Optimization of a catalytic combustor using electrosprayed liquid hydrocarbons for mesoscale power generation

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Abstract

A detailed study on the performance of a combustor to be used as a portable power source for mesoscale applications is presented. The burner operation is based on the combination of liquid fuel electrospray injection with combustion through a stack of catalytically coated grids, for the delivery of \( \approx 100 \) W of thermal power. The main design challenges relate to emission minimization, versatility for the coupling to power conversion modules, thermal management, and miniaturization. Combustion efficiency and emission reduction were pursued through catalyst optimization. Using two-dimensional infrared temperature measurements and gas chromatography/mass spectrometry/flame ionization detection exhaust gas analysis, we established a catalyst formulation which provides in excess of 99% combustion efficiency, based on the conversion of the parent hydrocarbon and air to CO\(_2\) and H\(_2\)O. Remarkably, reliable catalyst operation was achieved even using the notoriously polluting JP8, with as many as 1200 ppm of sulfur naturally present in the fuel. CO emission is undetectable and catalytic surface temperatures fall in the 900–1500 K range, which is appropriate for coupling with thermal-to-electric energy conversion systems, such as thermolectric and Stirling engines. The burner was tested for prolonged operation (500 h) for catalyst stability and aversion to coking, even under conditions of high air inlet temperature, to simulate conditions of heat recuperation that are indispensable to the design of high efficiency mesoscale devices. Droplet sizes reveal the need for fuel distributor multiplexing to minimize vaporization time and therefore the size of the necessary preheat chamber. The results of the characterization of a prototypical device led to an improved design utilizing multijet electrospray injection from a single fuel source, an electrospray ring extractor, and whirl, side-port air injection. In addition to reduced emissions and better temperature uniformity, this improved design relying on conventional fabrication resulted in optimal performance in a volume on the order of 10 cc.

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Keywords: Microcombustion; Electrospray; Catalytic combustion; Power generation; JP8; Microlith
1. Introduction

In his seminal lecture “for the year 2000” R.P. Feynman foresaw with nearly prophetic accuracy the miniaturization that would be accomplished in the subsequent 40 years in many fields of technology, from electronics to information storage, from manufacturing to (micro-)electro–mechanical systems [1]. To date it has been demonstrated in the realm of scales that Feynman paradoxically described as “plenty of room at the bottom” in his lecture title. Interestingly, power generation was not considered, perhaps not an accidental omission.

Indeed, the power generating component, invariably a battery, is the factor determining the size of a significant number of currently portable mesoscale devices and often limiting further miniaturization. In this quest for increased power density, liquid hydrocarbon combustion is a promising technology to explore. The power density of conventional liquid hydrocarbon fuels (on the order of 40 MJ/kg) exceeds that of state-of-the-art batteries by a few orders of magnitude. Even operating with efficiency as low as 5%, combustion-based devices can in principle be four to five times more power dense than batteries [2]. On the other hand, the main technical challenge for small-scale combustion is thermal management. Such devices inherently present significant heat losses because of their high surface-to-volume ratio, which at a sufficiently small scale may quench combustion, thus limiting the minimum size of the combustor. Moreover, even if steady combustion is sustained, the maximum efficiency of currently available direct energy conversion modules hardly ever exceeds 10% [3,4]. As a result, as much as 90% of the fuel chemical energy is transformed to heat, proper management of which is crucial for the efficient operation of the burner.

Research activity in the nascent field of mesoscale and “micro-” combustion was reviewed in [2]. A first approach involves direct miniaturization of conventional engines, using classical thermodynamic cycles, such as those adopted in internal combustion engines and gas turbines [2,5–8]. Problems with regard to sealing, balancing rotating components, and separating the “hot” from the “cold” side of the thermodynamic cycle and difficulties in microfabrication of the complex geometries of the necessary parts suggest that a second approach with a minimum of or no moving parts may be preferable. In such an approach, a first stage of combustion is coupled with either direct energy conversion modules, such as thermoelectric (TEG) [9,10], or thermo-photovoltaic (TPV) generators, or possibly Stirling engines. Several combustor designs, operating mainly on light hydrocarbon and alcohol fuels have been proposed [9–11]. Operation with light gaseous fuels is convenient for preliminary testing but is not an option for practical devices, since the high-power-density objective would be defeated by the requirement for gaseous fuel storage. The thermodynamics and heat transfer characteristics of a particular design of small-scale burners are discussed in detail in [9], although the validity of similarity arguments on the basis of nondimensional numbers and assumptions well justified in large-scale systems may be open to question as the length scales diminish.

