

Research for Fuel Cracking in Microchannels for Power MEMS Applications

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Abstract

This paper describes research challenges for the reformation (or “cracking”) of long hydrocarbon chains in microchannels for power MEMS applications. This approach leverages storage advantages of long hydrocarbon chain fuels, such as octane, with combustion advantages of lighter molecular weight fuels, such as hydrogen, methanol or ethylene. For portable power applications, internal combustion engines continue to be a viable option and several concepts are in development with displacements of a few cubic centimeters. These micro engines deliver higher specific power and typically operate at significantly greater speeds, due to operation with highly oxygenated fuels, than their macroscale counterparts. High operation speeds reduce the residence time for the combustion event to occur and successful micro engines perform better with faster burning, shorter hydrocarbon and oxygenated fuels. In this work, heavy or long chain hydrocarbon fuels are heated within micro fabricated silicon channels and the resulting fuel cracking is noted.

Keywords: Micro-engine, fuel cracking, micro fluidics

INTRODUCTION

Internal combustion engines for portable power applications require highly reactive fuels for improved performance due to the limitations imposed by the small size of the combustion chambers. Highly reactive fuels such as hydrogen have very high flame speeds and short quenching distances. For these reasons, the majority of commercial small scale engines operate with oxygenated fuels such as methanol, and shorter alkane hydrocarbons such as butane, as well as hydrogen. Unfortunately, these oxygenated and lighter fuels, such as methanol, suffer from a decreased storage energy density (W-hr/l) when compared to other hydrocarbon fuels. Given the energy storage requirements of portable power systems, an integrated fuel reformer which would break down heavy fuels into lighter constituents would increase the energy storage capability of small scale power generation systems. Further, fuel cracking or partial fuel reformation for portable power applications can potentially improve operational flexibility. Recent work at the University of California at Berkeley has shown that small rotary internal combustion engines are able to run on a variety of hydrocarbon based fuels, but engines have better performance for lighter end fuels [1]. Using microchannels to increase reactive surface to volume ratios and potentially microscale phase change techniques, longer hydrocarbon chains commonly found in gasoline or diesel fuel can be reformed into lighter end fuels. In practice, the enthalpy required to break down the fuel into lighter components will be provided by engine waste heat, improving the system thermal efficiency.

BACKGROUND

The University of California at Berkeley is developing a reduced scale Wankel-type rotary internal combustion engines for portable power applications. These micro engines are designed to operate at higher speeds than traditional engines, as previously noted. Our research group has shown that small (4.97 cm³) rotary engines are able to operate more effectively using methanol as a fuel which has a much smaller oxygenated hydrocarbon chain than either gasoline or diesel fuel, shown in Figure 1. This can be attributed to the increased reaction rate of the lighter end fuels, making possible operation at reduced Damkohler numbers. However, as the size of the hydrocarbon chain decreases (fewer C-C bonds), the energy density of the fuel also decreases, as can be seen in Table 1. This highlights the need for an energy conversion device which cracks the high stored energy density fuels into lighter components without adding significant system complexities or a large parasitic load. In addition to fuel energy density, system energy density must be compared to system efficiency because both are important for a complete system. Energy density at the cost of significant system efficiency does not yield an acceptable system.

To address system energy density there is a need to use large molecules for micro power applications. Fuel reformation on the micro and mesoscale is feasible using standard MEMS processes [2], [3]. However, integrated reformation systems are complex and energy intensive, creating a considerable parasitic energy load when coupled to an energy generation source such as a fuel cell or micro engine. Furthermore, compared to a micro fuel cell based

system, a high temperature micro heat engine system is far more tolerant to fuel impurities and can run on a wider range of fuels. Therefore, there is a need for a portable power system in which hydrocarbon fuels are cracked into lighter constituents but not fully reformed for portable power systems.

