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Micro-reactor design optimization and manufacturing for studying high temperature unimolecular decomposition of large molecules

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Abstract: Low residence time flow reactors (≤100 μs), when combined with photoionization mass spectrometry or matrix isolation/infrared spectroscopy, have the capability to directly probe the elementary pyrolytic reaction mechanism for various fuels. A qualitative analysis of flow inside these reactors (straight tubes approximately 1mm inner diameter and 3cm in length made of SiC) suggests pressure and velocity significantly change along the length of the reactor. This presents a challenge in determining actual flow conditions within the reactor making it complicated to establish conditions at which pyrolytic chemistry occurs. Computational and experimental testing have been used to optimize a new reactor geometry to control the flow profiles by adding a constriction at one end of the reactor. The nozzle has been shown computationally to stabilize fluid flow within the reactor. A review of available manufacturing processes and coating techniques to incorporate this constriction are presented along with the final processes selected. Further computational and experimental evaluations are discussed to highlight the performance of this new nozzle. The novel design of the micro-reactor will assist researchers in carrying out fundamental kinetic measurements of short residence time pyrolytic reactions of fuels influencing the creation of more efficient fuels and in sustainable engine technology.

Keywords: micro-reactor, thermal decomposition, fuels, ceramic manufacturing

1. Introduction

Micro-reactors are well suited to study the pyrolysis of fuels. When combined with sensitive diagnostic techniques such as photoionization mass spectrometry, PIMS, or Fourier-transform infrared spectroscopy, FTIR, micro-reactors can be used to probe the first chemical steps of a reactive mixture at controlled conditions. These reactors have been successfully used to probe the pyrolysis chemistry of a range of molecules such as the benzyl radical ($C_6H_5CH_2$) [1],

cycloheptatrienyl radical (C_7H_7) [2], 2-methoxyfuran ($C_5H_6O_2$) [3], cyclohexanone (C_6H_{10}=O) [4], and methyl acetate (CH_3COOCH_3) [5].

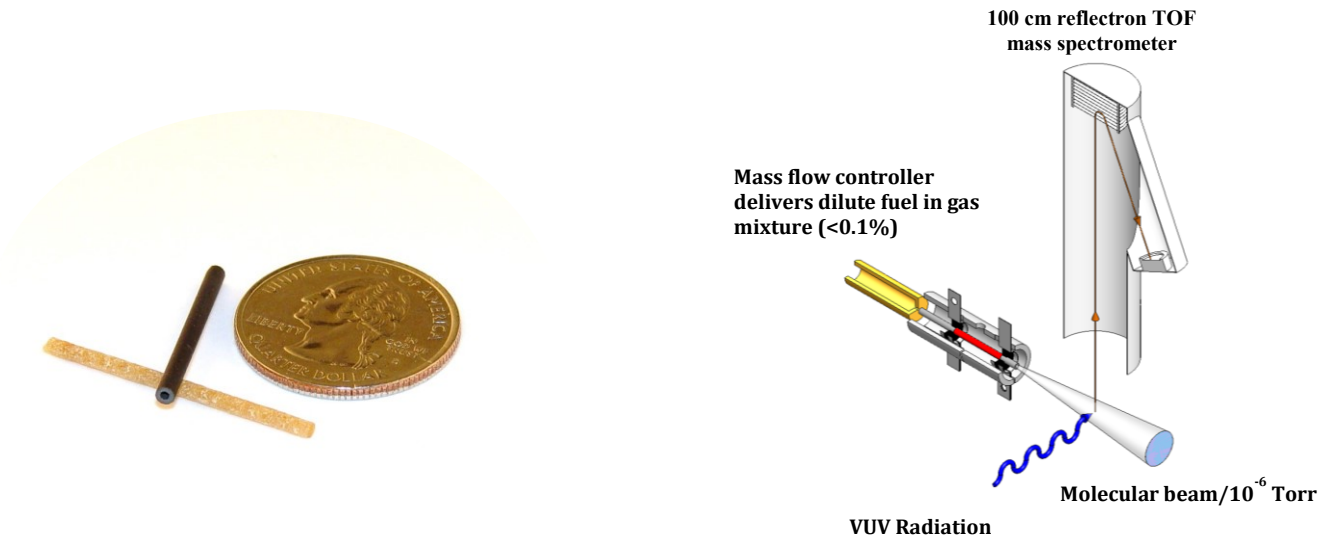

Figure 1: (L) Image of the reactor shown next to a quarter and a piece of linguini for comparison. (R) Schematic of the PIMS experiment

As described previously, the micro-reactor system is a vital component in the experimental setup to study the chemical pathways for the reactions of many fuels. There are however, shortcomings that warrant a review of the design of the setup. Among these is the issue that the pressure and temperature profiles vary drastically along the length of the reactor. Until now, it was assumed that the micro-reactor has a "sweet spot" [6] where the pressure and temperature are both high enough for reactions to occur, however, there is significant uncertainties associated with this assumption. In this work, we aim to redesign the micro-reactor to stabilize the temperature and pressure profiles for more quantitative kinetics experiments. Addditionally, we explore new methods for manufacturing micro-reactors with high aspect ratios out of silicon carbide, as well as various coating methods to make the surface of these reactors inert in oxidative conditions.

