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Gasoline Confined in Nano-porous Media
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1 Abstract

The heat of combustion was determined for gasoline confined in nano-porous media of differing pore size by bomb calorimetry. The heat of combustion of the confined fuels was comparable to that of bulk within the experimental uncertainty. This suggests that all of the confined fuel burns without any flame quenching and no chemical interactions at the interface between pore walls and fuel mitigate combustion.

2 Introduction

The goal of our work is to explore methods to extract energy more efficiently from gasoline. Specifically, by confining gasoline in nano-porous media. Previous work has seen increases in the viscosity and flash point of gasoline with the addition of nanoparticles and reduction in hydrocarbon emissions [1].

In the bulk combustion of gasoline, combustion occurs at the interface between fuel and air. A combustion wave travels downward through the fuel as it burns. The speed of the wave is controlled by the rate of reaction of gasoline. As the flame front travels, heat transfers to unburned fuel farther and propagates the combustion. The pressure of the system also plays a role, the rate of reaction is proportional to pressure [2]. The availability of oxygen is vital for combustion. Basic combustion creates Carbon Dioxide and Dihydrogen Monoxide whose presence can mitigate combustion.

In nano-porous media, there is a reduction in surface area where the reaction could occur. The smaller the pore size, the smaller the available surface area. If rate of combustion is proportional to surface area, then it follows that this might slow the rate of combustion of a fuel.

In this thesis, measurements were made using calorimetry. In general, calorimetry determines the heat produced during a reaction, in this case that reaction is combustion. Calorimetry with combustibles determines the calorific value of a sample at constant volume in an oxygen rich environment, or the amount of heat per mass of a sample. This is referred to as the Heat of Combustion (H_c°) and is calculated using the equation below.

$$H_c^\circ = \frac{W\Delta T - e}{m} \quad (1)$$

Where, W is the heat capacity of the calorimeter or the energy equivalence, ΔT denotes the change in temperature, m denotes the mass of the sample and e is any necessary thermochemical corrections. These corrections cover a variety of extraneous energy sources including the formation of nitric acid and sulfuric acid if sulfur is present in the sample [3].

3 Experimental

3.1 Samples

The fuel used was standard unleaded gasoline from a local service station. Prior to testing, the gasoline samples were mixed to ensure homogeneity. The first series of confined tests used 7.5 mm Whatman Anodiscs. These are nano-porous filters made from anodized aluminum, pore sizes of 0.2 μm and 0.02 μm were used. The last series used silica produced by Sorbent Technologies with pore sizes on the order of 20 nm. It is comprised on individual grains ranging from 5 – 7.5 μm in size. Example samples are shown in figure 1.

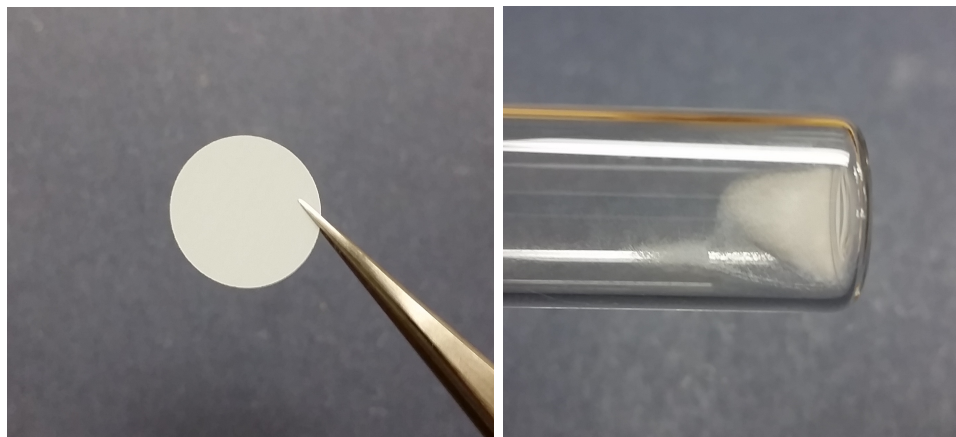


Figure 1: On the left is a face on view of a 0.2 μm Whatman Anodiscs. The filter is 7.5 mm in diameter and slightly translucent. They are fragile and prone to shatter if mishandled. The filters were thin and had very little volume. On average the 0.2 μm filters had a mass of 0.0095 g and the 0.02 μm filters had a mass of 0.0141 g. On the right is a sample of the silica. It is very fine, only appearing opaque when grains pile up.