Our objective is to present the detailed design of a clean and efficient burner which will exploit the high energy density of liquid hydrocarbons for mesoscale autonomous power generation. The burner size has to be on the same length scale as that of the widely available batteries (a few centimeters) and operate on commercially available liquid fuels. It also has to satisfy a series of requirements which relate to coupling with direct power generation modules. Since this device is envisioned as a “liquid fuel battery” with a wide range of applications, some emission standards are likely to be imposed on its operation. To the extent that indoor applications of the burner are possible, a solution to minimize CO emission has to be devised, despite miniaturization efforts that would inevitably result in short residence times. Furthermore, in the case of logistic fuels such as JP8, a jet propulsion fuel consisting of a blend of several liquid hydrocarbons with a high propensity to soot, the need to avoid sooting and the attending burner thermal signature is paramount. We discuss in detail the rationale that led us to the choice of a combination of electrospray for liquid fuel dispersion with catalytic combustion as the optimal solution for the power generation problem restricted by these design criteria. We elaborate on the principle of operation proposed in [12–14], present results on the optimization of the performance of various components of the prototypical burner, and address problems associated with the transition from the prototype to an engineering device.

2. Design criteria

The two main operational features of the proposed burner are catalytic combustion and electrospray atomization. Before proceeding with the quantitative analysis, it is worth justifying the design considerations that led to these particular choices and elaborating on strategies to enhance mixing through the air supply configuration, which is the third component of the burner.

2.1. Catalytic combustion

The temperature at the interface between the burner and the power generating module determines
the choice of the power generating strategy. Furthermore, available technologies (TEG, TPV, Stirling) tend to be restricted to narrow ranges of temperature for optimal operation. As a consequence, very good uniformity is required on the interface, with values lying in the 900–1500 K range, where catalytic combustion is a prerequisite for good stability. Particularly well-suited for small scale applications is a recently developed catalyst substrate design (Microlith) [15]. It consists of a number of catalytically coated grids or screens, each with short channel lengths, high cell density, and low thermal mass, stacked serially. The resulting reactor is compact, has rapid transient response and high energy density, and requires small loadings of precious metal catalysts. Under conditions of kinetic control, this design of staggered catalytic grids can pack significantly more active area into a given volume than the classical monolith designs, which consist of arrays of uninterrupted small-diameter channels. This means that insertion of such catalysts in a flow can provide more effective fuel conversion for a given pressure drop. Also, at the prevailing conditions, the thermal boundary layers around the grid wire are expected to be relatively thick for the laminar flows described here (Peclet number based on the cell opening is of unity order) and to affect the entire flow through the catalyst, thus facilitating reactions in the gaseous phase and efficient conversion of the fuel.

2.2. Electrospray fuel dispersion

Although spray injection is not the only route to liquid fuel dispersion (see, e.g., [11]), it is inevitable for heavy liquid hydrocarbons, since contact of the fuel with hot surfaces of the hardware may cause extensive coking [16]. For liquid hydrocarbon fuel flow rates on the order of 1–10 ml/h, which correspond to 10–100 W of thermal power, the electrospray allows for atomization with minimal power consumption and pressure drop. It can be operated in the cone-jet mode, characterized by the presence of a conical meniscus at the atomizer outlet, terminating into a fine liquid thread that, in turn, breaks into fine, self-repelling droplets (Fig. 1). In this mode the droplets are uniform in size (monodisperse) [17], thus providing a well-defined vaporization time to be matched with the residence time in the “preheat” chamber upstream of the catalysts.

Another feature of the electrospray is the dependence of droplet diameter size on flow rate. In [17,18], for example, this dependence is studied for heptane with 0.3% by weight of an electric conductivity enhancer. It is shown there that droplet size scales approximately as $D \propto Q^{-2/3}$ ($Q$, volumetric liquid flow rate) in sprays in the cone-jet mode. This means that the droplet diameter is decreasing with diminishing flow rate and that this decrease is particularly sharp for small flow rates ($dD/dQ \propto Q^{-1/3}$). So, if a given total flow rate, which is dictated by the thermal power required from the burner, is partitioned into $n$ electrosprays ($n > 1$), the droplet size at injection is reduced by $(1/n)^{2/3}$. Since the droplet evaporation time scales with the square of the droplet diameter, it will be reduced by $(1/n)^{4/3}$. This, in turn, should result in significant reduction of the dimensions of the chamber where the liquid fuel will vaporize and mix with air. Fuels other than heptane may have a power law differing from the 2/3 dependence of heptane. However, the monotonically increasing dependence of droplet size on flow rate is generally applicable to any electrosprayed liquid. As a result, regardless of fuels, this dependence points clearly to electrospray multiplexing as a route to miniaturization.

In parallel work [13], aimed at visualizing the mixing/evaporation process in the chamber, we found that optimal performance results from operating the electrospray in an unsteady regime accompanied by a characteristic hissing sound, slightly below the onset voltage for corona discharge. Although this mode is unlikely to yield monodisperse droplets, the introduction of unsteadiness into the otherwise steady laminar flow field from the whipping electrospray ligaments enhances mixing with the oxidizer, before combustion is initiated at the catalyst, which ultimately results in more uniform combustion temperature.