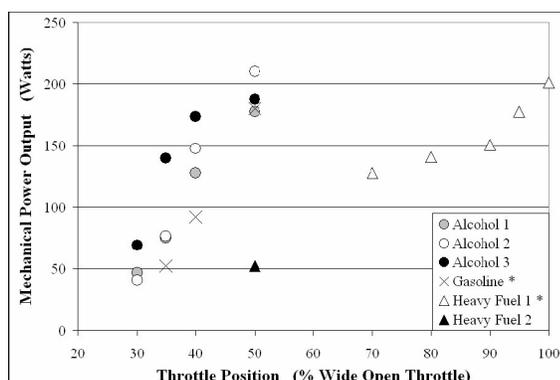


Figure 1. The 4.97 cm³ Wankel engine is capable of operation with heavier, higher energy density fuels, namely diesel and JP8, albeit with degraded performance. [1]

In experiments with a 4.97cm³ Wankel engine, the most efficient and most powerful operation was produced using alcohol fuels, namely nitro-methane/methanol/oil mixtures as the fuel. However, as Ameel et al. [4] note, while miniaturizing an engine dramatically increases the surface area to volume, size reduction does not affect the chemical reaction time of the combustion event given that the density of the reactants remains the same as the engine is scaled down. This again points to the need for a simple, on board, cracking system.

Table 1. Relevant chemical and physical properties of common liquid hydrocarbon fuels.

Molecule	Name	Energy Density kWhr/l	Boiling Temp K
CH ₄	Methane	6.56	112
CH ₃ OH	Methanol	4.43	338
C ₂ H ₆	Ethane	7.49	185
C ₂ H ₅ OH	Ethanol	5.88	352
C ₄ H ₁₀	n-Butane	7.28	273
C ₈ H ₁₈	n-Octane	8.65	399
C ₁₀ H ₂₂	n-Decane	8.98	447
C ₁₂ H ₂₄	n-Dodecene	9.59	489

REACTION KINETICS

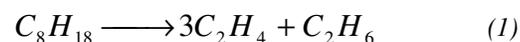
Fuels such as gasoline and diesel are blends, made up of hundreds of chemical components which vary greatly from process run to process run. The major components of these fuels are typically larger hydrocarbon molecules including, but not limited to n-octane, n-dodecane, toluene (methyl benzene), n-pentane and n-butane [5], as well as oxygenated components such as methanol, ethanol and dimethyl ether [6]. In Table 2 is listed the enthalpy of

formation at four temperatures for four major components that make up most commercial fuels and the enthalpy of formation for two smaller hydrocarbon molecules, ethane and ethene. The enthalpy of formation for n-dodecene was approximated by subtracting 4.926 kcal/g/mol from the enthalpy of formation for n-decane as is recommended by the CRC Handbook [7].

Table 2. The enthalpy of reaction for seven hydrocarbon chain fuels.

Molecule	Name	ΔH_f 400K kJ/mol	ΔH_f 600K kJ/mol	ΔH_f 800K kJ/mol	ΔH_f 1000K kJ/mol
C ₂ H ₄	Ethene	49.3	44.3	40.7	38.2
C ₂ H ₆	Ethane	-88.3	-96.2	-99.2	-101.7
C ₄ H ₁₀	n-Butane	-133.5	-145.2	-151.9	-154.8
C ₈ H ₁₈	n-Octane	-228.0	-246.9	-256.9	-261.1
C ₁₀ H ₂₂	n-Decane	-265.3	-287.9	-300.8	-306.7
C ₁₂ H ₂₄ *	n-Dodecene	-285.9	-308.5	-321.4	-327.3

Using the enthalpy of formation, different scenarios were investigated to determine the enthalpy difference between the initial and final (desired) states of the fuel. It can be seen from expressions (1) and (2) that fuel cracking reactions are endothermic and therefore require heat from the combustion process or another external source in order to proceed. Furthermore, kinetics studies indicate the larger the molecule, the greater the heat input needed for cracking [7].



ΔH_{rxn} 400K kJ/mol	ΔH_{rxn} 600K kJ/mol	ΔH_{rxn} 800K kJ/mol	ΔH_{rxn} 1000K kJ/mol
287.7	283.4	279.7	273.9



ΔH_{rxn} 400K kJ/mol	ΔH_{rxn} 600K kJ/mol	ΔH_{rxn} 800K kJ/mol	ΔH_{rxn} 1000K kJ/mol
425.3	423.9	419.6	413.7

The above analysis requires some consideration for the activation energy of the reaction. The activation energy for this process requires an additional approximately 50 kJ/mol for the process to proceed forward with n-octane [8] as the working fluid. The enthalpy change due to fuel cracking, the contribution of the activation energy to the total energy required, and the effect of adding a catalyst is shown graphically in Figure 3. The goal of this research is to break the larger hydrocarbon molecules (introduced as single components) into H₂, C₂H₄, and C₂H₆ as described in expressions (1) and (2).

