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A Study of Fuel and Reactor Design for Platinum Nanoparticle Catalyzed Microreactors

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Typical microcombustion-based power devices entail the use of catalyst to sustain combustion in less than millimeter scale channels. This work explores the use of several other candidate fuels for ~8 nm diameter Pt particle catalyzed combustion within 800 μm channel width cordierite substrates. The results demonstrate while commercial hydrocarbon fuels such as methane, propane, butane, and ethanol can be used to sustain catalytic combustion, room temperature ignition was only observed using methanol-air mixtures. Fuels, other than methanol, required preheating at temperatures >200°C, yet repeated catalytic cycling similar to methanol-air mixtures was demonstrated. Subsequently, a new reactor design was investigated to couple with thermoelectric generators. The modified reactor design enabled ignition of methanol-air mixtures at room temperature with the ability to achieve repeat catalytic cycles. Preliminary performance studies achieved a maximum temperature difference ΔT of 55°C with a flow rate of 800 mL/min. While the temperature difference indicates a respectable potential for power generation, reduced exhaust temperature and improved thermal management could significantly enhance the eventual device performance.

1. Introduction

Microreactors are actively studied for their potential for portable power generation, as documented by a number of exhaustive reviews [1–3]. Their large surface area-to-volume ratios and subsequent heat loss, however, make them susceptible to combustion instabilities and quenching [4]. While several approaches exist to mitigate these design challenges, catalytic combustion has been extensively studied as an effective strategy to address quenching [5]. Typically, metal nanoparticles are used to achieve ignition within submillimeter substrate channels using hydrocarbon fuels [6]. The current focus is on the specific combination of fuel, catalyst, and reactor design to optimize performance [1, 7]. Among the various reactor designs, direct conversion from thermal to electrical power using thermoelectric generators is preferred for its mechanical robustness and size [8, 9]. With thermoelectric power generation governed by temperature differential and thus an effective heat loss from the reactor, thermal management within the reactor becomes a key reactor design parameter [10, 11].

A variety of metal catalysts have been studied to sustain combustion reactions in micron-sized channels. Metal based catalysts are commonly used with nanometer dimensions to enhance reactivity via dramatically increased surface area [12–17]. Studies have also demonstrated Pt nanoparticles as the most active catalytic system when the fuel percent conversion or the fuel ignition behavior is compared [18–21]. Hu et al. [22] and subsequent studies [23–25] have demonstrated room temperature ignition of fuel using Pt nanoparticles. Further enhancements in reactivity can be achieved by alloyed or supported catalysts [26–30]. With respect to the choice of fuels, typically small hydrocarbon fuels or hydrogen [10, 31, 32] has been studied. Hydrocarbon fuels studied include commercially available alkanes such as methane [12, 14, 27, 33, 34], propane [11, 21, 28, 30, 35], and butane [36–38] and simple alcohols such as methanol [29, 39, 40] and ethanol [17, 41, 42]. While simplified catalytic mechanisms have been proposed for various fuels, they are not predictive in terms of their ignition and combustion behavior within microreactors [2, 21, 39, 43]. Most fuels require preheating or hydrogen assistance [43–45] to combat
reaction quenching. To further ameliorate thermal quenching, a variety of reactor design configurations have been explored, ranging from simple planar [10, 36, 38–40, 46] to counter-flow [11, 20, 47] and Swiss-roll geometries [35]. These and other studies serve as useful guides for catalytic microcombustor design. However, a thorough investigation of thermal design parameters specific to the system is warranted to drive further performance when the reactor designs deviate from the previously explored configurations.

Our previous studies involved catalytic combustion and room temperature ignition of methanol-air mixtures [48, 49]. These studies demonstrated sustained and repeatable methanol combustion using platinum nanoparticles within cordierite substrates. As a next step, this work examines the details of microreactor configuration and explores its dependence on the fuel type using Pt impregnated-cordierite substrate. This work also demonstrates the behavior of different fuels over multiple catalytic cycles. This study highlights the unique combination of factors important to microcombustor-thermoelectric coupled devices.