In general, samples were prepared according to the ASTM D4809 method for liquid hydrocarbons. This method is used to determine the heat of combustion of hydrocarbon fuels [4]. First the combustion capsule was cleaned with a soap solution, rinsed, dried and massed before each test. For confined tests, a filter or silica sand was added and massed next. The top side of the combustion capsule was covered with a piece of pressure sensitive tape as shown in figure 2.

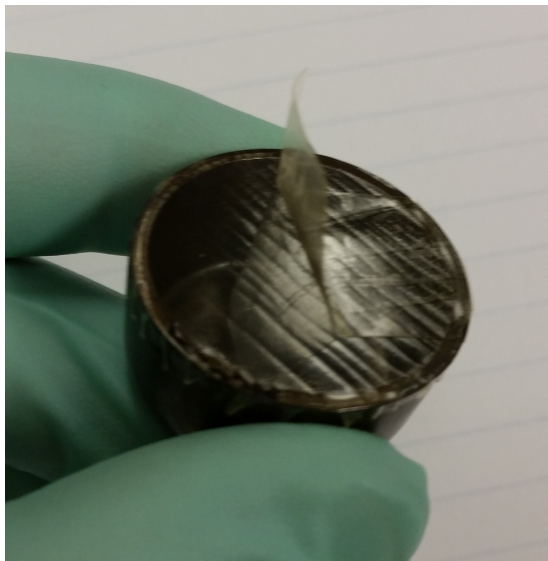


Figure 2: Combustion capsule prepared for bulk gasoline tests before the gasoline was injected. After the gasoline is injected the small flap is pressed down to seal the hole made by the needle. Effort was made to trim the tape flush with the edge of the combustion capsule to minimize the amount of tape.

3M Transparent Tape No. 610 was used as it is chlorine and sulfur free, so no additional thermo-chemical corrections are required [5]. The edges of the tape were trimmed with a razor such that tape only sat on the top of the combustion capsule. Gasoline was injected through the tape with a needle. Due to calorie limits on the calorimeter between 0.5 *g* and 0.75 *g* of gasoline were used per test. The hole made by the needle was sealed using an additional piece of tape. A small section of tape was left uncompressed to attach the fuse to later.

For confined tests using filters, one filter was used per test. The amount of gasoline used for filter tests was kept constant at about 0.47 *g*. For tests using silica, between 0.35 *g* and 0.4 *g* were used per test. A large portion of the silica test added gasoline until the sand was ‘saturated’; that is, until the silica could hold no more gasoline. Two series of tests were performed with saturated silica: one at an average of 0.3601 *g* of silica and an average of 0.4689 *g* of gasoline, and one at a larger average of 0.4075 *g* of silica and an average of 0.5453 *g* of gasoline.

3.2 Instrument

Measurements were made with a Parr 6200 Isooperibol Bomb Calorimeter. As we know, calorimeters measure the release of heat due to a chemical reaction. Specifically, bomb calorimeters measure the energy released during combustion under the constraint of constant volume.

The Parr 6200 Isoperibol Calorimeter has four components. The combustion vessel (bomb) which contains the combustion, the bucket which monitors the change in temperature, the jacket which insulates the bomb-bucket system and the water handling system which helps maintain the temperature of the bucket and jacket. A simple schematic of the apparatus is shown in figure 3. The jacket is held at 30°C . The bucket is filled with water from the water handling system which is heated to about 25°C .