If the constraint for monodisperse fuel droplets is relaxed, there are other operating modes of an electrospray that can be appealing. For example, by increasing the voltage applied to relatively large tubes, while pumping through flow rates within the range of relevance to the present application, one can operate in the so-called multitjet mode, in which several cone-jets are anchored at a relatively large tube outlet and spread out from the common source while disintegrating into fine droplets. Unless special efforts are made to ensure that the flow rate is partitioned uniformly among the various jets, it is likely that droplet sizes
may vary significantly from jet to jet. This may still be acceptable in light of the findings in [13,18]. Fig. 2 shows a picture of a multijet electrospray originating from a 1/8″ O.D. tube. The simplicity of having a single source, unlikely to ever clog up from coking, is apparent.

As a result there are essentially two ways to realize multiplexing: the first is by merely duplicating an individual capillary again and again to achieve a given level of multiplexing; the second, far simpler, is by using a single source operated in the multi-jet mode. Both were used in the present application. However, the risk of clogging of the multiplexed capillaries, with attending time-consuming maintenance, prompted us to resort to the second approach for the bulk of the experiments described below, especially those requiring burner operation over tens or hundreds of hours.

2.3. Air supply

Determination of an appropriate air supply scheme is an indispensable component of the burner optimization. Preliminary experiments showed that even a 10 m/s stream of air at atmospheric density in cross flow would not perturb the electrosprays. Therefore, rather than providing the oxidizer coaxially to each individual electrospray, as in the original design in [12], one or two lateral ports can be used for side air intake. If air is introduced from these side ports with a tangential velocity component, a whirling flow field is established in the burner. Yetter et al. [19] discuss the potential of whirl combustion for substantial reduction of pollutants in the range of very low overall equivalence ratio values (0.05–0.4). Motivated by these results, we discuss in a following section the application of whirl combustion in the burner under consideration. This entailed a single-source electrospray atomizer operated in the multijet mode coupled with a whirled air injection which “shaped” the electrosprays.

3. Experimental apparatus

A schematic representation of the principle of operation of one burner design is shown in Fig. 3. The flow was distributed through a polyetherketone manifold into a number of stainless steel capillaries (1.59 mm O.D., 127 μm I.D., 10 cm length) arranged in a hexagonal pattern. The principle of operation was demonstrated with seven capillaries arranged in a hexagonal ring [12] and the effect of further multiplexing was studied here with the addition of a second ring with twice the radius and the same pitch (19 needles in total). The capillaries were mounted through a machinable ceramic flange (zirconium phosphate). For experiments that required optical access for in-chamber observation, a cylindrical pyrex chamber 38.1 mm in I.D. and 38.1 mm in height was mounted on the flange. Air delivery through side ports was introduced as opposed to the coaxial delivery of [12]. To achieve overall ϕ = 0.30–0.70, air flow rates on the order of 5 g/min were required, corresponding to a speed through the supply ports on the order of 1 m/s. The chamber was capped at the top with a metal holder in which a number of Microlith catalyst screens were housed. Once the capillaries were charged to a voltage on the order of several kilovolts relative to the grounded catalyst holder, electrosprays were established at the capillary tips.

The fuel was metered with a syringe pump at a flow rate on the order of 10 g/h which corresponded to a thermal power of approximately 100 W.
The burner was operated with three fuels, all doped with an antistatic additive (Stadis 450; Octel America Inc.), a dilute solution of dinonylnaphthalenesulfonic acid in a mixture of aromatic solvents (C9–C16), which provided some electric conductivity. The fuels were JP8, n-dodecane which is the single component-fuel the physical properties of which are closest to JP8 [20], and 1,3 di-isopropyl-benzene which has structure and properties similar to the most common aromatics in JP8 [21]. The concentration of additive had to be kept as low as possible to minimize solid deposition during prolonged operation. A concentration of 0.05% yielded good spray quality for JP8, whereas 0.3% was necessary for pure-substance fuel surrogates. The pressure loss across the capillaries was minimal, i.e., approximately 20 cm of water ($\sim 2$ kPa), and so was the power consumption of the electrosprays. The current carried by the sprays was measured to be on the order of 100 nA, which yielded a parasitic loss of less than 1 mW. Even accounting for additional losses in the voltage multiplication process of high-voltage power supply, it is anticipated that the electrospray power requirements will be less than 1% of the thermal power generated by the combustor. This burner design was used in the tests to optimize the catalyst formulation.

