partial^2 T^*}{\partial x'^2} + Da \frac{Q}{C_p^* T_c} \omega^* + \frac{1}{\text{Pe}} \frac{\partial T^*}{\partial x^*},
\]

(2.18)

\[
\frac{L}{t_c u_c} \frac{\partial y_i^*}{\partial t^*} + u^* \frac{\partial y_i^*}{\partial x^*} = \frac{1}{\text{LePe}} D' \frac{\partial^2 y_i^*}{\partial x'^2} + Da \frac{1}{y_{ic}^*} \frac{\partial y_i^*}{\partial x^*}.
\]

(2.19)

The non-dimensionalized heat transfer equation on the solid wall can be represented in the following form:

\[
\frac{\partial T^*}{\partial t^*} = Fo \alpha^* \frac{\partial^2 T^*}{\partial x'^2}.
\]

(2.20)

The relevant normalized boundary conditions for these equations are

\[
u^* = 0, \quad \tau^* = \frac{\mu u}{\tau L} \frac{\partial u^*}{\partial y^*},
\]

(2.21)

\[
T^* = T_w^*, \quad \frac{\partial T^*}{\partial x^*} = \frac{\partial T^*}{\partial x^*} = Bi(T_w^* - 1),
\]

(2.22)

\[
y_i^* = 0, \quad \frac{\partial y_i^*}{\partial x^*} = (LePe)y_i^*.
\]

(2.23)

For a given fuel/oxidant mixture, the quenching distance also depends on the inert diluent used in the mixture. The order of quenching distances for common diluents is He > Ar > N\textsubscript{2} > CO\textsubscript{2}. This trend results from the rankings of thermal diffusivities. CO\textsubscript{2} has the smallest, while helium has the largest. This implies that the flame is more insulated from the walls by CO\textsubscript{2} than by helium.[118]

In macro-size combustors, the characteristic length is usually relatively large, and generally the Reynolds (Re) and Peclet (Pe) numbers are also large. The flows are mostly turbulent, and as seen in the above equations, the viscous and diffusive effects are small compared to the convective effects. As the size of the system is reduced, the Reynolds number and the Peclet number decrease indicating that the viscous and diffusive transports of heat and mass are now important.
Chemical Reaction Issues

Quenching

The chemical time scale, on the other hand, is not directly affected by length scale. It is dependent on the reactant concentrations, the reacting temperature and types of fuel and oxidizer, and can be expressed by the reaction rate and Arrhenius equations. Consider a simple bimolecular reaction

\[ F + O \rightarrow P \]  

The reaction rate expression is

\[ \tau_{\text{chem}} = \frac{\ln \left[ e + (1 - e) \frac{[F]_0}{[O]_0} \right]}{([O]_0 - [F]_0) Ae^\frac{E_{\text{chem}}}{RT}} \]  

As evident from this equation, the chemical characteristic time increases exponentially as the temperature decreases. The reacting temperature will be strongly influenced by the increased surface-to-volume ratio and the shortened flow residence time. As the combustion volume decreases, the surface-to-volume ratio increases; hence, the combustor surface heat loss increases as well as the potential destruction of radical species for sustaining reactions [77, 107, 119, 120]. The reduced combustion volume in small combustors enhances the possibility of radical termination by wall reactions. These radical terminating reactions on the wall break the reaction chains, preventing the buildup of radicals, which is essential for the branching and propagation of reaction chains that lead to efficient combustion of the reactants. However, the enhanced surface reactions due to the increased surface-to-volume ratio in the miniaturized combustion vessels makes catalytic combustion an attractive option in designing small scale combustors.

Thermal quenching of confined flames occurs when the heat generated by the combustion process fails to keep pace with the heat loss to the walls. Combustor bodies, in most cases, act as a thermal sink; consequently, as the surface-to-volume ratio increases with the decrease in combustor volume, the portion of heat lost to the combustor body increases and less enthalpy is preserved in the combustion product, which further lowers the combustion temperature and
retards the kinetic mechanism. The “excess enthalpy” concept mentioned in Chapter 1 has been introduced to extend the quenching limit of combustion in small combustors. The idea is to redirect the hot burnt gases to preheat the cold reactants without mass transfer. Only thermal energy is transferred to the reactants so that the total reactant enthalpy is higher than in the incoming cold reactants and therefore can sustain combustion under conditions that would normally lead to flame extinction without recirculation.

Ignition in Small Combustor

There are many ways in which a flame can be extinguished. For example, flames will extinguish while passing through narrow passageways. Other techniques for extinguishing flames are the addition of diluents, such as inert gases. Blowing the flame away from the reactants is also effective in extinguishing flames. Williams [121] gave the following two rules governing ignition: (1) ignition will only occur if enough energy is added to the gas to heat a slab about as thick as a steadily propagating laminar flame to the adiabatic flame temperature; (2) the rate of liberation of heat by chemical reactions must approximately balance the rate of heat loss from the slab by thermal conduction. The second criterion is the one applicable to the problem of flame quenching by a cold wall. In the combustor of small scale, this effect is especially strong.

Convection is the main mechanism that transports heat to side-walls. Before ignition, the wall temperature is the same as the surroundings. Flame quenching occurs if the total power generated inside the combustor is less than the loss to the wall. So, for ignition to occur,

\[ W_{\text{tot}} > W_{\text{trans}} \]  

(2.26)

The total heat generation and heat transfer to the walls can be expressed as:

\[ W_{\text{tot}} \sim \rho_g \Delta H_r U_g L^2 \]  

(2.27)
Substituting equations Equation 2.27 and Equation 2.28 into Equation 2.26, we have

\[ W_{trans} \sim Pr^{1/3}_g \left( \frac{\rho_g U_g}{\mu_g} \right)^{1/2} k_g \pi L^{3/2} (T_g - T_w) \]

\[ = Pr^{1/3}_g \left( \frac{\rho_g U_g}{R_g \mu_g} \right)^{1/2} k_g \pi L^{3/2} T_g^{-1/2} (T_g - T_w) \]  

(2.28)

In Equation 2.29, the adiabatic flame temperature \( T_f \) instead of gas temperature is used. Rearranging the above equation, we get the criterion for ignition

\[ \rho_g \Delta H_f U_g L^2 > Pr^{1/3}_g \left( \frac{\rho U}{\mu} \right)^{1/2} k_g \pi L^{2/3} (T_f - T_0) \]  

(2.29)

The relationship shows that for ignition to occur, an increase of combustor diameter, injection velocity and chamber pressure have positive effects since more reactants are injected into the chamber, which provides more energy to prevail over the heat loss to the solid wall.

**An Example: Analysis of Micro Thruster Performances**

The performance of a chemical thruster is largely decided by the combustion efficiency in the thruster chamber. For a thruster subjected to a specific thrust level, an increase in combustion efficiency increases the chamber temperature or a smaller value of \( \gamma \) provides a higher exit velocity. Hence, the specific impulse increases while the propellant consumption decreases. However, it is well known that the heat loss in a micro device usually goes up due to the increased surface to volume ratio [5,9,12,13]. On the other hand, the Reynolds number \( Re \) (UL/\( \nu \)) and Peclet number (UL/\( \alpha \)) is much smaller in the micro thruster than in the conventional macroscopic system, consequently, viscous effect and diffusive transport of mass and heat which are usually neglected in conventional analysis is now an important factor that affect the thruster performance. For micro thrusters with throat diameter on the order of a micrometer, rarefaction
effects can be an important issue when operating under low stagnation pressure [122]. Surface
imperfectness on micro scale nozzle will be amplified due to the enhanced relative roughness,
and can induce shock. The non-equilibrium effect and flow transition might also affect the
thruster performance.

Bruno et al.[123] investigated the scaling effect of a chemical micro thruster due to
combustion and heat transfer based on 1-D isentropic relationship and 1-D flame structure
analysis. They conclude that there is a dominating factor of $L^{2/3}$ on the ratio between heat loss and
heat generation of a chemical thruster. The scaling of viscous dissipations, heat transfer and
ionization has also been studied theoretically and numerically to explore the best micro nozzle
design parameters and performance [112-114], but no conclusive prediction on the performance
of the micro thruster has yet been successfully made due to the complexity of the problem itself
as well as the variety of design options available. Studies on the size effects of combustion
phenomena have also been widely studied; two major issues have been addressed: (1) an
enhanced surface to volume ratio that expedites flame quenching, (2) a shortened flow residence
time that degenerates the combustion completeness [2].

In this section, the performance of a mesoscale hot gas chemical thruster when scaling
down the nozzle throat is considered. Unlike analytical works that consider either vaporizing
liquid microthruster with no chemical reaction[124] or microcombustors alone[119], interactions
of combustion and thruster performances are analyzed here. A control volume thermal analysis
with 1-D isentropic relations has been set up. Hydrogen and air are the fuel and oxidizer for the
investigated thruster, which is working under a “choked” condition. The size of the nozzle throat
is the parameter investigated to show the scaling effects. It is found that the heat loss leads to a
decrease in the fraction of energy that can be transferred into kinetic energy as well as the energy
generated. Since the mass flow rate of a thruster working under “choked” condition is a function
of both the chamber temperature and nozzle throat area at a prescribed pressure, there would be a
point where the heat loss of the thruster is comparable to the heat generated such that the chamber
temperature is below the explosion limits of the fuel/oxidizer mixture. At this condition, the
thruster performance would drop significantly, and its operation would change from a hot-gas to a
cold-gas thruster.
Analysis of the Energy Balance

A schematic of the investigated microthruster is shown in Figure 2.1. A steady state model based on the first law of thermodynamics in the following form is developed to analyze a thruster of 1 cm in length and 1 cm in outer diameter with 5 mm inner diameter. The chamber volume is ~196 mm³.

\[ \dot{Q} = \dot{Q}_{\text{rad}} + \dot{Q}_{\text{conv}} = \dot{m}(\Delta h + \frac{V_c^2}{2}) \]  \hspace{1cm} (2.31)

\[ \Delta h = \sum_p (\bar{h}_{f,p}^0 + \bar{c}_{p,p}(T_i - T_0)) - \sum_r (\bar{h}_{f,r}^0 + \bar{c}_{p,r}(T_c - T_0)) \]  \hspace{1cm} (2.32)

Chamber pressures are set to be 2 to 10 atm so that the nozzle is kept choked. Stoichiometric mixture of hydrogen and air are considered. The chamber temperature is solved for nozzle diameters of 10 µm, 20 µm, 50 µm, and 100 µm. The following assumptions are utilized in the analysis:

1. The whole system is operating at steady state.
2. The nozzle flow is isentropic and choked.
3. The temperature in the combustion chamber is uniform, and the temperature of the combustion gas through the nozzle changes following the isentropic relations.
4. The chemistry in the nozzle is frozen.
5. The reaction in the combustion chamber is in equilibrium. As a result, the heat generation term in the energy equation can be solved provided that the temperature and pressure of the reaction are known.
6. The wall temperature equals to the reaction temperature. A thruster with a very thin wall or wall material with very large heat conductivity can actually approximate this limiting case. The homogeneity assumption is valid here since the Biot number for a meso/micro thruster is usually well below 0.119. Both natural convection and radiation account for the heat loss on the outer surface. The radiation heat transfer rate is given by

\[ \dot{Q}_{\text{rad}} = \epsilon \sigma \pi \left( \frac{D_i^2}{2} + DL \right)(T_c^4 - T_a^4) \]  \hspace{1cm} (2.33)
where \( D \) is the outer diameter of the thruster, \( L \) the length of the thruster, \( \varepsilon \) the emissivity, and \( \sigma \) the Stefan-Boltzmann constant. The emissivity is 0.85 in the calculation, and an ambient temperature of 298.15 K is assumed. The convection heat loss is given by

\[
\dot{Q}_{\text{conv}} = h \pi \left( \frac{D^2}{2} + DL \right) (T_e - T_a)
\]  

(2.34)

(7) The nozzle throat has no expansion, and hence the velocity at the exit corresponds to a Mach number equal to 1.

The equilibrium condition of minimum Gibb’s free energy,

\[
(dG)_{T,P}=0,
\]  

(2.35)

where \( G \) is the Gibbs free energy, along with Equation 2.12, which governs the mass flow rate through a choked nozzle at a specific nozzle throat diameter gives the two equations required to solve for the two unknowns \( T \) and the mass flow rate. The heat generation is obtained from by solving a TP problem in CEA software package[125, 126] at specific temperatures and pressures, the mass flow rate is then derived from Equation 2.12. Energy balance is calculated using a Matlab program, where heat loss term is introduced. The iteration continues until the energy equation in Equation 2.31 is balanced.

Figure 2.2 and Figure 2.3 show the results of the calculation. The effect of combustion and heat transfer on the performance of a chemical thruster is clearly demonstrated in Figure 2.2. The figure shows how the specific impulse changes with the diameter of the thruster nozzle throat when the combustion chamber pressure is at 2 atm. Figure 2.2 shows that as the nozzle size
decreases, a larger proportion of energy generated through the combustion process is lost through heat loss rather than being converted into thrust. The figure also shows that the specific impulse increases asymptotically to approximately 96 sec as the diameter of the nozzle throat reaches 1.5 mm, which corresponds to a contraction ratio of 0.3.

Figure 2.2: The effect of miniaturizing nozzle throat diameter with thruster size fixed on specific impulse.

Figure 2.3 shows the chamber temperature derived at different chamber pressures for each throat diameter. The explosion limit of stoichiometric H\textsubscript{2}/O\textsubscript{2} reaction in a spherical KCl coated vessel of 7.4 cm diameter\textsuperscript{[127]} is also depicted on the graph for comparison. Although the explosion limits are for H\textsubscript{2}/O\textsubscript{2} reaction, the trend still holds for an H\textsubscript{2}/Air system, as well as mixtures at other equivalence ratios. As a boundary between the fast and slow reaction, the explosion limit is an important criteria on the performance of a chemical hot-gas thruster as well as the ignitability. For flow conditions below the explosion limits, the production rate of radicals by chain branching reactions is less than the termination rate of radicals by chain termination reactions, and the reaction is non-explosive. The reaction temperature as well as combustion completeness in this kind of reaction is usually low; as a result, the thruster efficiency of a chemical thruster working in this region is expected to be poor. A recent study \textsuperscript{[128]} indicates
the existence of an “extended” second explosion limit which is located in the operating pressure range of the thruster. For conditions below the limits, ignition will be a problem.

![Figure 2.3: The calculated chamber temperature at the specific chamber pressure for each nozzle diameters.](image)

Explosion limits shown in Figure 2.3 is specifically for a combustion chamber 7.4 cm in diameter with potassium chloride coated wall. It is known that the first and the third explosion limits largely depend on the chamber size and wall material, while the second limit is mainly decided by the interaction between different gas-phase reaction pathways, which could still be affected indirectly by the combustion chamber dimension through thermal and radical quenching [99]. The third explosion limit is important for thruster applications because it is responsible for the occurrence of an explosion above ambient pressure condition. Both thermal and kinetic explosion are responsible for the explosion mechanism under these pressure conditions. The analysis reveals the existence of a critical nozzle throat dimension for successful operation of combustion based hot gas chemical thrusters.
The Critical Insulation Radius

In a cylindrical thermal system, there exists a critical insulation radius where the heat loss is a maximum. Let’s void the assumption that the wall temperature equals the reaction temperature as assumed above, and the heat transfer is one dimensional only in the radial direction and the inner side heat transfer is negligible, that is, the inner wall temperature equals to the combustion gas temperature. The total heat resistance per unit length is then

\[ R'_{tot} = \frac{\ln(D/d)}{2\pi \kappa} + \frac{1}{\pi D h_{eq}}, \]  

(2.36)

where \( \kappa \) is the thermal conductivity of the wall material, \( h_{eq} \) is the equivalent convective heat transfer coefficient, \( d \) the inner diameter and \( D \) the outer diameter, which is the variable to be solved here. By taking the first and second derivatives of Equation 2.36, the critical insulation diameter is solved [129],

\[ D_{cr} = \frac{2\kappa}{h_{eq}}. \]

(2.37)

At this diameter, the total thermal resistance is the smallest while the heat loss is the largest. The heat transfer will increase with the addition of wall thickness when \( D < D_{cr} \), and decrease when \( D > D_{cr} \). Consider an Inconel (\( \kappa \sim 20 \text{ W/mK} \)) combustor body under laminar forced convection with \( h_{eq} \) at around 200 W/m²K, \( D_{cr} \) is approximately 0.2 m, which is significantly larger than the usual characteristic length for meso/micro scale thrusters. This indicates that if we want to minimize the excessive heat loss in a miniaturized hot gas combustor, the wall thickness should be as thin as possible without considering the material constraints. And if we want to dissipate heat, the wall should be thicker but not exceeding the critical diameter.
CHAPTER 3

FABRICATION OF MICRO COMBUSTION SYSTEMS

Materials for Micro Combustion Systems

Material strength at high temperatures is currently one of the reasons preventing mass production of micro combustion systems by MEMS fabrication technologies. The high temperature nature of combustion devices has prevented bulk materials popularly used in other microfluidic devices such as SU-8 photoresist and elastomers from being applicable. Silicon and Pyrex, which are the most popular material for other MEMS devices, have softening temperatures up to ~1100 K [111], but the maximum temperatures for continuous operation are below 500 K [130]. The bonding of substrates of different materials is a big challenge due to the thermal expansion coefficient mismatch at high temperatures. Efforts have been made on applying more durable materials such as silicon nitride (Si$_3$N$_4$) [85, 131], silicon carbide (SiC) [28, 53, 66, 132], and aluminum oxide [98, 133]; however, the standardized manufacturing procedures for these materials are not yet available for mass production.

Conventional conductive materials such as stainless steel, aluminum, and other metal alloys can also be applied on micro combustion systems using electro-discharge machining (EDM) or laser machining. The applications of these materials are limited by the integration with other sub-components into a complete miniaturized system. For example, it is difficult to integrate the ignition spark electrodes into a sub-millimeter scale stainless steel combustion chamber due to the challenges on gas sealing and electrical insulation. Moreover, the relative higher thermal conductivities of metals make them unfavorable for micro combustion systems because of the larger surface to volume ratio.

Ceramic has drawn increasing interests as a material for micro combustion systems. Alumina (Al$_2$O$_3$) based ceramics such as mullite (60% Al$_2$O$_3$ and 40% SiO$_2$) have properties including good high temperature strength, good thermal shock resistance, excellent thermal
stability, and resistance to most chemical attack, all making it an excellent material for high temperature microsystems. There are few fabrication techniques that can construct alumina parts at sub-millimeter scales. However, the low temperature ceramic technologies originally developed for radio frequency microelectronic devices are recently found to be useful for fabricating micro reacting flow devices. The low temperature ceramic consists of a mixture of alumina, glass, and binders. The operating temperature is around 1200 K. Thermal properties of materials that have been considered to apply on micro combustion systems are summarized in Table 3.1

Table 3.1: Properties of materials commonly used for micro devices [41, 111, 129, 130].

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m³)</th>
<th>Melting Temperature (K)</th>
<th>Coefficient of Linear thermal expansion (10⁻⁶/K)</th>
<th>Thermal conductivity (W/m-K) @300K/@1000K</th>
<th>Specific heat capacity (J/Kg-K) @300K/@1000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel</td>
<td>8510</td>
<td>1665</td>
<td>17.3</td>
<td>11.7/24</td>
<td>439/626</td>
</tr>
<tr>
<td>Silicon</td>
<td>2328</td>
<td>~1690</td>
<td>2.6</td>
<td>148/-</td>
<td>700</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2270</td>
<td>1883</td>
<td>0.834</td>
<td>1.38/-</td>
<td>745</td>
</tr>
<tr>
<td>Si₃N₅</td>
<td>2400</td>
<td>2173</td>
<td>-</td>
<td>16/8.76</td>
<td>691/1155</td>
</tr>
<tr>
<td>SiC</td>
<td>3160</td>
<td>3100</td>
<td>230</td>
<td>490/87</td>
<td>675/1195</td>
</tr>
<tr>
<td>Pyrex 7740</td>
<td>2230</td>
<td>1094</td>
<td>3.25</td>
<td>1.1/-</td>
<td>753.6</td>
</tr>
<tr>
<td>LTCC (Dupont 951)</td>
<td>3100</td>
<td>~1200</td>
<td>5.8</td>
<td>3.3/-</td>
<td>-</td>
</tr>
<tr>
<td>Quartz</td>
<td>2650</td>
<td>1883</td>
<td>0.59</td>
<td>10.4</td>
<td>-</td>
</tr>
<tr>
<td>Sapphire</td>
<td>3980</td>
<td>2323</td>
<td>15.1</td>
<td>46/10.5</td>
<td>765/1225</td>
</tr>
<tr>
<td>99.5% alumina</td>
<td>3890</td>
<td>2323</td>
<td>11.9</td>
<td>36/7.85</td>
<td>765/1225</td>
</tr>
<tr>
<td>Mullite</td>
<td>2800</td>
<td>1923</td>
<td>5.4</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>Propellant</td>
<td>1526</td>
<td>-</td>
<td>-</td>
<td>0.25/-</td>
<td>1852</td>
</tr>
</tbody>
</table>

Fabrication Technologies of Micro Combustion Systems

Several fabrication techniques were considered and pursued to build the microcombustion systems for the present study. Electro-discharge machining (EDM) was utilized to build combustors made of stainless steel and Inconel. Micro channels reactors were etched on
silicon substrates using both wet and dry etchings to investigate the feasibility producing an integrated combustion system using silicon based microfabrication technologies. Ceramic based techniques including stereolitography and low temperature ceramic tape (LTCC) technologies were also carried out to build a variety of microcombustion systems. These latter techniques are sometimes classified as nontraditional microfabrication methods as compared to silicon based technologies [134]. For high temperature flows, they provide an important alternative.

**Electro-discharge Machining (EDM)**

Unlike conventional machining methods in which the material is removed physically by cutting and milling, electrical discharge machining (EDM) utilizes the erosive action of electrical discharges (sparks) provided by a generator to cut the material. The discharges result from an electrical voltage that is applied between the tool electrode and the workpiece electrode. These electrodes are separated by the dielectric fluid in a work tank. Every discharge (or spark) melts a small amount of material on both electrodes. Part of this material is removed by the dielectric fluid and the remaining solidifies on the surface of the electrodes [135, 136]. The net result is that each discharge leaves a small crater on both workpiece and tool electrode. With this high energy electro-thermal erosion (instead of mechanical cutting forces) to remove material, EDM is capable of machining mechanically difficult-to-cut materials such as hardened steels, carbides, high strength alloys, and even the ultra-hard conductive materials like polycrystalline diamond and ceramics [137]. However, the surface roughness of an EDM machined surface is typically on the order of hundreds of nanometers to microns depending on the discharge parameters. Furthermore, the materials compatible with EDM are limited to conductive and semi-conductive materials.

The working principles of EDM are applied at the micron and nano level for micromachining.[138] The process is called as micro-EDM. The amount of material removed is proportional to the energy which crosses the discharge gap in EDM. Higher energy results in a higher removal rate but a rougher surface. As a result, the key in micro-EDM is to limit the energy in the discharge. In order to make micro products with high accuracy and good surface finish, the energy per single discharge should be minimized and discharge frequency should be increased. It is required for micromachining to maintain the energy of a single discharge in the
order of $10^{-6}$ J to $10^{-7}$ J. The minimum width of channels that can be machined by an usual wire EDM is approximately 300 μm. Micro-EDM can drill holes down to 5 μm [139], but 10 to 50 μm are more typical [140]. The largest aspect ratio of features that EDMs can fabricate is around 5 for feature size on the order of 100 μm [141].

Figure 3.1: A micro counterflow burner fabricated using EDM.

Stainless steel channels and Inconel vortex combustors were built using EDM in present study. Figure 3.1 is an example of stainless steel channels fabricated using EDM. The magnified views at the intersection of the crossed channels and at one end of the smaller channel are also shown in the same figure. The channel sizes are 0.3 and 1 mm. Irregularities at the edges can be seen in the pictures taken through a microscope. The thickness of the piece is 1 mm.

**Ceramic Stereolithography**

Stereolithography is a widely used rapid prototyping technology to build plastic parts. This technology was adapted to fabricate meso and micro-scale ceramic parts [142-151]. Objects fabricated using stereolithography are built in a layer by layer fashion. By scanning a laser beam over a liquid monomer resin, the resin cures into solid polymer layer by layer. This class of
materials originally developed for the printing and packaging industries, quickly solidifies wherever the laser beam strikes the surface of the liquid. Once one layer is completely traced, the part is lowered a small distance into a vat and a second layer is traced right on top of the first. The self-adhesive property of the material causes the layers to bond to one another and a complete three-dimensional object will consist of layers of various contours.

Ceramic parts are fabricated from both the aqueous and non-aqueous alumina suspensions in liquid photosensitive monomers. The cured solid polymer is burned out during the sintering process afterwards. Inhomogeneity [147, 148, 152] in the alumina solution and absorption and scattering in the dense ceramic colloid solution [150, 153-157] are among the two major challenges for ceramic stereolithography.

Three-dimensional stereolithography [158] was utilized to manufacture the microthrusters for present research. This process starts with the design of the part to be made as a three dimensional virtual solid in a computer aided design program. The solid is then sliced finely by another computer program (Maestro) along the Z-axis, creating a build file that consists of a stack of X-Y layers. The build file is transferred to the build station used for the manufacture of the part; a schematic of this process is shown in Figure 3.2 (3-D Systems Inc. SLA-250, Valencia, CA).