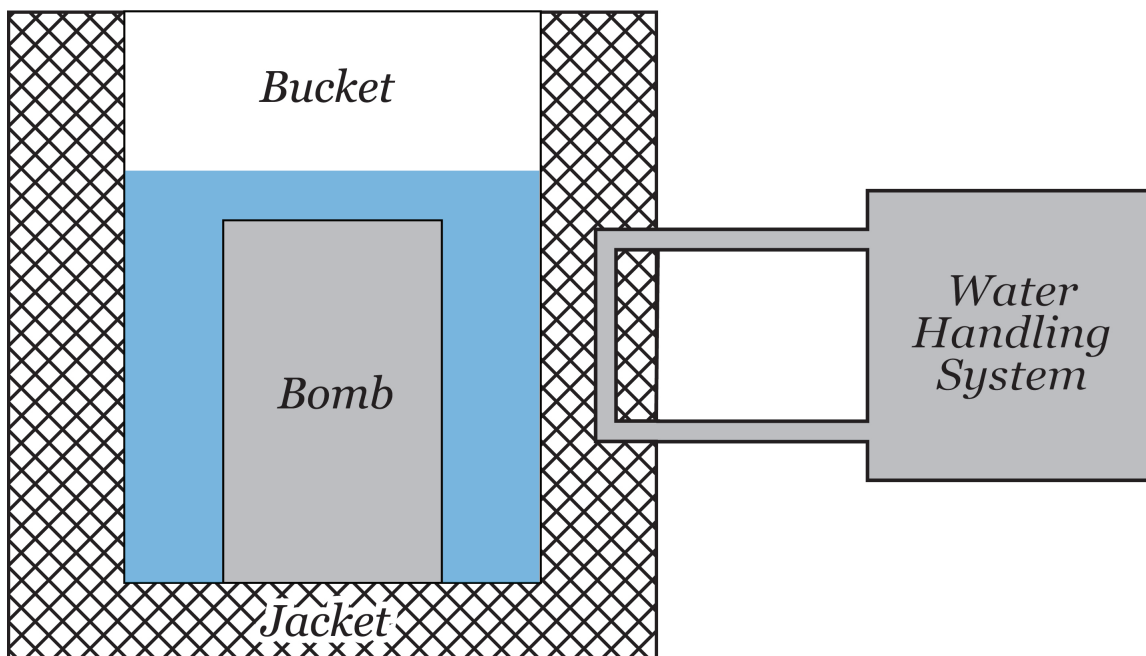


Figure 3: Schematic of the calorimeter's major components. The bomb rests in the bucket which is filled with two liters distilled water. The bucket is isolated from thermal fluctuations by the jacket. The calorimeter holds the jacket at a constant temperature, using water from the handling system to help stabilize the system's temperature. The water in the handling system and the jacket are isolated from one another.

The bomb used was a Parr 1108P Oxygen Combustion Vessel. This bomb is built from a niobium-stabilized stainless steel to resist corrosives produced during combustion. It is built to withstand combustion from most hydrocarbons and carbonaceous materials, high explosives withstanding. A labeled diagram of the bomb is shown in figure 4.

When performing a test, a sample of known mass is placed in the combustion capsule. A fuse is tied about the ignition wire and laid over the sample with ample contact surface. Once the fuse is tied, the bomb head is lowered into the main body and secured with the screw cap. The outlet valve is closed and the bomb is pressurized with 30 *psi* O_2 . The ample available oxygen ensures complete combustion of the sample.

The prepared bomb is placed in the bucket which contains two liters of deionized water. During a test, the sample combusts and heats the bomb and water. A thermometer measures

the change in temperature of the bucket. Using the heat capacity of water, we can determine how much heat was released by the sample.