2. Experimental

2.1. Material Synthesis. Pt nanoparticles were synthesized using a colloidal synthesis technique delineated by Bonet et al. [50] and further specifics detailed elsewhere [48]. The ethylene glycol-based (EG, 99.8% purity, Sigma Aldrich) synthesis incorporated hexachloroplatinic acid precursor (H₂PtCl₆, ACS reagent grade, Sigma Aldrich) stabilized by polyvinylpyrrolidone (PVP, MW 29,000, Sigma Aldrich). Particles were cleaned through centrifugation using methanol followed by deionized water yielding Pt nanoparticles suspended in water.

XRD analysis confirmed metallic platinum particles were present in the synthesized solution with an average crystallite diameter of 8.9 nm. TEM analysis provided an average primary particle diameter of 8 nm. Figures 1(a) and 1(b) provide TEM images of representative particles with appreciable agglomeration. Particle agglomeration can be attributed to the drop-coating method used to deposit samples on to TEM grids. It is expected that the particle morphology shown in Figure 1 is representative of deposited particles on catalytic cordierite substrates using draw-coating.

2.2. Substrate Preparation and Reactors. A bulk cordierite monolith was used for uniform nanoparticle distribution and unhindered reactant flow (Corning Inc., 900 cells/in², 800μm internal channel width). Octagonal substrates 13.5 mm wide and 19 mm long were prepared from the bulk monolith. The substrates were coated with cleaned Pt nanoparticles using a draw-coating method and allowed to dry at ambient conditions. Refer to Applegate et al. [48] for preparation details. This technique deposited a single coating to the base of each channel (estimated to be 10 mg Pt per deposition). The square-channeled substrate was rotated 180°, 90°, and 180° with respect to previous coatings to obtain two, three, and four Pt coated sides, respectively. A layer of quartz wool (0.6–1.6 mm thick) was added around the substrate to prevent reactant bypass through the gap existing between the substrate and the reactor inner wall. Figure 2(c) shows an image of the substrate prepared using the methods described here. The substrate was then inserted within an aluminum reactor. Two reactor configurations were used based on the study parameters. Alternative fuel study used a cylindrical reactor shown in Figures 2(a) and 2(b), while the power device study used a rectangular reactor shown in Figure 2(d) to accommodate the planar thermoelectric generators.

2.3. Alternative Fuel Study. Since previous work focused only on methanol as the reactant fuel, four alternative fuels were explored for Pt-based cyclic catalytic microcombustion. One liquid fuel and three gaseous fuels were investigated as alternatives to liquid methanol. Liquid-phase ethanol (≥99.5% purity, Sigma Aldrich) was combined with synthetic air (99.9% purity, Airgas) via a bubbler assembly. Fuel content in the reactor flow was adjusted to achieve stoichiometric mixtures of fuel and air. A flow controller was...
used to achieve bubbler inlet flow rates of 800 mL/min and 1000 mL/min. To achieve stoichiometric ethanol-air mixture (based on vapor pressure), the ethanol contained in the bubbler was maintained at 45°C using an oil bath, while the reactor inlet line was maintained at ~105°C to avoid condensation. Gaseous fuels included methane (99% purity, Praxair), propane (99% purity, Praxair), and butane (99.5%, Praxair). The gaseous fuels and air were premixed in the dry bubbler prior to introduction to the reactor at flow rates of 800 mL/min and 1000 mL/min. Preliminary studies, discussed later, indicated the inability of all alternative fuels to ignite without preheating. Preheating of the gaseous fuels involved heating the inlet line using an insulated electrical heater to achieve inlet mixture temperatures of ~210°C.