During the build, each layer is formed by raster scanning an ultra-violet laser across the surface of a photo-curable bath of liquid resin. The solidified layer is moved down by one layer thickness inside the liquid bath so that the resin flows across the previously cured layer and the patterned curing process is repeated to form the next layer on the top of the immediately previous layer. In this work the resin is a highly concentrated colloidal dispersion prepared by dispersing alumina powder in an aqueous solution of ultraviolet curable polymers. The ceramic green body manufactured is subsequently dried, the photo-curable binder is burned out, and the part is sintered to full density.
Figure 3.2: Ceramic stereolithography [158].

Figure 3.3: Alumina thruster body (top), wire-frame of thruster body (bottom left) and cross-section of the throat (bottom right)
Figure 3.3 shows the initial prototype design of a thruster based on the asymmetric whirl concept and consists of a combined combustion chamber and nozzle fabricated using ceramic stereolithography. The chamber is open at the front end, but sealed by a gasket and manifold system to enable rapid development and testing of various reactant supply and ignition concepts in the combustion chamber. Several thruster bodies have been fabricated from aluminum oxide. The ceramic thrusters have throat diameters ranging from approximately 700 - 300 μm, an exit area / throat area ratio of 2, and a conical nozzle divergence half angle of 14°. The combustion chamber has a volume of approximately 60 mm³.

**Low Temperature Co-fired Ceramic (LTCC)**

LTTC tapes are glass-ceramic composite materials. The ceramic filler is usually alumina, Al₂O₃, but could also be any other ceramic system, including high thermal conductive BeO, ferroelectric perovskites, ferromagnetic spinels and “smart” (photovoltaic-piezoelectric) ceramics. The usual composition also includes a glass frit binder to lower processing temperature as well as rendering the material compatible with thick film technology. A third component of the composite is an organic compound for binding and viscosity control of the tape before sintering [159]. The tapes are commercially produced in flat tapes of various thicknesses, but are usually in the range of 100-400 μm. Tapes with larger thicknesses can be obtained by laminating multiple layers of tapes. As many as 80 layers can be laminated together. The tapes before being fired and sintered are called green ceramic tapes. They are usually machined to the desired profile in the green stage.

Figure 3.4 is a schematic representation of the general fabrication process of the LTCC tapes [160]. The tapes are usually shipped on a roll from the manufacturer. The preconditioning and blanking procedures make the tapes into flat sheets that can be handled by the tools in the following processing steps. One of the most fascinating features of LTCC technology is the possibility of fabricating 3D structures using multiple layers of green tapes. Each layer (before firing) is processed green separately with features such as vias, cavities, channels, and electrical elements. Vias, cavities, and channels can be cut out with several machining methods such as high speed mechanical punching machine, lasers, and CNC milling. The smallest size that a punching machine can generate is ~ 100 μm. The smallest feature that CNC milling can create is
slightly larger than the punching method; however, the CNC milling can fabricate shallow cavities and thin membranes by milling off a portion of the tape thickness. Laser machining has the ability of shaping features as small as 50 μm on both fired and green tapes [161]. The ability to sculpture the fired LTCC makes dimension control easier and more precise. For example; not only does the shrinkage of the LTCC after firing not have to be taken into consideration during the design phase, but the dimensional tolerances of the parts can also be significantly improved. Hot embossing has also being investigated as a way to fabricate small features on LTCC tapes. The electrical elements, such as resistors and conductors, can be deposited on the tapes using a thick film screen printer [159].

Figure 3.4: Typical fabrication procedures of LTCC [160].
After all layers are processed to the desired profiles, they are stacked in sequence on a platform with alignment pins. The layer to layer alignment tolerance is around 25 μm. This process is called collating. The next step is usually laminating the stacked blanks by applying pressure (~ 3000 psi) and heat (~ 70 °C) using a press. A holding time at peak temperature of typically 3-10 min is required to reach a homogeneous temperature profile in the entire stack. The applied pressure can also be accomplished with an isostatic press. The stacked tapes are vacuum packaged and pressed in hot water under the same condition as mentioned above. The thermo-compression squeezes the particles into the neighboring layers so that the layered stack merge into one single block after firing. However, this compression process causes problems for internal cavities and channels essential in microfluidic applications. The cavities and channels collapse and deform during this thermo-compression lamination process because mass flow is created as the particles from both un-sintered tapes interpenetrate into each other.

Two approaches are available to eliminate the problem: cold low pressure lamination [162] and lamination using organic fluids. In the cold low pressure lamination method, the green tapes are stuck with each other by double sided polyacrylate based adhesive tapes 12-25 μm thick at room temperature under low pressures. The lamination mechanism in this process is due to a low viscosity melt derived from the polyester carrier film of the adhesive tape, which occurs at higher temperatures of around 350 °C during the binder burnout process. This liquid phase which occurs at the interface of the porous microstructure of the green tapes causes capillary forces. These forces pull the neighboring ceramic layers towards each other, and finally in a re-arrangement of the particles in the interface of the tapes. The binders of both the LTCC green tapes as well as the adhesive layers are already burned out, but the sintering phase has not started. The movement of the particles in the presence of the melt results in an interpenetration of the particles of adjacent tapes. The following sintering process transfers this structure to defect free joining. The organic fluid approach uses a similar lamination mechanism; however, it has the advantage of being able to be deposited on complex shapes and non-uniform surfaces. One of the most common organic fluids being applied is honey.

Sagging of suspended structures, such as the top wall of a wide channel, is another common problem related to the lamination process of LTCC. Several approaches are developed to reduce the sagging effect. For a bridge structure, a shrinkage matched paste can be screen printed on top of the bridge layer to provide the tensile stresses upon sintering. Graphite powders
mixed with high viscosity organic fluid can be filled into the internal channels to prevent the top and bottom layers of a buried void from sagging [163]. The graphite mixture is oxidized into carbon dioxide or carbon monoxide during the sintering cycle. Materials such as a lead bi-silicate frit that can be preferentially etched away after sintering have also been explored as a sacrificial layer to eliminate the sagging problem. Sagging for holes with diameters less than 400 μm are found to be negligible [164].

The last step of the LTCC fabrication process is sintering. The laminated LTCC stack is placed in an oven with a specific programmed multi-step temperature profile. The typical profile starts with a slow rising temperature at about 2-5 °C per minute up to around 450 °C and holds for approximately 2 hours for the organic binder to be burned out. The temperature is then raised up to between 850 and 875 °C with a dwell time of about 10 to 15 minutes. The sintering takes place at this temperature for LTCC.

![Figure 3.5: Micro counterflow burner fabricated with LTCC tape technologies.](image)

One system developed using LTCC in the present research was a burner design, consisting of two channels crossing each other at the midpoint. The reaction channel is 1 mm × 1 mm in cross-section. The cross-sectional dimension of the reactants inlet channel was
approximately 221 μm wide and 216 μm high. The lengths of the channels are 12.7 mm. The features were constructed by punching and stacking of Dupont 951 green tapes. Thick layers for building up the burner thickness were pre-laminated with the isostatic press. The blocks were then laminated using an organic fluid. The smallest lateral dimension of the current process was limited by the punch size, which is 152 μm in diameter. The fabricated burner is shown in Figure 3.5. The overall size of the combustor is comparable to a US quarter coin, but the reaction zone volume is less than 12.7 mm². Sapphire windows 6.5 mm in diameter and 0.5 mm thick are co-fired with the LTCC tapes to seal the burner. At the same time, the windows provide optical access for in-situ diagnostics.

**System Integration Issues**

For most micro devices, communication and interconnection with other macro scale components are still unavoidable. For example, even if the pump and valves are integrated onto the micro combustion device on the same chip, fuel tanks at a relatively larger scale will still be required for extended operation. The interconnection of components at different length scales is a challenge. Micro-to-Macro interconnections, good sealing, and temperature sensitive materials have been identified as the three major difficulties that have to be resolved for successful microfluidic systems [165, 166]. The most common method for fluidic micro-to-macro interconnection is by attaching the microfabricated microfluidic chips to aligned manifold blocks machined by traditional techniques using commercially available compression fittings (e.g., Swagelok). Reliable gas tight and temperature resisting interconnect adapters are essential for microcombustion systems.

Among the microfabrication technologies discussed, LTCC technology has the potential to serve as a core technology for highly integrated high temperature micro thermal fluidic applications. Such microsystems are able to integrate, e.g., electrical, mechanical, and micro fluid mechanic functions. The relatively lower conductivity of LTCC is also a plus for micro combustion applications. Table 3.2 below is a comparison of various microfabrication technologies modified from Ref. [159]. This technique may also serve as a bridge between fabricated parts from silicon devices and high temperature ceramics.
Table 3.2: Comparison of various MEMS technologies (modified from [159])

<table>
<thead>
<tr>
<th></th>
<th>Hybrid LTCC</th>
<th>X-ray</th>
<th>Bulk Si micromachining</th>
<th>Surface Si micromachining</th>
<th>EDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feature height</td>
<td>100 μm per layer, easily up to 10 mm laminating layers</td>
<td>100 μm to 1 cm</td>
<td>500 μm to 1 mm with bonding</td>
<td>10-20 μm to a few mm</td>
<td></td>
</tr>
<tr>
<td>Internal surface roughness of channels</td>
<td>Very good</td>
<td>Very good</td>
<td>Very good</td>
<td>Very good</td>
<td>Good</td>
</tr>
<tr>
<td>Cross-sectional shape variation with depth</td>
<td>Fair</td>
<td>Good</td>
<td>Fixed Angle</td>
<td>Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Materials</td>
<td>Wide range</td>
<td>New materials</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Conductive metals</td>
</tr>
<tr>
<td>Compatibility with integrated devices</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Difficult</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>Large</td>
<td>Large</td>
<td>Small</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Low volume production</td>
<td>Excellent</td>
<td>Poor</td>
<td>Fair</td>
<td>Poor</td>
<td>Excellent</td>
</tr>
<tr>
<td>High volume production</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good</td>
</tr>
</tbody>
</table>
CHAPTER 4

EXPERIMENTAL METHODS

To investigate flame structure and dynamics in meso/micro scale combustion systems, several diagnostic tools were applied. The techniques can be put into three categories based on the targeted properties of the measurements: species, velocity, and temperature. The experimental techniques for species measurements applied in this thesis include gas chromatography (GC), Fourier transform infrared spectrometry (FTIR), chemiluminescence, and imaging spectroscopy. GC and FTIR are capable of quantifying the species concentrations, while chemiluminescence and spectroscopy studies further reveal the spatial distribution of chemical compounds. Thermocouples were applied for temperature measurements.

Species Measurements

Gas chromatography was applied to quantify stable species in the combustion products. Spectroscopy techniques were also utilized to analyze species involved in the combustion process. Three types of spectroscopy techniques were applied: dispersive, filter based, and Fourier-transform spectrometers.

Gas chromatography (GC)

Principles of Operation

Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, stationary and mobile phases, as they move through a tube (column). In gas chromatography (GC), the mobile phase is a gas. A typical gas chromatograph consists of carrier gas, flow controller, injector, column, detector, and data system. The column and the detector are the essential parts of the system. There are two major
categories of columns: the packed column and the open tubular column. There are three types of open tubular columns (OT): wall coated (WCOT), support coated (SCOT), and porous layer (PLOT). The WCOT column, also called capillary column, is a fused silica capillary tube with the stationary liquid phase coated on the inner surface of the tube wall. SCOT columns are columns that contain an absorbed layer of very small solid support coated with liquid phase, and PLOT columns contain a porous layer of a solid adsorbent. The packed columns are metal tubes packed with inert supports on which stationary liquids are coated. Many GC detectors have been invented, but the most popular ones are the flame ionization detector (FID), the thermal conductivity cell (TCD), and the electron capture detector (ECD). [167]

In a chromatographic process, a gas mixture consisting of, for example, components A and B are introduced into the column. As the mixture is carried through the column by the carrier gas, partitions between the mobile phase and the stationary phase occur. Different molecules have unique partitioning characteristics between the column substrate and the carrier gas. The column is less absorptive to component A; consequently, component A is carried down the column faster than component B because of the higher concentration in the mobile phase. Component A leaves the column and passes through the detector before component B. The output signal of the detector gives rise to a chromatogram, in which the areas of the peaks represent concentrations of the components.

**Agilent MicroGC 3000**

The GC system applied in the present study was an Agilent 3000 MicroGC equipped with two porous layer open tube (PLOT) columns and thermal conductivity detectors (TCDs). The column materials of the system are Molsieve 5A for column A and PLOTQ for column B. Channel A is also equipped with a 3 m long PLOT U pre-column and a 1 μL backflush injector. The inner diameter of the columns is 0.32 mm. The Molsieve 5A main column is 10 m long, while the PLOT Q column of channel B is 8 m long. The backflush injector works in the following manner. One end of the pre-column is installed into the injector and the other end into one port of the backflush valve. The inlet to the analytical column is connected then to the second port of the backflush valve. During injection, carrier gas is supplied through the injector rather than through the back flush valve. The sample enters the pre-column and progresses toward the
backflush valve. After the analytes of interest elute from the pre-column, the carrier gas supply is switched from the injector to the backflush valve. The analytes of interest continue down the analytical column while the unwanted analytes on the pre-column, such as water in a molecular sieve channel, are backflushed out through the injector. This keeps the analytical column clean and allows the system to hold a calibration longer. Moreover, the backflush injector on column A behaves like a fixed volume injector when run with a zero-millisecond injection time. At longer injection times, a larger quantity of the sample is introduced to the pre-column and the injector behaves like a variable volume injector. This latter mode of operation improves system detection limits.

The TCD is a differential detector that measures the thermal conductivity of the analyte in carrier gas, compared to the thermal conductivity of pure carrier gas; therefore, the carrier gas used with the TCD must have a thermal conductivity that is very different from the samples to be analyzed. It is also worth noting that a TCD measures the concentration of the analyte, which means that as the flow rate is decreased, the signal peak remains unchanged, but the area increases. Helium is the most common carrier gas used since it has a very high thermal conductivity compared to hydrocarbons. However, argon was utilized as the carrier gas for most of the systems studied here because the thermal conductivity of helium is too close to hydrogen, which was one of the fuels studied in the micro combustion systems.

**Quantitative Analysis**

The external standard method was utilized for quantification. Water vapor was measured separately in the PLOT-Q column of the micro GC. Chromatograms of known amounts of water vapor were obtained from which a calibration curve was determined. The analysis method then compares the measured area of the peak with the calibrated data. A custom built heated bubbler was used for water vapor calibration. The bubbler was basically an aluminum bottle wrapped with three band drum heaters and insulation. The container was half filled with distilled water. Air was flowed into the container through a tube from the top. A sintered stainless steel filter (7 μm) was welded on the end of the tube. Air was broken up into tiny bubbles by the filter. As the bubbles flowed through the heated water, they reached thermal equilibrium with the water. The temperature of the vapor was monitored by a J-type thermocouple near the gas exit inside the
container. Temperature was adjusted manually by changing the voltage applied to the band heaters. Water vapor concentrations were back calculated based on the temperature measured using the saturated vapor table at atmospheric pressure.[168]

![Figure 4.1: Gas chromatogram of hydrogen and air in column A of the micro GC. The concentrations of 11.1% hydrogen, 18.7% oxygen, and 70.2% nitrogen for the spectrum](image1)

Figure 4.1: Gas chromatogram of hydrogen and air in column A of the micro GC. The concentrations of 11.1% hydrogen, 18.7% oxygen, and 70.2% nitrogen for the spectrum.

![Figure 4.2: Gas chromatogram of water vapor in column B of the micro GC. The concentration of the vapor in the air is 60 °C saturated which is 19.686 %](image2)

Figure 4.2: Gas chromatogram of water vapor in column B of the micro GC. The concentration of the vapor in the air is 60 °C saturated which is 19.686 %.

Figure 4.1 shows a typical chromatogram for hydrogen and air mixture. The three peaks in the figure correspond to the elution of hydrogen, oxygen, and nitrogen, respectively. The first peak in Figure 4.2 is the combined effect of oxygen and nitrogen in air, while the second peak comes from water vapor in the solution. Table 4.1 gives the GC operational parameters.
corresponding to the measurement shown in Figure 4.1 and Figure 4.2. The temperatures are set well beyond the boiling point of water at atmospheric pressure to ensure that no water condensation occurs in the chromatograph. The calibration curves for hydrogen, water vapor, oxygen, and nitrogen are shown in Figure 4.3 (a), (b), (c), and (d), respectively.

(a) Hydrogen

\[ \text{[H}_2\text{]} = 0.06 + 8.78 \times 10^{-5} \times \text{Area} \]

(b) Water vapor in air, 1 L/min

\[ \text{[H}_2\text{O]} = -0.13 + 9.50 \times 10^{-4} \times \text{Area} \]

(c) Oxygen

\[ \text{[O}_2\text{]} = 3.712 + 2.44 \times 10^{-3} \times \text{Area} \]

(d) Nitrogen

\[ \text{[N}_2\text{]} = 11.51 + 2.45 \times 10^{-3} \times \text{Area} \]

Figure 4.3: Calibration curves for (a) hydrogen, (b) water vapor, (c) oxygen, and (d) nitrogen. The calibration curve for water vapor corresponding to the parameter settings in Table 4.1.
Table 4.1: Typical settings of the GC.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Column A</th>
<th>Column B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Inlet Temperature (C)</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>Injector Temperature</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>Column Temperature</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>Sampling Time (sec)</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Injection Time (ms)</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Run Time (sec)</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>Pressure Equilibration Time (sec)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Column Pressure (psi)</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>Post Run Pressure (psi)</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>Backflush Time (sec)</td>
<td>9.75</td>
<td>-</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>Standard</td>
<td>Standard</td>
</tr>
<tr>
<td>Baseline Offset (mV)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carrier Gas</td>
<td>Argon</td>
<td>Argon</td>
</tr>
</tbody>
</table>

**Fourier transform infrared-red spectrometry (FTIR)**

**Principles of Operation**

Fourier transform infrared (FTIR) spectroscopy is a type of vibrational spectroscopy in which absorption corresponding to transitions of both vibrational and rotational states of a molecule are changed. A FTIR system usually consists of four major components: a near to mid infrared light source, an interferometer, a detector, and a data acquisition system.

The FTIR spectrometry is based on the Michelson interferometer. A monochromatic light wave can be represented in the complex form as

\[ U = A(\cos \phi + i \sin \phi) = Ae^{i\phi}, \]  

(4.1)
where $A$ is an amplitude constant, and

$$\phi = kx - kv t = \frac{2\pi}{\lambda}x - \omega t,$$

(4.2)

which $k$ is known as the propagation number, $v$ is the phase velocity of the wave, and $\omega$ is the angular temporal frequency. When two monochromatic waves $U_1$ and $U_2$ of the same wavelength $\lambda$ are summed, the intensity of the combined wave is

$$I = (U_1 + U_2)^2$$

$$= [\text{Re}(U_1) + \text{Re}(U_2)]^2 + [\text{Im}(U_1) + \text{Im}(U_2)]^2.$$ (4.3)

$$= I_1 + I_2 + 2(I_1 I_2)^{1/2} \cos(\phi_2 - \phi_1)$$

The equation can be rearranged as

$$I = (I_1 + I_2) \left[ 1 + \frac{2(I_1 I_2)^{1/2} \cos \delta}{I_1 + I_2} \right].$$ (4.4)

For ideal optics, $I_1$ and $I_2$ will be 50% of the total irradiance from the light source. Moreover, the modulated part of the interference, which is represented by the second term in the bracket of Equation 4.4 is of interest,

$$I_{ac} = 0.5I_s \cos \delta,$$ (4.5)

where,

$$\delta = \frac{4\pi}{\lambda} = \frac{2\pi}{\lambda} (2v_d t),$$ (4.6)

and $v_d$ is the speed of the mirror in the FT-IR spectrometer. The detector will obtain signals of constructive interference at $x=n\lambda$, and destructive interference at $x=(n+1/2)\lambda$. The frequency of the measured modulated signal can then be obtained using a Fourier transform

$$F(f) = \frac{1}{2\pi} \int I_{ac} e^{i2\pi f} dt,$$ (4.7)

where the frequency, $f$, is equal to the speed of the wave, $c$, divided by the wavelength: $f=c/\lambda$. In a real application, a digital Fourier transform is used instead of the form shown in the equation above. For a broadband radiation, which contains a wide range of frequencies, the interference function is given by
The Fourier transform of the interferogram will give the entire power spectrum by plotting the absolute value of \( F(f)^2 \) versus \( f \).

The FT-IR absorption spectrum is taken by measuring two frequency spectra, one with the sample cell containing no absorption species in the frequency range investigated, and the second with the cell containing the material whose spectrum is to be measured. The difference in the power spectra yields the desired absorption spectrum. Since radiation at every frequency reaches the detector and all this radiation is used to compute the power spectrum, an FT-IR spectrometer gives a better signal-to-noise ratio than a simple dispersion instrument. Approximately 50% of the light progressing through the optical arrangement can be collected.

**Thermo-Nicolet 600**

A Thermo-Nicolet 600 FT-IR spectrometer was utilized in the current study. The system is equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT-A) detector. The detector is capable of detecting radiation from 650 to 4000 cm\(^{-1} \). Figure 4.4 shows the layout of the FT-IR system. The spectrometer is equipped with dual sources: a white light source for near IR and a separate IR source. Only the IR source was utilized in the study for the wavelength range investigated. A helium-neon laser in the system provides the calibration benchmark of light wavelength. A 100 mL gas cell with 10 cm long optical path was installed in the sample compartment. Instead of common KBr windows, ZnSe side windows are used on the cell to enable the capability of characterizing nitric oxide in the gas mixture. Energy screen labeled Screen A, which attenuates the incident radiation onto the detector by 70% (30% transmittance) was installed.
The whole system was purged with gas generated by a FT-IR purge gas generator (Parker Balston 75-52NA), which removes the water vapor and carbon dioxide contents in the air to below 100 °C dew point and 1 ppm, respectively. Figure 4.5 shows the difference in the background spectrum under conditions with and without the system being purged. Ultra-high-purity (UHP) nitrogen, which is optically inert, was the gas flowing through the gas cell for both spectra. Very clean background spectrum could be obtained after the whole system was purged. A stable and clean spectrum is important for quantitative analysis of the gas components. Fully computerized measurements can be conducted with the custom-built gas distribution system as shown in Figure 4.6.
Figure 4.5: The background spectrograph when the FT-IR is purged with (a) dry air and (b) with purging gas.

Figure 4.6: Gas distribution system for FTIR.
Quantitative Analysis

The methods for quantitative analysis of FTIR are based on the Beer-Lambert-Bouguet equation, often referred to as Beer’s law,

\[ A = \varepsilon l c , \quad (4.9) \]

where \( A \) is the absorbance, \( \varepsilon \) is the molar absorptivity or extinction coefficient, \( l \) is the path length or sample thickness, and \( c \) is the concentration of the substance. The absorbance is derived from the measured transmittance (T) of the sample

\[ A = -\log T , \quad (4.10) \]

and the value of the extinction coefficient depends on the frequency of light, and is the intrinsic light absorption characteristic of a species. By comparing either the peak area or peak height over a range of frequencies between the unknown sample and a reference with known concentration of the investigated species, the concentration of the species investigated can be obtained using

\[ c(S) = c(R) \frac{\int A(S)}{\int A(R)} , \quad (4.11) \]

where \( c(S) \) and \( c(R) \) are the concentrations of the sample and the reference. Using peak areas instead of peak heights is significantly better, since it tends to average out any noise that is present in the data, assuming the noise varies randomly across the spectrum. Moreover, the peak height detected might not be accurately resolved when the frequency resolution is not high enough, which often occurs when faster measurement rates are desirable.

In most FTIR measurements, overlapping of absorption frequencies between species will occur and the simple analysis mentioned above will fail. The absorbance at the interfered frequency becomes the summation of the absorbance of all species with non-zero extinction coefficient in the mixture,

\[ A(S, f) = \sum_i c(S, i) \frac{A(R, f)}{c(R, i)} , \quad (4.12) \]
where \( i \) is the component number. By measuring absorbance at more frequencies than the unknown species, an over constrained mathematical system can be obtained. The unknowns, species concentrations, can be further solved using least squares analysis. The quantitative analysis software, QuantPad, bundled with the Thermo-Nicolet 600 FTIR applies algorithms to carry out the least squares analysis. Corrections for nonlinear absorbance, nonzero baselines, component interaction can also be implemented.

When carrying out quantitative analysis, the following steps were followed to choose analysis regions:

1. Measure a spectrum of each of the components at the highest concentration that will be encountered in the samples. For non-dilute combustion product of hydrocarbon/air or oxygen mixture, \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) can be up to 10-20%. Most other components will typically be in the range of 0.1 to 1.0% (1000 to 10000 ppm).

2. Eliminate from consideration frequency ranges in which any of the components are effectively opaque (\( A > 1 \), i.e \( T < 10\% \)).

3. Choose for each component a region of the spectrum where the analysis will be performed (quantified). Other components may also absorb in the region selected, but none of the high-absorbance frequency ranges eliminated in the previous step can be considered for any component. It is possible (and often necessary) to quantify several of the components using the same region of the spectrum.

Table 4.2 provides information on the quantification method used to quantify the \( \text{CO} \), \( \text{CO}_2 \), \( \text{CH}_4 \), in the product of hydrocarbon combustion. “S” in the species column is the region where the species was quantified, while regions labeled as “I” are those regions where interferences occurred between species. Interferences only occurred at in the region of 2149-2185 cm\(^{-1}\) between the \( \text{CO}_2 \) and \( \text{CO} \) spectra for the quantification method shown.
Figure 4.7 shows a typical FT-IR spectrum for a combustor fueled with methane and oxygen. The parameters for the spectra collection are listed in Table 4.3. For the overall fuel rich conditions (overall equivalence ratio of approximately 1.42) as shown in Figure 4.7(a), small quantities of acetylene (C\textsubscript{2}H\textsubscript{2}) and ethylene (C\textsubscript{2}H\textsubscript{4}) are also measured. The concentrations of acetylene and ethylene are below the sensitivity limit of the current measurement method in most fuel lean cases as shown in Figure 4.7(b). The concentrations of the gas components quantified using the method shown in Table 4.2 are 9.5 %, 7470 ppm, 875 ppm for CO\textsubscript{2}, CO, CH\textsubscript{4} in Figure 4.7(b), respectively.