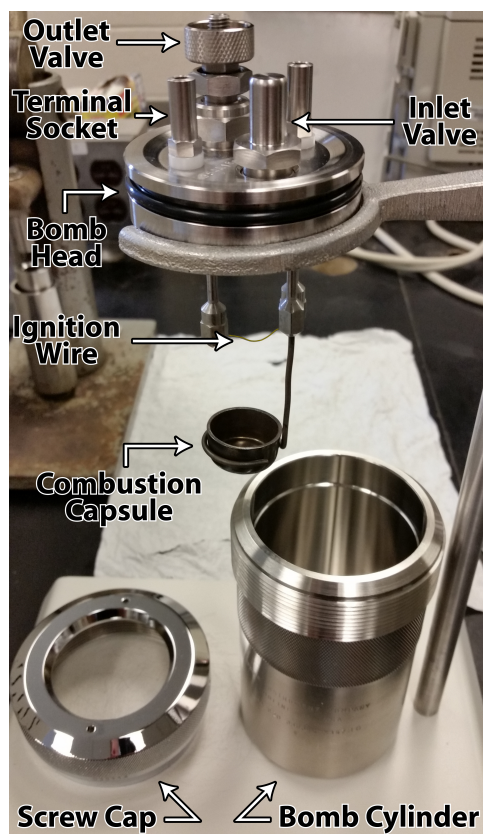


Figure 4: The Parr 1108P Oxygen Combustion Vessel with important components labeled. The combustion capsule holds samples during tests. A fuse (typically a cotton thread) hangs from the ignition wire into the combustion capsule. The two terminal sockets connect to the ignition wire and allow a current to be run through it, igniting the fuse then the sample. The bomb cylinder is the main body of the vessel, into it fits the bomb head which holds the combustion capsule. The screw cap then tightens down over the bomb head to seal the vessel. The inlet and outlet valves allow for pressurizing and depressurizing the bomb respectively [6].

The jacket serves as an insulator for the system. It helps to mitigate heat exchange between the bucket and its surroundings. In an isoperibol system the jacket is kept at a constant temperature. The calorimeter then calculates the heat leakage between the bucket and jacket and adjusts the resulting heat of combustion accordingly. The water handling systems assists in this role by providing the jacket with additional temperature controlled water to cool the jacket if need be; functionally increasing its heat reservoir.

Periodic standardization is performed to ensure the energy equivalence of the calorimeter (W) remains accurate. To standardize the calorimeter tests are performed on a sample

whose ΔH_c° is well known, typically Benzoic Acid (6318 cal/g) [3]. Using the known ΔH_c° for Benzoic acid, W can be calculated for a given test. The Parr 6200 Isoperibol Calorimeter calculates W from an average of ten standardization runs.

In addition to calculating heat leakage between the bucket and the jacket, the calorimeter also automatically accounts for typical environmental corrections that would otherwise skew results. The two corrections taken into account are the formation of nitric acid, and the extra calories produced by burning the fuse. Nitric acid forms because the environment in the bomb during combustion is hot enough to oxidize ambient nitrogen, which release energy; about ten calories. The fuses are estimated at 50 calories a piece. Both are taken into account in e in equation 1.

3.3 Methods

In general, tests were performed according to the ASTM D4809 method for liquid hydrocarbons. For bulk gasoline, D4809 was followed exactly. Other tests required slight modification. Initially, the calorimeter and water handling system was turned on. The jacket warms to 30°C in a matter of minutes but the water handling system takes much longer. No tests were made until the water handling system's temperature stabilized to 25°C .

Samples were prepared as described in section 3.1 then placed in the rack attached to the bomb head. Using a pipette, 1 ml of deionized water was added to the bottom of the bomb to collect any residue formed during combustion. A cotton fuse is then tied to the ignition wire with a simple overhand knot. One end of the fuse is left with sufficient slack to reach the sample. Typically, the fuse was tucked under the tab of tape left over from sample preparation, thereby ensuring contact.

Once the bomb was sealed, it was charged with O_2 and the bucket was filled with two liters of heated, deionized water from the water handling system. The bucket was placed in the jacket followed by the bomb and the calorimeter was closed.

Posttest, the bomb was removed from the bucket, dried and decompressed. The water in the bucket was poured back into the water handling system to acclimate. The bucket must be dried completely, excess water during a test will skew results. The bomb was opened and any residue was documented. The bomb and combustion capsule were cleaned to reset for the next test.

4 Results

For tests of individual samples, the calorimeter calculates a heat of combustion. Multiplying this quantity by the mass of the sample gives the energy released during combustion. By plotting the energy released against sample mass for all the data in one series we can find the average heat of combustion by fitting a line to the data. Multiplying both sides of equation 1 by mass gives the following:

$$E = H_c^\circ m + C \tag{2}$$

where C is some extra energy provided by other sources. In every series the value of C is similar, it is likely due to the combustion of tape which is otherwise unaccounted for. The error was taken to be the standard deviation of each series.

Bulk gasoline was tested first to determine a baseline to compare with the confined tests. The data for these tests is plotted in figure 5. The baseline heat of combustion was determined to be $44.425 \pm 0.034 \text{ MJ/kg}$.