EXPERIMENTAL RESULTS

Testing was conducted using n-octane and iso-octane (also known as 2,2,4 trimethylpentane) as the working fluid. The difference in the arrangement of the atoms for these two molecules is depicted graphically in Figure 2. What is not shown is that the methyl groups give iso-octane a three dimensional structure while n-octane is more planar. The

boiling point for iso-octane is 371K while the boiling point for n-octane is 398K. These fuels were chosen for testing due to their widespread availability, common use as a fuel, and because of their intermediate size (larger than n-butane but smaller than n-decane).

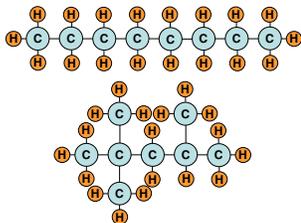


Figure 2. The molecular configuration of n-octane (top) and iso-octane (bottom).

Using a straight 6 mm long and 167 μm hydraulic diameter microchannel etched in silicon with a Pyrex top plate, preliminary tests have been conducted. The channel was heated uniformly using a mineral oil bath on a hot plate and the temperature was regulated using a closed loop proportional-integral-derivative (PID) controller. Results were obtained by analyzing one milliliter samples taken of the fuel before and after boiling in the microchannel using an Agilent 6890 gas chromatograph (GC) with a flame ionization detector, a 50 meter HP-1 methylsilicone column and an injector temperature at 150°C. The exhaust fuel, which was in vapor form, was condensed by chilling the exhaust collection beaker before each sample was analyzed.

Initial test parameters were based on test results for average external temperature of the 4.97cm³ Wankel engine [1] during engine operation with high degree of engine cooling from external fans. These tests determined temperature setpoints between 398K and 473K [8]. This corresponds to 25 and 50 degrees above the boiling point for iso-octane and zero and 25 degrees of superheat for n-octane. It is important to note that if the engine was redesigned to include a fuel cracking system in good thermal contact with the combustion chamber, significantly higher temperatures are expected.

For a micro engine to output 50 Watts of power for an hour, assuming an efficiency of 10%, 500 Watt-hours of fuel will be required. For n-octane, which has an energy density of 8.65 kW-hr/l, a density of 703 kg/m³, and an atomic weight of 114 g/mol, a steady flow rate of 0.963 ml/min of fuel will be required. Therefore, for a channel fuel flow rate of 0.25 ml/min, a network of four channels is required.

GC analysis of the samples with the noted superheat (up to 50 K) showed that no fuel cracking occurred for a fuel flow rate of 0.25 ml/min. Using n-octane as the working fluid with fifty (50) degrees of superheat and 0.25 ml/min flow rate resulting in 15.3 kJ/mol of heat input, or

approximately 5% of the required energy for fuel cracking to occur. Therefore, for effective fuel cracking, the flow rate will have to be dropped by an order of magnitude and the superheat doubled. This can readily be achieved by massively parallel microfabrication of multiple channels. In this case, 40 parallel channels are required. The experiment was repeated reducing the flow rate to 0.01 ml/min with the same superheat levels but again no fuel cracking was measured. Testing is currently underway conducting this experiment using higher superheats and other working fluids.

REACTOR DESIGN

To maximize exposure of the channels to the combustion chamber and to give the appropriate residence time (or space velocity) for the reactions to occur, a serpentine microchannel with multiple passes has been designed. By maintaining the channels with a hydraulic diameter on the order of 100 μm , the microscale boiling phase change of the fuel will be characterized by an abrupt change from liquid to vapor with few or no bubbles in the stream [9]. To aid in heat transfer from the combustion chamber to the reactor, this microchannel design leverages the small spatial distance enabled by the thin, planar design. Excessive pressure drop is prevented by sizing the microchannels on the order of 100 μm using a multiple channel system design. To fully leverage the advantages of microscale boiling and the high thermal conductivity of silicon, good thermal contact between the combustion chamber and the fuel cracking system must be maintained.