The reactor redesign is organized into two phases. The first phase involves carrying out computational fluid dynamics (CFD) modeling of the reactor to predict its thermodynamic profile and to define an ideal reactor geometry to achieve uniform temperature, pressure and velocity profiles within the reactor. The next phase is to explore different designs to achieve the optimum geometry and to manufacture these reactors using conventional casting processes and exploring the application of additive manufacturing. An evaluation of appropriate reactor coatings to sustain oxidative combustion is also included.

2. Micro-Reactor Redesign

2.1 PIMS Experimental Methods

In the PIMS setup under pyrolysis condiditions, the primary reactant (≤ 0.1 mol %) is diluted with Helium to limit bimolecular chemistry. This mixture is introduced into the micro-reactor which is held at a constant temperature within the range of 300 – 1700 K. The reactants undergo thermal dissociation during the short residence time within the reactor, ~150 μs, after which all reactions are stalled as the mixture exits the reactor, forming a supersonic jet. The products then are skimmed to form a molecular beam using a 0.2 mm diameter skimmer and enter a vacuum chamber maintained at 1 X 10^{-7} Torr. The molecular beam is then ionized by the 9^{th} harmonic of an Nd:YAg laser, corresponding to 118.2 nm or 10.487 eV. An electric field in the Z-axis causes the ions to fly into the reflection time-of-flight spectrometer where they are detected.

2.2 Micro-Reactor Design

At the University of Colorado, Boulder, the micro-reactor used is based on the Chen-Nozzle [7], shown in Figure 1. These reactors are straight tubes with an inner diameter of ~1mm and 2-3 cm length. One of the key advantages of using a tubular micro-reactor is the fluid flow within the reactor is laminar. The reactor is made of silicon carbide, SiC, because SiC has a high heat transfer coefficient, is chemically inert, and has a high melting point. Silicon carbide also has low thermal expansion, ensuring that it does not affect the fluid properties within the reactor. It is inert in ultra-vacuum environments (up to 1700K) and has low susceptibility to thermal fatigue and creep failure. While SiC has sidngificant advantages, there also exists significant challenges to working with SiC. High hardness and great brittleness make the process of manufacturing small scale, high aspect ratio geometries complex [8].

The current design features a geometry that is relatively well understood and can be modeled using standard CFD solvers. The flow within the tube is laminar and the pressure drop across the length of the reactor can be calculated as a function of the Reynolds number. There is a dramatic pressure drop from the inlet to the exit of the reactor from around 0.1-0.3 atm at the entrance to near vacuum at the exit along the centerline of the reactor. This leads to significant uncertainty in the pressure at which reactions are occurring within the micro-reactor.

In order to stabilize this pressure profile and reduce these uncertainties, we have designed a new micro-reactor with a converging nozzle section at the exit of the micro-reactor. Our calculations suggest that it is possible to control the upstream pressure by varying the choke area while ensuring the mass flow rate of the fluid in the reactor is kept constant. Figure 2 shows key design parameters, that influence fluid flow within the reactor. These are the length, L, of the reactor, the converging section length, G, and the exit diameter, d. This redesign process was carried out while maintaining the main micro-reactor body inner diameter as a constant and varying L, G, and d to deterimine the optimal final geometry of the reactor.