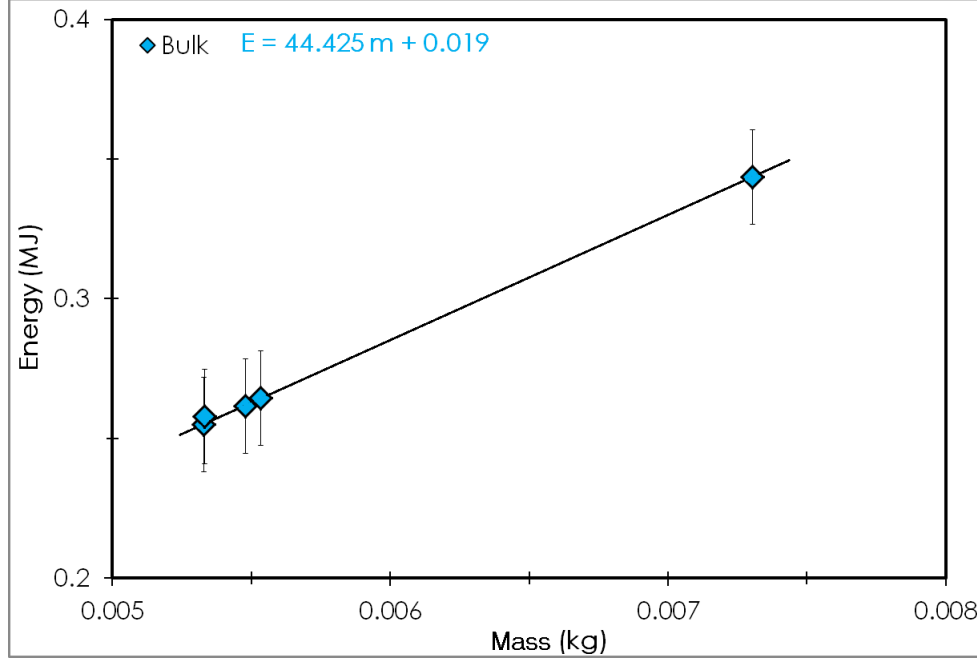


Figure 5: Results from burning gasoline in bulk. Gasoline was mixed prior to testing to ensure a homogeneous sample during testing.

The first confined test put Gasoline in $0.2 \mu\text{m}$ nanofilters. Data for these tests are plotted in figure 6. The average heat of combustion was $45.782 \pm 0.044 \text{ MJ/kg}$.