For the alternative fuel studies, the cylindrical aluminum continuous flow reactor shown in Figures 2(a) and 2(b) was used. Detailed dimensions and features of the cylindrical reactor were provided previously [48]. The catalyst coated substrate was positioned within the reactor with a K-type thermocouple (KMTXL-020G, Omega Engineering) cemented 7.6 mm deep from the substrate exit into the center channel, hereon referred to as the “substrate temperature.” Temperature data was collected at 10 Hz via a LabView-based DAQ system. Each test comprised three repeat cycles in which heated air and fuel mixtures at the indicated flow rates were introduced in intervals of 30 minutes. All experiments were conducted at atmospheric pressure.

2.4. MTC Device Study. The microcombustion-thermoelectric coupled (MTC) device consisted of three primary components: an aluminum (Al) reactor, thermoelectric generators (TEG’s), and heat sinks. A rectangular reactor shown
in Figure 2(d) was designed to match the planar geometry of the TEGs while keeping a 14.3 mm diameter cylindrical substrate cavity. The reactor was placed between two 1 in$^2$ 2.5 W bismuth telluride thermoelectric modules (HZ-2, Hi-Z Technology, Inc.). The Al reactor formed the hot side of the TEGs, while folded sheet-metal computer heat sinks were placed on either side of the two TEGs as cold junctions. A thermal grease (Hi-Z Technology, Inc.) was applied to the TEG faces for improved thermal contact. A constant mechanical compression was maintained for every MTC experiment. K-type thermocouples (KMTXL-020G, Omega Engineering) were used to monitor hot- and cold-side temperatures as well as the substrate temperature using LabView-based DAQ. In addition, exhaust product gas temperature was monitored to account for heat loss. Figure 2(e) provides a complete schematic of the MTC assembly. The schematic is a cross section top view of the MTC device. The orientation was selected to optimize convective heat transfer from the heat sinks.

Material and substrate preparation methods described earlier were used to produce the catalytic substrate shown in Figure 2(c). All MTC device tests were conducted using methanol (99.8% purity, Sigma Aldrich) as the reactant fuel introduced by bubbling synthetic air through a glass bubbler. Previous work has demonstrated such a process to yield near stoichiometric mixture of methanol and air. Air flow rates ranged from 400 mL/min to 800 mL/min. A threaded exhaust tube was screwed into the reactor outlet to secure the substrate and to reduce exhaust heat loss. Experiments were conducted at ambient conditions by introducing the reactants into the microcombustor which subsequently ignited to provide a stable heat source for the TEGs to produce power.

3. Results and Discussion

3.1. Alternative Fuel Study. Our previous work has already demonstrated successful room temperature ignition of methanol-air mixture with platinum nanoparticles [48]. Furthermore, this previous work has presented the effect of reactant flow rate and mass loading (in the form of a number of coated sides) on the catalytic performance of the microreactor. Therefore, the selected test parameters for the alternative fuel study were based on previous trends observed with methanol-air mixtures. Figure 3 shows the Pt coated substrate undergoing a single catalytic combustion of methanol within the cylindrical reactor. As the resulting glow suggests, heat generation is concentrated in the center core of the substrate; subsequent temperature measurements at radial locations have indicated <10% drop in average temperatures from the substrate center. This is in contrast to the axial locations that demonstrate a more dramatic reduction of ~35% in temperature when inlet temperatures are compared to the outlet temperatures within the center channel, a feature that is common with low conductivity substrates [31]. While thermal map of the substrate is sufficiently described here, additional temperature and ignition time mapping studies are reported elsewhere [51].

As opposed to methanol ignition at room temperature, preliminary tests conducted using ethanol, methane, propane, and butane failed to ignite at room temperature. Ethanol, in particular, as the only liquid-phase alternative to methanol, yielded fuel-lean mixtures at room temperature and failed to ignite. For combustion to proceed, the ethanol flask was submerged in an oil bath maintained at 45°C and the reactor inlet line was heated to 105°C to maintain near stoichiometric mixtures. The gaseous fuels, methane, propane, and butane, were preheated to achieve ignition. Preheating was achieved using a resistive heating wire to raise the inlet reactant temperatures up to ~210°C. It is important to note that the preheating temperature is appreciably higher than individual fuel light-off temperatures. Figure 4 provides representative results of catalysis experiments conducted
for ethanol, propane, and butane flowing at 800 mL/min with two-sided Pt coated substrates. Methane results were excluded from Figure 4 because only a single catalytic cycle was observed at the higher flow rate of 1000 mL/min. The need for thermal activation for these fuels is in agreement with similar studies of various Pt catalytic combustion systems [12, 19, 21, 28, 30, 31, 41].