Table 4.2: Investigation windows for hydrocarbon combustion product quantification.

<table>
<thead>
<tr>
<th>Region</th>
<th>Window</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>End</td>
<td>Start</td>
</tr>
<tr>
<td>758</td>
<td>796</td>
<td>758</td>
</tr>
<tr>
<td>2149</td>
<td>2185</td>
<td>2149</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2867.84</td>
</tr>
</tbody>
</table>

Table 4.3: Parameters set on the FTIR for hydrocarbon combustion efficiencies characterization.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Numer of sample scans</td>
<td>16</td>
</tr>
<tr>
<td>Resolution (cm\textsuperscript{-1})</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample gain</td>
<td>1.0</td>
</tr>
<tr>
<td>Mirror velocity (cm/s)</td>
<td>0.6329</td>
</tr>
<tr>
<td>Aperture</td>
<td>17</td>
</tr>
<tr>
<td>Attenuator installed</td>
<td>A</td>
</tr>
</tbody>
</table>
Chemiluminescence

Chemiluminescence, sometimes called chemoluminescence in other fields such as forensic science, is the emission of light as a result of a chemical reaction. The chemical reaction generates a species at an excited electronic state, and as the excited species is relaxed to the ground state, energy is released in the form of radiation at certain wavelengths corresponding to the energy change between the states. The energies involved in the transitions between different electronic states of molecules are generally in the range from $10^3$ to $10^4$ kJ/mol. The corresponding resonant electromagnetic radiation is in the UV-to-visible range (100 to 1000...
nm). Species that are commonly observed in hydrocarbon flames are $\text{OH}^*$, $\text{C}_2^*$, $\text{C}_3^*$, $\text{CH}^*$, $\text{HCO}^*$. The origins of the luminescence of these species will be discussed in this section.

Measurement techniques including spatially filtered imaging and dispersive imaging spectroscopy will also be introduced. Chemiluminescence, most of the time, is an intrinsic mechanism of the combustion process, the measurements and observations are therefore non-intrusive, not only physically but also chemically. However, the species that can be resolved are limited to the existing chemical process in the combustion phenomena as well as the sensitivity of the detectors. The technique has been demonstrated for measuring heat release, local equivalence ratio, and burning rate for premixed and partially premixed flames through the correlations of the species luminescence intensities in laboratory scale flames [169-172].

**Origin of the Luminescence**

The formation of excited $\text{OH}^*$, $\text{CH}^*$, and $\text{C}_2^*$ species in flames are from the following reactions [173-183]. For $\text{OH}^*$, several possible reaction routes have been proposed. In hydrocarbon systems, $\text{OH}^*$ is formed via,

$$\text{CH} + \text{O}_2 \rightarrow \text{CO} + \text{OH}^*.$$  
When no carbon species exist in the system like the hydrogen flame, the possible reactions are

$$\text{O} + \text{H} \rightarrow \text{OH}^*$$  
$$\text{H} + \text{O}_2 \rightarrow \text{OH}^* + \text{O}$$

An OH radical can be raised from the ground state into the excited state when it is involved as a third partner in a recombination reaction between two other particles

$$\text{OH} + \text{H} + \text{M} \rightarrow \text{OH}^* + \text{HM}.$$  
This reaction explains why the presence of H and OH radical in hydrogen and acetylene flames in excess of their equilibrium concentration also leads to a superthermal excitation of the OH band above the primary combustion zone. However, $\text{OH}^*$ radicals are generally produced by the reaction between formyl radicals and oxygen atoms as well as the oxidation of CH radicals [174]:

$$\text{HCO} + \text{O} \rightarrow \text{CO} + \text{OH}^*$$  
$$\text{CH} + \text{O}_2 \rightarrow \text{CO} + \text{OH}^*.$$  
Chemiluminescence is observed as the $\text{OH}^*$ radical relaxes back to the ground state
\[ \text{OH}^* \rightarrow \text{OH} + \text{hv} \]

\( \text{OH}^* \) can also be consumed or deactivated by collision with other species in the system such as \( \text{H}_2, \text{N}_2, \text{O}_2, \text{H}_2\text{O}, \text{CH}_4, \text{CO}, \text{and CO}_2 \). A detailed model for \( \text{OH}^* \) chemiluminescence can be found in Ref [174]. Emission of \( \text{OH}^* \) at 308 nm is usually used to characterize the reaction in hydrocarbon and hydrogen flames, but the ultraviolet emission is unable to transmit through the optics of the microscope (Nikon TE2000U) available for the present study. The light intensities for wavelengths below 340 nm are sharply cut in the microscope. As a result, \( \text{OH}^* \) emission diagnostics will not be pursued in the study of microscopic dispersive imaging spectroscopy, only filter based measurements will be utilized.

The intense blue emission observed in hydrocarbon flames is attributed to the \( \text{CH} (\text{A}^2\Delta - \text{X}^2\Pi) \) electronic transition. \( \text{CH}^* \) is not formed by direct breakdown of hydrocarbons but by side reactions. Although the exact processes of these reactions are not totally understood, the observation that \( \text{CH}^* \) in the \( \text{A}^2\Delta \) electronic state that emits luminescence at 431.3 nm usually occurs higher in the reaction zone than \( \text{C}_2 \). Gaydon [182, 183] therefore suggested that \( \text{CH}^* \) might be formed from \( \text{C}_2 \) by the reactions:

\[ \text{C}_2 + \text{OH} \rightarrow \text{CO} + \text{CH}^* \]

The reaction mechanism above, however, was experimentally rejected by experimental results that show no observable \( \text{CH}^* \) in systems containing \( \text{C}_2 \) and \( \text{OH} \) when \( \text{O} \) atoms are not present [184]. The following mechanisms are alternatively proposed [179, 180, 185-189],

\[ \text{C}_2\text{H} + \text{O} \rightarrow \text{CO} + \text{CH}^* \quad \Delta \text{H}^0_{298K} = -46 \text{ kJ/mol} \]
\[ \text{C}_2\text{H} + \text{O}_2 \rightarrow \text{CO}_2 + \text{CH}^* \quad \Delta \text{H}^0_{298K} = -80 \text{ kJ/mol} \]

The energetic of these reactions is sufficient to excite \( \text{CH} \) to the A and B electronic states. The rates for the two reactions are \( 1.8 \times 10^{-11} \) and \( 3.6 \times 10^{-14} \text{ cm}^3/\text{mol/s} \) at room temperature. Although the rate constants for the \( \text{O} \) atom reaction is much higher, the reaction with \( \text{O}_2 \) is as important in producing \( \text{CH}^* \) because the concentration of \( \text{O}_2 \) in typical hydrocarbon flames is much higher. The luminescence from the relaxation of \( \text{CH}^* \) from the \( \text{A}^2\Delta \) and \( \text{B}^2\Sigma^- \) states back to the ground \( \text{X}^2\Pi \) state are the most common transitions of \( \text{CH}^* \) chemiluminescence. Relaxation can also occur through quenching collisions of the excited \( \text{CH}^* \) with other species in the system. The reaction rates of quenching reactions can be found in Ref. [177]. The wavelengths of the (0,0) transitions for the two systems are around 431 and 390 nm, respectively.
As for C$_2^*$, the following reactions are usually considered as the mechanisms that generate excited C$_2^*$:

$$\text{CH}_2+\text{C} \rightarrow \text{H}_2+\text{C}_2^*$$
$$\text{CH}+\text{C} \rightarrow \text{H}+\text{C}_2^*.$$  

The Swan system is the most well known among the seven known C$_2$ emission bands. The Swan band is the origin of the green emission from the fuel rich zone of the flame. It is the transition between $\Lambda^3\Pi_g$ and $X^1\Pi_u$ electronic states of the C$_2$ molecule, which has a gap energy of 2.4025 eV. The strongest groups of emission of the Swan band come from the emission of $\Delta \nu=1$, 0 and -1 vibrational transitions, which have outstanding heads at 473.71, 516.52, and 573.55 nm, respectively [190]. Besides the Swan band, other band systems can also be observed in hydrocarbon flames. Further information can be found in Ref [182, 183].

The formation mechanism of excited CO$_2^*$ has been debated considerably. According to recent investigations, this blue continuum is not given by simple recombination reactions. It is possible to show that the flame radiation is not really a continuum, but has rotational fine structure which is smeared out at only moderate spectral resolution. The origin of the emission is given by the following three-body collision:

$$^1\text{CO}+^3\text{O}+\text{M} \rightarrow ^1\text{CO}_2^*+\text{M},$$

where M is a molecule in the flame, $^1$CO denotes a CO molecule in the singlet state, $^3$O is an O atom in the triplet ground state and $^1$CO$_2^*$ is a CO$_2$ molecule in an excited triplet state. The third-body M acts as a stabilizer of the newly formed $^1$CO$_2^*$ molecule. This molecule then transitions, without radiating, into a neighboring excited singlet state ($^1$CO$_2^*$) from which it can make an allowed radiative transition to the electronic singlet ground state

$$^1\text{CO}_2^* \rightarrow ^1\text{CO}_2+\nu.$$  

In this transition, the emission frequencies can have discrete values because both the initial and the ground states are stable. The complexity of the spectrum results in the quasi-continuum spectra obtained with a low resolution spectrometer. The excited CO$_2^*$ molecule can also fall back to the ground state without radiation through collisional deactivation,

$$^1\text{CO}_2^*+\text{M} \leftrightarrow ^1\text{CO}_2+\text{M}.$$
The collision partner M will absorb the released excitation energy. The reversibility of the reaction above suggests that the \( \text{CO}_2^* \) molecule can also be formed through collisional excitation of a \( \text{CO}_2 \) molecule in the ground state in addition to the recombination reaction of CO and O.

**Filter Based Chemiluminescence Imaging**

Filter based chemiluminescence imaging was used in the studies of micro ethylene jet flame and meso vortex combustion. Figures 4.8 demonstrates the technique with images of spatially filtered \( \text{CH}^* \) chemiluminescence of methanol jet flames. Liquid methanol was dispensed from a stainless steel hypodermic tube with inner diameter of 584 \( \mu \text{m} \) from the bottom of the frames. The volumetric flow rates are 0.75, 1, 2, and 3 mL/hr.

![Figure 4.8: Pseudo-color images of \( \text{CH}^* \) chemiluminescence of methanol jet flames with flow rates at 0.75, 1, 2, and 3 mL/hr.](image)

The images were captured with a TSI PIV14-10 camera in high gain mode. Nikon Micro UV Nikkor lens coupled with an extension bellow were used to project the millimeter scale flames onto the CCD. An exposure time of 500 ms was required to obtain quality images although the aperture had been fully opened at F2.8. Photons captured in this extended exposure period accumulate enough charges on the CCD to stretch the image intensity depth across a whole 8 bit span. A 1 inch diameter optical filter (Ealings, 35-3300) was installed between the flame and the lens so that only emission from \( \text{CH}^* \) radicals passed through to the CCD. The center frequency of the filter is 430 nm, and the full width at half maximum (FWHM) of the filter is 7.8 nm. Consequently, the captured images depict the reaction zone distribution, which corresponds to the strong emission of \( \text{CH}^* \) at 431.5 nm in a hydrocarbon flame.
Imaging Dispersive Spectroscopy

Although filter based chemiluminescence imaging can provide information on two-dimensional spatial species distribution, only one species can be monitored with each CCD at a time. Dispersive imaging spectroscopy can measure the emission from several species simultaneously by sacrificing one dimension of the CCD array to accommodate the frequency information of the emitted luminescence. A unique microscopic imaging dispersive spectroscopy system was developed to investigate meso and micro scale combustion systems in the present study.

Figure 4.9 is a schematic of the system layout. The system consists of three major components: an inverted optical microscope (Nikon, TE2000U), an imaging dispersive spectrometer (Acton, SpectraPro-2560), and an intensified CCD camera (Princeton Instruments, PI-MAX, GenIII UniGen Intensifier). The emission of the reaction is first collected by the microscope objective. The light beam is then relayed and refocused on the plane of the spectrometer entrance slit through the microscope tube lens. The grating in the spectrometer disperses the collimated light from the collimating mirror onto the focusing mirror.

The spectrum is focused onto the CCD through the focusing mirror. One axis of the CCD array (usually the horizontal axis) records the intensities of the frequency dispersed emissions, while the information of the spatial distribution along a line parallel to the entrance slit is registered along the other axis of the CCD. The dispersion wavelength coverage of the current setup is 85.2 nm for the 150 g/mm grating, and 173.1 nm for the 300 g/mm grating. A two-dimensional map of the emission spectra from a flame in a steady state can be obtained by the scanning method.

Figure 4.10 shows a diffusion flame stabilized in a micro burner. Methane was injected from a fuel port on the left of the figure, while oxygen was fed into the reaction zone from the right. A miniature flame with luminous zone approximately 1 mm long and 250 μm was stabilized in the 1 mm cross section reaction channel as shown in the figure. The picture was taken using a Nikon Coolpix 990 digital camera through a Nikon TE2000U inverted microscope with 4X objective. The exposure time was 4 sec. The volumetric flow rates for methane and oxygen were 4.55 sccm and 9.28 sccm, respectively.
Figure 4.9: Schematics of the layout of microscopic imaging spectroscopy.

Figure 4.10: Typical diffusion flame stabilized in the LTCC micro burner.
Figure 4.11 is the image spectrogram of the micro diffusion flame along the centerline. The horizontal axis of the figure represents wavelength, and the vertical axis is the spatial dimension across the flame along its centerline. The luminescence of the flame is dispersed by the grating and refocused on the CCD. The slit opening on the spectrometer entrance was 70 μm. The gating pulse width on the ICCD was set at 0.5 μs. Exposure of 2000 pulses were accumulated on the CCD chip. The readout from the CCD was further accumulated 10 times on the computer. As a result, the equivalent exposure time of the picture shown is 10 ms. Background noises is preferentially eliminated using this method. The gain of the photocathode on the ICCD was set at 196. The 300 g/mm grating blazed at 500 nm was selected for the measurement. The bright zone on the left comes from the strong emission of from the CH*(AΔ-XΣ) transition on top of CO2* chemiluminescence. The dimmer spots towards the right originate from the chemiluminescence during the relaxation of excited C2* and CO* radicals.

The processed spectrograms of Figure 4.11 are shown in Figure 4.12. Each strip represents emission from a region of 75 × 25 μm section on the centerline of the flame. The distance between neighboring strips is 63 μm. The maximum resolving power achievable with the current setup using a 10X objective is approximately 4.9 μm. The strips in Figure 4.12 are labeled from 1 to 10 with corresponding locations from top to down on Figure 4.11. Strip #1 corresponds to the fuel rich side in the diffusion flame, while strip #10 represents the emission spectrum from the oxidizer side of the flame. Only emissions from CH*, C2*, CO*, and CO2* are observed in the spectra. OH* radicals, which emit strong luminescence at 306 nm as they transit from the ΛΣ to ground ΧΠ electronic states, can not be detected with this setup due to the strong cut-off on the
transmission efficiency of the microscope optics below 340 nm. Special UV optics as well as gratings blazed at 300 nm (the gratings utilized in the present study are blazed at 500 nm) will be required to study OH emissions.

Figure 4.12: Three dimensional spectrogram of the micro diffusion flame. The spectrograms are labeled 1 to 10, starting from the fuel side.

Figure 4.13 is the standalone spectrum of strip #5 in Figure 4.12. The strong peak at 431.5 comes from the emission of CH$^\text{+}$($\Sigma$-$\Delta$). The weak peaks at around 390 nm seems to be from CH$^\text{+}$ going through B-X transitions. Greenish C$_2^*$ emissions from the well-known Swan system are detected at approximately 438.2, 473.7, and 516.5 nm. The three peaks represents the transitions of (2,0), (1,0), and (0,0) vibrational states, respectively. The peaks at around 600 nm are probably due to the A-X transition of CO$^*$ radicals, known as the fourth positive system. The emission intensities of vibrational transitions, $\Delta v$=1, 2, 3 and 4, occurring between 550 and 640 nm are relatively strong. The hump underneath the CH$^\text{+}$ and C$_2^*$ peaks is from the broadband emission of CO$_2^*$, which extends from 280 nm all the way into infrared-red regime [172, 182, 183].
Temperature Measurements

Thermocouples were applied for surface and gas temperature measurements in the present study. N-type thermocouples were generally installed for flame temperature measurements inside the combustor, while E-type thermocouples were applied to obtain the temperature readings elsewhere. The N-type thermocouple has a more stable Seeback voltage output than the popular K-type thermocouple at high temperatures. A semiconductor temperature sensor on the terminal block (National Instruments SCB-68) measures the reference junction temperature. The Seeback voltages of the thermocouples are digitized by a 12 bit data acquisition board (National Instruments, NI-6040) before being processed and recorded in the computer. The accuracy of the data acquisition system corresponds to a temperature uncertainty of ±3 K.

Figure 4.13: Spectrogram #5 in Figure 17.
CHAPTER 5

MICRO DIFFUSION FLAMES

Flames fed by opposing jets of fuel and oxidizer have been extensively utilized as a fundamental configuration to study flame characteristics due to their approximate one-dimensional nature and because residence times within the flame zone can be easily varied. Most studies on micro-scale combustion systems so far have been focused on premixed systems partly due to their relative simplicity of analyses and system fabrication. But non-premixed combustion systems, which introduce fuel and oxidizer separately into a millimeter scale reaction chamber, are more prevalent in practical systems not only because of the safety consideration but also the controllability of burning rates and flame locations. The laminar counterflow flame has also been proposed as a fundamental element in the complex structure of turbulent non-premixed flames [191].

Miesse et al. [107, 192-194] studied the flame dynamics in a mesoscale burner with a semi-counterflow configuration. Their design introduces fuel and oxidizer separately from the two legs of an inverted Y channel. The two streams merged and mixed in the exhaust channel, which is 0.75 mm thick. Although the channel depth is sub-millimeter, the lateral dimension is relatively large at 5 mm. They observed flame cells along the channel, which they suggest to be a cellular instability that appears to be unique to microcombustion systems. However, the flame in their configuration is probably more a premixed (or partially premixed) flame than a diffusion flame in nature.

In the present study, a micro counterflow diffusion flame burner is designed and fabricated to investigate the characteristics of diffusion flames at sub-millimeter scale. Diffusion flames were stabilized in a millimeter scale channel by introducing fuel and oxidizer jets from injection ports located on opposite sides of the channel. The flame structures were investigated with imaging spectroscopy to reveal the combustion characteristics in small confinements, as well as their response to changes in the flow field characteristics, e.g., strain rates and dilution. These
studies will provide insight into the effects of length scale on flame stabilization and stretch with coupled heat loss, which will provide data for designs of future microcombustors.

**Design and Fabrication of the LTCC Counterflow Diffusion Flame Burner**

The design of the micro counterflow diffusion flame burner is shown in Figure 5.1. In a typical counterflow diffusion flame burner, fuel and oxidizer free jets (often sheathed by an co-flow inert gas) impinge each other in a unconfined volume [195]. Counterflow burners with partly confined impingement region has also been utilized to investigate the one-dimensional diffusion flame [196]. These macroscale designs usually have port sizes and gap distances of several centimeters. For the counterflow burner studied in this thesis, the injection port size for both the fuel and oxidizer is 221 μm wide and 216 μm in height. The cross section of the impingement region is approximately 1.2 mm by 1.2 mm. The length of the impingement region is around 5 times the hydraulic length of the injection port. The reaction zone is confined at the top and bottom by sapphire windows and the sides by side walls. The total length of the confined reaction channel of the burner is 12.7 mm (6.35 mm on each side of the impingement plane). The overall size of the combustor is 25.4 mm square and 3.3 mm thick.

The microcombustor was fabricated using the LTCC tape technique described in Chapter 3. The fabrication procedure is shown in Figure 5.2. Internal channels can be conveniently integrated in the current burner design with this fabrication technique. The burner consists of seven pre-laminated blocks and two sapphire windows as shown in Figure 5.1. The sapphire windows are co-fired with the LTCC tapes. Table 5.1 shows the layers of LTCC tapes pre-laminated in each block. A combination of Dupont 951 AT and AX tapes, which have different thickness, was used to obtain the desired thickness of each block. The fired thickness of AT and AX tapes are 96.52 μm, and 215.9 μm, respectively. The blocks were laminated using an isostatic lamination which applied 3000 psi at 70 °C to the stack for 10 min. The features were then cut out on each block with a punching machine. Honey was brushed on the interface between blocks before they are stacked together. Pressurized lamination could not be utilized due to the existence of internal channels and cavities, but the whole burner stack was placed in a plastic bag and a vacuum was pulled on the bag to ensure that the honey was uniformly distributed over the
interfaces. The burner stack was then retrieved from the plastic bag and diced (4 burners on a tape stack) using a dicing chopper.

![Figure 5.1: Design of the LTCC counterflow diffusion flame burner.](image)

The burners are sintered (co-fired) in a programmed oven with the temperature profile shown in Figure 5.3. The time duration for the burn-out phase was extended due to the utilization of honey for lamination. Stainless steel back ferrules for 1/16” tubes (Swagelok) were placed on the inlets and fired together. The stainless steel ferrules do not bond to the LTCC tapes, but can be tightly held on the burner due to the shrinkage of the ceramic around the edges of the ferrules after co-firing. The shrinkage factor for the LTCC tapes is 0.872 in x and y directions. Tubes can be more easily aligned and glued to the burner with the existence of these ferrules. Stainless steel tubes are glued onto the fuel and oxidizer ports using vacuum epoxy (Varian, Torr Seal). Sapphire windows, on the other hand, were bonded to the LTCC tapes after co-firing process. The bonding causes non-uniform shrinkage of the LTCC because the sapphire will not shrink after co-firing. As a result, the actual width of the reaction channel at cross sections where the sapphire
windows form the top and bottom walls was approximately 1.2 mm, instead of the 1.0 mm, which it would have been without the windows.

![Fabrication flow of the LTCC micro burner.](image)

**Figure 5.2:** Fabrication flow of the LTCC micro burner.

<table>
<thead>
<tr>
<th>Block</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7×AT</td>
</tr>
<tr>
<td>2</td>
<td>3×AT + 1×AX</td>
</tr>
<tr>
<td>3</td>
<td>5×AT</td>
</tr>
<tr>
<td>4</td>
<td>1×AX</td>
</tr>
<tr>
<td>5</td>
<td>5×AT</td>
</tr>
<tr>
<td>6</td>
<td>3×AT+1×AX</td>
</tr>
<tr>
<td>7</td>
<td>2×AX</td>
</tr>
<tr>
<td></td>
<td><strong>Sapphire window</strong> 0.5 mm thick</td>
</tr>
</tbody>
</table>

**Table 5.1:** Constituents of the pre-laminated blocks.
The LTCC counterflow diffusion flame burner after the firing procedure was shown in Figure 3.5. Figure 5.4 is a magnified view of the reaction channel and the injection port. Rectangular injection ports with no signs of sagging were obtained for the burner. The sidewalls of the reaction channel are, however, jigsawed along the vertical direction in the picture. The irregularity is probably unavoidable since the block to block alignment tolerance is approximately 25 μm. The channel is smooth along the horizontal direction with the high punching density applied (center to center distance of 109 μm between 635 μm punching holes). Lower punching density was used for the observation holes on blocks 1 and 7. As a result, a jigsawed pattern on the side wall along the circumference of the opening can be clearly seen in Figure 5.4.
Numerical simulation using CFD software, FLUENT, was carried out to study the influence of wall thermal boundary conditions in the configuration. Adiabatic and cold wall (constant at 600 K) was set as the wall boundary conditions in the three dimensional numerical study. In order to compare the simulation results with the chemiluminescence observed in the diffusion flame burner, GRI-Mech 3.0 reaction mechanism [197] and the chemiluminescence reaction mechanisms shown in Table 5.2 were applied for the methane/oxygen combustion. The added chemiluminescence reactions are obtained from Ref. [175] for CH°(A) and OH°(A) and from Ref. [198] for C_2°(d). The letters in the parentheses after CH°, OH° and C_2° represent the electronic states of the excited species. The majority of emission for hydrocarbon flames in the visible range originates from CH(A-X) at around 430 nm, CH(B-X) at 390 nm, C_2(d-a) between 470 and 550 nm, and from the CO_2 continuum band and HCO bands between 300 to 500 nm. The CH(B-X) chemiluminescence contribute approximately 20% of the total CH° emission [175].
Kojima et al. [173] have also assembled a reaction set for OH*(A), CH*(A), and C_2*(d), but the extra reactions for C_2 formation and quenching reactions for C_2* are neglected in their mechanism. The current kinetic model consists of 39 species and 246 reactions. Species and reactions that involve the nitrogen atom in the GRI-Mech 3.0 and in Ref. [175, 198] were neglected.