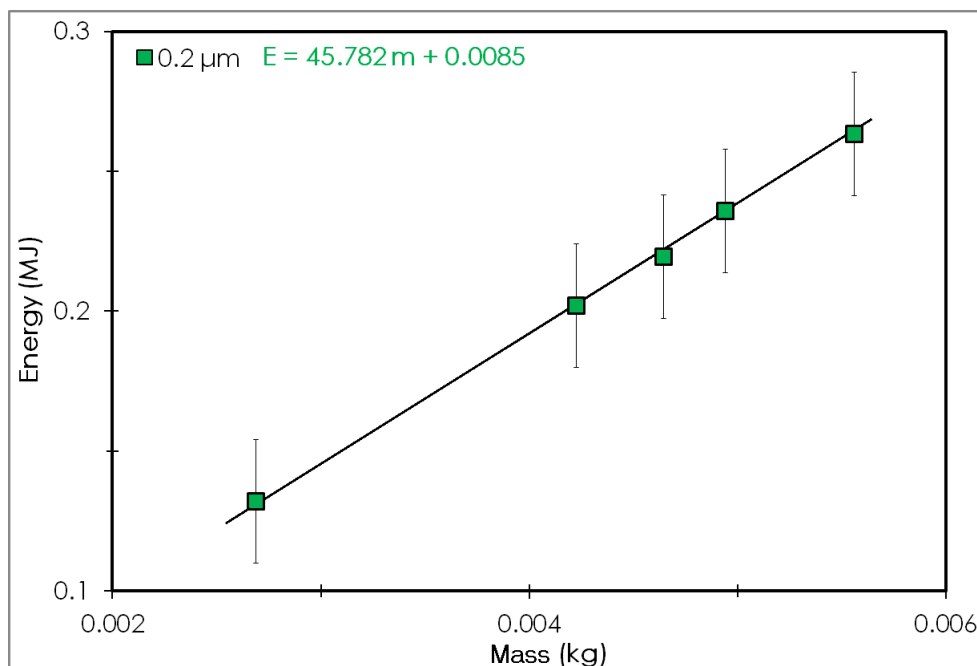


Figure 6: Results from combusting gasoline in $0.2\mu m$ nanofilters. The larger ΔH_c° may be due to the lowest point pulling the regression.

The second confined test put Gasoline in $0.02\mu m$ nanofilters. Data for these tests are plotted in figure 7. The average heat of combustion was determined to be $44.496 \pm 0.016 MJ/kg$.

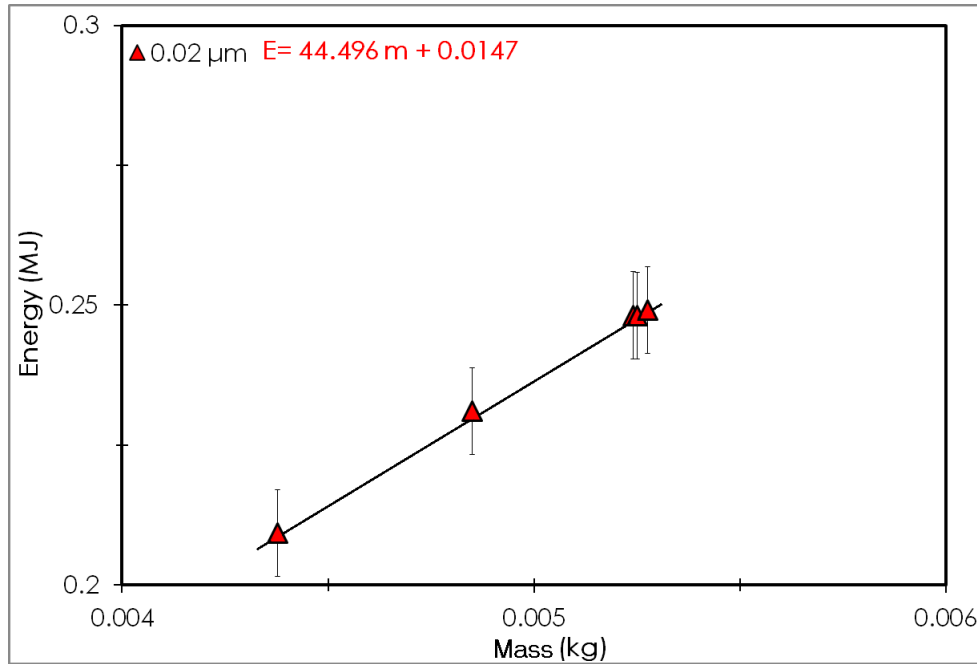


Figure 7: Results from combusting gasoline in 0.02 μm nanofilters.

When combusted, the filters are deformed or completely destroyed. Minimum damage typically included cracking and some warping. Serious damage leaves just a small sliver of the filter remaining. The 0.02 μm pore size filters tended to withstand combustion better. Two examples are shown in figure 8. Typically, filters experienced serious deformation. No filter could be reused.