It was observed that after multiple turnoffs of the burner, the capillary lines often became obstructed by solid deposits in the capillary tubes. To tackle this problem, the fuel distributor was redesigned. Instead of emerging from several capillary tubes, the electrospray emerged from a single large tube (1/8″ O.D.) and was operated in the multijet mode [22], as discussed above. This configuration proved ideal for tests of very long duration (100–500 h) for catalyst evaluation, requiring minimal periodic cleaning every 75 h of continuous operation. Air was admitted through the chimney side walls and the catalyst grids were used as ground electrode. With this configuration, the durability tests were performed.

The third and last configuration on the path toward burner optimization incorporated the whirl air addition, with a tangential injection of the air. A schematic of the optimized burner is shown in Fig. 4. In this case a 38.5-mm-diameter ring acting as electric ground (ring extractor) was mounted on the Teflon atomizer base and a circular Teflon flap in the inner side of the ring was used to improve electric insulation and prevent sparking. To establish a whirl flow, two 6-mm-I.D. Pyrex tubes were mounted tangentially, in diametrically opposed positions, on a Pyrex chimney measuring 38.5 mm in inner diameter and 20 mm in height. The chamber height was adjustable down to a minimum of 11.4 mm, by sliding the chimney over the bottom Teflon flange. Teflon tape was used to provide leak-tight tolerance. The chamber was capped by several layers of catalytic meshes, housed in a metal holder. Interposed between the catalyst and the atomizer were a few uncoated high-density cell screens, the purpose of which was to prevent direct impingement of the droplets on the catalyst and contribute to the mixture uniformity at the entrance of the catalytic reactor. The air intake was heated to simulate heat recuperation in an operating device.

4. Diagnostic techniques

Exhaust gas sampling downstream of the catalyst was used to determine exhaust gas composition. Major combustion products and light species ($N_2$, $O_2$, $H_2$, $CO_2$, $CO$, $CH_4$, $C_2H_6$, and in general hydrocarbons with three or fewer atoms of carbon) were measured using a two-channel Micro-Gas Chromatograph of Agilent Technologies. The device employs two channels, one with a molesieve and one with a PorapLOT backflush injector. Acquisition of an exhaust gas sample lasted 60 s and argon was used as a carrier gas for both injectors. In some targeted tests to identify the unburned hydrocarbons in the exhaust gas, we sampled gas and analyzed it with an Agilent gas chromatograph/mass selective detector/flame ionization detector (GC/MSD/FID) system (Agilent 5973N MSD, 6890 GC). Three columns were used in the GC: a Supelco Carboxen column, able to separate CO$_2$ and light gaseous hydrocarbons, an HP-1 well-suited to separating hydrocarbons up to C$_{12}$ and even higher; and a third column, Molesieve, well-suited to the separation of CO. The Supelco column, in fact, could separate CO from $N_2$ only with a small sampling loop, which would have adversely affected the instrument sensitivity to trace species. Two columns were connected to the MSD and one was connected to the FID through an elaborate system.
with two 10-port valves, allowing for backflushing of one of the columns. The GC oven was programmed for 35 °C, hold 10 min, ramp at 5 °C/min to 230 °C, hold 40 min. Sampling the exhaust gases of the burner was done using a quartz probe positioned approximately 1 cm above the catalytic grid into a chimney, located on top of the burner, to avoid dilution of the gases with the atmosphere. The tubing connecting the probe to the sampling rig was heated at 200 °C to avoid condensation. The sampling loops were filled at a pressure of 400 mm Hg before injection into the capillary columns.

The temperature at the catalyst surface was measured using a PV-320 Electrophysics infrared video camera and a germanium objective lens. To avoid signal saturation, a glass filter of 0.3 optical density and a 2.5-µm cutoff was used, so that the recorded signal on the camera chip was from the 1.5–2.5-µm part of the spectrum. The temperature measurements were calibrated using a K-type thermocouple coated with the catalyst material.

To characterize the droplet size behavior for the fuels of interest as a function of flow rate, a commercial Phase Doppler Anemometer (Dantec Electronik) was used and operated at Brewster’s angle for the fuels of interest.

5. Results and discussion

5.1. Catalyst optimization

In [12] we demonstrated the principle of combustor operation using a catalyst that was not targeted specifically for liquid hydrocarbon fuels but was rather optimized for light gaseous hydrocarbon combustion. The 97% efficiency thus achieved was certainly encouraging. However, the presence of amounts of CO as high as 2% per volume in the flue gases necessitated optimization of the catalyst so that more efficient conversion to CO2 could be achieved, since CO emissions at that level would restrict significantly the use of such burners in indoor applications. During catalyst optimization, both catalyst and support formulation and substrate geometry were considered, as shown in Table 1. The catalyst on sample A was palladium on stabilized alumina and was the same formulation as that used in [12]. The catalyst precious metal ratios on samples B and C were 8/2 Pd/Pt. The catalyst support used on B and C was stabilized alumina. Additionally, sample C was doped with Ce and Ni for enhanced sulfur resistance. The meshes used for samples A, B, and C were approximately orthogonal grids of 125-µm wires with 1 mm pitch. For sample D, the formulation was kept the same as that of sample B, but the pitch on the mesh was reduced to 0.8 mm; the catalytic grid therefore was denser and the geometric area was thus increased. In summary, samples A, B, and C had different catalyst and/or support formulations with the same substrate, whereas sample D had the exact same catalyst formulation as sample B but different geometric characteristics. In all cases the total catalyst loading was significantly less than 1 g.