Figure 5.5 shows the reaction channel and the computational domain of the simulation (gray region). Symmetry was assumed across the x-z and y-z planes; as a result, only a quarter of the reaction zone was solved during the computation. Physical dimensions of the computational domain are 1.5 mm in the x direction, 0.5 mm in the y direction, and 1 mm in the z direction. Although the overall length of the reaction channel is 12.7 mm in the LTCC burner, it is experimentally observed that the size of the flame luminous zone extends less than 2 mm in the x direction. The length of the computational domain is therefore set as 1.5 mm (3 mm overall due to the symmetric condition at x = 0 plane). Dimensions of fuel and oxidizer inlets are 200 μm square. An isothermal wall at 600 K with no-slip was assigned as the wall boundary conditions. The inlet velocities for both methane and oxygen streams were 1 m/s, and the stream temperatures was 300 K. The computation domain contained 9025 node, and the smallest cell volume was 20 × 20 × 40 μm.
Table 5.2: OH*, CH* and C2* chemiluminescence reactions [175, 198] added to GRI-Mech 3.0 mechanism.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A (cm³/mol/s)</th>
<th>n</th>
<th>Eₐ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactions related to C₂</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂+H₂=C₂H+H</td>
<td>4.000E+05</td>
<td>2.400</td>
<td>1000.00</td>
</tr>
<tr>
<td>CH+CH=C₂H₂+H₂</td>
<td>5.000E+12</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>C+C+M=C₂+M</td>
<td>3.000E+14</td>
<td>0.000</td>
<td>-1000.00</td>
</tr>
<tr>
<td>C+CH=C₂+H</td>
<td>5.000E+13</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>O+C₂=C+CO</td>
<td>5.000E+13</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>C₂+O₂=CO+CO</td>
<td>9.000E+12</td>
<td>0.000</td>
<td>980.00</td>
</tr>
<tr>
<td><strong>Reactions related to CH</strong>*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H+O=CH*+CO</td>
<td>6.200E+12</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>C₂H+O₂=CH*+CO₂</td>
<td>4.100E+13</td>
<td>0.000</td>
<td>4500.00</td>
</tr>
<tr>
<td>CH*=&gt;CH</td>
<td>1.860E+06</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>CH*+O₂=CH+O₂</td>
<td>2.480E+06</td>
<td>2.140</td>
<td>-1720.00</td>
</tr>
<tr>
<td>CH*+H₂O=CH+H₂O</td>
<td>5.300E+13</td>
<td>.000</td>
<td>0.00</td>
</tr>
<tr>
<td>CH*+H₂=CH+H₂</td>
<td>1.470E+14</td>
<td>.000</td>
<td>1361.00</td>
</tr>
<tr>
<td>CH*+CO₂=CH+CO₂</td>
<td>2.400E-01</td>
<td>4.300</td>
<td>-1694.00</td>
</tr>
<tr>
<td>CH*+CO=CH+CO</td>
<td>2.440E+12</td>
<td>0.500</td>
<td>0.00</td>
</tr>
<tr>
<td>CH*+CH₄=CH+CH₄</td>
<td>1.730E+13</td>
<td>.000</td>
<td>167.00</td>
</tr>
<tr>
<td><strong>Reactions related to OH</strong>*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH+O₂=OH*+CO</td>
<td>6.000E+10</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>OH*=&gt;OH</td>
<td>1.450E+06</td>
<td>.000</td>
<td>0.00</td>
</tr>
<tr>
<td>OH*+O₂=OH+O₂</td>
<td>2.100E+12</td>
<td>0.500</td>
<td>-482.00</td>
</tr>
<tr>
<td>OH*+H₂O=OH+H₂O</td>
<td>5.920E+12</td>
<td>0.500</td>
<td>-861.00</td>
</tr>
<tr>
<td>OH*+H₂=OH+H₂</td>
<td>2.950E+12</td>
<td>0.500</td>
<td>-444.00</td>
</tr>
<tr>
<td>OH*+CO₂=OH+CO₂</td>
<td>2.750E+12</td>
<td>0.500</td>
<td>-968.00</td>
</tr>
<tr>
<td>OH*+CO=OH+CO</td>
<td>3.230E+12</td>
<td>0.500</td>
<td>-787.00</td>
</tr>
<tr>
<td>OH*+CH₄=OH+CH₄</td>
<td>3.360E+12</td>
<td>0.500</td>
<td>-635.00</td>
</tr>
<tr>
<td><strong>Reactions related C₂</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C+CH₂=&gt;C₂*+H₂</td>
<td>2.400E+12</td>
<td>.000</td>
<td>0.00</td>
</tr>
<tr>
<td>C₂*=&gt;C₂</td>
<td>1.000E+07</td>
<td>.000</td>
<td>0.00</td>
</tr>
<tr>
<td>C₂*+M=C₂+M</td>
<td>4.800E+13</td>
<td>.000</td>
<td>0.00</td>
</tr>
</tbody>
</table>
CH\(^*\) and C\(_2\)^* emissions are the mechanisms that contribute to the bluish green luminescence typically observed from a hydrocarbon flame. Figure 5.6 is a comparison of the CH\(^*\) and C\(_2\)^* chemiluminescence obtained from the CFD calculation and the experimentally observed flame. The intensity contours shown in Figure 5.6(a) and (b) are derived by multiplying the Arrenhius reaction rates, \(k_i\), and the mole concentration, \(y_i\), of the excited species obtained from the simulation,
where the reaction rates,

\[ I_i = k_i y_i, \]  

(5.1)

\[ k_i = A_i T_i^{n_i} \exp\left(\frac{E_{a,i}}{RT}\right), \]  

(5.2)

can be obtained directly from the computational results. The contours correspond to the plane at \( y=0 \) in the computational domain, and the contour of \( C_2^* \) intensity is horizontally flipped for easier visual comparison. Experimental line-of-sight observation of the flame shown in Figure 5.6(c) was taken with a cooled CCD (TSI 14-10) through a microscope (Nikon, TE-2000U). Both computational and experimental visualizations reveal that the flame curved towards the oxidizer side. The computational results also reveal that the chemiluminescence of \( C_2^* \) occurs more towards the methane side than \( CH^* \).

Figure 5.7: The calculated temperature distributions in the \( x = 0 \) and \( y = 0 \) planes. The oxygen side is labeled on the figure, and the methane is on the opposite side of the \( z \) axis.
The temperature distributions in the $x = 0$ and $y = 0$ planes of the reaction zone are shown in Figures 5.7. Maximum temperature in the reaction zone is 2727 K for the boundary conditions applied. The results also show that the high temperature zone is concentrated in the center region of the micro burner, which is essential for the applicability of LTCC. The serviceable temperature for LTCC is higher than silicon (see Table 3.1), but wall temperatures over 1200 K might cause cracks in the material. The velocity fields in the $x = 0$ and $y = 0$ planes from the numerical simulation are shown in Figure 5.8. Part (a) of the figure shows the distribution of the velocity magnitude, and part (b) reveals the contour of the z velocity vectors. The stagnation plane positioned at 2/3 of the separation gap away from the oxygen side.

**Experimental Diagnostics of the Chemiluminescence**

Flame structure characterization was carried out using the microscopic imaging spectroscopy technique described in Chapter 4. Figure 5.9 shows the spectral intensity maps of methane/oxygen combustion in the LTCC burner. The width of the slit at the entrance of the spectrometer was 100 μm. The gate time of on the ICCD was 10 μs and 1000 exposures were taken.
accumulated on the CCD. The equivalent exposure time was 10 ms. The spectra shown in the figures are the summations of 10 accumulations. The grating utilized was 150 g/mm centered at 475 nm. Each strip shown in the figures represents the binning of 25 horizontal lines on the CCD. The spatial resolution of the measurement is therefore 31.5 μm for the 10X objective used. The resolution in the present case is limited by the sensitivity of the system. A spatial resolution of around 1.3 μm is theoretically achievable if pixel binning does not have to be applied to overcome the low luminescence of micro flames; however, the current resolution limit is restricted by the sensitivity of the detector (or the chemiluminescence yield per unit volume of the reaction).

The inlet volumetric flow rate of methane was kept constant at 13.8 sccm, while the volumetric flow rates of oxygen were varied from 19.7, 22.5, 25.3, to 28.1 sccm for parts (a), (b), (c), and (d) of Figure 5.9, respectively. The corresponding average exit velocity for the methane jet was 4.82 m/s, and the average velocities for the oxygen jets were 6.87, 7.85, 8.83, and 9.82 m/s. The Reynolds numbers evaluated using gas properties at 300 K and the hydrodynamic diameter of the rectangular inlet port are 93, 106.3, 119.6, and 132.9 for the four oxygen flow rates and 63.9 for the methane jet. As the flow rate for the oxidizer is increased, it can be clearly seen in Figure 5.9 that the spectral peaks shift toward the fuel side. The emission intensities of CH* at around 431 nm were enhanced as the oxidizer flow rate increased from 19.7 to 25.3 sccm, but begin to decrease as the oxidizer flow rates were further increased. This is due to the fact that at 13.8 sccm methane and 25.3 sccm oxygen, the reactants are almost fully consumed. There are relative fewer possibilities of quenching reactions by excessive O₂ and CH₄ molecules to occur.
Figure 5.10 shows the location of maximum CH\textsuperscript{*} emission intensities and the full width at half maximum for a methane flow rate equal to 13.8 sccm. The CH\textsuperscript{*} emission intensity is evaluated by summing the intensity values obtained on each strip between 426 and 436 nm. This wavelength region corresponds to the Q-branch emission of the CH\textsuperscript{*} A\textsuperscript{2}\Delta – X\textsuperscript{2}\Pi (0,0) transition. The locations of the CH\textsuperscript{*} emission maxima change linearly with oxygen flow rates until the flow rate reaches 27 sccm, at which point, the maxima location remains nearly constant. The flame width is the narrowest when the oxygen flow rate is approximately 20 sccm and increases as more oxygen is injected. The full width at half maximum can be considered as the flame width [199].

Figure 5.9: Intensity maps of the diffusion flame along the centerline (x = 0, y = 0).
Intuitively, the flame width should decrease as the oxygen flow rate increases since the strain rate increases.

The variation of CH* intensity with respect to flow conditions is shown in Figure 5.11. For all three CH₄ flow rates investigated, the CH* luminescence first increases with the increase of the oxygen flow rate and then decreases. The enhancement of CH* chemiluminescence is due to the formation of steeper concentration gradients at the reaction front and consequently faster diffusive rates. Since diffusion controls the reaction rate, a faster production rate of CH* is achieved. But when the oxygen flow is further increased, an excessive amount of oxygen diffuses into the reaction zone not allowing sufficient time for reaction. Instead of acting as the reaction partner for C₂H to generate excited CH*, oxygen becomes a quenching molecule for CH* resulting in the decrease of chemiluminescence. The dataset corresponding to a CH₄ flowrate of 13.8 sccm shows that CH* intensity does not changes for O₂ flow rates above 28 sccm. The location of the reaction zone in this case is very close to the wall of the fuel side, the amount of oxidizer that can be convected into the reaction zone is probably limited by the wall viscous effect. Most of the oxygen is deflected and flows directly toward the exhaust ports before reaching the reaction zone.

Figure 5.10: Locations of the maximum CH* emission (431 ± 5nm) intensities and the full width at half maximum (FWHM) as CH₄ flow rate is kept at 13.8 sccm. The location of 0 corresponds to the oxygen side, while 1000 corresponds to the methane side of the reaction channel.

The variation of CH* intensity with respect to flow conditions is shown in Figure 5.11. For all three CH₄ flow rates investigated, the CH* luminescence first increases with the increase of the oxygen flow rate and then decreases. The enhancement of CH* chemiluminescence is due to the formation of steeper concentration gradients at the reaction front and consequently faster diffusive rates. Since diffusion controls the reaction rate, a faster production rate of CH* is achieved. But when the oxygen flow is further increased, an excessive amount of oxygen diffuses into the reaction zone not allowing sufficient time for reaction. Instead of acting as the reaction partner for C₂H to generate excited CH*, oxygen becomes a quenching molecule for CH* resulting in the decrease of chemiluminescence. The dataset corresponding to a CH₄ flowrate of 13.8 sccm shows that CH* intensity does not changes for O₂ flow rates above 28 sccm. The location of the reaction zone in this case is very close to the wall of the fuel side, the amount of oxidizer that can be convected into the reaction zone is probably limited by the wall viscous effect. Most of the oxygen is deflected and flows directly toward the exhaust ports before reaching the reaction zone.
A similar plateau is found for the low oxygen flow rate conditions of the 17.3 sccm CH₄ dataset. Here, the reaction zone is squeezed towards the oxygen side instead of the fuel side.

The overall characteristics of the counterflow flame are shown in Figure 5.12. The total intensity ratios of C₂* and CH* are plotted against the overall equivalence ratio of the reactants. The overall equivalence ratio is defined here by the mass flow rates of methane and oxygen into the reactor channel. C₂* intensity is quantified between 514.5 and 517.5 nm in order to capture the (0, 0) transition at 516.5 nm of the Swan band chemiluminescence. The overall intensities of C₂* are the summations over the 32 strips using intensity values in the quantification range for the overall equivalence ratios. The same approach was used to obtain the CH* overall intensities using intensity values between 426 and 436 nm. It is found that the C₂*/CH* ratio increases monotonically with the overall equivalence ratio between 1.0 and 1.3 for the three methane flow rates investigated. For equivalence ratios outside the range, the linear correlation fails. For higher equivalence ratios, the linear correlation fails probably because the transfer of C₂* chemiluminescence from (0, 0) transitions to higher order transitions like Δv= 1 and -1. The correlation also fails as the equivalence ratio goes below 1.0 for the 13.8 sccm CH₄ dataset shown in the figure; however, this might be because part of the flame is outside of the observable region.
of the spectrogram. The $\text{C}_2^*/\text{CH}^*$ correlation is slightly improved when the luminescence from $\Delta v = 1$ transitions is utilized for $\text{C}_2^*$ (see Figure 5.13). The intensities from wavelengths between 466 and 475 nm, which include (1, 0), (2, 1), (3, 2), (4, 3), (5, 4) and (6, 5) transitions, are used for the quantification. The $\Delta v = 2$ transitions of $\text{C}_2^*$ located around 438 nm are difficult for quantification because the peaks are partly overlapped by the P branch of $\text{CH}^*$ A-X (0, 0) transitions.

Figure 5.12: The ratio of overall $\text{C}_2^*$ to $\text{CH}^*$ intensities grows linearly for overall equivalence ratios between 1.0 and 1.3 when CH$_4$ flow rate is at 13.8 sccm.

Figure 5.14 shows the spatial distribution of $\text{CH}^*$ and $\text{C}_2^*$ intensities as well as the corresponding local $\text{C}_2^*/\text{CH}^*$ ratios. The $\text{CH}^*$ intensities and the $\text{C}_2^*$ intensities are quantified using the same criteria as in Figure 5.12. The methane and oxidizer flow rates for the case shown are 13.8 and 22.8 sccm, respectively. The FWHM of the $\text{CH}^*$ profile is slightly larger than that of the $\text{C}_2^*$. The largest intensity of $\text{C}_2^*$ luminescence falls slightly towards the fuel side compared to the maximum intensity for $\text{CH}^*$, which is consistent with the results of the numerical simulation shown in Figures 5.6(a) and (b). In general, $\text{C}_2^*/\text{CH}^*$ declines as the measuring region moves toward the oxygen side.
The full width at half maximum of the CH\(^+\) and C\(_2\)^+ profiles are plotted in Figure 5.15 as a function of strain rate. The C\(_2\)^+ chemiluminescence is quantified for two transition modes: \(\Delta v = 0\), and \(\Delta v = 1\). The quantification region for \(\Delta v = 0\) is between 508.5 and 517.5 nm, which covers the (0, 0), (1, 1), and (2, 2) transitions of the Swan band of C\(_2\)^+ emission. The \(\Delta v = 1\) region is the same as that in Figure 5.13. The strain rate is defined as the mean of the methane and oxygen flow rates divided by the width of the reaction channel. The strain rates are increased by proportionally increasing both the methane and oxygen flow rates. The figure shows that the widths of luminous CH\(^+\) and C\(_2\)^+ increase with the strain rates. This might be the result of better mixing due to the larger injection velocities (strain rate), which expand the width of the reaction zone.

Figure 5.13: The overall intensity ratios of C\(_2\)^+ (\(\Delta = 1\))/CH\(^+\).
An interesting comparison could be made between the current data and the data shown in Ref. [199, 200], which equal volumetric flow rates of 23% methane in nitrogen and 23% oxygen in nitrogen were fed into a Wolfhard-Parker slot burner with 14 mm exit diameters and the exits were spaced 13 mm apart. The flame thickness, defined as the FWHM of the temperature profile, was found to correlate inversely with the square root of strain root, i.e., the higher the strain, the thinner the flame. In contrast, the flame width, which is defined as the FWHM of the CH* profile, increase with strain rate. This is primarily due to the fact that the peak temperature in a diffusion flame does not vary significantly with the volumetric flow rates of the reactants (strain rate), but the peak CH* intensity does.

Figure 5.14: The intensities distributions of CH* and C2* across the flame. The methane and oxidizer flow rates are 13.8 and 22.8 sccm, respectively.
However, if the peak temperature/intensity to FWHM ratio is compared, both the millimeter thick CH$_4$/O$_2$/N$_2$ diffusion flame studied in Ref. [200] and the current sub-millimeter sized CH$_4$/O$_2$ flame have the same trend as shown in Figure 5.16. The ratio goes up with increasing strain rates, which means that the temperature and concentration gradients become steeper as the strain rate increases.

Figure 5.15: Full width at half maximum values for CH$^*$, C$_2$*(Δν = 0), and C$_2$*(Δν = 1) under different strain rates.
Summary

In this chapter, microscale counterflow diffusion flame burners were built using the low temperature co-fired ceramic technology. Sapphire windows that provide gas seal and optical accessibility into the reaction channels were successfully co-fired with the LTCC tapes. Micro diffusion flames with a luminous zone of approximately 250 μm in width and 1 mm in length were stabilized in the reaction channel. The flame structure observed was consistent with the distributions of the CH* and C2* luminescence revealed by three dimensional numerical simulation with detailed chemistry.

Microscopic imaging spectroscopy was utilized to study the structure of microscale counterflow diffusion flames. The results show that for a constant fuel flow rate, the CH* intensity increases initially with increasing oxidizer flow rate due to the enhancement of the diffusive rate, but later decreases as the rate of oxygen diffusing into the reaction zone is too fast to allow sufficient residence time for reaction. The intensity ratio between C2*(Δv=1) and CH*

Figure 5.16: The comparison of peak temperature/CH* intensity ratio versus strain rate.
chemiluminescence were found to be linearly correlated with the overall equivalence ratio of the reactant mixture between 1.0 and 1.4. C₂^*/CH* were also found to decline towards the oxygen side quasi-linearly with respect to the location of the measuring region. The study shows that the microscopic imaging spectroscopy technique is able to provide detailed species distribution information across a micro diffusion flame. Also shown is the feasibility of using LTCC tapes to build high temperature reactors.
CHAPTER 6
GASEOUS AND LIQUID REACTANT COMBUSTION IN SMALL VOLUMES

The flame characteristics of sub-millimeter scale non-premixed combustion were demonstrated in the previous chapter using burners with simple geometries. These burners, although helpful in understanding the flame dynamics in small scale, are not practical for most applications. For example, wider range of flow ratios with stable combustion is required for high thrust or power generation. Moreover, complete mixing of fuel and oxidizer is needed to achieve high efficiency and low emission in those applications. Better thermal management is also necessary. In macroscale combustion, flow recirculation has been used to extend flammability limits. At small scales, flow recirculation may be used to increase residence times of a portion of the flow, thereby enabling formation of high temperature reaction zones to stabilize the reaction in the remainder of the flow. In the present research, a vortex flow generating enthalpy and species recirculation was investigated. The vortex combustion chamber was based on an asymmetric whirl combustion concept [201], developed to improve the lean combustion performance in macroscale burners. Experimental characterization of the mesoscale combustor was performed with various types of reactants including gaseous, liquid/gas, and pure liquid monopropellants.

Asymmetric Whirl Combustion Concept

The asymmetric whirl concept, which demonstrates unusual stability characteristics at lean overall equivalence ratios, inspired the design of the current vortex meso scale combustor. In the asymmetric whirl concept, fuel is injected off-axis of a rotating air flow, which enters the combustor tangentially without an axial component (see Figure 6.1). The axial component is determined by mass conservation in which fresh mixture displaces the reacting mixture forcing it down the combustor axis. The air continues its rotating flow pattern by exiting tangentially at the opposite end of the combustor. Depending upon the exit location about the circumference, the
flow can continue in the same direction as the inlet flow or in a direction counter to the inlet flow. The concept introduces fuel and air separately; the danger and complexity of lean premixed combustion are avoided.

![Figure 6.1: (a) Schematics of the combustor configuration based on asymmetric whirl combustion concept and its operation in (b) symmetric and (c) asymmetric fuel injection mode. Shorter flame lengths are observed when the combustor was used in asymmetric fuel injection [201].](image)

The much higher swirl number, defined as the ratio of azimuthal momentum to axial momentum, of the whirl combustor distinguishes it from the conventional swirl combustors. Moreover, the whirl flames should have a relatively quiescent center, while swirl flames have been characterized by a vigorously burning central recirculation zone produced by vortex breakdown of the strong swirling flow. This feature is favorable for micro combustors since the hot quiescent center may serve as the enthalpy and radical source to sustain the reaction, and the cooler outer zone consists of un-reacted reactants protects the combustors wall from being damaged by the high combustion temperature.

**Combustor Construction and Experimental Setup**

A series of five millimeter-scale vortex combustors made of Inconel were fabricated by electro-discharge machining (EDM). The combustion volume ranged from 10.6 mm$^3$ for the smallest to 107.8 mm$^3$ for the largest (see Figure 6.2). Diameters of the injection and exhaust ports were scaled with the combustor length. Exact values of the combustor dimensions designed are listed in Table 6.1.
Figure 6.2: Meso scale vortex combustors made of Inconel using EDM.

Table 6.1: Dimensions of the micro vortex combustors.

<table>
<thead>
<tr>
<th>Combustor</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber volume (mm³)</td>
<td>10.6</td>
<td>25.1</td>
<td>49.1</td>
<td>84.8</td>
<td>107.8</td>
</tr>
<tr>
<td>Chamber diameter (mm)</td>
<td>2.38</td>
<td>3.18</td>
<td>3.97</td>
<td>4.76</td>
<td>5.16</td>
</tr>
<tr>
<td>Chamber length (mm)</td>
<td>2.38</td>
<td>3.17</td>
<td>3.97</td>
<td>4.76</td>
<td>5.16</td>
</tr>
<tr>
<td>Fuel port diameter (mm)</td>
<td>0.2540</td>
<td>0.3302</td>
<td>0.4064</td>
<td>0.5080</td>
<td>0.5080</td>
</tr>
<tr>
<td>Oxidizer port diameter (mm)</td>
<td>0.4064</td>
<td>0.5080</td>
<td>0.5842</td>
<td>0.7620</td>
<td>0.7620</td>
</tr>
<tr>
<td>Exhaust port diameter (mm)</td>
<td>0.5842</td>
<td>0.8382</td>
<td>1.016</td>
<td>1.1684</td>
<td>1.1684</td>
</tr>
<tr>
<td>Liquid fuel port diameter (mm)</td>
<td>0.3302</td>
<td>-</td>
<td>0.4064</td>
<td>-</td>
<td>0.508</td>
</tr>
<tr>
<td>Outside length of the</td>
<td>7.94</td>
<td>8.73</td>
<td>9.53</td>
<td>10.32</td>
<td>10.72</td>
</tr>
<tr>
<td>combustor cube (mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.3 shows the configuration of the combustor. The fuel is injected perpendicularly to the tangentially injected oxidizer and exits the combustion chamber tangentially. Although the fuel jet enters the combustor radially inward instead of down the length of the combustor like the macroscopic whirl combustor prototype, the fuel jet still intersects the tangential air jet immediately upon the separate flows entering the combustor. As the reacting flow whirls downstream to the exhaust, the centrifugal force drives cold flow with higher density to the wall, and the lighter hot flow to the core. This flow pattern and temperature stratification result in a lower temperature flow that protects the Inconel combustor body from achieving too high a temperature since the flame temperatures of both hydrogen and hydrocarbon combustion may far exceed the melting point of Inconel (~1700K). Meanwhile, the flame is stabilized by a low-pressure trough along the centerline of the combustor predicted by the Rayleigh criterion. The center core acts as a source of enthalpy and radicals.
During the experiment, the reactant mixtures are ignited by either a glow or a spark igniter located in the center of the combustor. When taking core temperature measurements, an end port cap replaces the sapphire observation window on the combustor. Figure 6.4 is a schematic representation of the test rig. The cooling water heat exchanger was only installed during methane/enriched oxygen experiment to protect the exhaust tube from being melting and oxidation by the high temperature exhaust gases. Moreover, it also helps to quench the high temperature methane oxidation reaction at the exhaust port so that the combustion efficiency is better evaluated. Gas flow rates were regulated with commercial mass flow controllers (Hastings, HFC-202). For oxygen enriched air experiments, oxygen and nitrogen were premixed at the desired ratio before being injected into the combustion chamber through the oxidizer port. Temperatures were measured with N Type thermocouples with sheath diameter 0.01” (Omega). Combustor pressures were measured with a piezo-resistive pressure transducer (Omega, PX-176). Hydrogen (99.5 % purity), methane (99.5 % purity), oxygen (99.5 % purity), dry air and nitrogen (99.9 % purity) were supplied by compressed gas cylinders.
A Fourier transform infrared spectrometer and a gas chromatograph described in Chapter 4 were utilized for emission measurements. The FTIR (ThermoNicolet, Nexus 670) was used to obtain absorption spectra from the methane/oxygen enriched air combustion products. The cell path length was 10 cm with a volume of 100 cm³. The exhaust gas from the combustor was kept above the saturation vapor temperature of the water vapor in the transmission line and the FTIR gas cell. The resolution of the acquired spectrum was 0.5 cm⁻¹. In order to obtain concentration measurements from gas molecules that lack permanent dipole moments, such as hydrogen, oxygen, and nitrogen, the gas chromatograph (Agilent, 3000 MicroGC) was used. The carrier gas was argon for both columns and the column temperature was set at 130 °C. The parameters used to sample and quantify exhaust species during hydrogen/air combustion are listed in Table 4.1. A thermocouple was installed at the entrance of the GC using a cross fitting to monitor the gas temperature. The exhaust gas was kept above 100 °C by wrapping heating rope and insulation around the tube to prevent water condensation on the tube wall.