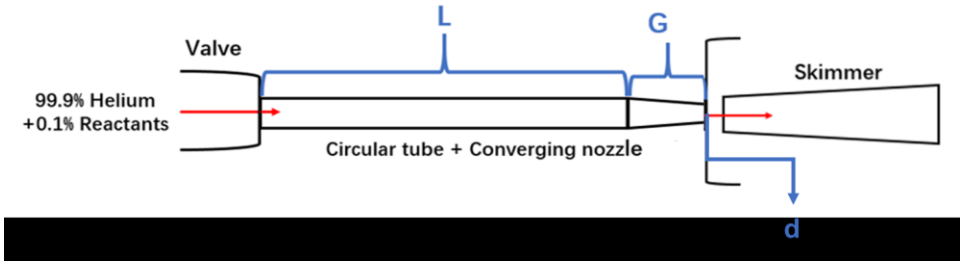

Figure 2: Schematic representation of the redesigned reactor geometry

For the CFD modeling, Helium was chosen as the carrier gas as it is monoatomic, inert, has high thermal conductivity, and is used in the PIMS setup currently. The modeling involves solving the continuity equation, conservation of linear momentum equation, and conservation of energy equation for steady state, compressible, ideal gas flow. For the modeling to be accurate it is estimated that at the inlet the fluid is at room temperature and the wall temperature is held at 1500 K. As it flows through the reactor it experiences a dramatic temperature change. To account for this, valid thermodynamic functions for the thermal conductivity and thermodynamic viscosity of Helium are calculated from previously verified experimental data [9].

This system of equations has been implemented using ANSYS Fluent [10] and MATLAB. Varying configurations of the reactor have been rendered in three dimensions in ICEM [11] using the tetrahedral mesh. This particular type of mesh allowed for quick iterations in geometry to verify its effectiveness on stabilizing fluid flow. The density-based solver was applied with the SIMPLE scheme [12, 13], using a second-order upwind discretization method.

2.3 Selected CFD Results

The exit diameter, d, was found to have the most significant impact on the fluid flow within the micro-reactor. Here we present the influence of varying the exit diameter, d, on the center line pressure and velocity profiles is simulated for different inlet mass flow rates. The exit diameter is varied while keeping all other geometric dimensions constant. The results shown in Figure 3 depict how, without the constriction (see dashed lines) the pressure profile rapidly decreases to near zero and there is a steady increase in velocity through the length of the reactor. When including the constriction (see solid lines), the pressure distribution becomes stable for a significant portion of the length of the reactor. Along with stabilization in pressure, there is a corresponding plateauing of the center line velocity with the addition of the nozzle. Both the centerline pressure and velocity vary with the exit diameter, and thus, the properties of the reactor can be tuned by varying either the exit diameter or flow rate. Varying the length of the reactor was found to have much less impact on the overall fluid properties within the micro-reactor. The only effect observed was changing the residence time.

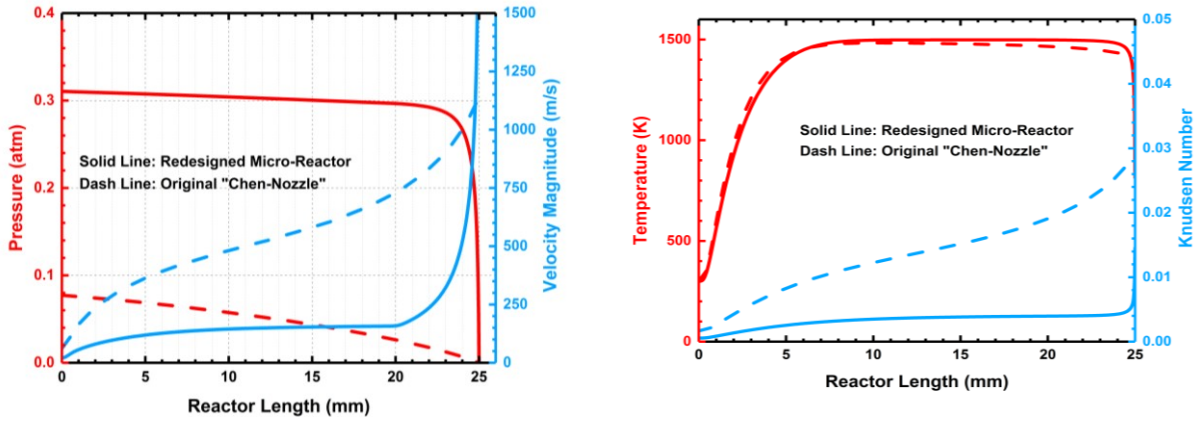

Figure 3: (L) Center line pressure and velocity distributions along reactor length for original reactor geometry and redesigned reactor. (R) Center line temperature and Knudsen number distributions along reactor length for original reactor geometry and redesigned reactor.

3. Micro-Reactor Manufacturing

3.1 Manufacturing Techniques

Different nozzle configurations were evaluated for ease of manufacturing in addition to providing the desired flow properties. In particular, two final designs were compared for their effectiveness in stabilizing pressure and velocity profiles of the fluid in the reactor (Figure 4). The first design incorporates a step nozzle, with a sharp transition in diameters from 1 mm to 0.5 mm at the exit. The second design features a more gradual transition into the constriction. It was identified that the presence of sharp transitions could lead to localized recirculation of products, would result in a non-uniform temperature zone, and poorer surface finish. An improved surface finish would reduce radical trapping, reduce boundary effects, and improve reliability of the reactor in general. Based on these conclusions it was decided to manufacture the reactor with a tapered constriction.

