

A Method for Microscale Combustion of Near Stoichiometric Energy Dense Liquid Fuel Mixtures

E D Tolmachoff, W R Allmon and C M Waits

United States Army Research Lab Sensors and Electronic Devices Directorate, 2800 Powder Mill Rd Adelphi, MD 20912, USA

E-mail: erik.d.tolmachoff.ctr@mail.mil

This paper reports on the potential of a heterogeneous/homogeneous (HH) reactor for use as a fuel-flexible heat source, meeting the needs of the next generation of high temperature thermal-to-electric (TEC) portable power converters. In this class of reactor, low activation energy catalytic reactions provide a means to stabilize high activation energy homogeneous reactions. Diffusion limited surface reactions play a critical role in HH reactor operation. Surface conversion must be sufficiently fast to generate the high temperatures (~1000 K) necessary to initiate gas phase reactions. Therefore, fuel diffusivity and the reactor dimension are important parameters in governing HH reactor operation. We examine the performance of an HH reactor fuelled by propane and n-dodecane, representing two extremes of liquid hydrocarbon diffusivity, as a function of confining reactor dimension. Unburned fuel/air mixtures are close to stoichiometric, which is an important factor in minimizing the amount of excess air and, therefore, balance of plant energy costs. At moderate levels of confinement, the reactor is capable producing high, uniform temperatures for both fuels.

1. Introduction

To date, most microcombustion based energy conversion devices have focused on available thermoelectric (TE) modules limiting, them to ~200-500 °C. As both TE and thermophotovoltaic (TPV) improve, efficient TEC energy conversion will require higher operating temperatures (800 to >1000 °C) [1]. Reaching these high temperatures requires a high mass flow rate through a small reactor. High flow rates limit residence time of the reacting flow and diminishing reactor size results in reaction quenching heat losses as the ratio of surface area to volume increases; both factors adversely affect fuel conversion, reactor stability and temperature. A HH flow reactor with catalyst-lined walls separated by small distance in order to tune reactor operation may provide a platform to fully oxidize fuel in very small reactors with large heat losses. Low activation energy catalytic reactions at the reactor's inner surface provide stability against heat loss while heating up the unburned gas to a point where significant homogeneous reactions occur. Homogeneous reactions are less energetic since the fuel content has been partially depleted by surface reaction; they consume fuel and CO that may otherwise escape a small residence time heterogeneous reactor, completing the conversion of chemical energy to heat while avoiding the extreme gas phase temperatures characteristic of ordinary flames ~2000 K. The net result is that HH reactors are capable improved fuel conversion and heat release over the length of the reactor [2-5].

It is well established in the field of gas phase combustion that while hydrocarbon reaction pathways are complex and fuel specific, overall fuel conversion rates are largely determined by



reaction rates of propane and smaller species [6]. It follows that it may be possible to engineer a reactor so that a variety of fuels decompose in such a way that they yield similar distributions of these rate determining smaller species, and therefore, that the reactor behaves in similar ways with different fuels and is fuel-flexible. For fuel flexibility to be achieved this way in a HH reactor, the confining dimension between the catalytic walls would likely play a critical role. This distance, g , determines the characteristic transverse diffusion time scale ($\tau \propto g^2/D$ where D is the diffusivity). Transport to the catalytic surfaces must be fast enough to generate the high temperatures required to initiate gas phase reactions. Since diffusive transport plays such a large role in determining the stability limits of HH reactors [4], it is not immediately clear if there exists a gap such that a HH reactor can operate in a fuel flexible manner over a significant range of practical fuels. Here, we investigate the role of gap size on the performance of a HH reactor. Propane and dodecane (a jet fuel surrogate) were examined to assess how the reactor operates under conditions of light and heavy fuels.