**Hydrogen/Air Combustion**

Figure 6.5 shows the line-of-sight integrated OH* distribution of hydrogen/air combustion in the 107.8 mm³ combustor. The chemiluminescence pictures were taken with an intensified CCD camera (PI-MAX, UNI-GEN III) coupled with extension bellows and UV macro lens (Nikkor UV f/4.5). A 306 nm filter was aligned between the combustor observation window and the camera lens. The filter has a FWHM of 10 nm, and is able to pick up the strong (0, 0) vibrational transition of the \( \text{A}^2\Sigma^+ - \text{X}^2\Pi \) transition of the excited OH* radicals. The ICCD camera was in the gated mode, and the gating time was 10 ms. Gain of the photo-intensifier was set at 128. No background subtraction was applied for the pictures shown. The hydrogen was injected from the right of the figure, while the air stream came into the cylindrical combustion chamber from the top right side of the figure. The exhaust gas left the chamber from the opposite end of the combustor as the arrow shown on the top left side of the figure. The rotational flow is evident from the general shape of the OH* emission.
The short reaction zones of hydrogen/air as indicated by the OH* emission suggest that the residence time is sufficient for complete combustion in a volume of 107.8 mm$^3$. The results confirm the prediction of a three-dimensional numerical simulation [202] of an identical combustor design using a one-step hydrogen/air reaction mechanism. The three figures show the effect of the hydrogen and air volumetric flow rates on the reaction zones. The luminosity of OH* emission becomes less intense as the air flow rate was decreased from 1.69 L/min (see Figure 6.5(a)) to 0.94 L/min (see Figure 6.5(b)), although the amount of fuel injected was kept constant. This phenomenon is probably due to the weaker mixing between reactant streams as the inlet Reynolds number of the oxidizer decreases from 5844 to 3250, estimated using the cold flow kinematic viscosity. The reaction zone therefore becomes less concentrated and diffuses across a larger region. Figure 6.5(c) is the OH* chemiluminescence of the combustion with 0.15 L/min hydrogen and 0.94 L/min air. The figure shows that the reaction zone not only become less intense but shorter as both the fuel and oxidizer flow rates decrease since the flow residence time increases.
The flammability limits for hydrogen-air mixtures were obtained for three different combustion volumes of 10.6, 49.1, and 107.8 mm$^3$. Figure 6.6 shows the results for the 49.1 mm$^3$ combustor as a function of total mass flow rate. The overall equivalence ratio at the lean blow-off limit is around 0.25, whereas the rich limit varies from 3 to 6 depending on the reactant flow rate. The existence of the flame front was determined by temperature measurements with thermocouples located at the head-end center and exhaust port of the combustor. Results were confirmed independently by OH$^*$ emission measurements. The OH$^*$ emission measurements were accomplished by focusing the emission from the combustion volume onto a photodiode. The focusing lens was a 50.4 mm biconvex fused silica lens. The same filter used for OH$^*$ chemiluminescence visualization in Figure 6.5 was installed in front of the photodiode. The uncertainty of the measured blow-off limits are ±0.05 due to hysteresis effects in approaching the limits, the perturbation effects on the flame location by the presence of the thermocouple probe, and to the low intensity of OH$^*$ emission near extinction. It is worth noting that a piercing humming noise took place before blown-off occurred.

Figure 6.6: The operating space of hydrogen/air combustion in the 49.1 mm$^3$ combustor.
Figure 6.7 shows a typical gas chromatograph chromatogram output for hydrogen/air combustion. The equivalence ratio was 0.67, and the air mass flow rate was 0.2g/s for the case shown. No hydrogen peak was detected for the condition suggesting the complete conversion of hydrogen fuel into water vapor. Figures 6.9, 6.8, and 6.10 show the combustion efficiency of the combustor with chamber volumes of 10.6, 49.1, and 107.8 mm$^3$, respectively. For fuel lean cases, the combustion efficiency can be defined as the percentage of the H atoms that exist in water vapor, which is the reaction product for complete combustion of a hydrogen and air mixture,

$$\eta = \frac{[H_2O]}{[H_2] + [H_2O]} \times 100\% .$$

(6.1)

The quantity of the combustion product was decided by gas chromatography measurement. No species other than H$_2$, O$_2$, N$_2$, and H$_2$O were observed in the chromatograms. The results further reveal that over 97% of H$_2$ can be efficiently converted into H$_2$O in the vortex combustor for overall equivalence ratio above 0.4. In the lower equivalence ratio region, the combustion efficiency decays quickly and no stabilized flame can be sustained when the overall equivalence ratio is smaller than ~0.25 for flow rates investigated.
Figure 6.8: Chemical efficiencies of hydrogen/air combustion in the 49.1 mm$^3$ vortex combustor operating.

Figure 6.9: Chemical efficiencies of hydrogen/air combustion in the 10.6 mm$^3$ vortex combustor operating.
Figure 6.11 shows the chemical efficiency of the three combustors. The total mass flow rate is 0.02 g/s for each combustor. The chemical efficiency for hydrogen/air combustion is

Figure 6.10: Chemical efficiencies of hydrogen/air combustion in the 107.8 mm³ vortex combustor operating.

Figure 6.11: Comparison of the chemical efficiencies of hydrogen/air combustion in the 10.6, 49.1, and 107.8 mm³ micro combustors. The total flow rates was 0.02 g/s.
defined as the ratio of the measured water vapor concentration to the summation of unburned hydrogen and water vapor concentrations in the product as shown in Equation 6.1. Complete combustion was achieved in all three combustors when the overall equivalence ratio exceeds 0.4. The 49.1 mm$^3$ combustor gives a slightly larger operating space as the lean extinction limit is approached compared to the other two combustors. In these experiments, identical reactant flow rates were used for each combustor. Although the residence time was highest for the largest combustor, it also experienced the greatest heat loss. The residence time of the 10.6 mm$^3$ combustor was the smallest (~ 0.2 ms) and therefore least efficient in chemical conversion. Consequently, the 49.1 mm$^3$ was a compromise between the largest combustor with the greatest heat loss and the smallest combustor with the shortest residence time.

![Figure 6.12](image)

Figure 6.12: Chemical efficiencies and temperatures of hydrogen/air combustion in the 107.8 mm$^3$ and 49.1 mm$^3$ combustors operating under identical flow residence time.

Figure 6.12 shows the combustion performance of the 107.8 mm$^3$ and 49.1 mm$^3$ combustors operating at the same residence-time and power-density condition. The flow residence time, evaluated using the measured temperature, is approximately 2 ms. The total mass flow rates for the two combustors are 0.02 and 0.01 g/s, respectively. The two combustors have similar chemical efficiencies as well as the temperatures measured inside the combustor after scaling the chemical power input with the combustion chamber volume. The temperatures (not necessarily the maximum) were measured at the head-end on the center-line of the combustor
approximately 0.3 diameter into the chamber. The reason why the measured temperature is not necessarily the maximum is because the flame location is likely more close to the rim as shown in the chemiluminescence pictures in Figure 6.5 than to the middle of the combustor where the thermocouple was located. The delivered chemical power output under the conditions shown in Figure 6.12 covers a range of 20-50 W.

Figure 6.13: Temperatures measured in the micro combustors comparing with the adiabatic flame temperatures and the temperatures of a perfectly stirred reactor.

Figure 6.13 shows the temperatures measured for a range of equivalence ratios from 0.2-0.6. The temperature for the 49.1 mm$^3$ combustor increases from 981 to 1319 K as the overall equivalence ratio increases from 0.3 to 0.5. Also included are the adiabatic flame temperatures and the outlet temperature of a perfectly stirred reactor (PSR) with chamber volume of 10.6 mm$^3$. The latter may provide a more reasonable benchmark for comparison since it takes into account the finite rate combustion kinetics as well as the thermal exchange of hot products with cold incoming reactants. Various definitions of thermal efficiency can be found in the literature [52, 203] depending on the way in which the generated thermal energy is utilized. For example, for a heater and a thermal-photovoltaic power generator, the usable thermal energy is regarded as the portion that is transferred through the wall, whereas this is generally considered as heat “loss” for applications where high sensible energy is desired in the exhaust gas. In the present study, the thermal efficiency is defined as the ratio of the sensible energy in the combustion products to the
total chemical power input. Such a definition is more suited for power plants or micro propulsion systems. It can be written mathematically in the following form:

$$
\eta_i = \frac{\sum_k \dot{m}_k c_{p,k} (T_c - T_i)}{\sum_i \dot{m}_i h_{c,i}} \times 100\%
$$

(6.2)

where $\dot{m}_i$ and $h_{c,i}$ are the mass flow rate and heat of combustion of reactant species $i$, respectively, and $\dot{m}_k$ is the mass flow rate of species $k$ in the product. The constant-pressure heat capacity of species $k$, $c_{p,k}$, is evaluated at the measured temperature, $T_c$, and the inlet temperature $T_i$ is set at 298K. The thermal efficiencies for the 49.1 mm$^3$ combustor were estimated to be 62 % and 58 % for $\phi = 0.3$ and 0.5. Their counterparts for the 107.8 mm$^3$ combustor were 40 % and 32 %, respectively. No temperature measurements were conducted in the 10.6 mm$^3$ volume due to the space constraints for installing thermocouples. As mentioned above, the measured temperatures were not necessarily the combustor average temperatures. Furthermore, attempts control thermal losses were not considered, and consequently, thermal efficiencies were low while the chemical efficiencies were high.

**Hydrocarbon Combustion**

Combustion of hydrocarbon fuels in chamber volumes of tens of cubic millimeters is known to be challenging. The residence time required for efficient energy conversion is on the order of milliseconds, which is the same order as the characteristic chemical time for hydrocarbon/air combustion at room conditions. Methane and propane combustion with air was found more difficult as the combustor volumes were reduced. Self-sustained propane/air and methane/air flames were successfully stabilized in the 124 mm$^3$ combustor. However, stable methane combustion could only be achieved at atmospheric pressure in the smallest 10.6 mm$^3$ volume combustor by means of oxygen enrichment of the air.
Efforts were also applied to characterize the chemical efficiency and flame stability from hydrocarbon air systems. Figure 6.14 shows the front view of a propane/air flame with an overall equivalence ratio, $\phi$, of 0.8. The chamber volume is 124 mm$^3$. The flame exhibits a luminous blue ring with a non-luminous core. The quenching distance is approximately 0.5 mm. The flame becomes bluish-green for fuel-rich mixtures. Under no conditions did the flame have a yellow emission characteristic of soot formation. Furthermore, carbon deposits were not observed on the inside of the chamber surface. The absence of soot formation suggests that the temperature inside the combustion zone was under 1650 K [195]. As inferred from the numerical calculations, the swirling flame structure observed herein results from the injection of fuel into the region of the highest kinetic energy of the whirling air flow, thereby producing rapid fuel-air mixing. The resulting flow produces a central hot combustion product core and a spinning outer flame zone.

Figure 6.14: Propane/air combustion in the 124 mm$^3$ vortex combustor.
Figure 6.15 shows a typical flame structure of the methane/oxygen-enriched-air system in the 49.1 mm$^3$ combustor. The oxidizer contains 50% nitrogen and 50% oxygen, and the overall equivalence ratio is 0.3. A luminous blue swirling flame rotating along the chamber is clearly observed. The higher luminous zone intensity comparing with the propane/air flame was a result of more vigorous reactions of the higher oxygen concentration in air. The two bright spots in the center are caused by radiation from the spark igniter. Platinum glow-igniters were melted routinely, suggesting that the temperature at the combustor core might exceed the melting point of platinum, which is above 2000 K.

Figure 6.16 shows some of the other flame structures observed in the 10.6 mm$^3$ combustor. In Figure 6.16(a), pure oxygen is used as the oxidizer, and a tiny blue diffusion flame is stabilized right at the fuel inlet, indicating that chemical reaction rates are fast, and mixing controls the combustion process. The U-shaped structure near the combustor center is caused by radiation from the igniter. Figure 6.16(b) shows that the reaction zone expands as nitrogen is added to the mixture, which results from a lower flame temperature and hence slower kinetics relative to its mixing ratio of the reactants. As shown in Figure 6.16(c), the reaction becomes more vigorous and engulfs the entire volume as the overall mixture equivalence ratio is increased.
Figure 6.17 shows the effect of total mass flow rate on the lean and rich blow-off limits for the propane/air system in the 124 mm$^3$ combustor. The limits appear to increase with increasing flow rate. At a total mass flow rate of 0.2 g/s, the lean and rich blow-off limits occurred at equivalence ratios of approximately 0.4 and 1.6, respectively. The corresponding flammability limits for well-mixed propane in air are 0.56 and 2.7, respectively. The difference of flammability between the present combustor and a premixed system suggests that stratification remains in the mixture during combustion. The measured temperatures in the flow core region along the centerline are approximately 1500 K for an equivalence ratio of 0.75 (see Figure 6.18).
Figure 6.17: Operating space of propane/air combustion in the 124 mm$^3$ micro combustor.

Figure 6.18: Measured temperatures at the inlet and exit ends of the combustors operating with propane/air.
In the present research, only exhaust gas composition of the vortex combustors fueled with methane were obtained. Measurements were conducted using the FTIR analyzer to obtain absolute concentrations. Since no other carbon containing species except CO₂, CO, and unburned CH₄ were observed in the FTIR spectra under fuel-lean conditions, the chemical efficiency of methane combustion was defined as the ratio of the measured concentration between carbon dioxide and all carbon-containing species. The CO and unburned CH₄ concentrations were generally higher for lower oxygen enrichment. Quantitative analysis was applied to the spectrums to obtain absolute concentrations. A chemical combustion efficiency can be defined as

\[
\eta = \frac{[CO_2]}{[CO_2] + [CO] + [CH_4]}
\]  

(6.3)

where the terms on the right hand side of the equation are the mole concentrations of CO₂, CO, and CH₄. The settings of the FT-IR are given in Table 4.3.

Figure 6.19: The temperatures in the middle of the combustion chamber, on the combustor surfaces at the side of the auxiliary fuel port, and the side of the water cooled exhaust tube for methane and oxygen enriched air (80% oxygen, 20% nitrogen) mixture in the 107.8 mm³ combustor.

Figure 6.19 shows the temperatures at four different locations inside and on the surface of the 107.8 mm³ combustor. The temperature inside of the combustor was measured with an R type thermocouple inserted in the middle of the combustor. Temperatures at the inlet end and the outlet end were measured separately by changing the insertion length of the thermocouple. E type
thermocouples glued on the outer surface of the Inconel combustor using high temperature ceramic adhesives were utilized for surface temperature measurements. Methane concentrations from approximately 5 % to 40%, which corresponds to overall mixture equivalence ratios from 0.3 to 1.5 for the 80% oxygen and 20% nitrogen oxygen enriched air mixture, were investigated. It should be noted that the temperature readings have not been corrected for the radiation heat lost and catalytic reactions taking place on the platinum thermocouple wires. The total flow rate of the fuel and oxidizer flow was kept constant at 1000 sccm for all cases.

For equivalence ratios below approximately 0.3 and near the rich blow off limit, tiny blue diffusion flames were found to be stabilized right outside the fuel inlet as shown in Figure 6.16(a). The localized reaction is reflected in the low temperatures measured by both the R thermocouple in the middle of the chamber and the E thermocouple on the auxiliary fuel port side wall. Flames with overall mixture equivalence ratios from 0.3 to 0.8 appeared as spinning rings and the temperature readings of the thermocouple in the middle of the chamber were independent of equivalence ratio. As the equivalence ratio approached stoichiometric, a bright red core was observed. The temperature on the outer surface of the combustor at the exhaust side ($T_e$) was lower than that at the auxiliary fuel port side primarily due to the cooling effect of the water heat exchanger installed on the exhaust tube.

![Temperature vs. Methane Concentration](image)

Figure 6.20: The temperature in the middle of the 107.8 mm$^3$ combustion chamber operating with 100% oxygen as oxidizer. The total flow rates were approximately 1000 sccm.
Comparison of the temperature readings in the middle of the combustor with 80% oxygen and 100% oxygen was shown in Figure 6.20. The temperature profiles peak at approximately 33% methane, which is the stoichiometric concentration for methane/oxygen combustion. The peak temperature is nonetheless much lower than the adiabatic flame temperature. The reason could be due to both the uncorrected thermocouple readings, the relative locations of the thermocouple probe and the flame zone, and the excessive heat loss of the combustor.

![Graphs showing CO₂, CO, and CH₄ concentrations vs. CH₄ concentration](image-url)

Figure 6.21: Effect of oxygen concentration on (a) CO₂, (b) CO, and (c) CH₄ emission from the 107.8 mm³ combustor operating with methane and an oxidizer consisting of 50% O₂ and 50% N₂ (square), and 33% O₂ and 67% N₂ (circle). The total flow rates were 1000 sccm.
Figure 6.21 compares the concentrations of CO$_2$, CO, and CH$_4$ quantified using FTIR spectra obtained from the combustion products of methane/oxygen enriched air mixtures. The combustor utilized was the one with a 107.8 mm$^3$ chamber volume. The oxygen enrichment of the air was 50% and 33% oxygen, shown as open square and circle symbols, respectively, in the figure. The results show that the combustion was effectively enhanced with larger concentrations of O$_2$ in the oxidizer. The unburned methane was lower than 1000 ppm for all cases investigated as the air was enriched to 50% oxygen.

Figure 6.22: The effect of oxygen concentration in the oxidizer on the combustion efficiencies.

Figure 6.22 is the combustion efficiencies calculated using Equation 6.3 based on the concentrations of carbon containing species measured. The total flow rates for the measurements shown in the figure were kept constant at 1000 sccm for both 33% and 50% oxygen enrichment. Better combustion efficiencies were obtained as the air was enriched to 50% oxygen, comparing with the efficiencies with 33% oxygen. The trend shows that oxygen enrichment can effectively enhance the combustion kinetics such that the chemical time scale is reduced to a level that
complete combustion can be achieved. In other words, flow residence times for the flow condition applied were insufficient for complete combustion in the 49.1 mm$^3$ combustor.

Figure 6.23 shows the chemical efficiencies of methane/oxygen enriched air combustion in the 49.1 and 10.6 mm$^3$ combustors. The oxidizer consists of 40% oxygen and 60% nitrogen.

Figure 6.23 shows the chemical efficiencies of methane/air combustion with oxygen enrichment in the 10.6 and 49.1 mm$^3$ combustors. The oxidizer mixture contains 40% O$_2$ and 60% N$_2$, and the total mass flow rate remained constant at 1000 sccm (0.02 g/s). As expected, efficiency is lower for a smaller volume due to the shorter flow residence time. The efficiency was also lower than those for 50% oxygen enrichment in the 107.8 mm$^3$ combustor shown in Figure 6.22, but higher than the cases with 33% oxygen. The delivered chemical output from the 10.6 mm$^3$ combustor ranged from approximately 25 to 174 W. The residence time for the flow rate evaluated at standard conditions was approximately 0.6 ms. With stable combustion, the results of Figure 6.23 show that good chemical efficiencies are attainable in the smallest combustors with hydrocarbons which were even higher in the larger combustors.
Operation with Liquid Nitromethane

To take full advantage of the high specific energy of hydrocarbon fuels, liquid phase storage and operations are necessary. At the macro-scale, liquid fuels are typically sprayed into a combustor as droplets to enhance the vaporization and the burning rate. For application to the microscale, sprays with small droplet diameters are required [2]. At the micro-scale, the feasibility of liquid fuel combustion by utilizing wall film evaporation was recently demonstrated in a 3.14 cm³ volume combustor [204, 205]. Sirignano et al. [204, 205] concluded that a 10 mm diameter combustor will have a film surface area comparable with a droplet spray having a 10 μm Sauter mean radius. Consequently, atomizers that are capable of producing sub-micron scale droplet may not be needed for liquid fuel combustion in meso and micro scale combustors. Wall film evaporation creates a favorably distributed temperature profile for the meso and micro scale combustors since the wall liquid film prevents heat losses while cooling the combustor surfaces. Thus, part of the increased heat loss due to the increased surface-to-volume ratio in small combustors is utilized for fuel film vaporization. In another approach, Liedtke and Schulz [206] proposed fuel film evaporation as a mechanism for fuel preparation by pre-vaporizing the liquid fuel by recovering thermal energy from the hot combustion products.

Since separate oxidizers are required for liquid hydrocarbon combustion, the diffusive time for mixing in addition to the times for evaporation and gas phase combustion have to be less than the limited residence time of the fuel and oxidizer mixture in the combustor. Unfortunately, the residence time for non-premixed gaseous hydrocarbon combustion in a meso-scale combustor with ~100 mm³ chamber volume at atmospheric pressure is often too short for complete combustion. To address the residence time issues and greater heat losses in small scale systems, the usage of liquid monopropellants, such as nitromethane, CH₃NO₂, and wall film vaporization was studied. In this case, the liquid reactant is injected tangentially into the combustion chamber to form a film along the surface of the combustor walls. This film may be used to cool the wall because of both endothermic liquid decomposition reactions and gasification, which can produce improved thermal management at the small scales. With the use of the monopropellant as the liquid fuel, mixing of fuel and oxidizer in the same phase or initially different phases is not necessary. The fuel liquid film is vaporized and decomposed by the heat release of the combustion of the decomposed reactants from the vaporized liquid fuel to generate a self-sustained flame in the meso scale combustor.
Liquid Nitromethane/Air Combustion

The combustor was adapted to liquid reactant flows as shown in Figure 6.24. The experimental setup includes the combustion chamber, the inlet and outlet, the exhaust heat exchanger, and the fuel syringe pump. In the figure, the liquid reactant is injected tangentially into the combustion chamber just as the bulk air flow was in the gaseous reactant systems. However, in this configuration, the liquid flow can form a film along the surface of the combustor walls. This film may be used to cool the wall because of both endothermic liquid decomposition reactions and gasification, which can produce improved thermal management at the small scales of the present system [204, 205]. Note that with the use of the monopropellant as the liquid fuel, mixing of fuel and oxidizer in the same phase or initially different phases is not necessary.

To investigate the capability to operate on liquid fuels, studies were initially conducted with the combustion chamber operating on liquid nitromethane and a small amount of oxygen at atmospheric pressure (1 atm). Liquid nitromethane is injected tangentially along the wall of the combustion chamber. In the same direction, but on the opposite side of the combustor, a small amount of gaseous oxygen is also injected tangentially. Three different mass loadings of nitromethane (80, 89, and 94% by volume) with constant oxygen flow rate have been investigated. The chemical energy into the system increased from 70, 100, and 160 W. In all three cases, the combustion temperature and flow field are essentially determined by the nitromethane alone. Thermodynamically, if the oxygen is eliminated from the mixture with 94% nitromethane, predicted flame temperatures decreased from ~ 2520 to 2400 K. Ignition is achieved by first igniting a methane-oxygen pilot flame and then adding liquid nitromethane while removing methane until all the methane is eliminated from the mixture. An example of the resulting flame is shown in Figure 6.25 and is dominated by the combustion of nitromethane as is evident by the yellowish, bright-white emission from the flame. As in the combustion of the gaseous hydrocarbon/air mixtures, no soot or carbon deposits were observed to form on the surfaces. Much of the liquid nitromethane appeared to be vaporized shortly after being injected into the chamber. At atmospheric pressure, combustion with nitromethane alone was not achievable.

Nitromethane, CH₃NO₂, is a monopropellant that is relatively unreactive at one atmosphere in an inert environment. The need for the small amount of oxygen at one atmosphere
can be understood by looking at its combustion kinetics relative to that of a hydrocarbon-oxygen system. The most important steps to nitromethane combustion are as follows:

\[
\begin{align*}
\text{CH}_3\text{NO}_2+\text{M} & \rightarrow \text{CH}_3+\text{NO}_2+\text{M} \\
\text{CH}_3+\text{NO}_2 & \rightarrow \text{CH}_2\text{O}+\text{NO} \\
\text{CH}_2\text{O}+\text{M} & \rightarrow \text{CH}_2\text{O}+\text{H}+\text{M} \\
\text{H}+\text{NO}_2 & \rightarrow \text{NO}+\text{OH} \\
\text{OH}+\text{CH}_3\text{NO}_2 & \rightarrow \text{H}_2\text{O}+\text{CH}_2\text{NO}_2 \\
\text{CH}_2\text{NO}_2+\text{M} & \rightarrow \text{CH}_2\text{O}+\text{NO}+\text{M} \\
\text{CH}_2\text{O}+\text{OH} & \rightarrow \text{HCO}+\text{H}_2\text{O}
\end{align*}
\]

Figure 6.24: Experimental setup for liquid nitromethane/air combustion experiments.
Unlike hydrocarbon oxidation which has significant chain branching due to the presence of molecular oxygen (via. \( \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \)), no equivalent branching reactions occur in the nitromethane system. The main source of radicals is through pressure dependent dissociation reactions. Consequently, at low pressures, nitromethane kinetics are rather slow, but accelerate dramatically with pressure. Because of chain branching in hydrocarbon systems, reaction rates at low pressure can be fast and do no increase as much with pressure as in the case of nitromethane, which is often used to fuel racecars because of the strong dependence of kinetic rates on pressure. Note when nitromethane is burned in race cars, oxygen from the air is still used as an oxidizer. This is because nitromethane by itself is extremely fuel rich, with an equivalence ratio of 1.75. In the present experiments, the little amount of oxygen added to the system provides the initiation chain branching necessary at low pressure to achieve stable combustion. This added oxygen can be eliminated from the system by simply operating at higher pressures.