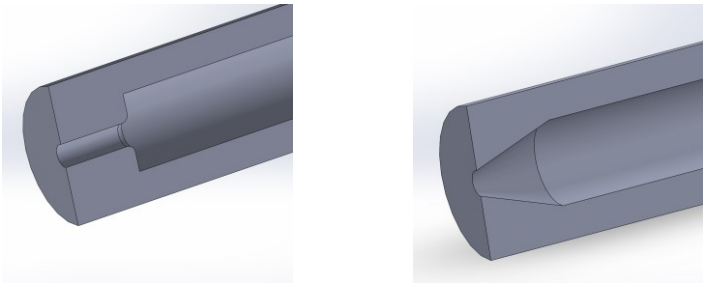

Figure 4: (L) Redesigned reactor showing step nozzle (R) Redesigned reactor featuring taper nozzle

Considering the impact of varying exit diameters on the reactor performance, five different variants are proposed, featuring exit diameters ranging from 0.5 mm to 0.1 mm. All other geometrical parameters are identical in these reactors, except for a change in transition length for exit diameters 0.2 mm and 0.1 mm to accommodate the extreme change in diameters (from a main diameter of 1 mm to 0.2/0.1 mm).

Two concurrent routes to manufacture the redesigned reactors are being employed. The first process involves using additive manufacturing to produce the reactor design. Additive manufacturing presents a highly flexible process which can be used to make quick, iterative changes. With the capabilities present at the University of Colorado, Boulder, this process would be ideally suited to test and validate the reactors. Extensive research has been carried out to manufacture SiC using Stereolithography (SLA) and Selective Laser Sintering (SLS) [14]. To validate the applicability of these processes in manufacturing the geometry, existing 3D printing resources at the University of Colorado, Boulder were leveraged. A standard off the shelf stereolithography printer was used to re-create the geometries created using CAD. The reactors produced through this process were shown to have defects such as cracks, localized deformations

and improper binding of the resin. The geometry of the reactor along with the associated tolerances were deemed too complex to be manufactured using conventional SLA printers.

An alternative additive manufacturing technique currently being evaluated is the use of powder-bed inkjet printing. This process involves layering a binder phase into a bed of ceramic powder. This technique can be used to create complex geometries with high aspect ratios. For this process to be successful, stable ceramic inks must be developed which can dry sufficiently fast enough for the process to be viable. Additionally, these processes are limited by the resolution of the printer and ink combination. Tests are currently being carried out at the University of Colorado using a ZCorp Z650 printer to obtain the ideal SiC grain size to adhere uniformly and produce the desired surface finish.

The second manufacturing technique being adopted involves using a specialized casting process to manufacture the reactor. Casting is among the most commonly used large scale process used to produce ceramic components. Based on geometry there are different process routes that can be chosen to manufacture these components. The different processes were reviewed considering the unique requirements of the reactor and squeeze casting was chosen This technique is a liquid material forging process, in which the material in the liquid state solidifies when closed dies are positioned between the plates of a hydraulic press. The combination of the pressure applied and the contact between the liquid metal and the die surface produces an environment that is ideally suited to produce a pore free, fine-grain structure.

The process involves creating an aqueous slurry of SiC combined with organic binding agents. These binding agents help keep the slurry in a semi-solid form without drying out too rapidly. These additives also help lubricate the punch ensuring it travels in a smooth, single operation and can be withdrawn from the assembly without compromising the component. The liquid ceramic is then poured into the die, which contains the exterior contour of the reactor. The punch, contains the inner geometry of the reactor including the constriction towards the exit of the reactor. As the punch closes into the die, it creates the shape of the inner reactor geometry. Once the die is in position, a hydraulic press is used to apply uniform pressure forcing the material into position. The time duration for which the pressure is applied can vary from 30 to 120 seconds, depending on the weight of the casting. In the case of the reactor, considering the material nature, the load is retained for 145 seconds. The load is removed, but the punch is not drawn out for over 4 hours. This ensures that the material solidifies uniformly, and the integrity of the casting is retained. The punch is then withdrawn from the die, exposing the reactor. Care is taken to ensure that the punch is drawn out at a uniform rate to avoid damaging the reactor. The reactor is then removed from the die – the ceramic in this state is considered to be in the green state. The component is then fired in a closed vent oven up to 2000K during which the ceramic is sintered. The sintering process binds the ceramics together while burning out the organic binders that were added to the slurry. This process imparts high strength to the ceramic and eliminates any impurities that could have entered the component during the manufacturing process.