The results of catalyst optimization for JP8 combustion are shown in Figs. 5 and 6 where the ratio of CO to CO2 concentration in the flue gases and maximum catalyst temperature are presented as a function of equivalence ratio and mass flow rate through the burner. The maximum temperature can be used as a reasonable estimate of the average temperature,
Fig. 6. Maximum temperature on the catalytic screens for JP8 combustion (a) as a function of overall equivalence ratio for a constant fuel flow rate of 12.6 ml/h and (b) as a function of fuel flow rate for an overall equivalence ratio of 0.48. The symbols indicate catalyst formulations from Table 1.

since it was shown in [12] that a ±5% uniformity is achieved. It was preferred only because it was easier to acquire from infrared thermography images. If we ignore other carbon-containing species in the flue gas, the ordinates in Figs. 5a and 5b can be interpreted as approximately the per-volume compositions of the burner exhaust in CO or, equivalently, the percentage of carbon which was not oxidized completely. This CO/(CO + CO₂) ratio is presented as a function of the equivalence ratio for a constant volumetric fuel flow rate of 12.6 ml/h in Fig. 5a and as a function of mass flow rate for ϕ = 0.48 in Fig. 5b. In the former case the equivalence ratio varies by varying the mass flow rate of air, whereas in the latter case the total mass flow rate is proportional to fuel flow rate, since ϕ is kept constant.

To interpret the results of Fig. 5, one should keep in mind that the operation of the burner is heat transfer limited as explained in [12]. As combustion becomes leaner, heat loss (the rate of which depends much more strongly on the physical properties of the burner hardware and the environment rather than on the burner operation parameters) prevails over combustion-related heat release. In such a case, oxidation is not completed; i.e., CO concentration in the flue gases increases. If, on the other hand, the equivalence ratio approaches the stoichiometric value, heat losses cannot hinder full oxidation and the conversion to CO₂ is more complete. The scenario is complicated somewhat for the case when the equivalence ratio is kept constant and the fuel mass flow rate varies. In that case, fuel flow rate is proportional to total flow rate and therefore inversely proportional to residence time in the burner and in the vicinity of the catalytic grid. At increased flow rates, we provide increased heat input to the system; however, the residence time in the catalytic burner decreases. Competition between these two effects is expected to yield an optimum flow rate with regard to completeness of combustion.

Fig. 5 shows that under all conditions of operation, catalyst D, i.e., the one with the finest grid, gives significantly more complete conversion. Actually in most cases, CO is close to or below the detection limit of the employed GC technique (10 ppm). On the other hand, it is difficult to decipher any substantial difference between samples A–C which have the same geometric surface areas, despite significant differences in their formulation. Using the process outlined in [13] (carbon atom balance) to estimate combustion efficiency from such data, we evaluate that in all conditions of operation it exceeds 99% for operation with catalyst D. The stoichiometry of complete combustion was calculated using the average C–H ratio for JP8, which is close to that of n-dodecane.

Increased combustion efficiency caused an almost 5% increase of maximum catalyst temperature for operation with catalyst D at elevated equivalence ratios (Fig. 6a). Since the combustion was almost complete (approximate efficiency of 97%) even for preliminary results with a nontargeted catalyst [13], we did not expect a drastic increase in temperature. An energy balance in a control volume surrounding the catalyst bed yields

\[
\frac{dm}{dr} Q_{\text{LHV}} = \frac{dm}{dr} c_p(T - T_0) + \varepsilon \sigma A(T^4 - T_0^4) + Q'_{\text{cond}},
\]

where \( m \) and \( m_f \) are total and fuel mass, respectively, \( Q_{\text{LHV}} \) is the lower heating value of the fuel, \( \varepsilon \) is the emissivity of the catalyst material which was approximated as that of the steel material of the wires, \( A \) is the radiating surface which can be estimated from the dimensions of the grid wires for catalyst D, and \( Q_{\text{cond}} \) is the heat loss due to conduction through the catalyst material and the rest of the burner hardware. \( Q_{\text{cond}} \) is difficult to measure directly but substitution into Eq. (1) yields that it must be on the order of 12% of the total energy input, which is entirely conceivable for the current experimental setup. Without detailed knowledge of what happens with 12% of the fuel heat release, the results of Fig. 6b that show practically no
difference between the various catalyst formulations are not surprising. Heat management in the burner is discussed further in the context of heat recuperation in the following section.