Figure 6.26 shows the effect of combustion pressure on the ignition delay of pure nitromethane compared to the effect of adding oxygen using CHEMKIN [207] simulation. The result shows that the enhancement of reaction branching by adding oxygen reaches an asymptotic
value at around 10% oxygen addition. The reduction of ignition delay by increasing the combustion pressure is equivalent to that by adding oxygen as the pressure is increased above 20 atm.

High Pressure Liquid Nitromethane Combustion

The experimental system is shown in Figure 6.27. A needle valve was utilized at the exhaust port of the combustor to regulate the chamber pressure. A commercial high pressure syringe pump (Harvard Instruments, PHD 4400) was used for liquid nitromethane injection. A 2 mm thick sapphire window capable of withstanding pressure up to 400 psig was installed on the combustor for the visualization experiments. The window was replaced with an end cap with a thermocouple port when temperature measurements were conducted. The chamber pressure was regulated manually with the needle valve on the exhaust tube and monitored by a pressure
transducer (Setra, Model 207). Ignition is achieved by first igniting a hydrogen-air flame. Liquid nitromethane is then added while closing the back-pressure valve to increase the chamber pressure up over 100 psig. The hydrogen is then shut off. Air was removed gradually as the flow rate of nitromethane and the chamber pressure were increased to the desired values. The mass flow rate of the liquid nitromethane can be controlled by the varying the feeding speed of the high pressure pump, while input gas flows were regulated by commercial mass flow controllers (Hastings, HFC-202). Hydrogen and air were shut off as soon as stable combustion was observed at pressures, meanwhile, flow rate of nitromethane was increased to compensate for the power input reduction by the removal of hydrogen air.

Figure 6.28 shows two typical operating sequences of the experiment. The temperature and pressure in the combustor as well as the evolution of the hydrogen and air flow rates during the run were recorded. The operating pressure in Figure 6.28(a) is slightly higher than that in Figure 6.28(b); as a result, less temperature fluctuations are recorded. The spike of air flow rate at the end of the experiment in Figure 6.28(a) is due to the purging of cold air for cooling down the combustor. Temperature surges in the early stage of the experiment as well as the dips during liquid nitromethane combustion in Figure 6.28(b) might result from insufficient pressurization in the combustion chamber. These surges and dips are not seen in higher pressure operations as shown in Figure 6.28(a).
Figure 6.28: The evolution of hydrogen, oxygen flow rates, the chamber temperature and the chamber pressure in the combustor during the nitromethane combustion at maximum pressures of (a) 280, and (b) 150 psig.
The exhaust products were diluted with helium (99.999%) and then analyzed by FT-IR (Thermo-Nicolet 670). The cell of the FT-IR was equipped with ZnSe windows and the optical path was 10 cm. The cell volume was 100 cm$^3$ and the temperature was kept at 130 °C. The resolution of the spectra acquired was 1 cm$^{-1}$. The experimental settings of the FT-IR are listed on Table 6.2. Figure 6.29 is an exemplary FTIR spectrum of 1.52 % vol. pure nitromethane vapor in argon (99.999%). Calibration of the nitromethane spectra was accomplished by analyzing known concentrations of different nitromethane/argon mixtures. The mixtures were prepared by passing ultra high purity argon gas through a bubbler filled with liquid nitromethane at different temperatures. The bubbler was half-submerged in a thermostat tank such that the temperature could be controlled. The temperature of the sample gas was monitored at the exit of the bubbler. The concentration of nitromethane in the sample stream was calculated at the corresponding temperature using an empirical nitromethane vapor pressure correlation [208].

Table 6.2: Configurations of FTIR for characterizing nitromethane combustion.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Numer of sample scans</td>
<td>8</td>
</tr>
<tr>
<td>Resolution (cm$^{-1}$)</td>
<td>1</td>
</tr>
<tr>
<td>Sample gain</td>
<td>4.0</td>
</tr>
<tr>
<td>Mirror velocity (cm/s)</td>
<td>0.6329</td>
</tr>
<tr>
<td>Aperture</td>
<td>34</td>
</tr>
<tr>
<td>Attenuator installed</td>
<td>A</td>
</tr>
</tbody>
</table>
The volume of the combustion chamber was 107.8 mm$^3$ (chamber diameter is 5.16 mm). The injection and the exhaust ports both intersect the circumference of the cylindrical combustion chamber tangentially but at opposite ends. The tangential inlet and outlet creates a swirling flow that is able to enhance gaseous combustion stability.

Figure 6.30 shows the combustion of liquid nitromethane at ~350 psi in the 107.8 mm$^3$ vortex combustor. Pressures mentioned throughout this section are gage pressures. In this picture, the liquid nitromethane entered the combustor through the top tube on the left hand side of the photograph at the back end of the combustor. Exhaust products exit the cylindrical combustion chamber tangentially at the front end through the tube shown on the bottom left side of the photograph. The mass flow rate of nitromethane was ~ 0.021 g/s, which corresponded to a linear liquid feeding rate of 10.2 cm/s in the injection port. Interestingly, the continuous yellowish-bright white flame recorded when a small amount of oxygen is added is no more observed. Instead, a very dim nearly uniform white emission accompanied with bright red-white emission from small particles (possibly soot), which form and rapidly disappear, is seen. The existence of soot indicates the temperature in the combustor might be well above 1650 K [195]. More effort
has to be made to clarify the mechanism and spectral emission for nitromethane at high pressures in the future.

As the pressure in the combustor was reduced, intermittent brownish white flames were observed more and more frequently, which finally turn into an oscillatory-like mode as the chamber pressure was decreased below 300 psig. A low pressure limit of ~ 500 psi has been observed for nitromethane burning rate measurements in a strand burner [209]. The current results show that stable combustion can be achieved in the vortex combustor at pressures as low as at least 260 psig. The extended burning conditions are likely due to preheat effects through both the combustor body and the recirculation zone in the chamber created by the swirl flow. At the highest pressures considered, the combustor body had a reddish emission indicating that the combustor body is likely above the vaporization temperature of liquid nitromethane at 374 K under normal pressures. At one atmosphere, the decomposition temperature of nitromethane is 520 K. Consequently, no liquid nitromethane is likely to exist in the combustor during high pressure conditions. During high pressure combustion, liquid was not visually observed within the combustor as it was with the atmospheric experiments and oxygen addition.

![Flame Oscillation Sequence in the Vortex Combustor](image)

Figure 6.31: The flame oscillation sequence in the vortex combustor. The mass flow rate of nitromethane was 0.0127 g/s.
The erratic evolutions of the flame zone for nitromethane combustion at lower injection flow rates as well as operating pressures are shown in Figure 6.31. Nitromethane was injected tangentially into the combustor from the lower right corner at a mass flow rate of 0.0127 g/s. The time interval between each frame is 33 ms. The frame sequence was randomly picked to show the unsteadiness of the visible flame zone. The periodicity of the evolution was not identified in the recorded clips obtained. The registered chamber pressure was ~ 330 psig. A similar intermittent bright brownish white flame was also observed for combustion at lower pressures but higher flow rates. Apparently, an energy balance between the generated heat and the heat feedback to evaporate and decompose the liquid nitromethane has to be reached for steady combustion. The vaporization energy required for evaporating 0.00127 grams of nitromethane is ~ 8 W, while the chemical energy input is ~ 144 W, which far exceeds the required energy for vaporization. However, the amount of energy that is able to contribute to the vaporization and decomposition is largely affected by the combustor configuration as well as the thermal distribution of both the reaction zone and the combustor body. The fluctuation of the flame zone at low injection flow rates might be due to the insufficient thermal feedback to generate a steady flow of decomposed gaseous nitromethane and consequently the reaction quenches intermittently. At high input flow rates and low operating pressures, the insufficient residence time for complete combustion might result in less energy generation that leads to similar effects as discussed above.

Figure 6.32 shows the FT-IR spectra acquired at steady-state operation with chamber pressures of 260 (17.7), 290 (19.7), 320 (21.7), and 350 (23.8) psig (atm). The mass flow rate of the experiment is maintained at 0.02 g/s, while the pressure was controlled by regulating the cross-sectional area at the choked orifice in the needle valve. Various hydrocarbon compounds, such as CH₄, C₂H₂, and C₂H₄ are found in the exhaust gas along with the major products, CO, CO₂, and water vapor, at the lower combustion pressures cases of 260 and 290 psig (see Figure 6.32(a) and (b)). Nitromethane was not found in the exhaust gas. The unburned hydrocarbons are almost totally undetectable as the pressure is increased (see Figure 6.32(d)).
Figure 6.32: The FTIR spectra of liquid nitromethane combustion in the 107.8 mm³ combustor at (a) 260, (b) 290, (c) 320, and (d) 350 psig.
Carbon in nitromethane is converted more efficiently to CO and CO$_2$ at higher pressures, while the existence of unburned hydrocarbons indicates incomplete combustion. Flow residence time can be increased by lowering the injection flow rate of nitromethane; however, the lower chemical input power might result in insufficient heat feedback to evaporate liquid nitromethane and decompose the vaporized reactant. Nitric oxide was also not found in the spectra indicating that most of the nitrogen in nitromethane was converted into molecular nitrogen, which is undetectable using infrared-red spectrometry due to the lack of a dipole in the diatomic molecule. Similarly, hydrogen, which is also a major product of nitromethane combustion, was not detectable using FTIR. Identification and quantification of these molecules can be obtained by further characterization of the combustion products using gas chromatography.

Figure 6.33 shows the predicted unburned hydrocarbon concentrations and temperatures at various chamber pressures in a perfectly stirred reactor (PSR) using CHEMKIN [207]. The mass flow rate and the combustion volume is the same as the experimental values at 0.02 g/s and 107.8 mm$^3$, respectively. The result shows that the unburned hydrocarbon concentration is almost zero as the pressure increases up to above 20 atm (279.3 psig). The chamber temperature also reaches an asymptotic value at around 2800K. The trends of these results are in agreement with our qualitative observations on the disappearance of unburned hydrocarbons in Figure 6.32 as the pressure is increased over 300 psig.
The calculation also suggests that the major unburned hydrocarbon species are methane and acetylene. However, the predicted methane concentration in the combustion products of the PSR calculation are less than the quantified values from the FTIR spectra, which are 3500, 2700, 700, and 600 ppm at 260, 290, 320, and 350 psig, respectively. The PSR model assumes the perfect mixing of the product and reactants such that the temperature is homogeneous in the combustor. In reality, the vortex combustor creates a temperature gradient along the radial direction and the injection of liquid nitromethane from one end of the cylindrical combustor and exit from the opposite end may generate a temperature gradient in the axial direction as well. The heat loss of the vortex combustor also contributes to the higher concentrations of unburned hydrocarbon compared to the PSR modeling predictions.

The mole concentrations of major carbon containing species are shown in Figure 6.34. The mole fraction of CO and CO₂ both increase slightly as the pressure goes up, while the mole fraction of CH₄, C₂H₂, and C₂H₄ decrease significantly and almost disappear as the pressure goes beyond 20 atm. Soot formation observed in the combustor is not included in the current nitromethane chemical mechanism, which consists of 35 species and 134 gas phase reactions. At the highest operating pressures reported here, the estimated total concentration of unburned
carbon in the measured hydrocarbons is well below 1 %, thus indicating very high chemical combustion efficiencies with liquid nitromethane.

![predicted temperatures and methane, ethylene, acetylene, carbon monoxide, and carbon dioxide concentrations of PSR calculation at various chamber pressures.](image)

**Summary**

The concept of asymmetric injection and vortex combustion has been successfully implemented and demonstrated to stabilize flames in small volumes ranging from 10.6 to 124 mm³. Both gaseous hydrogen and hydrocarbon (methane and propane) in air were treated. Methane was the most difficult to stabilize, but oxygen enrichment was found to be an effective approach to reduce the chemical time scale so that the relatively shorter flow residence time in the meso/micro scale combustors could be matched. With an enrichment level of 50% oxygen in air by volume, combustion efficiencies for the methane/oxygen enriched air were above 95%. Combustion efficiencies for hydrogen/air combustion in the mesoscale vortex combustors generally exceeded 97 %. 
Stable combustion of nitromethane in a combustor with 107.8 mm$^3$ volume was not found achievable at one atmosphere, although combustion can be self-sustained by enhancing the kinetic rates of reactions with the addition of a small amount of oxygen. Pressurization of the combustor had an equivalent effect as oxygen enrichment on flame stabilization due to the high sensitivity of nitromethane kinetic rates to pressure. Stable combustion in the vortex combustor was achieved at pressures higher than 260 psig, although various hydrocarbon compounds such as CH$_4$, C$_2$H$_2$, and C$_2$H$_4$ are found in the FTIR spectra of the combustion products at low pressures, suggesting incomplete combustion due to insufficient flow residence time. Complete combustion was achieved at chamber pressures above 350 psig. The chemical power input was ~ 230W for all the cases investigated.
CHAPTER 7

GASEOUS FLAME PROPAGATION IN SMALL CHANNELS

Vortex flows and oxygen enrichment were applied to accomplish steady-state meso scale combustion in Chapter 6. In addition, transient combustion may be another important approach for microcombustion applications. Many of the thermal management problems of microscale combustion can be overcome with a propagating flame. This can be understood by utilizing the simple scaling laws discussed in Chapter 2. The volume of combustion for a propagating reaction front scales with $L^2$ for a constant propagating velocity, instead of the $L^3$ dependence for steady-state systems. Thus, the surface-to-volume ratio becomes 1 for transient systems.

Numerical studies have shown that the laminar boundary layer generated by the laminar reaction front in a small tube (2.54 mm ID) can increase the flame propagation velocity exponentially [210, 211]. However, whether the effect can be experimentally observed, and the acceleration can be continued to detonation is unknown. At the macroscale, the compression due to hydraulic resistance has been considered as the mechanism for deflagration-to-detonation transition (DDT) [212-215]. Motivated by these theoretically and numerical studies, DDT in capillary tubes of stoichiometric ethylene/oxygen were examined in this chapter. A unique experiment where ignition by a spark or hot wire is used in the center of an open tube was implemented. This creates a symmetric boundary at the center with less heat loss than ignitions at the closed end of a tube. The gaseous reactant ignition and flame propagation all occur in the smooth circular capillary tubes with diameters as small as 500 μm.

Background

There appear to be no studies of DDT in microscale tubes (millimeter scale or smaller). Only some studies have been made of detonation limits and behavior in narrow tubes or gaps in which detonations are initiated in a large diameter tube before propagating into a narrow channel.
or tube [216-218]. These studies determine the critical gap for detonation to propagate successfully. Different modes of steady detonation, such as the subsonic (much faster than normal deflagration) and the supersonic (near Chapman-Jouguet (CJ) velocity or somewhat slower) waves are observed. These waves are observed because of the effects of the walls that cannot be neglected as in large geometries. This is because gaseous deflagration-to-detonation transition (DDT) is a complex process with highly disparate time and spatial scales. The overall evolution is known from experimental observations: flame acceleration yields weak shocks, which interact, strengthen, and adiabatically compress the fresh fuel mixture, eventually leading to thermal explosion somewhere between the leading shock and the flame front, and detonation is finally achieved.

Even in larger scales, the acceleration and transition to detonation of premixed flames is still an important, yet relatively poorly understood problem in combustion science. The details of the flame acceleration and the final transitional step to detonation have been vigorously investigated and debated [212, 219]. Turbulent or Darrieus–Landau instabilities have often been speculated to play a dominant role in flame acceleration. Recent theoretical work has renewed interest in other mechanisms playing a critical role, such as viscous effects in the multi- dimensional analyses (also hydraulic resistance in one-dimensional analyses) or flame structure (e.g., tulip flames) in the acceleration of the flame [210, 212-214, 220]. Bychkov [212], for example, predicts a strong increase of the acceleration rate with decreasing Reynolds number (decreasing diameter). It is unclear if DDT can actually occur without the onset of turbulence as some recent calculations predict [212, 220]. However, combustion experiments are seldom performed in extremely small diameter tubes, and likewise lower Reynolds numbers, other than in the context of flammability or detonation limits.

A variety of reactive waves are also observed in inert porous media (e.g., [221]) where a tortuous path also contributes to the overall fluid dynamic drag of the solid on the gas. Up to five reactive waves are observed in these porous systems: low-speed flames (0.1 mm/s to 10 cm/s), higher-speed isobaric flames (0.1 to 10 m/s), sonic waves involving convective flows driven by pressure gradients (100 to 300 m/s), low-velocity detonations (500 - 1000 m/s) where shock waves become important, and detonations near CJ speeds. The first two waves could be interpreted as essentially laminar and turbulent flame propagation modified by the fluid and thermal interactions with the porous media. Likewise, the highest velocity wave can be viewed
as a perturbation from homogeneous gaseous detonation. However, the intermediate-speed reactive waves appear to be distinct phenomena, corresponding to a subsonic or supersonic convective mechanism (i.e., convective deflagration or detonation) that is unique to porous media and micro-channels. Some analyses of these convective detonations are found in the literature [222, 223].

It is important to better understand the mechanisms and limits of DDT so gaseous systems can be designed to be safer. Similar to gaseous systems, convective burning is also observed in pores (e.g., Ref. [224]) and gaps/cracks of energetic materials (e.g., Ref. [225, 226]). Of course, with reacting solids there are differences from gaseous systems because the reactants are initially solids. However, in thermal explosion of energetic materials (cook-off), slow heating produces a material with connected porosity that is filled with reactive decomposition gases before ignition occurs. Upon ignition, fast reactive waves are observed to propagate through the porous material.

In addition to safety, improved understanding in this area could lead to possible microscale combustion applications such as energy production, propulsion or actuation [2, 227, 228], or as the predetonator of a pulsed detonation engine (PDE). For energetic materials, microscale applications may include deflagration or detonation that will also interact with the microstructure [47, 229, 230]. A nanoscale composite energetic material that has promise as a microenergetic material also has been shown to exhibit a supersonic convective reactive wave (no sharp shock) structure [231].

**Experiment**

Heavy-walled quartz capillary tubes with inner diameters of 0.5 mm, 1 mm, and 2 mm as illustrated in Figure 7.1 were used to study the flame propagation mechanism in microscale. A 0.762 mm (0.030 in) hole for the igniter was drilled in the middle of the tube. Ignition at the center creates a symmetric adiabatic axial boundary condition. The hole was sealed by vacuum epoxy sealant (Varian, Torr Seal). Both spark and hot-wire ignition systems were used. For the hot-wire igniter, it consisted of a 0.254 mm (0.01 in) tantalum filament stretched across the channel diameter and spot welded to two 0.508 mm (0.02 in) Alumel leads. Tungsten wires of
0.508 mm (0.02 in) were used as the electrodes for spark ignition. Electrodes were installed carefully so that the tips did not intrude into the capillary. The total length of the capillary tubes was 1.22 m (4 ft); consequently, the equivalent tube length for a tube closed at one end is 0.61 m (2 ft). No baffles or orifices are installed in the tube to trip turbulence in order to facilitate detonation in the current experimental configuration.

Figure 7.1: Schematic of the capillary tube investigated. Diameters of the tubes are 0.5 mm, 1 mm and 2 mm with the igniter at the center of the tube (figure not to scale).

Stoichiometric ethylene and oxygen were premixed in a 0.914 m (3 ft.) long, 3.175 mm (1/8 in.) I.D. polyethylene tube (7.236 mL mixing volume) before feeding into the capillary from one end. The ethylene and oxygen flows were both regulated by commercial mass flow controllers (Hastings, HFC-202). The absolute uncertainty of the equivalence ratio was ±0.05. During ignition, a triggering pulse (15ms duration) was sent to an AC relay which regulates the current from a variable transformer to a high voltage ignition coil (Carlin, model 41000) that can provide 14KV at 35mA. Current was transmitted directly to the tantalum filament with a resistance of 0.3 Ω for hot-wire ignited tubes. The ignition pulse duration transmitted to the relay was 75ms. The test rig is schematically shown in Figure 7.2.
Flame propagation in the capillary tube was recorded by a high speed CCD camera (Vision Research, Phantom V7.1). High resolution single-frame pictures were taken by a Peltier cooled high sensitivity camera (TSI, 14-10). The exposure time can be set to as short as 500ns to freeze the flame motion so that flame structures can be better visualized. The single shot photography method was triggered by a photodiode that detects the flame zone before it enters the view of the camera. Time delay was controlled by the onboard counter (1.5 $\mu$s resolution) in a multi-functional data acquisition board (National Instrument, PCI-6040E).

**Ignition and Flame Acceleration**

Most of the studies on flame and detonation wave propagation in narrow tubes have the ignition source outside the channel in a much larger tube. It is well known that below a certain (hydraulic) diameter, thermal and radical quenching will prevent the flame from propagating in the tube; detonation can also be inhibited in a small tube. However, it is unclear what scenario results when the ignition source is in the capillary tube.
The evolution of the visible flame zone on one side of the 1 mm capillary tube is shown in Figure 7.3. The stoichiometric ethylene/oxygen mixture was spark ignited. The total energy deposited through the ignition coil is no more than 7.35 J, while the chemical energy can be released in the 1 mm diameter tube during constant-volume combustion is approximately 100.5 J. The frame rate of the high speed CCD camera was set at 80000 fps (inter-frame time was 12.5 μs). Exposure time for each frame was 10 s. The flame ignited on the left side of the picture and propagated toward the right. The flame propagating towards the left is not shown. The brightness of the flame is relatively dim and the flame zone is relatively short in this initial stage. The flame zone becomes brighter as it accelerates downstream. At 185 μs, an abrupt burst in brightness is observed due to the transition to detonation, which can be confirmed in the processed flame tip location data. The brightness of the flame saturated the CCD and even blooms the surrounding pixels. The detonation front continues to propagate downstream while a retonation wave can be seen moving upstream.
Figure 7.3: High speed photography images showing the flame evolution in the capillary tube. The diameter of the tube is 1mm and time between each frame is 12.5 μs. The exposure time for each frame is 10 μs.
Experiments have also been conducted with hot-wire ignited capillary tubes. The energy transmitted to the ignition circuit by the transformer was approximately 1.5 J. Ignition energy had been varied by changing the voltage and the duration of the input pulse. The setting with the lowest input energy that was able to ignite the flame in the capillary tube was then used for the experiments. Similar flame acceleration and DDT are observed, although a longer DDT time was recorded for the hot-wire ignited tube. Both evolutions of ensemble averaged flame tip locations in the 1 mm tube with spark and hot-wire ignitions are shown in Figure 7.4. The error bar represents the data scatter at each time point. The length of the error bar is a standard deviation of the 4 datasets on each side of the averaged datapoint. There is also an inherent error in the time axis due to the uncertainty of the ignition instant for the current discretized sampling method. The frame before a visible flame was observed was taken as the first frame for each sequence. Therefore, an uncertainty as large as 12.5 µs exists in the time axis for the 1 mm sequences taken at 80000 fps and 16.5 µs for the 2 mm tube data sampled at 60606 fps. The uncertainty of the frame interval is less than 1 s.

Figure 7.4: Comparison of the x-t evolution of spark and hot-wire ignitions in 1 mm I.D. capillary tubes.
Figure 7.5 shows the velocity evolution of the flame tip location of the 1 mm and 2 mm I.D. tubes. The spatial resolution of the flame tip measurements for the current set of data is on the order of 1 mm/pixel. As a consequence, a misinterpretation of one pixel represents an uncertainty of ~ 80 m/s in the velocity data presented. The fast growth of the visible flame zone to 100 - 300 m/s in less than 20 μs is probably due to the fast laminar flame speed (~5.5 m/s) and large expansion ratio (~ 16) for the stoichiometric ethylene/oxygen mixture [232]. The effect of the initial velocity surge starts to dissipate at ~ 50 μs. Either a shock wave or a strong compression wave might also be generated by the ignition. The flame in the 1 mm tube further accelerates after the initial stage, while the flame in the 2 mm tube slows down before accelerating again. The acceleration can be related to the effect of the no-slip boundary condition on the wall that drives the plane laminar flame into a stretched parabolic shaped flame front [210, 233], in addition to the possible Darrieus–Landau instability [220]. The increased flame surface area then accelerates the energy generation and the flow ahead of the flame. Such effect will be less important in large diameter tubes since the boundary layer is relatively thin compared to the tube diameter.
When the wall is isothermal instead of adiabatic, the products formed in the boundary layer first jet radially inward, and can then convect in both upstream and downstream directions. As a result, the flame either accelerates less than it does with an adiabatic wall or can even decelerate [210]. The time scale for the study shown in Ref. [210] is on the order of milliseconds due to the low initial pressures. For the current experiment, the initial pressure is 1 atm, so the flame speed of the ethylene/oxygen flame is much faster such that the transition is typically accomplished in a few hundred microseconds in the 0.61 m long half-length tube for the spark ignited cases. Consequently, heat loss effects will be minor since the time scale for heat transfer is at least an order of magnitude more than that required for the flame to propagate through the capillary.

However, for the 2 mm tube and the hot-wire ignited tubes, the effect of heat loss to the side wall may be playing a small role on flame propagation, although heat loss to the closed end is minimized in the present configuration by igniting the flame at the tube center. The Reynolds numbers of the flow evaluated with the tube diameter as the characteristic length and the unburned gas properties at 300K traveling at the sound speed (330 m/s) is $2.3 \times 10^4$ for the 1 mm tube, which suggests that the flame could be turbulent.