Squeeze casting produces components that have excellent surface finish. The process has good repeatability creating components that present very high level of dimensional fidelity across batches. This technique also needs very low post processing, requiring little or no machining or finishing, producing near net components. The technique, however, mandates the creation of

complex tooling and multiple set up trials making this process expensive and not suitable for making iterative changes.

3.2 Research on Oxidation Resistant Coatings for SiC

The existing reactor material, SiC, is ideally suited for operations in high temperature environments and is resistant to corrosion in the absence of oxygen. This limits the reactor to being suitable for carrying out only pyrolytic reactions. With an onus on being able to simulate combustion, new materials which can operate in oxygenated environments, that can be coated on the reactor are being investigated.

The material, would ideally have to be able to sustain temperature beyond 2000 K, be chemically inert in the presence of oxygen, and be easy to apply/coat on the existing reactor setup. Different materials are currently being evaluated for their suitability, with tests being carried out on the current reactor geometry. Materials such as Alumina (Al_2O_3), Mullite ($3Al_2O_32SiO_2$), and Zirconium Oxide (ZrO_2) are being studied for their effectiveness as reaction barriers. One of the process employed to apply these coatings is Atomic Layer Deposition (ALD), which can be used to deposit a 5 nm thick layer of Alumina on the reactor. This system is currently being tested for its applicability on the PIMS setup at the University of Colorado, Boulder.

4. Initial Experimental Results

To simulate the effect of having a constriction on the reaction chemistry, a prototype reactor was manufactured. The prototype was made of SiC, has a main body diameter of 1 mm and a length of 28 mm. The constriction was created by inserting an Alumina section with a 1 mm outer diameter and 0.5 mm inner diameter into the reactor. The prototype features a step nozzle as shown in the Figure 5 as compared to the ideal tapered geometry described previously. The effects of having the nozzle section on the reactor pressure and velocity for different flow rates is also shown in Figure 5.

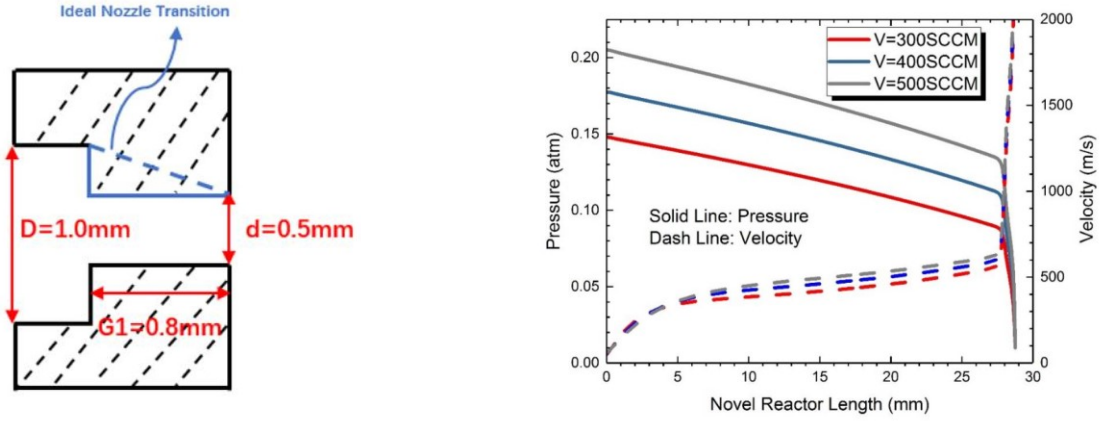

Figure 5: (L) Schematic of reactor prototype insert (R) Centerline pressure and velocity variation along the reactor length for different mass flow rates

5. Conclusions

This paper presents an overview of the redesign of a micro-reactor for studying short residence time pyrolysis. The research details the modeling, redesign, material selection, and manufacturing process chosen to create this novel reactor design.

In the modeling and design phase, the current design used at the University of Colorado, Boulder is characterized and the effects of including a nozzle is studied. The impact of various exit diameters in stabilizing the pressure and velocity is presented. The influences of including a constriction at the exit of the reactor are also evaluated from a thermodynamics perspective. The experimental setup to study pyrolysis at the University of Colorado, Boulder is presented along with the selection of materials to manufacture the redesigned reactor. Two manufacturing processes are presented with details of the capabilities of each technique. Lastly, experiments are proposed to establish the quantitative differences of products/reactants ratio between the original and novel prototype are outlined.

6. Acknowledgements

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