2. Experimental

The reactor used in this study was designed after the reactor in [7]. It consists of two thin stainless steel plates (0.9 mm thick) separated by an interchangeable stainless steel gasket. Welded to the top plate are stainless steel tubes, one for reactant inlet and one for exhaust outlet. Inside the reactor chamber, stainless steel screens (250 μm openings) are placed immediately before and after the reactor section in order to straighten flow and prevent “jetting”. In the middle, the reaction zone consists of catalyst coated alumina inserts separated by thin strips of fibrous alumina insulation. The length of the reaction zone is 5 cm, the width is 1cm and the gap between catalyst inserts is governed by the thickness of the gasket chosen. The assembly is held together by a series of screws around the perimeter. Inside, compressed alumina insulation maintains a snug fit between the catalytic inserts and the stainless steel walls. A photograph and schematic of the reactor are seen in figures 1 and 2.

The catalytic inserts are developed on solid thin amorphous alumina sheets (15x50x0.65 mm). A thin porous layer of γ -alumina nanoparticles are screen printed and annealed onto the solid alumina sheets. The inserts are masked and 0.2 ml of chloroplatinic acid (Aldrich, 8 wt. % in H_2O) is delivered on the porous layer. After drying, the loaded inserts are baked for 5 hours at 923 K to reduce the chloroplatinic acid into platinum. Each insert is loaded with 5 mg of platinum.

The unburned fuel/air stream is preheated to 423 K in order to vaporize the dodecane; the stream is also preheated when running propane for consistency. A butane torch is used to heat the reactor to a point where autothermal operation is possible. Six K type thermocouples welded along the centre of the bottom plate of the reactor are used to monitor reactor temperature. The thermocouples are placed in 1 cm intervals coinciding with the location of the catalytic insert. The reactor assembly is sandwiched between two 5 cm thick needled silica mats (AVSil AB100S) wrapped in aluminium tape. Here we examine equivalence ratio ($\phi = \text{fuel/oxidizer}/(\text{fuel/oxidizer})_{\text{stoichiometric}}$) $\phi=0.9$ and three gap heights (0.5, 1.0, 2.0 mm) with volumetric flow rates varying from 1.5 to 3 SLPM. The conditions chosen are power input rates, flow rates, and gap distances that are representative of values that would be present in a small scale portable power converter (Table 1).

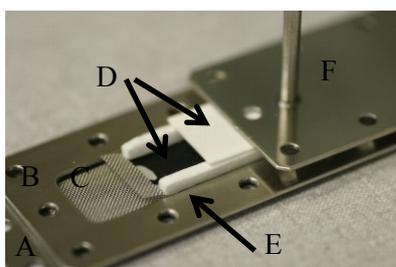


Figure 1. Disassembled HH reactor. A. Reactor bottom. B. Gasket controlling the gap size between reactive walls. C. Flow straightening mesh. D. Catalytic inserts. E. Alumina foam separating catalytic inserts. F. Reactor top.

| \dot{V} (SLPM) | \dot{H} (W) dodecane | \dot{H} (W) propane |
|------------------|------------------------|-----------------------|
| 3 | 156 | 169 |
| 2.5 | 130 | 141 |
| 2 | 104 | 113 |
| 1.5 | 78 | 85 |

Table 1. Summary of reactor conditions. The parameters chosen are representative of values expected to be present in a TPV based portable power conversion device.