The fact that complete combustion is achieved at the low temperatures indicated in Fig. 6 suggests that heterogeneous reactions play significant roles affecting the bulk of fuel conversion and do not simply initiate gas phase chemistry. However, the range of temperatures is such that homogeneous reactions are likely to be also significant. The study of the relative importance between homogeneous and heterogeneous chemistry will be addressed in the future.

5.2. Prolonged operation of the burner

For continuous operation during time intervals from a few hours to hundreds of hours, there are additional design concerns pertaining to coke formation and catalyst durability.

An efficient use of the heat rejected by either the burner or any potential direct energy conversion module coupled to it would be to heat the air fed to the burner, which could then also be used to warm the liquid fuel to facilitate vaporization. Since, as explained above, at a minimum 85% of the chemical energy of the fuel is expected to convert to heat, the temperature of the preheated air stream could be elevated to levels close to the combustion temperature of the burner, in something akin to a regime of mild combustion [23]. For a maximum temperature of 1200 K, it is not unreasonable to expect air intake temperatures on the order of 700 K. Although this is a thermodynamically advantageous mode of operation, it has been established that, when heated on solid surfaces, liquid hydrocarbons present a very strong coking tendency [16,21]. Any form of solid deposition is unwanted for the operation of the burner. Coke can obstruct capillary fuel delivery lines and solid depositions at the burner walls may alter the heat transfer characteristics and cause the operational point to drift from a desired steady state. Moreover, since the shape of the tip of the fuel injector is important for the formation of the electrospray, even minimal depositions on the tip may alter drastically the atomization characteristics.

Early indications of limited solid deposition on the burner walls prompted us to examine the phenomenon in a more systematic manner. First, it was established that the amount of antistatic additive had a significant effect on solid deposition. Decreasing the antistatic additive content to 0.05%, as described above, tackled the problem successfully for approximately 1-h-long experimental runs. To test possible obstruction of the capillaries by coking, we increased the air intake temperature to 750 K to simulate extensive recuperation in an actual device and ran the burner for approximately 3½ h at a JP8 flow rate of 11 g/h and overall equivalence ratio of 0.48.

To exacerbate possible coking formation, we deliberately increased the protrusion of the steel capillaries by a factor of 10 to a total length of 5 mm to increase the contact time of fuel and hot surface. This affected adversely the uniformity of temperature on the catalyst. However, even on this time scale, no effect on the macroscopic characteristics of the burner operation (maximum temperature, temperature nonuniformities of the catalyst) was observed. The main reasons for this are that the capillary length in contact with the hot air stream is short and that the fuel residence time in contact with the hot surface is too brief, on the order of 1 ms, for coking to take place in the tube. Minor solid deposition was only observed on the spray tip, where the “cone” of liquid from which the spray forms sat.

The results of a 500-h test of the catalyst are shown in Fig. 7, where CO and unburnt hydrocarbon emission measurements are presented as a function of time during the test. The experiment was interrupted 10 times for fuel distributor cleaning, since a highly viscous deposit, the apparent quantity of which depended directly on the amount of antistatic additive, formed at the exit of fuel supply tubes, although no obstruction of the supply lines due to coking was observed. The results indicate practically stable operation of the catalyst, despite the presence of as much as 1200 ppm of sulfur in the fuel. It is likely that the observed cyclic variability is related to the periodic interruptions of operation for the distributor cleaning. After 500 h of aging, scanning electron microscopy analysis of the washcoat support surface showed a well-dispersed Pd phase (bright spots) covering the entire surface with average particle diameter of up to ~ 1 μm (Fig. 8). This indicates relatively low catalyst sintering. Comparison of energy dispersive spectroscopy signals in catalyst exposed to the gas flow and catalyst sheltered from the flow did not re-
Fig. 8. Particle size distribution of catalyst surface after 500 h aging.

Fig. 9. Droplet diameter as a function of JP8 flow rate through 127-µm (0.005″) I.D. capillaries for electrosprays at the cone-jet mode.

veal meaningful differences, suggesting little change in morphology. The washcoat integrity remained unaffected with no indications of distress, e.g., delamination. These results suggest that catalyst performance should be durable for periods much longer than 500 h.