Figure 4 shows catalytic cycling and relatively constant peak temperatures for propane and butane fuels consistent with previous methanol studies. Ethanol, however, demonstrated unstable catalytic combustion temperatures. In other words, while catalytic cycling similar to methanol can be achieved with propane, butane and ethanol, preheating is necessary to achieve light-off at room temperature. Results in Figure 4 are representative of multiple runs conducted with each fuel. In order to discuss quantitative trends, Table 1 lists the average peak temperature, time constant, and heat production rate for each fuel. The average peak temperature is defined as the average of temperature data after reaching 95% of the peak cycle value. The average and standard deviation of peak temperatures for each fuel were evaluated for three cycles within a test. The mean time constants for each fuel ignition were similarly calculated. The analysis was performed using a MATLAB algorithm. Table 1 includes a theoretical estimate of heat production rate based on the assumption that 100% of the fuel is converted to products. Standard Lower Heating Values (LHV) found in combustion literature were used for comparison. Table 1 shows propane attained the highest average temperature of combustion at 820 ± 22°C, while the lowest average temperature was achieved by ethanol at 667 ± 59°C. These trends do not correlate with the heat production rate, suggesting fuel-specific interaction with platinum nanoparticles that potentially controls fuel conversion and in turn heat production rate. A fuel conversion rate study as a function of fuel type is required to thoroughly explain the observed trends. While the alternative fuel study established methanol as the fuel of choice for its ability to combust from room temperature, one can easily integrate the alternative fuels in self-preheating reactor configurations or with hydrogen blended ignition considering that ethanol, propane, and butane successfully yielded the cyclical catalytic combustion desired for an MTC device.

### 3.2. MTC Device Study

In development of the MTC device, the design requirements were governed by existing and previously tested cordierite-based octagonal catalytic substrate. Therefore, to maximize potential power output, according to the previous study [48] substrates with 4-coated sides were primarily used instead of substrates with 2-coated sides used in the alternative fuel study. As a reminder, all MTC device studies utilized near stoichiometric methanol-air mixtures for performance tests. TEG modules that best matched the substrate dimensions were selected. The aluminum reactor dimensions and geometry were dependent on both the substrate and TEG devices, at the same time minimizing thermal mass of the system. Large reactor thermal mass prompts quenching due to excessive heat loss at the heterogeneous combustion stage, eventually requiring reactant preheating. Considering a theoretical model of the ignition characteristics and the quenching mechanisms that are challenging to develop for such a system, a combination of steady state thermal simulations and empirical results were used to guide the final design. A substrate placement location study was conducted to determine the optimal substrate position for uniform temperatures on the “hot side” of the TEG modules. Simulations concluded that a substrate located closer to the fuel-air mixture inlet was ideal. The location, verified by experiments, yielded reactor surface temperatures that were within 10°C of each other. In addition, three heat sink pairs (with 3.5 cm, 8 cm, and 15 cm contact widths) were tested for combustion stability and the temperature difference across the TEGs. Analogous to the reactor thermal mass discussion, the large 15 cm heat sinks promoted quenching, while the smaller heat sinks yielded minimal temperature difference across the TEG modules. As a result 8 cm heat sinks were selected for the MTC device. The final MTC device included a 7.6 cm long aluminum exhaust tube attached to the reactor outlet, which was shown to increase substrate temperature by ~50°C.