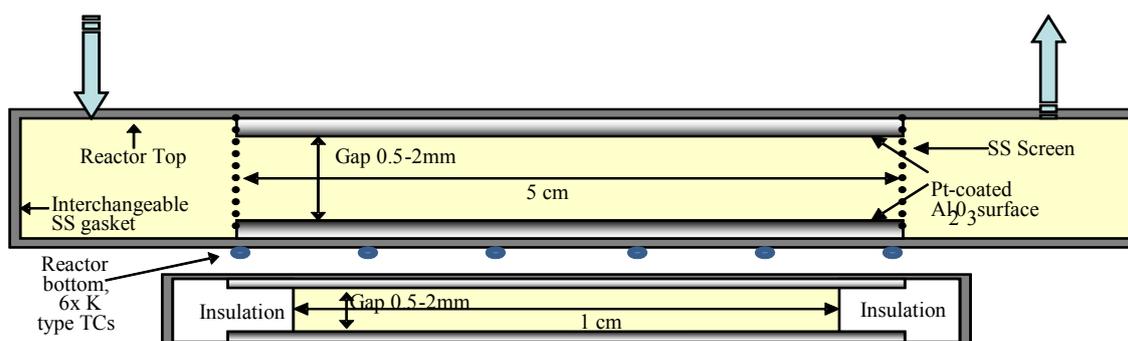


Figure 2. (Top, lengthwise cross section) fuel/air enters from the left, passing through a SS flow-straightening mesh, through the reaction region, finally passing through a SS mesh and out the reactor. Thermocouples record location-dependent temperature. The gap between the reactor walls is controlled by an interchangeable gasket. (Bottom, cross section of width, not to scale).

3. Results and Discussion

The results examined here are based primarily on the steady state location-dependent temperature of the reactor, though some transient behaviour is worth mentioning. For both fuels, transients approaching high steady state temperatures for the reactors with $g = 1\text{ mm}$ and 2 mm showed temperature discontinuities near the middle of the reactor, suggesting that flames were established nearby. Similarly, the transients from high to low steady states temperatures show downward temperature discontinuities, suggesting a flame inside the reactor was blown out (extinguished).

Each condition was run multiple times. The data is the average of 2-4 sets of experimental values with the error bars representing two standard deviations. At high temperatures uncertainty is rather large, however, it is comparable with similar systems [7] and has been attributed to deviations of both flow conditions and catalyst uniformity [8]. It should be noted that steady operation could not be achieved for any conditions without catalyst.

In spite of being well insulated, heat losses are significant and unavoidable for small scale reactors. Norton *et al.* [7] calculated a Biot number of ~ 100 for a thin walled reactor similar to the ones examined here. The same analysis yields Biot numbers >10 for the reactors in this study. Large Biot numbers are characteristic of systems in which the effects of conduction can be largely ignored. A CFD analysis of the reactor (not shown) confirmed this fact. Since the effects of heat conduction are minimized, wall temperatures are highly representative of the phenomena occurring locally. Since microcombustors cannot accommodate traditional combustion diagnostics and numerical modelling is computationally intractable for complex reacting flows, analysis of wall temperatures in a high Biot number HH reactor can provide valuable information about its operation. For example, it can be shown that, under conditions in which the heat releasing reactions are limited by mass diffusion of reactants to the reactor walls, temperature is flow rate independent. Similarly, a strong flow rate dependence on reactor temperature is evidence that the reactor is not transport limited and that a significant amount of homogeneous reactions occur.

Figure 3 shows the data for $g=2\text{ mm}$. Under the least confined conditions in this study, surface reactions play a smaller role and favour lighter species. For dodecane, reactor temperatures are essentially independent of flow rate, a characteristic of transport limited surface reactions. Fuel

decomposition, which readily occurs at high temperatures, is not expected to be appreciable at the reactor temperatures observed for dodecane in Figure 3 [9]. With transport limited operation and minimal homogeneous reactions, reactor temperatures are low. Under propane operation, however, there is a strong dependence of reactor temperature on flow rate, with temperatures rising from 1.5 SLPM to 2.5 SLPM. The residence time dependent temperature behaviour suggests that gas phase reactions play an important role for propane. This is consistent with the understanding that homogeneous reactions are highly sensitive to fuel diffusivity as reactors become less confined [4]. The drop in reactor temperature seen for the flow rate of 3 SLPM, however, suggests that these homogeneous reactions are susceptible to blowout for short residence times. In the case of intermediate confinement $g=1$ mm (figure 4), reactor temperatures are in good agreement for both dodecane and propane. This is the desired behaviour for fuel flexible operation. While the experimental results are promising, modelling work is underway to try to understand the underlying mechanisms allowing this fuel flexible operation.