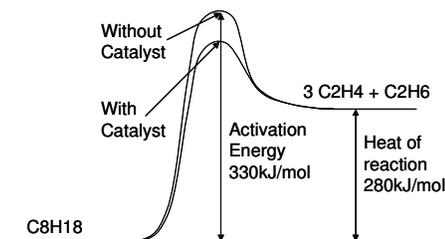


Figure 3. The effect of catalyst on the energy required for fuel cracking.

While the microreactor can crack fuel by using thermal energy alone, a catalyst coating will help reduce the activation energy and thus reduce the amount of thermal energy required to break up the long hydrocarbon chains, as is shown in Figure 3. Therefore, a portion of the microchannel will be coated with a catalyst microscale structure. Research has shown that the zeolite HZSM-5* impregnated with platinum acts as a highly selective catalyst to crack n-dodecane and other large hydrocarbon chain molecules into C₂-C₅ hydrocarbon chains [10]. In that experiment [10] HZSM-5 was implemented on the

* ZSM-5 stands for Zeolite Socony Mobile number five, the H refers to the zeolite being configured in proton form.

macro scale. Other research has built zeolite micro membrane structures on microchannels using standard MEMS fabrication processes [11]; however, these structures were not used for fuel cracking. In order to create a MEMS fuel cracking system, the zeolite micro membrane will be grown in the fabricated silicon microchannel and then impregnated with metal catalyst, using a selective sputtering process. In addition to reducing the amount of thermal energy required for the reaction to occur, the catalyst will increase the rate of fuel cracking, in turn enabling higher mass flow rates through the system and/or smaller structures.

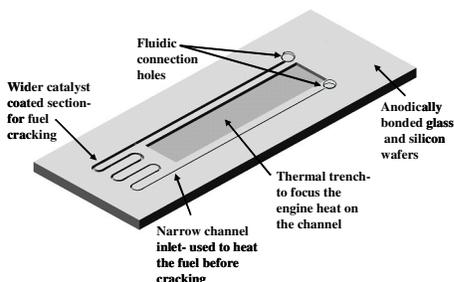


Figure 4. Schematic of the microchannel fuel cracking system showing an entry length for fuel vaporization followed by a catalyst coated region.

A schematic of the microchannel fuel cracking system is shown in Figure 4. In the final design, the fuel cracking system will be adjacent to the combustion chamber which will serve two purposes. First, the combustion chamber will provide the latent heat required for fuel cracking to proceed. Second, this design utilizes thermal energy from the heat engine, increasing the system thermal efficiency. Burning the cracked fuels is expected to result in a more robust combustion event, increasing system specific power.

CONCLUSIONS

To leverage the high energy density of long hydrocarbon chain liquid fuels, such as octane, and gain the combustion advantages of short hydrocarbon chain fuels, such as ethane, a micro fuel cracking system is in development. Fuel cracking enables significantly lower parasitic losses than is required for a complete fuel reformation system including partial oxidation and water-gas shift reactors. Initial results were unsuccessful, but subsequent analysis is encouraging. Catalytic cracking of long hydrocarbon chain, high specific energy liquid fuels into smaller, hydrocarbon constituents is necessary for a micro engine based MEMS power system. Cracking fuel at the system level maintains the high energy density of the stored fuel because the endothermic reforming process utilizes the enthalpy created by the combustion chamber in the form of recovered waste heat.

Recent research has shown that the partial fuel cracking for Power MEMS may soon be feasible using proven

fabrication techniques. This microscale fuel cracking system will build on existing fuel cracking technologies and adapt these systems to be compatible with micro fluidic structures. A three dimensional crystal zeolite structure will be deposited into part of the channel and impregnated with a metal catalyst. Inclusion of this fuel cracking system enables the use of heavy fuels for micro engines by improving combustion performance and utilizing waste heat which will result in improved system conversion efficiency and improved stored energy density. Beyond powering micro engines, the thermal cracking of heavy fuels can also be used as a pre-treatment step before complete fuel reforming. This work has shown that this approach is feasible and that there are distinct advantages at the system level to integrating a fuel cracking system.

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