Figure 5 presents representative temperature histories from thermocouple probes placed at key locations (namely, two hot- and cold-side temperatures, exhaust temperature, and the substrate temperature) within the final MTC device during a preliminary test to assess device performance. With a flow rate of 400 mL/min, this substrate with two-coated sides experiences the highest substrate temperature that stabilizes within ~7 min of operation. The substrate maintains the high substrate temperature of 500°C before returning to room temperature as the reactant mixture supply is stopped. The device symmetry is evident from the pair of hot-side and cold-side temperature profiles in Figure 5. The pair of hot- and cold-side temperatures directly overlap each other. The temperature difference between the hot-side and the cold-side temperature is defined as the TEG temperature difference ΔT, and that drives thermoelectric conversion. Considering

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<tr>
<td>Ethanol</td>
<td>800</td>
<td>667 ± 59</td>
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<tr>
<td>Methane</td>
<td>1000</td>
<td>740 ± 6.8</td>
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<tr>
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<td>10.1</td>
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<td>Butane</td>
<td>800</td>
<td>790 ± 9.1</td>
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Table 1: Alternative fuel study using preheated inlet results summary. Ethanol reservoir was maintained at 45°C.
an MTC device that operates at steady conditions, $\Delta T$ at the end of a cycle is a reasonable metric to estimate device performance. Figure 5 also provides the product gas exhaust temperature, which is noticeably higher than the hot-side temperature, indicating the future potential for harvesting the heat energy or using the exhaust heat for reactant flow preheat. Alternatively, the substrate temperature can be raised by increasing the flow rate through the substrate resulting in higher heat production rate due to an increase in reactant mixture content.

Figure 6 provides a summary of $\Delta T$ as a function of reactant flow rate. $\Delta T$ represent the mean temperature difference between the hot-side and the cold-side temperatures of a pair of TEGs over three consecutive catalytic cycles. The error bars represent a single standard deviation within the data subset. As indicated in Figure 6, the $\Delta T$ increases with increasing reactant flow rate up to $\sim 60^\circ C$ with 800 mL/min. The increase in $\Delta T$ can be explained by the increased heat release as documented by our previous work [48]. Due to system limitations, thermoelectric conversion performance was not conducted with these experiments. Instead, theoretical values for potential power output based on TEG module specifications and operational parameters (such as TEG temperature and $\Delta T$) were obtained and plotted alongside. Calculations used a Seebeck coefficient of 200 $\mu V K^{-1}$ provided by the manufacturer. Figure 6 indicates the maximum power output at 300 mW for the highest flow rate. Considering the methanol LHV and the flow rate, the thermal conversion efficiency of the system is estimated at 0.1%. While this value is low in comparison to hydrocarbon based power production, the state-of-the-art conversion efficiencies for microcombustion-TEG power devices are in the range of 2-3% [36, 38, 39, 46]. Furthermore, a number of parameters remain to be optimized within the MTC device that minimizes exhaust gas temperature and maximizes the $\Delta T$. The critical design parameters that can drive further enhancements include improved substrate-reactor geometry match, custom heat sink design, optimized reactant residence time, and exhaust heat management, to name a few. Already, the extension of the substrate length has demonstrated notable improvement in fuel conversion (methanol-conversion is estimated at 60% for the substrates used in these studies). Further investigation on the reactant flows, as investigated by Leu et al. [47], is warranted for achieving higher fuel conversion rates.

4. Conclusion

This work provided important experimental results on design of a microcombustion-thermoelectric power device using Pt nanoparticles as the catalyst. The alternative fuel study demonstrated methanol-air mixture as the ideal fuel of choice if a self-starting device is desired. At the same time, the ethanol, propane, and butane can be used in catalytic microcombustion if preheating or an ignition source is integrated. The new reactor design provided a functional device with the ability to achieve repeatable catalytic cycles. While the efficiency of the new reactor is low, this work indicated multiple aspects of the design that can be modified to enhance performance. The results elucidate important influencing factors for further optimization of the thermal design. More importantly, the results provide a viable template towards a highly miniaturized design for a microcombustion-thermoelectric coupled power device.
Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

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