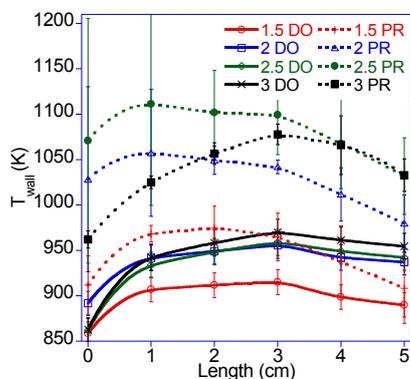


Figure 3. Results for $g=2$ mm. The reactor operating on dodecane (DO) is limited by transport of fuel species to the reactor wall, evidenced by the flow rate independent temperature profiles. Gas phase reactions play a significant role in the reactor operating on propane (PR). However, at flow rates above 2.5 SLPM, the gas does not have sufficient residence time to react and homogeneous reactions are blown out, leading lower temperatures.

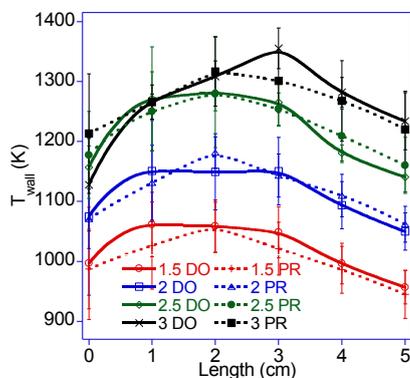


Figure 4. Results for $g = 1$ mm (DO = dodecane, PR = propane). At this gap size, temperature jumps in transients, occurring near the middle of the reactor, suggest flames can be sustained under certain conditions. The temperature characteristics are quite similar for the two fuels, though the underlying reason for this is not well understood at this time.

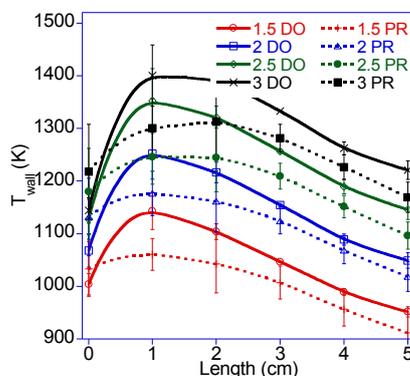


Figure 5. Results for $g = 0.5$ mm reactor. It is remarkable that propane (PR), the lighter fuel, results in lower peak and average temperatures. This suggests that, dodecane (DO) readily decomposed into smaller highly diffusive species near the reactor inlet, resulting in a rapid temperature rise.

The results for the $g=0.5$ mm reactor are shown in figure 5. It is remarkable that when the reactor is fuelled by dodecane, both the peak and mean temperatures are greater than when the reactor is

fuelled by propane. Since propane is a smaller molecule with a greater diffusivity than dodecane, it would be expected that it is more readily transported to the reactor walls and, therefore, that it would lead to higher reactor temperatures. Modelling work on this reactor shows that a transport limited C_2H_4 (the most abundant intermediate of dodecane decomposition [9]) reaction can account for this rapid temperature rise near the reactor inlet. Although a heat source in a power conversion device would experience greater heat losses than those encountered in this work, the rapid coupling between surface and gas phase reaction and temperature gradients seen in both modelling and experiments can be detrimental to the performance and longevity of a heat source. Therefore, there may be a lower limit to level of confinement for a HH heat source to act in a way that is both fuel flexible and optimal.

4. Conclusions

HH reactors show fuel flexible characteristics, capable of maintaining similar reactor temperatures with dissimilar alkane fuels. The underlying reason for the observed fuel flexibility cannot be conclusively determined without detailed modeling or advanced diagnostics capable of seeing into the microcombustor, however, it is clear that the confining dimension in these reactors plays an important role. There is a fuel dependent upper limit on the confining dimension in HH reactor operation. Above this limit, fuel cannot diffuse quickly enough to the reactor walls to react and generate the temperatures necessary to sustain gas phase reactions. There may also be lower limit to this dimension, below which the heat generated by surface reactions causes large and slowly diffusing but unstable fuel species to decompose fast enough to generate undesirably high temperatures and temperature gradients.

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