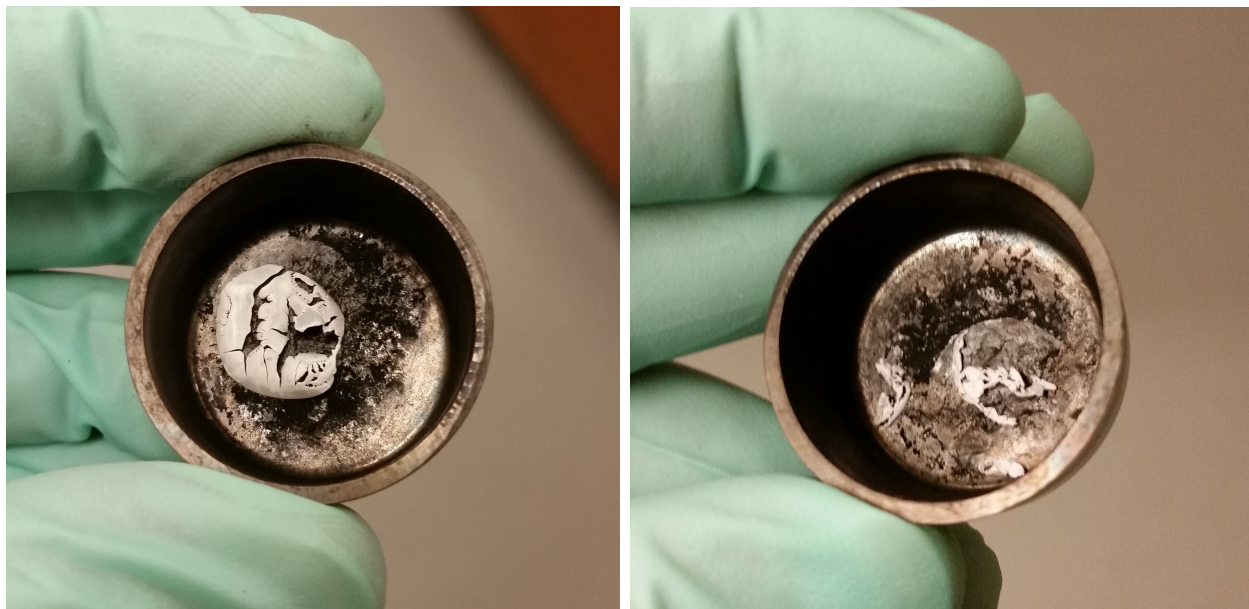


Figure 8: Two examples of damage to nanofilters sustained during combustion. The left was a $0.02\ \mu\text{m}$ filter and the right a $0.2\ \mu\text{m}$ filter.

The last series used silica with pores roughly $20\ \text{nm}$ in diameter. Data for these runs are plotted in figure 9. The average heat of combustion was determined to be $45.764 \pm 0.049\ \text{MJ/kg}$.

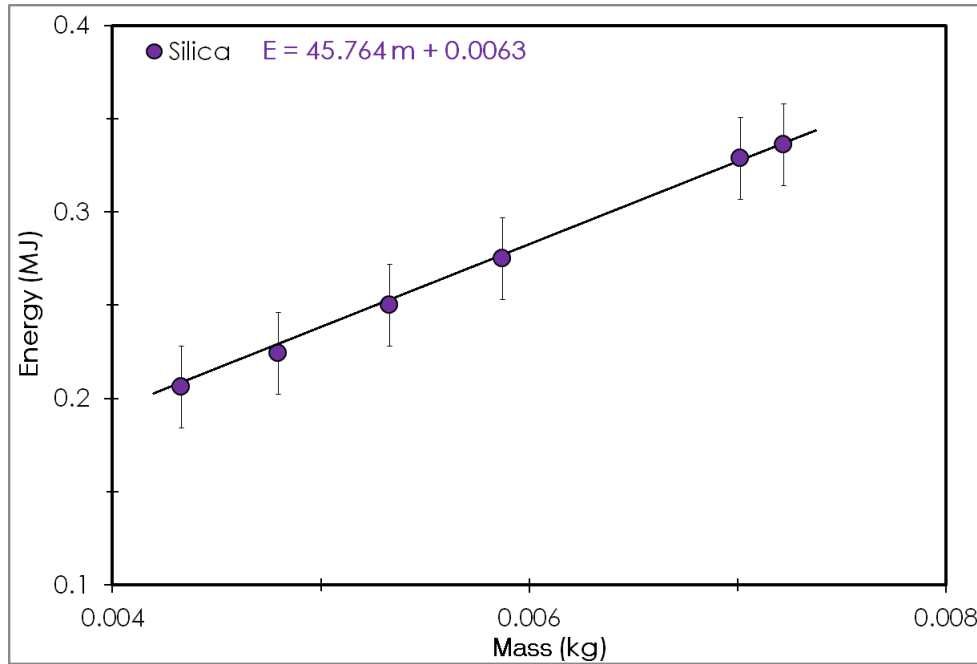


Figure 9: Results from burning gasoline in silica with pore diameters on the order of $20nm$.