Figure 7.6: The flame structure at (a) 25 mm, (b) 85 mm, (c) 140 mm, and (d) 280 mm from the ignition spark in the 2 mm tube.
The flame structures at different downstream locations in the 2 mm capillary tube with spark ignition are shown in Figure 7.6. The images were obtained using the triggered single frame method with the Peltier cooled camera. Note that the intensities of the images do not show the relative brightness of the flame zone since the exposure settings of each frame are different. Figure 7.6(a) shows the flame structure to have a very thin reaction zone at ~ 25 mm from the ignition spot, which corresponds to approximately 130 μs after ignition in Figure 7.4. This is the region where the initial ramp, which is believed to be due to ignition, starts to diminish. The exposure time for this picture is 2.5 μs. Figure 7.6(b) shows the flame structure at ~85 mm from the ignition point. The exposure time for the frame was 500 ns. The comet-like flame structure might be an indication of the boundary layer affecting the flame. The reaction zone is distorted due to the viscous effect in the unburned gas flow; the reacted gases in the boundary layer are expanded radially inward, which leave a trace in the center region of the tube when observed from the side. As the flame moves even faster, the comet shaped flame might not be able to exist; instead, a turbulent flame which is known to have irregular shape is more likely to be observed. Figure 7.6(c) is the flame structure at 140 mm. The exposure time is 500 ns. One of the possible scenarios for the flame shape at this stage is an annular flame since the reaction front is traveling at around 1500 m/s on the laboratory coordinate. The velocity gradient between the centerline and the no-slip wall in the millimeter diameter tube might be too large for the flame to stabilize. It is difficult to fully confirm the existence of a tubular flame structure from the images. Figure 7.6(d) shows the detonation at 280 mm. A nearly flat flame front can be clearly seen.

Gas Detonation and the Scaling of Detonation Distance

The flame tip velocity traces shown in Figure 7.5 indicate that the flame tip reaches detonation velocity (CJ velocity = 2373.5 m/s) in both 1 mm and 2 mm I.D. tubes. The viscous effects that drive a planar flame to a stretched parabolic flame mentioned above can be the mechanism that accelerates the laminar flame to become a turbulent one, which has a faster flame velocity. In the turbulent flame regime, the flame structure becomes more irregular. The turbulent flame speed in the ethylene/oxygen mixture can be estimated perhaps as high as 10 - 50 m/s [195]. Alternatively, this fast wave could be a sonic velocity wave driven by a pressure gradient
These speeds are fast enough to build up pre-heat and pre-compression in the unburned gas.

Recently, theoretical and numerical analyses have argued that the auto-ignition of the pre-compressed gas between the leading shock wave and the reaction zone might be a mechanism for deflagration to detonation based on one-dimensional models [214, 215, 234-236]. This coupling between combustion and sound waves might be the triggering event for DDT in narrow tubes. The flow in front of the flame zone is pushed outward by the burned gas, and can be choked due to the friction force along the long tube. The accelerating reaction front then further compresses the unburned gas between the shock and the flame. The preheated unburned gas further enhances the reaction rate, and thus, the flame speed as the reaction front travels, and finally leads to a thermal explosion when the preheated and pre-compressed conditions are right in the unburned gas somewhere ahead of the flame zone.

Figure 7.7 shows a picture captured right at the moment of detonation in the 2 mm tube. The location of the bright spot is 210 mm downstream from the ignition spark.

Figure 7.7: The picture captured right at the moment of detonation in the 2 mm tube. The location of the bright spot is 210 mm downstream from the ignition spark.
Figure 7.8: Flame evolutions in the 0.5 mm I.D. tubes: (a) regular detonation, (b) initial detonation followed by failure and extinction, and (c) the flame accelerates to a constant speed lower than the detonation velocity.
The final flame tip velocities in the 1 mm and 2 mm I.D. tubes are both approximately 2300 m/s as shown in Figure 7.5, which is close to the detonation speed for the stoichiometric ethylene/oxygen mixture (2373.5 m/s). Figure 7.8 shows the evolution of flame tip locations in the 0.5 mm I.D. tube with spark ignition. The experimental results show diverse behavior of the flame propagation. Three types of flame propagation behaviors were observed: (a) DDT occurs and the reaction front travels at a near CJ detonation speed (approximately 2300 m/s), (b) initial detonation but the detonation wave fails to propagate, and (c) the flame accelerates to a constant speed of approximately 1600 m/s. The flame evolutions of the three cases are shown in Figure 7.9 (a), (b), and (c), respectively. Figure 7.9 shows the velocity traces of the three cases in the 0.5 mm tubes.

Quenching diameter for detonation and deflagration are known to be different. Generally, deflagration can be self-sustained in a smaller diameter than detonation [213]. It is known that the critical diameter for the single-head spin detonation wave to propagate is approximately $\lambda/\pi$, where $\lambda$ is the cell size of the detonation wave [237-239]. The cell width for the detonation wave of the stoichiometric ethylene/oxygen mixture was found to be around 0.58 - 0.8 mm [238, 240];
consequently, the critical diameter is approximately 0.19 - 0.27 mm. However, detonation waves are known to travel in a “galloping” mode or at a lower detonation velocity in the near detonation limit regime. These phenomena could correspond to the case (b) and case (c) of our observation in the 0.5 mm I.D. tube, although the galloping and low velocity detonation was observed in the literature under conditions where the detonation wave was initiated before propagating into the narrow tube, while here the reaction front actually evolves all the way from stagnant stationary initiation to detonation in the capillary tube.

Figure 7.10 shows the scaling of the flame tip velocities in the tubes of the three diameters studied. The evolution of the flame tip velocity in the 1 mm and the 2 mm tubes can be scaled with x/d, where x is the distance between the flame tip location and the ignition point and d is the diameter of the tube. The evolution of the flame tip velocity in our case (a) for the 0.5 mm tube scales with x/d before x/d ~ 100; however, the flame seems to try to stabilize in some lower speed mode before it accelerates abruptly to the near CJ velocity at a location further downstream than the tubes with larger diameters.

Figure 7.10: Scaling of flame tip velocity evolution.
Summary

For the first time, deflagration-to-detonation was observed in sub-millimeter scale tubes. The flame acceleration in the capillary tube from stationary ignition to detonation was discussed in terms of the known theories, such as the boundary layer effect for laminar flame acceleration, turbulence, and the autoignition of the pre-compressed and pre-heated unburned gas. The detonation distance in terms of tube diameters, x/d, is approximately 100 for the stoichiometric ethylene/oxygen flames in smooth-walled capillary tubes with diameters as small as 0.5 mm. The evolution of the flame tip velocity was found to scale with x/d in the 1.0 and 2.0 mm tubes. Several flame structures were observed during different stages of the acceleration process. Three different propagation scenarios were observed in the 0.5 mm ID tube for the ethylene/oxygen flame: (a) CJ detonation initiation, (b) CJ detonation initiation followed by failure and extinction, and (c) the flame acceleration to a constant speed of approximately 1600 m/s. The different propagation modes can potentially give more insight to the long debating issues on the deflagration versus detonation limits in combustion science. Furthermore, the results on flame accelerations observed here are valuable to the design of micro pulse detonation engines, micro shock tubes, and detonation ignition systems to name a few.
CHAPTER 8

NANOTHERMITE REACTION PROPAGATION IN SMALL CHANNELS

In the previous chapter, it was shown that gaseous mixtures could be detonated in submillimeter diameter dimensions. Because of the boundary layer growth, transition occurs relatively rapidly in terms of the diameters. However, quenching diameters still appear to remain at a few hundred micrometers depending on the fuel oxidizer mixture. In the present chapter, the reaction propagation of nanothermites in micro tubes and channels is studied. The propagation rate, as a function of the size of the microchannel, was experimentally determined. A thermite reaction is a type of reaction in which metal is oxidized by the oxide of another metal. Here, mixtures of nanoscale aluminum (nAl) and molybdic oxide (MoO3) nanoparticles were used. By using the nanothermite, extremely high temperatures and pressures could be produced for a short duration in channels smaller than the gaseous reaction could propagate. The adiabatic temperature for stoichiometric Al/MoO3 is around 3800 K.

Background

The combustion of EMs in microscale channels has been referred to as either micropyrotechnics [47] or microenergetics [230]. Because of potential advantages, there is a growing interest in applying energetic materials in microscale applications [2, 16, 19, 23, 24, 42, 45-47, 229, 230, 241-246]. Applications include thrust, actuation (including injection or moving fluids), ignition, power, welding, and rapid switching. Energetic materials have a relatively lower chemical energy potential (as low as ~ 5 MJ/kg for some propellants) [244] compared with hydrocarbon fuels; however, their burning rate can be far superior to many hydrocarbons making them appealing for micropropulsion and actuation devices where the rate of energy release as well as the total energy potential is a concern. EMs do not require additional oxidizer for reaction and include propellants, explosives, and pyrotechnics. The fast reaction rate (deflagration or detonation) of some energetic materials is also an advantage for minimizing heat losses, which is
one of the most challenging issues to be solved in micro systems. Fuel tanks, valves, pumps, may be eliminated or reduced in microscale devices using solid EMs, resulting in simpler systems. In addition, fast propagation rates can result in lower heat loss, better combustion efficiency, and successful reaction in smaller channels.

Often energetic materials commonly used for macroscale applications are not ideal for microscale applications. Many will not ignite or the combustion efficiency is low. There is a need to consider materials that may have properties that are best suited for microscale applications. Nanoscale energetic composites (also called metastable intermolecular composites or MIC) exhibit extremely fast reactions and propagation rates [247-252]. Consequently, nanoscale composites could have advantageous over other materials in microenergetics applications. Tappan et al. [230] performed the first experiments with nanocomposite EMs in microchannels. Recently Tappan has successfully propagated these materials in channels as small as $300 \times 100 \, \mu m$ [253]. Several other EMs were also evaluated by Tappan and co-workers. However, the propagation rate was not determined as a function of the size of the microchannel. The aim of this work is to quantify the propagation rate for an optimized mixture for a variety of sizes of microchannels, in both circular and rectangular cross-sections. In addition, a more complex geometry with lateral channels was considered to further demonstrate the applicability of these materials to microscale applications.

**Experiments**

The materials used in this study were mixtures of nanoscale Al and MoO$_3$. Spherical nano-aluminum (nominally 79 nm, 81% active Al content) was obtained from Nanotechnologies, Inc. with a surface area of 26.5 m$^2$/g. The MoO$_3$ used was obtained from Technanogy with a surface area of 64 m$^2$/g and has a sheet-like morphology with typical dimensions of about $30 \times 200$ nm. Hexane was used as the solvent in the sonication mixing. In this study 0.25g batches of reactants were used with about 10 ml of hexane. Following sonication, the mixtures were placed onto a steel pan and allowed to dry on a hot plate at ~ 40°C.
Note: These are experimental materials and care should be exercised when handling the composites because of their sensitivity to impact, spark, and friction. Very small samples (< 1 gram) should be handled and appropriate mitigation used.

Two experimental configurations were used. Figure 8.1 is a schematic of the microtube experiment. Thick walled capillary tubes were used for the three smallest sizes (inner diameters of 0.48, 1.01, and 1.85 mm) and an acrylic tube was used for the largest tube (inner diameter of 3.63 m). A small section of rubber tube held a spark igniter at the top of the tube (Figure 8.1). A small spark ignited the material. These materials require very little ignition energy, which is an advantage. Vibration was used to fill the tubes with Al/MoO₃ powder. The density of the mixture was about 0.35 g/cm³ or about 9% of theoretical maximum density (TMD). For Al/MoO₃, the TMD is 3.81 g/cm³. A small amount of the composite is placed on the top of the capillary tube in the rubber tube.

Figure 8.1: Schematic of tube experiments. The largest tube used was acrylic. The smaller tubes are borosilicate glass thick walled capillary tubes.
Figure 8.2 shows the configuration for slot experiments. Stainless steel sheets were cut using electrical discharge machining (or EDM). The slots were sandwiched in a holder, as shown in Figure 8.2 with poly(methyl methacrylate) windows. Figure 8.3 shows magnified views of two of the slots. The walls appear to have rough surfaces. A Phantom 5.1 (Vision Research, Inc.) high speed video camera was used to monitor the reaction progress. The camera record was triggered by light emission.

Figure 8.2: Part (a) is an exploded schematic of the slot experiments. A photograph of the experiment is shown in part (b).
To determine the optimal mixture ratio for fastest propagation, we varied the ratio of nano-aluminum (nAl) to MoO$_3$ was varied. Thick-walled 1.85 mm inside diameter tubes were used. The stoichiometric mass fraction of nAl, accounting for the initial oxide, was 31.6% nAl with 68.4% MoO$_3$ by weight. As seen in Figure 8.4, the maximum propagation velocity occurs near 38% nAl and 62% MoO$_3$ by weight. It is not unusual for fuel-rich thermite mixtures to have higher propagation velocities [254], but explanations for this have not been adequate. If stoichiometric portions were used, the propagation velocity would have been decreased by more.

Figure 8.3: Type Caption Here Parts (a) and (c) are example photographs of the wider steel slots used. Parts (b) and (d) are the examples of the narrower slots.
than 10% from the maximum. In addition, the temperature is predicted to be much lower (over 800K) at the maximum propagation velocity compared to the stoichiometric ratio. Consequently, if temperature is important in applications of interest more than propagation rate, a stoichiometric ratio may be preferred. In addition, some applications demand even higher gas production. This could be accomplished by the addition of gas generants or by choosing other reactants. The goal here is not to direct this material to any particular application, but to study the effect of diameter on the propagation.

**Tube Experiments**

The mixture ratio resulting in the fastest propagation was considered because this may minimize heat losses. Four tube diameters were considered. A framing rate of 88888 fps with a shutter speed of 3 μs was used. The aperture was adjusted between experiments to keep the exposure adequate. The intensity increased with diameter, as expected. Figure 8.5 shows a

![Figure 8.4: The measured propagation rate as a function of mass fraction of nAl (%).](image)
snapshot of four experiments with various diameters. There are no qualitative differences in appearance.

Figure 8.6 shows a time sequence for a typical tube (2 mm diameter) experiment. There is a short initial transient, followed by propagation that appears steady. The expansion of the rubber tube used to hold the spark igniter and some blow-by of products from the ignition event is seen near the top of the image.

Decreasing the diameter decreases the propagation velocity. Figure 8.7(a) shows the propagation velocity as a function of diameter for the tubes considered. The uncertainty is very conservatively estimated to be about 10%. Density variations of the powders could introduce the most significant uncertainties. The speed appears to be approaching a limit as the losses to the walls become negligible with larger diameters. Heat or momentum losses to the walls are the likely cause of the slower propagation. This functional dependence is similar to unconfined explosive rate stick results [254]. In high explosives the divergence of the expanding downstream flow reduces the energy available to propagate the detonation.

The propagation speed can also be plotted as a function of the inverse of the diameter, $d$ (see Figure 8.7(b)). For unconfined explosives having large diameters, a linear dependence is observed for unconfined explosives followed by a more rapid drop in detonation velocity [254]. Since the tube walls are not deflected significantly in these experiments as the reactive wave propagates, the loss mechanism is not likely the same as high explosives. However, Figure 8.7(b) shows that these results produce a linear dependence on $1/d$ for the diameters considered. This may indicate that the failure diameter is far less than the smallest tube used. The linear regression, $V=V_\infty - a/d$, is shown in Figure 8.7(b). The maximum available energy is proportional to the volume, or the cross sectional area on a per length basis.
Figure 8.5: Single frame images from experiments in the four different diameters used.

Figure 8.6: Image sequence of a single tube experiment. The time between images is 13.8 μs.
The energy lost by heat transfer or viscous loss would be proportional to the surface area, or perimeter in specific terms. The ratio of the energy lost to available energy for propagation would then be proportional to $1/d$. It is not obvious why this effect on propagation rate would be a simple relationship, such as a linear dependence as it appears. The wall losses become negligible as $d$ becomes large. For infinite diameter, the fit extrapolates to a value of 1090 m/s for $V_\infty$. This result shows that larger tubes would not produce much of an increase in propagation speed beyond the largest diameter considered here. The parameter, $a$, is a material property with units of m$^2$/s that is expected to change for different materials and initial conditions, such as density and temperature. The ratio, $\xi = a/V$, is a material dependent length scale. For explosives, $\xi$ is roughly correlated to the failure diameter [254, 255]. Consequently, may be a useful way to compare materials for use in microenergetic applications.

Specifically, materials with smaller $a$, and large $V$ (smaller $\xi$) would be expected to have smaller failure diameters, and likely better combustion efficiency too. The length scale of this

Figure 8.7: Propagation velocity (a) as a function of tube diameter, (b) as a function of inverse diameter.
material (ξ), under these conditions, is on the order of 100 nm using the measured results. This is on the same order as the size of the particles used. Explosive failure diameters are on the order of $10^\xi$ [255]. If this also holds for the materials considered here, then the failure diameter for this material would be estimated to be on the order of 1000 nm or 1 m. It is a huge engineering challenge to load these materials in 1 m channels. However, if a similarly sized and reactive nanoscale material were assembled in some manner, reaction on the micron scale may be possible. Perhaps smaller failure diameters would be possible for even finer scaled materials. In any case, measuring for different materials and configurations (such as density) of interest could prove to be a useful way to rank materials for their application in microenergetics.

### Stainless Steel Microchannels

In addition to the glass and acrylic tube configurations, stainless steel slots were investigated. Two widths were considered, 487 and 299 μm. Depths for the 487 μm width slots were 508, 1016, 1397, and 1829 μm. Corresponding hydraulic diameters are 497, 658, 722, and 769 μm, respectively. Depths for the 299 μm were 76.2, 177.8, 330.2, 508, 812.8, and 1016 μm. Corresponding hydraulic diameters are 121, 223, 314, 376, 437, and 462 μm, respectively. Figure 8.8 shows a sequence of images obtained for the smallest slot considered (hydraulic diameter of 121 μm). The two smallest sizes showed unsteady propagation. The other results were remarkably steady for such short slots (25.4 mm). Figure 8.8(b) shows the position-time location of the ignition front of the smallest slot. The unsteadiness is clearly seen.

Figure 8.9 summarize the slot results. With the exception of the two smallest hydraulic diameters the data are qualitatively similar to the tube results. It was difficult to pack the two smallest slots with the composite because the depths were so small makes it difficult to obtain a continuous fill of material, and this may have significantly affected the results. Also, as mentioned above, the flame propagation was not steady. The rest of the data are shifted down to lower velocities compared to the tube data. There are several reasons this may be the case. The walls of the steel slots are much rougher than the acrylic and glass tubes and this could increase the heat and momentum loss to the walls. Also, there is some leakage of gases between the steel and windows, as can be seen in Figure 8.8 and this would be an additional loss. Moreover, the
shorter slot lengths may not have allowed a propagating flame to become fully developed. It is also possible that the rectangular shape does appropriately scale to the hydraulic diameter. Nevertheless, the parameter measuring is on the same order of magnitude as obtained for the tubes and the implications are the same for the slots as the tubes.

![Figure 8.8](image)

Figure 8.8: Part (a) is a sequence of images from the smallest slot measured. Time difference between images is 11.3μs. Part (b) shows position as a function of time for the ignition front.
Connected Slots

Some possible applications may require turns or other more complex geometries. Figure 8.10 shows a more complex slot configuration consisting of a small slot crossing a larger slot. The width of the larger channel was 487 μm, and that of the smaller one was 299 μm. The depth of the channel was 1016 μm. The figure clearly shows that the small slot ignites the wider slots, and propagation then proceeds much faster than in the thinner slot demonstrating that the reaction wave can readily turn corners. This characteristic is useful for future design of microenergetics applications, for example, Swiss-roll patterned channels can be utilized to enhance the energy densities of the devices.

Figure 8.9: Propagation velocity of the steel slots (a) as a function of the hydraulic diameter, (b) as a function of the inverse of hydraulic diameter. Uncertainties are not estimated for the smallest slots because these may be much higher than other experiments and not easy to estimate.
The applicability of a nanoscale thermite (nAl/MoO$_3$) in microchannels was examined with both tubes and slots. The results show that the highest propagation speed did not occur at stoichiometric mixture ratio where the temperature is normally the highest. Therefore, the dominant mechanism of the propagation is potentially more by hot gas products that propel liquid Mo forward and transfer heat via convection and the solidification of the liquid Mo. The propagation speed of the reaction in smooth walled tubes is a function of diameter. The propagation velocity varies inversely with diameter, controlled mainly by wall losses (heat transfer or viscous effects). Steel slots with two widths and several thicknesses were also considered, extending to a hydraulic diameter of 121 μm. The propagation velocity also varies inversely with hydraulic diameter for all but the smallest two slots. The propagation velocity in even the smallest slots is near 100 m/s. Classical energetic material would have difficulty igniting

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**Summary**

The applicability of a nanoscale thermite (nAl/MoO$_3$) in microchannels was examined with both tubes and slots. The results show that the highest propagation speed did not occur at stoichiometric mixture ratio where the temperature is normally the highest. Therefore, the dominant mechanism of the propagation is potentially more by hot gas products that propel liquid Mo forward and transfer heat via convection and the solidification of the liquid Mo. The propagation speed of the reaction in smooth walled tubes is a function of diameter. The propagation velocity varies inversely with diameter, controlled mainly by wall losses (heat transfer or viscous effects). Steel slots with two widths and several thicknesses were also considered, extending to a hydraulic diameter of 121 μm. The propagation velocity also varies inversely with hydraulic diameter for all but the smallest two slots. The propagation velocity in even the smallest slots is near 100 m/s. Classical energetic material would have difficulty igniting
and propagating in these small tubes and slots. These results show the nanoscale thermites can ignite and propagate well in microchannels. These results show that the nanoscale composites such as those considered here may be successfully applied in nanoenergetic applications in very small channels (on the order of at least 100 μm or smaller).
CHAPTER 9

CONCLUSIONS

Summary

Millimeter and sub-millimeter scale combustion systems are studied in this thesis to obtain understandings of combustion, heat transfer, and fluid mechanics of chemically reacting flows in small volumes and channels as well as the fabrication and diagnostic aspects of the systems. A series of small scale combustion systems were investigated that operated with gaseous, liquid, and solid reactants. Both steady-state and transient modes of combustion were studied in confinements where the characteristic length scale of the combustion volume approached that of the reaction zone.

Low temperature co-fired ceramic tape technology was utilized to fabricate a millimeter scale counterflow diffusion flame burner. The successful integration of sapphire windows into the LTCC allowed for in situ optical diagnostics of the micro diffusion flames. The luminous zone size of the flame stabilized in the micro burner is less than 1 mm in length and 250 μm in width. The experimentally observed flame structure is consistent with the contours obtained from the numerical simulation, which incorporates a detailed chemiluminescence reaction mechanism. Microscopic imaging emission spectroscopy revealed that the total chemiluminescence intensity ratio of \( C_2^*/CH^* \) is a good measure of overall equivalence ratio of the reactant mixture. Quasi-linear \( C_2^*/CH^* \) correlation is also found across the flame luminous zone. The effects of strain rate on flame shape are generally consistent with larger burners; however, the correlation between flame width and strain rate appears to differ from the square root relationship in larger scale diffusion flames.

Vortex flows were utilized as a means to stabilize gaseous flames in meso/micro scale non-premixed combustors for use in small-scale power and propulsion systems. Flame stabilization was achieved by a large, relatively quiescent, hot core flow that was formed by the
flow recirculation at the head- and tail-ends of the combustor. Scaling studies were performed with a series of combustors ranging in size from ~10.6 to 124 mm$^3$ (i.e., combustor diameters of 2.4-6.4 mm). Combustor performance was evaluated by analyzing the stability limit and chemical efficiency. Both hydrogen and hydrocarbons (methane and propane) have been studied with the chemical energy varying from 25 to 174 W. The stability limits for hydrogen/air mixtures in the 49 mm$^3$ combustor, in terms of the overall equivalence ratio, were found to be ~0.25 on the lean-side and in the range of 3 - 6 on the rich-side. The corresponding chemical efficiency exceeded 97%.

For the largest combustion volume, hydrogen and hydrocarbons burned efficiently in air. For smaller volumes, oxygen enrichment in air was found to be an effective approach to stabilize hydrocarbon flames. For propane/air combustion, the stability limits ranged from ~ 0.25 to 2 for the 124 mm$^3$ combustor. Methane was the most difficult fuel to stabilize the flame and required oxygen-enriched air containing 40% O$_2$ and 60% N$_2$ by volume to operate in the 10.6 mm$^3$ combustor with a chemical efficiency of more than 85%.

Combustion of liquid monopropellant in the mesoscale vortex combustor was also investigated. Oxygen enrichment and pressurization were found to be the feasible approaches for liquid nitromethane combustion in the mesoscale vortex combustors. Self-sustained liquid nitromethane combustion in the 107.8 mm$^3$ vortex with no additional fuel or oxidizer was achieved at elevated chamber pressures. If atmospheric operation was desired, oxygen could be injected to enhance the chemical kinetic rates of the combustion process. The temperature at the combustor core for pure nitromethane combustion is ~ 1700K according to the thermocouple measurements. FTIR characterization of the combustion product showed no unburned hydrocarbons exist in the exhaust stream when the combustion pressure exceeded 300 psig.

For the transient propagation of combustion in millimeter and sub-millimeter tubes, stoichiometric ethylene/oxygen flames were found to be able to accelerate from deflagration to detonation in smooth-walled capillary tubes having diameters as small as 0.5 mm. Transition occurred at a distance of x/d of approximately 100. The evolution of the flame tip velocity was also found to scale with x/d in the 1.0 and 2.0 mm tubes. Several flame structures were observed during different stages of the acceleration process. The flame acceleration in the capillary tube from stationary ignition to detonation was discussed in terms of the known theories, such as the
boundary layer effect for laminar flame acceleration, turbulence, and the autoignition of the pre-compressed and pre-heated unburned gas.