5.3. Droplet sizing

JP8 droplet size measurements in the cone-jet mode are reported in Fig. 9. In this mode of operation, the electrospray is practically monodisperse. The relative standard deviation in the reported sizes is less than 0.10. The exponent of a power law regression through the data is significantly smaller than that for the heptane case ($n \approx 0.4$), which indicates a milder dependence on flow rate at higher flow rates and a drastic one for smaller flows. If we assume that this relationship can be extrapolated to very low flow rates, as shown in Fig. 9, the need for extensive multiplexing is exacerbated, since only for very small flow rates per spray can a substantial decrease in droplet size and therefore vaporization time be observed. The necessary increase of the number of fuel electrosprays can be pursued for the designs of Figs. 3 and 4 only through microfabrication of extensive arrays of tips. However, the ring extractor configurations of Figs. 2 and 4 offer the perspective of geometries much easier to manufacture and will be discussed in more detail in the following sections. A word of caution should be spent on the use of droplet size data for other, possibly unstable, operating modes of the electrospray. The monotonic behavior of size versus flow rate still holds but only qualitatively, and the distribution of droplet sizes for a given flow rate broadens significantly. Thus, the functional dependence of Fig. 9 can be used only for qualitative guidance.

5.4. Optimized combustor: multijet electrospray with ring extractor and whirl air injection

Our analysis so far has demonstrated significant advantages of pursuing multijet electrospray injection from a relatively large (1/16–1/8″ O.D.) tube (Fig. 2) over distributing the flow through an array of capillaries (Figs. 3 and 4). In summary, multijet configurations are significantly easier to manufacture for the same degree of electrospray multiplexation and they are much less vulnerable to solid or highly viscous deposits or to fuel line obstruction after burner switch-off.

An important additional modification toward the optimization of the particular geometry is the addition of an electrospray ring extractor, which, to some extent, decouples the electric ground of the system from the catalytic screens. To get a more “radial” atomization, a metal ring was grounded and mounted at the base of the chimney, coaxially with the electrospray nozzle. Individual cone-jets are extracted as a “fountain” (see Fig. 2). The catalytic screens do not attract the droplets electrostatically. The droplet streams move toward the ring, thus “lingering” at the bottom of the preheat chamber. This extends the residence time of the fuel into the mixing chamber for a given chamber size. Equivalently, the necessary preheat chamber height for the vaporization of a given flow rate of fuel can be decreased. Indeed a decrease in chamber height by a factor of approximately 3 was observed compared to the prototypes of [12,13].

Whirl air intake is expected to improve temperature uniformity on the catalytic surface, which is crucial for efficient coupling with direct energy modules. In fact, uniformity of temperature relates directly to the homogeneity of the local equivalence ratio. Quantification of the combustion uniformity is performed with the IR camera over a range of overall equivalence ratios, using JP8 at a constant flow rate of
temperature of 1170 K is reached when burning JP8 at an equivalence ratio of 0.6. There does not seem to be a substantial increase of temperature as the equivalence ratio increases from 0.6 to 0.7. This was observed also in some of the catalyst tests of Fig. 6 and is attributed to details of the heat transfer from the burner. The temperature can be increased for any value of the equivalence ratio by reducing the heat loss due to conduction through the burner hardware as indicated by Eq. (1) with a selection of appropriate insulating material, such as a ceramic blanket. The presence of a low-temperature area at the outer periphery of the catalyst screens is mainly attributed to the whirl flow. Because of the lateral air injection, the mixture is leaner on the side of the combustor and the air injection can locally cool the catalytic screens. Consequently, combustion is weak in this area. This low-temperature area can be minimized by insulating the burner sidewall and by blocking the outlet of the combustor with a suitable disk to ensure that the only exposed surface is at uniform temperature.

The extent to which the combination of more compact size provided by the ring extractor with increased temperature uniformity provided by whirl air intake can be sustained is illustrated in Fig. 12. At a fixed overall equivalence ratio of 0.5, attempts were made to minimize the chamber height and temperature distributions were measured at heights of \( h = 16.5 \text{ mm} \) (Fig. 12a) and 11.5 mm (Fig. 12b). In the first case, temperature was uniform over a relatively large area of the catalyst, although the temperature fluctuations were larger than those in Fig. 11. A temperature within 10% of the maximum value is indicated with a horizontal line in the related profiles. This corresponds to a variation of \( \pm 5\% \) around a mean value of 1088 K, which was the criterion used in [12]. In the case of the shortest chimney (Fig. 12b), the electrospays impinged on the catalytic grid before evaporating and the reactor bed was lengthened to prevent fuel loss. During operation, fuel accumulated on the screens before evaporating. Good uniformity in temperature is achieved also in this case (Fig. 12b), i.e., with a variation of \( \pm 5\% \) around a mean value of 958 K, when air was injected at a temperature of 523 K. In this last case, temperature was uniform over a smaller area and the mean combustion temperature was lower. This decrease in mean temperature indicated that the minimum acceptable burner height for the particular configuration was between 11.5 and 16.5 mm. The effect of air whirl is evidenced by a comparison of Figs. 12a and 12c. In both cases experimental parameters are identical, but for Fig. 12c, whirl injection was substituted with coaxial air injection from the burner bottom.
which was obviously detrimental to temperature uniformity.