The silica was deformed during combustion in a similar manner to the filters. Typically, a top layer of silica would sinter together and create a solid, brittle crust. Beneath the top layer the remaining silica was unharmed. For tests using more silica, the width of the crust remained constant leaving more unharmed silica below it. A typical result is shown in figure 10.

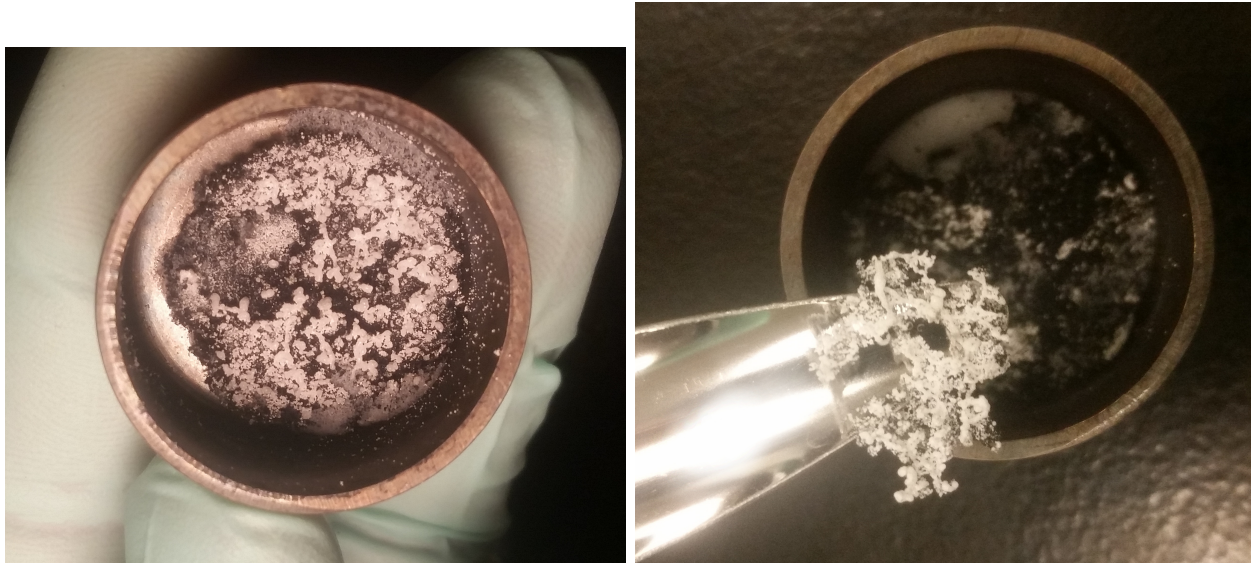


Figure 10: Post combustion silica sand. On the left, the white pieces and black below it comprise the crust, unharmed silica is visible below it. The right picture shows the crust in more detail.

5 Conclusions

The purpose of this research was to determine if an appreciable change in heat of combustion occurs through the physical confinement of gasoline. Gasoline was confined in $0.2\ \mu m$, $0.02\ \mu m$, and $20\ nm$ pores and compared against bulk. It was found that no large change in heat of combustion occurs. The $0.02\ \mu m$ ($44.496 \pm 0.016\ MJ/kg$) and $20\ nm$ ($45.764 \pm 0.049\ MJ/kg$) series compared well with the bulk test of $44.425 \pm 0.034\ MJ/kg$. The outlier was the $0.2\ \mu m$ series which yielded a heat of combustion of $45.782 \pm 0.044\ MJ/kg$. This series has a 3.1% difference from the bulk which is not significant given the standard deviation of the data. This suggests that combustion on the very small scale acts in a similar fashion as on a macroscopic scale. This also suggests that the gasoline is not binding in any odd manner to the walls of the channels it is confined in.

The damage to the filters and silica sand is not altogether unexpected. The filters are prone to shatter and combustion in a pure oxygen environment is violent and would produce a rapid change in temperature within the bomb. High heat may also explain the crust that formed during the silica test. Since the flame propagates downward [2] the surface of the silica would experience the greatest heat during combustion.

References

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