Three different propagation scenarios were observed in the 0.5 mm I.D. tube for the ethylene/oxygen flame: (a) CJ detonation initiation, (b) CJ detonation initiation followed by failure and extinction, and (c) the flame acceleration to a constant speed of approximately 1600 m/s. These different behaviors indicate that the size of the tube might be reaching the detonation quenching limit for this particular gas mixture. The present low speed mode of flame propagation might be some low speed detonation previously observed in the literature for detonation in narrow gaps or porous media.

The feasibility of reaction propagation of a nanoscale thermite (Al/MoO$_3$) in microchannels was investigated in both tubes and slots. The propagation velocity of the thermite reaction was found to vary inversely with diameter, controlled mainly by wall losses (heat transfer or viscous effects). Steel slots with two widths and several thicknesses were also considered, extending to a hydraulic diameter of 121 μm. The propagation velocity also varies inversely with hydraulic diameter for all but the two smallest slots. The propagation velocity in the smallest slots was near 100 m/s. Classical energetic materials would have difficulty igniting and propagating in these small tubes and slots. These results show that nanoscale thermites can ignite and propagate well in microchannels. Consequently, these materials may have applications in various microenergetic (or micropyrotecnic) applications. The issue will be, nonetheless, in loading the nanoenergetics onto the application platform precisely and safely. Porous silicon and silicon grass as described in Appendix B provide interesting opportunities to address this challenge.

Both ceramic and Inconel uni-body thrusters consisting of a combustion chamber and nozzle were constructed. The ceramic thruster was fabricated with stereolithography techniques, while Inconel thrusters were made with EDM technologies. These thruster bodies were integrated with a manifold block for testing. Schlieren and shadowgraph visualization of the thruster plumes were carried out in both cold and hot gas flow conditions. Initial characterization showed promising thruster performance using hydrogen-air as the reactants.
In general, the following key achievements represent major accomplishments of this research:

- Demonstrated vortex flame stabilization in volumes as small as 10.6 mm$^3$ using an asymmetric whirl combustion concept as a means to obtain sustained gas phase combustion over a wide range of operating conditions and extended duration.
- Demonstrated oxygen enrichment as an effective approach for sustaining hydrocarbon combustion in millimeter to sub-millimeter scale confinements.
- Performed experimental scaling studies of combustion in small volumes ranging from 10.6 to 124 mm$^3$.
- Demonstrated continuous combustion of nitromethane, a liquid monopropellant, by making use of tangential injection into the vortex chamber and wall vaporization.
- Developed the hardware and scientific knowledge to operate the combustor using entirely liquid monopropellants.
- Demonstrated stable combustion of nitromethane in high pressure conditions.
- Performed diagnostics on the flame structure inside the combustion chamber as well as characterize the combustion efficiencies.
- Fabricated millimeter and sub-millimeter scale counterflow diffusion flame burners using low temperature co-fired ceramic tape technologies.
- Developed a microscopic imaging spectroscopy system to study the chemiluminescence of micro diffusion flames in a counterflow burner.
- Analyzed the luminescence and the spatial distributions of excited species of sub-millimeter methane/oxygen diffusion flames.
- Analyzed flame propagation in millimeter to sub-millimeter size tubes using gaseous ethylene/oxygen mixture.
- Analyzed reaction propagation of nano thermites in microchannels and tubes.
- Characterized non-reacting and reacting operations of the first ceramic axisymmetric meso-scale thrusters fabricated using stereolithography techniques.
Aspects of microcombustion covered in the thesis include steady-state gaseous and liquid combustion, transient gas and solid reaction propagation, as well as the fabrication and diagnostic methods of combustion systems. Significant unknowns still exist in the many facets of microcombustion, not to say the unlimited development opportunities in this relatively new field of research. Research topics that are essential continuations of current research efforts and some directions for future research are briefly discussed in the following section.

**Future Work**

**Meso and micro scale liquid monopropellant combustion**

High pressure combustion and oxygen enrichment were strategies successfully applied for liquid nitromethane combustion in the current study. Preliminary studies have shown that HAN (hydroxylamine nitrate, \( \text{NH}_2\text{OHNO}_3 \)) based propellants can be combusted in the vortex microcombustor at relatively lower pressures. Figure 9.1 is a frame shot extracted from the video recording of the combustion of the HAN based monopropellant in the 107.8 mm\(^3\) combustor. The operating pressure was only slightly above atmospheric with the valve at the exhaust fully open.

The electrochemical properties of HAN based monopropellants offer an interesting opportunity for ignition. In the current effort, ignition of liquid propellants was achieved by utilizing \( \text{H}_2/\text{air} \) pilot flames. However, electrolytic ignition is potentially feasible for HAN based monopropellants. Electrolysis of the liquid propellant decomposes liquid into gases. Thermal feedback from the exothermic decomposition reactions further vaporizes the liquid as well as building up the pressure to achieve ignition. Moreover, this technique is more compatible with microscale applications because extra components for pilot flames are not necessary. Since the energy is directly deposited into the propellant during electrolytic ignition, it may be more advantageous than catalytic ignition in terms of thermal and power management.
DDT in microtubes

In Chapter 7, the process of flame acceleration from stationary ignition to detonation in a sub-millimeter scale tube was shown for the first time. Considering the simplicity and effective cost of the setup, it can be easily modified to study many unresolved topics during the DDT process. For example, could deflagration propagate without being accelerated into detonation in the capillary tube? The detonation limits are traditionally studied in a setup where DDT is initiated in a larger chamber before being propagated into a small channel. Are the detonation limits still the same when the deflagration-to-detonation transition also occurs in the small channel? Which stage of the flame acceleration process is most affected by the increased proportion of the boundary layer? Can the setup be applied to micro PDEs and microthrusters? There are many open questions which still need to be answered in this subject.

Study of combustion phenomena with microscopic imaging spectroscopy

Although imaging spectroscopy has been widely used in research fields such as geophysics (they called it hyperspectrum), astrophysics and recently biochemistry
(spectrophotometry is the keyword), it is a relatively new diagnostic tool for studying combustion phenomena especially when combined with microscopy. The current research efforts further integrate the imaging spectrometry to study microscale flames. This setup could be used to resolve the one-dimensional spatial species distributions in other reacting systems, for example, the combustion of nanothermites as discussed in Chapter 8. In addition to the measurements of the intrinsic chemiluminescence of the reactions, laser induced fluorescence can be carried out with this technique. Temperature information can then be obtained using this laser-spectroscopic technique.

**Ceramic high temperature reactors**

Polymer and silicon are the most popular materials for fabricating micro devices. A wealth of fabrication techniques has been accumulated for these two materials in the literature, but both materials are not able to withstand the high temperatures typical in microcombustors, which can reach 3000 K. Ceramic is considered as a promising material for high temperature micro reactors; unfortunately, no reliable and cost-effective microfabrication technique has yet emerged. However, developments in low temperature co-fired ceramic (LTCC) tape technology as described in Chapters 3 and 5 could potentially provide a competitive fabrication method for high temperature micro reactors. More engineering techniques and applications based on this relatively new technology nonetheless still need to be explored. For example, the fabrication and integration of alumina and zirconia based high temperature ceramic tapes to sustain higher temperatures than LTCC and the integration of silicon based diagnostic and control circuit with the ceramic tapes is an area requires further research. Many high temperature micro reactor applications can be pursued with these technologies, to name a few, micro fuel reformers, micro incinerators, microthrusters, micro actuators, micro flame sensors, etc. In particular, liquid monopropellant micro thrusters with integrated elements for electrolytic ignition are currently being built with the LTCC tape technology.
Silicon combustion

Silicon is the most common material in the semiconductor industry. It is also known that potential explosion hazards exist for silicon dust. However, very few studies have been made on characterizing silicon combustion. Combustion behavior (explosion) of porous silicon has recently been reported [256-258], but the mechanism of the explosion is still poorly understood. Figure 9.2 shows SEM pictures of porous silicon at different views. The porous silicon was provided by Prof. Tony Huang in the Department of Engineering Science at Penn State, and was fabricated at UCLA. The silicon fraction in these porous silicon pieces are visually characterized with a Matlab image processing program. The results show that 45-50 % of the total area is occupied by silicon. The pore size is, however, on the order of a few microns.

Figure 9.2: Structures of micro porous silicon revealed under SEM. Picture (a) represents the overall view, (b) the close-up view of the pores, (c) the vertically top view, and (d) the close-up view of the pore channels.
The dense silicon grasses described in Appendix B provide another potential alternative for studying the combustion of silicon with different liquid or solid oxidizers that could be filled into the channels. The fraction of silicon grass shown in Appendix A per unit area is approximately 15%. Oxidizers would have to be chosen to yield the desired stoichiometry and would be different for the porous silicon and silicon grass fabrication techniques. The silicon grass can be fabricated directly on the silicon wafer with desired patterns, which is advantageous for it to be integrated to potential applications.

**Field velocity characterization tool for high speed gaseous micro reacting flows**

Most of the optical diagnostic techniques were originally developed for macro scale flows. Micro sensor technologies exist, but very often these sensors offer only “one point measurements”, and are tailored to be used in specific circumstances and devices. Micro particle image velocimetry (PIV) might be by far the most versatile non-intrusive tool to provide whole-field flow information, but its usage is limited to liquid flows at low flow velocities. New research tools need to be developed for studying high speed gaseous reacting flows, which are more typical in high temperature reacting systems.

Significant research opportunities exist beyond the few topics mentioned above particularly on the applications relevant to high temperature reacting flows. To name a few, miniaturization of a spectroscopy system combined with ceramic tape technologies could lead to an innovative micro flame sensor for reaction controls in harsh combustion environments. A microcombustor could be used to generate hydrogen through partial oxidation of hydrocarbons; the combustor when further being packaged with micro fuel cells becomes a portable micro power generator. The successfullness of the partial oxidation systems largely relies on the controllability of the reaction environments. A small scale reactor is therefore advantageous due to its relatively smaller thermal mass and inertia. Micro high temperature reacting systems are also an excellent testbed for direct investigation of hazardous reactions and experiments that are difficult to conduct at the macroscale.
Bibliography


APPENDIX A

MICRO THRUSTER WITH VORTEX THRUSTER CHAMBER

An initial prototype thruster based on the asymmetric whirl concept was designed and fabricated. The thruster consists of a combined combustion chamber and nozzle. The chamber is open at the front end, but sealed by a gasket and manifold system to enable rapid development and testing of various reactant supply and ignition concepts in the combustion chamber. Several thruster bodies have been fabricated from aluminum oxide using stereolithography techniques. These thrusters were built by Prof. Ilhan Aksay and Mr. David Milius in the Chemical Engineering Department of Princeton University [259]. The ceramic thrusters (see Figure 3.3) have throat diameters ranging from approximately 300-700 μm, an exit area/throat area ratio of 2, and a conical nozzle divergence half angle of 14 degrees. The combustion chamber has a volume of approximately 60 mm³.

Figure A.1: Inconel microthrusters fabricated with EDM.
In addition, Inconel thrusters have been fabricated using electric discharge machining (EDM) (see Figure A.1) for comparison studies with the ceramic thrusters. Both the Inconel and aluminum oxide thrusters have similarly roughness. The thermal diffusivity of Inconel is smaller than aluminum oxide at room temperature \((3.1 \times 10^{-6} \text{ versus } 1.2 \times 10^{-5} \text{ m}^2/\text{s})\), however, the thermal diffusivity of Inconel increases slightly with the temperature, while the thermal diffusivity of aluminum oxide decreases. The thermal diffusivity of aluminum oxide at 1000 K is \(1.6 \times 10^{-6} \text{ m/s}\), and that of Inconel is \(4.5 \times 10^{-6} \text{ m}^2/\text{s}\). As a result, aluminum oxide may be a better material for hot gas thrusters than Inconel because thermal energy is stored rather than being conducted away by the material.

Pressure loaded small Inconel flanges are mounted at each end of the thruster to seal the combustion chamber and provide a means for injection and ignition of the reactants. A pressure tap, and thermocouple port, and an igniter port are also positioned in the upstream(back) flange. Tangential ports at the upstream end of the combustor are available for gaseous air injection and liquid monopropellant injection. Gaseous fuel injection occurs perpendicular to the air injection port. High temperature gaskets are used to seal the thruster bodies with the upstream flange.

Figure A.2: Shadowgraph images (top) of plumes from two different ceramic thrusters with helium and a chamber pressure of 10 atm. Schlieren image (bottom) of helium plume from a third ceramic thruster with a chamber pressure of 7 atm.
Both cold flow and hot fire combustion experiments have been conducted on the prototype thrusters. Shadowgraph and schlieren techniques have been used to visualize thruster plumes. Figure A.2 shows shadowgraph (top) and schlieren images of plumes from ceramic thrusters operated under cold flow conditions with helium.

![Figure A.2: Shadowgraph and schlieren images of plumes](image)

Figure A.2: Shadowgraph and schlieren images of plumes from ceramic thrusters.

Examples of the measured characteristic velocity and C* efficiency for one of the thrusters as a function of chamber pressure is shown in Figure A.3. For cold airflow conditions, C* was approximately 325 m/s and remains nearly constant independent of pressure. For this particular thruster, C* efficiencies were initially calculated to be about 80%. This lower than expected efficiency is attributed to uncertainties in the measurement of the nozzle throat area. The throat cross-sections of the ceramic thrusters are not perfectly circular and additional microscopic measurements of the throat diameters have yielded slightly different results depending on the side from which the diameters are measured. Characteristic velocity efficiency measurements from the Inconel thrusters were 95±10%.

![Figure A.3: Characteristic velocity and C* efficiency for cold flow operation](image)

Figure A.3: Characteristic velocity and C* efficiency for cold flow operation.
Hot fire tests without forced external cooling have been performed with H\textsubscript{2}/air mixtures. Continuous operation has been performed in addition to many start-up and shut-down sequences. Ignition was obtained via either a spark across two small electrodes or a platinum glow wire. Photographs of the thruster and the plume are shown in Figure A.4. The thruster body in these photographs appeared as a reddish-orange color. Surface temperatures of the ceramic thruster body from a thermocouple located on the top surface near the outer diameter of the thruster body were generally near 600 K.

Figure A.5(a) shows a short exposure schlieren image of the cold jet at the exit of the microthruster. The exposure time of the image was 10 μs. The chamber pressure in the thruster was 2.5 atm, and the working fluid was helium. Turbulent structures can be clearly seen in the picture starting at around 3.5 d downstream of the thruster exit. The system layout of the schlieren setup using high intensity light emitting diodes (LED) as the illumination source is shown in Figure A.5(b). The high pulsing rate and short pulse duration of the LED can turn the setup into a high speed schlieren system when the LED is synchronized with a high speed camera.
An example of the start-up and shut-down of the thruster is shown in Figure A.6. Here the thruster is operated on a non-premixed hydrogen-air mixture with an overall equivalence ratio of 1.6. The chamber adiabatic temperature is calculated to be approximately 2100K. The Reynolds numbers of the inlet air, hydrogen, combustion chamber, and throat were, 7500, 550, 330, and 2300, respectively. For this condition, the experimental C* was determined as 970 m/s and the theoretical vacuum specific impulse was 214 sec. The start-up procedure consisted of setting the air flow rate, followed by firing the spark, and then injecting the hydrogen. Ignition is rapidly achieved as indicated by the jump in pressure and temperature around 35 sec. The internal setup.
temperature measurement is located at the upstream end of the combustion chamber near the combustor wall, but no in contact with the wall. The slight increase in chamber temperature at 90 sec is a result of a change in the hydrogen flow rate. Shut-down is achieved by closing the hydrogen flow to the chamber.

Successful operation of the prototype mesoscale thrusters in hot gas mode using the vortex combustion concept discussed in Chapter 6 is demonstrated. The experimental \( C^*_\text{exp} \) and the theoretical vacuum specific impulse characterized at equivalence ratio of 1.6 and total reactant volumetric flow rate of 4.5 L/min with hydrogen and air were 970 m/s and 214 sec, respectively.

Figure A.6: Start-up and shut-down of the thruster under hot-gas conditions.
Shadowgraph and schlieren techniques were used to visualize thruster plumes. A high speed schlieren technique was developed using high intensity LEDs as the illumination source. The technique can potentially be used to study the transient start-up and shut-down dynamics of microthrusters.
APPENDIX B

FABRICATION OF SILICON MICROCHANNELS

Preliminary studies on microchannel fabrication using silicon based techniques were carried out. The channels are aimed to be used as a platform for studying reaction propagation of nanoscale thermites as discussed in Chapter 8, and potentially as a reaction channel for steady state combustion (see Chapter 5). This appendix outlines the procedures that were implemented to fabricate the microchannels on silicon wafers as well the diagnostic layers on Pyrex.

Figure B.1: Design of the microchannel.

Figure B.1 shows the design of the microchannel assembly. It consists of a channel layer made of silicon and a metal circuit layer deposited on Pyrex, which will be called the diagnostic layer. After bonding the two layers together, the assembly becomes an integrated diagnostic platform for studying reaction propagations. In the design, the resist heater (igniter) is matched to one end of the channel, and surface ion probes are patterned along the channel. The tips of the ion probes are 50 μm apart, while the widths of the channels are 100, 300, and 500 μm. The line width of the heater elements is 25 μm.
Figure B.2 shows the mask drawings for the design. The drawings shown are in positive, the actual masks were made in negative (feature area transparent). Six chips are accommodated on a 4” wafer in the current design. Since the smallest feature size is much larger than 10 μm (25 μm for the heater element), high resolution laser photoplots on transparencies, which have tolerances at approximately ±5 μm, were used instead of chrome masks. During the lithography
process, the transparency was taped on a 5” × 5” glass so that the transparency mask could be easier handled to ensure satisfactory alignment and exposure under the mask aligner. A chrome mask for the diagnostic layer with 1 μm resolution was later built using a laser writer system (Heidelberg, DWL-66).

Figure B.3: Planned fabrication process flows of the channel layer (left) and the diagnostic layer (right).
The fabrication flow of the channel layer is shown on the left side of Figure B.3. Both dry and wet etching techniques were investigated. A 1 μm oxide, double side polished, 525 μm thick 4” <100> silicon wafer was the substrate for the layer. The oxide layer was the “hard mask” for silicon etching. The procedure began from carrying out the standard lithography process. The wafer was cleaned and the photoresist was spin coated. A primer layer of hexamethyldisilazane (HMDS) that enhanced the adhesion of photoresist was first spin coated at 4000 rpm until dry, then Shipley 3012 positive photoresist was spin coated at 4000 rpm for about 1 min until the color on the spinning wafer stopped changing. The wafers were pre-baked on a hot-plate at 95 °C for 1 min before being exposed under the mask aligner. The parameters utilized to expose the channel patterns using the laser photoplots mask was 10 mW/cm² for 5 sec on Karl Suss MA6 contact aligner. The exposed wafers were developed in CD-26 developer for 1 min and rinsed in de-ionized water before being post-baked (hot-plate, 115 °C, 1 min).

Table B.1: The recipe for SiO₂ RIE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>200 W</td>
</tr>
<tr>
<td>DC power</td>
<td>297 W</td>
</tr>
<tr>
<td>Pressure</td>
<td>100 mtorr</td>
</tr>
<tr>
<td>Etching phase</td>
<td>2 min 10 sec</td>
</tr>
<tr>
<td>CF₄ flow rate</td>
<td>45 sccm</td>
</tr>
<tr>
<td>O₂ flow rate</td>
<td>5 sccm</td>
</tr>
<tr>
<td>Purging phase</td>
<td>3 min 30 sec</td>
</tr>
<tr>
<td>N₂</td>
<td>100 mtorr</td>
</tr>
</tbody>
</table>

Two types of etching processes were used to remove the exposed oxide layers on the wafers. Wet etching with buffered oxide etch (BOE, 6 parts of 40 % NH₄F and 1 part of 49 % HF) was first used to remove silicon oxide (SiO₂) at the areas unprotected by the photoresist and thereby expose the silicon underneath. The etch rate of the BOE was approximately 70 nm/min. As a result, it took less than 10 min to etch away the 1 μm thick oxide layers on the wafers. A dry etch technique, using reactive ion etching (RIE), was also investigated. A Plasma Therm 720 RIE system set up with the parameters listed in Table B.1 was used for the SiO₂ etching. Since the
Plasma Therm 720 system was water cooled, alternating etching and purging were applied to prevent overheating, which will cause the photoresist being burned out. An etch rate of approximately 15 nm/min was achieved with the parameters used. However, a very thin layer of oxide (~ 50 nm) was found to always remain on the etched area using this method. The wafers after the SiO₂ ripping process are shown in Figure B.4. Shinny surfaces were obtained after BOE as shown in Figure B.4(a), while brown residues were found on the surface of reactive ion etched surfaces (see Figure B.4(b)).

![Figure B.4](image)

Figure B.4: The wafer etched in (a) BOE, and (b) RIE.

The next step of the procedure was silicon etching. Similarly, both wet etching using tretramethylammonium hydroxide (TMAH) and dry etching with deep reactive ion etch (DRIE) were pursued. TMAH was chosen as the etchant because it has a better selective etching rate than potassium hydroxide (KOH) for SiO₂/Si. TMAH was known to have an etch rate of approximately 1 μm/min with 20% TMAH in water at 90 °C. However, the management temperature and solution evaporation (keeping constant solution concentration) during the 8-10 hour required to etch through the 525 μm wafer was found to be difficult. Figure B.5 is a scanning electron microscope (SEM) picture focused on a corner of a TMAH etched channel. Undercuts and the effects of different etching rates of TMAH on <100> and <110> surfaces of the silicon are clearly seen.
In the DRIE etch, SF$_6$ (300 sccm, 3.5 sec) was used for the etching phase while C$_4$F$_8$ (300 sccm, 1.5 sec) and O$_2$ (100 sccm, 1 sec) were the chemicals used for the passivation of the side wall in a liquid nitrogen cooled reactor (Adixe AMS100 i-speeder). The chamber temperature and pressure were set at 20 °C and $2.5 \times 10^{-2}$ mbar (18 mtorr), respectively. The depth of the channels was approximately 40 μm for a 30 min etch. The etching rate was therefore approximately 1.3 μm/min.

Vertical side walls can be obtained with the cyclic alternations of etching and passivation in the DRIE process, but scalloping is known to be a typical side effect. Scalloping is clearly seen on the side wall of the channels (see Figure B.6). The wavelength of the scalloping structure is

Figure B.5: SEM picture of the corner of the TMAH etched channel.

Figure B.6: Scalloping structure on the side wall of the deep reactive ion etched channel.

Vertical side walls can be obtained with the cyclic alternations of etching and passivation in the DRIE process, but scalloping is known to be a typical side effect. Scalloping is clearly seen on the side wall of the channels (see Figure B.6). The wavelength of the scalloping structure is
less than 1 μm. However, a step change on the width of the channel is observed in the SEM pictures of Figure B.6, B.7(a), and B.7(c). The reason for the formation of the stepped walls is still unknown.

Silicon grass was known to be another side effect of the DRIE process [111]. However, dense grasses are found on both silicon and SiO$_2$ covered regions after deep reactive ion etch (see Figure B.7). Further studies will be needed to clarify the reason for the formation of the grass structure on SiO$_2$ covered regions. Figure B.8 shows close-up views of the silicon grasses. The SEM pictures are taken from an angle near perpendicular to the grasses to reveal the height of the grass. The edge of the investigated piece was scratched by a knife edge to provide a well-defined edge for SEM imaging. The height of the grass measured from the pictures is on the order of 50 μm and the diameter is approximately 1 μm, giving an aspect ratio of around 50. Further
investigations of the reasons that cause the dense grass are necessary. Although these dense grasses may not be desirable for flow channels, they can provide unique opportunities for studying the combustion of silicon with different liquid or solid oxidizers that could be filled into the channels.

Figure B.8: The grass formed on the surface of the wafer after 60 min of DRIE process. The messy area in front of the grassy region was due to the scratching of a knife edge before taking the SEM.

Figure B.9: The Pyrex chip with titanium ignition heater and ion probe electrodes deposited.
A standard lift-off and evaporation process, as shown in the right side of Figure B.3, was utilized to fabricate the diagnostic layer. LOR photoresist was spin coated (4000 rpm, 40 sec) on the Pyrex wafers. The pattern was transferred from the mask onto the photoresist with a 5 sec exposure on the MA6 aligner. After the wafers were developed, titanium (Ti) was evaporated onto the wafers in an E-gun evaporator (Kurt Lesker). Titanium was chosen as the electrode material not only because of its better bonding characteristics to Pyrex but also due to of its high electric resistively, which is beneficial for both heater and ion probes. The thickness of the titanium evaporated was 525 Angstrom. The lift-off procedure was accomplished by soaking the wafers in a stripping bath (Remove PG). This step removed the bi-layer stack of photoresist and titanium in the clear region, while the electrode region, where titanium was adhered directly onto the Pyrex surface, was kept. Figure B.9 shows a diagnostic layer chip diced from the wafer. A magnified view of the heater is also shown in the figure.

In summary, silicon microchannels for studying reaction propagation for studying reaction propagation of nanoscale thermites were fabricated. Ion probes and microheaters were successfully patterned on Pyrex wafers, which can be bonded to the silicon microchannel chips leading to an integrated testing chip for nanoenergetics. When silicon is used as the fuel, the dense silicon grasses unexpectedly obtained can be developed into a unique self-loading mechanism. However, more future studies will be necessary to explore these opportunities.
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