5.5. Exhaust gas analysis by GC/MSD/FID

The micro-GC results of Fig. 5 indicate a minimal amount of CO in the burner flue gas which for most operational conditions was below the detection limit of the micro-GC technique. However, given the strict emission requirements expected for devices that may be required to operate in closed spaces of human activity, we pursued a detailed characterization of emissions for the optimized configuration determined above. Exhaust gas analyses from the optimized whirl combustor were performed over a range of overall equivalence ratios (0.4–0.7). For this test dodecane was used as a fuel, since its combustion products can be identified with less ambiguity than those of JP8 using chemical analytical techniques. The catalytic reactor was sized to ensure complete conversion by stacking several grids. For the optimized whirl air intake burner, CO could not be detected by GC/MS over the explored range of equivalence ratios, with a threshold concentration detectable by the GC/MS on the order of 1 ppm.
A sample MSD chromatogram, obtained with the burner operated at equivalence ratio of 0.4 (which Fig. 5 indicates is marginal with regard to emissions), is shown in Fig. 13a. Alkenes, aldehydes, and ketones with carbon atom numbers smaller or equal than the parent fuel were detected. The peaks located for retention times larger than 35 min were neither well separated nor identified. The results of Fig. 13a are not typical for all conditions of operation. For operation at overall equivalence ratios closer to the 0.55–0.65 optimal region suggested by Fig. 5 the structure of the chromatograms is drastically simplified with only the peaks of alkenes and dodecane (C_{12}H_{26}) being present. FID was used for quantification of the species present in the chromatogram. Fig. 13b shows the FID spectrum for these optimized conditions. Of the species that could be detected with our diagnostics, the dominant emission is unburnt vapor of the parent fuel at a level on the order of 10 ppm. This indicates clean combustion of heavy liquid hydrocarbons, which are notorious for the environmental concerns that their combustion entails, except for the inevitable sulfur emission, which could be curtailed only with scrubbing approaches unsuitable for a miniaturized combustor.

6. Conclusions

We demonstrated that the combination of electrosprays of liquid fuels with combustion on appropriately formulated fine catalytic grids is a promising route toward combustion-based power generation in the mesoscale, even in the case of fuel blends of heavy hydrocarbons such as JP8 (jet propulsion fuel) with their notorious emission challenges. We optimized a prototype burner based on this combination using JP8 at flow rates on the order of 10 ml/h with overall equivalence ratios of 0.35–0.70 to produce thermal power on the order of 100 W in a volume on the order of 15 cc. Uniform temperatures were demonstrated on the incandescing catalytic screens at the combustor output in the 900–1500 K range, which are appropriate for coupling with TEG, TPV, and Stirling systems. The stability of the catalyst formulation for prolonged burner operation (> 500 h) was demonstrated, despite the presence of as many as 1200 ppm of sulfur in the fuel. Even when tested with air inlet temperatures as high as 700 K, to simulate the extensive heat recuperation expected in small-scale combustors, the burner exhibited durability over several hour-long tests. Fuel supply line obstruction due to coking was not observed, because of the limited surface of contact of
the fuel capillaries with the hot air flow. Key ingredients to the optimization are the following:

(a) catalyst formulation and geometric characteristics, with a Pt/Pd formulation used to achieve combustion efficiency in excess of 99% and to reduce CO emission below the detection limit of analytical instrumentation;

(b) a modification of the initial prototypical design which involved the establishment of a multijet electrospray at the exit of a relatively large (1/8’’ O.D.) tube, which eliminated general concerns about the robustness of a fuel delivery system based on easily cloggable capillary supply lines and simplified the manufacturing of the fuel distributor system; and

(c) the introduction of a whirl air supply, which resulted in enhanced mixing in relatively small volumes.

These results provide the basis for consideration of the proposed combustors from an engineering systems analysis perspective. This can include the study of manufacturing techniques for such prototypes with a particular emphasis on the application of microfabrication techniques and the study of integrated power producing devices which will combine the combustor with direct energy conversion modules. Although this study was motivated by the search for power devices at the level of tens of watts, there is no a priori reason that the approach could not be scaled up (down) by a few orders (one order) of magnitude, without dramatic departures from the proposed design. Drastic miniaturization will necessitate a careful study of the microfabrication and thermal management issues involved.

Acknowledgments

We acknowledge Dr. R.S. Tranter of the University of Illinois at Chicago for his consulting in setting up the GC/MSD/FID, Mr. R.W. Dean of PCI for his assistance with the micro-GC measurements, Mr. N. Bernardo of Yale University for machining the hardware, and Mr. P.A. Dobrowolski of Yale University for acquiring the photograph of Fig. 1. The support of DARPA under Grant No. DAAD19-01-1-0664 (Dr. Richard J. Paur, Contract Monitor) is gratefully acknowledged. Microlith is a trademark of Precision Combustion Inc.

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