Fisher Space Systems, LLC

PLA Infused with $KMnO_4$ as a Hybrid Fuel for HTP

by
Jerry F. Fisher

"Simplicity is the ultimate sophistication."
- Leonardo da Vinci

Abstract

I infused PLA with $KMnO_4$ and used it as a fuel core for fuel grade hydrogen peroxide. The PLA fuel core can be segmented and printed on a desk top 3D printer, infused with $KMnO_4$ at high temperature and pressure, and encased in a CPVC casing with parts glued together with CPVC cement. The infusion takes less than an hour and results in the $KMnO_4$ being evenly distributed throughout the PLA. As such, it is possible to change a parameter, print out and infuse a new fuel core, and test a rocket one to two times a week. At 100 psi the theoretical O/F ratio is 2.5, resulting in a very compact rocket design. My objective is to develop a class I HTP/PLA/$KMnO_4$ rocket and launch from my back yard.

1.0 Introduction

Hydrogen peroxide was first used as an energy source for underwater propulsion in Germany in 1934[1]. This work led to its subsequent application during World War II for auxiliary propulsion and gas generator concepts in aircraft and rockets. Systems that have used hydrogen peroxide as a gas generators include the V2 Rocket, Redstone, and the X-15. Systems that have used hydrogen peroxide for auxiliary propulsion (mainly reaction control systems) include the Mercury Spacecraft, Little Joe II, Lunar Landing Simulator, Astronaut Maneuvering System, Personnel Rocket Belt, X-15, and other systems[1].

However, prior to the late 1960s, hydrogen peroxide's use in operational bi-propellant systems were limited to high performance rocket aircraft. The interest in using hydrogen peroxide in concentrations greater than 70% led to a detailed compilation of the physical, chemical, and handling properties of this important oxidizer. The Hydrogen Peroxide Handbook[1] is the compilation of the engineering properties of propellant-grade hydrogen peroxide (HTP). HTP in this paper refers to propellant-grade hydrogen peroxide in concentrations greater than 70%.

Disclaimer: As an oxidizer, HTP is relatively safe if you follow the handling and safety procedures outlined in the Hydrogen Peroxide Handbook. The greatest danger in handling HTP comes from complacency; skipping steps and taking shortcuts. HTP, like any potentially explosive material, requires careful handling and the observation of proper safety procedures.

The use of HTP as a bi-propellant oxidizer waned in the 50s and 60s probably due to the search of higher energy fuels[2]. However, recent system studies[3,4,5] point to potential benefits of using HTP as an oxidizer in hybrid systems due to its high density, ease of handling, non-toxicity, and mono-propellant characteristic.

The current research presented in this paper is based on the results from my own study[6] of HTP/RP-1 propellants, showing the overall mass of the system is comparable to that of a system based on cryogenic propellants. In my opinion, using HTP as the oxidizer and a hybrid fuel produced by fused deposition manufacturing (colloquially known as 3D printing) will also be comparable in mass and performance to a system based on cryogenic oxidizer and fuels.

In a recent report[7], acrylonitrilebutadiene-styrene (ABS) thermoplastic is compared to Hydroxyl-Terminated Polybutadien (HTPB). Nitrous oxide is used as the oxidizer. Test results showed that the ABS hybrid fuel did not perform as well as the HTPB. The reduced performance was attributed to lower combustion efficiency for the ABS fuel grain. The authors believe that efficiency could be improved by adjusting the ABS mixture ratio.

The rocket performance of commercially available poly-lactic acid (PLA) was experimentally investigated with 90% HTP and compared with HTPB[8]. The characteristic velocity efficiencies were calculated as 89.5% for HTPB and 93.1% for PLA. This implies that PLA has a high potential to substitute for HTPB. However, the fuel inlet partially melted down in the gravity direction due to the inlet surface being directly exposed to the hot decomposed gas (~741 ^{o}C). A manganese oxide/gamma phase alumina catalyst was used to decompose the 90% HTP.

There are two primary methods to initiate and maintain controlled decomposition of HTP: catalytic and thermal[1]. Thermal decomposition can often be the easiest method, as it only requires an auxiliary heat source to initiate the process. However, thermal decomposition alone can not sustain decomposition at high flow rates (sic). The HTP squelches the combustion. As such, both catalytic and thermal methods are required to sustain controlled combustion at high flow rates.

Catalytic decomposition of HTP uses a catalyst; either as a liquid mixed with the fuel, or a solid in a fixed bed chamber. The liquid catalysts normally employed are aqueous solutions of calcium or potassium permanganate ($KMnO_4$). $KMnO_4$ mixed with the fuel was used to decompose HTP in the gas generators for the V2 rocket. In my experience with $KMnO_4$, it was most likely the blocking of injector ports, condensation of $KMnO_4$ on the turbine blades, making seals brittle, and clogging the plumbing system that prompted the switch to a solid catalyst.

Solid catalyst beds consist of packed columns of porous materials or screens. Porous materials are the least expensive and often consist of extrusions of manganese dioxide and alumina. Extrudates tend towards shrinking non-uniformly while drying and expanding when sintered in a kiln. As such, it is difficult to get the proper size needed in the post injector. Alternatively, a consumable ignition device[9] can be used. Ignition occurs quickly, the catalyst washes out of the post injector and combustion is sustained by thermal decomposition. However, as mentioned, thermal decomposition alone cannot sustain combustion at high flow rates.

Both silver and platinum screens have been used as solid catalyst beds[1]. Due to the structural integrity of these metals, especially at high temperatures, the silver and platinum are often deposited on screens made of brass, nickel, or stainless steel. The working screens are alternated with stainless steel screens and loaded under high pressure in the catalyst bed. However, such screens are subject to catalyst stripping during operation. This limits the lifetime of the catalyst bed. Another disadvantage is the pressure drop across the bed. Bed pressure drops typically range from 75 to 125 psi. This is especially relevant to pressure driven propulsion systems, higher pressure requirements impact system mass.

For the last two years, I have worked on a porous ceramic infused with mixed cobalt, manganese, and aluminum oxides. After some success, a problem arose while introducing decomposed HTP into a PLA fuel core. The inlet to the fuel core would melt and plug the nozzle, resulting in shut down and in one case a small explosion.

In the middle of summer, May 2020, I was having trouble printing brackets with PLA. The print would come out spongy and weak. Research on a web forum led to the speculation that PLA absorbs moisture, especially in high humidity. The moisture in the PLA expands as it passes through the extruder and produces a spongy build. I knew that $KMnO_4$ was soluble in water, so why not infuse PLA with $KMnO_4$ and use it as a fuel core for HTP? Mixing $KMnO_4$ with the fuel was a good idea in the 30s and it might even be a better idea today.

2.0 Infusing PLA with $KMnO_4$

My goal was now to make a hybrid fuel core that is catalytic with HTP. First, I infused test coupons to test my hypothesis, next I infused PLA segments with $KMnO_4$, then I assembled the segments into a PLA/$KMnO_4$ fuel core, and finally, I tested the rocket engine.

2.1 PLA Test Coupons

For the test coupons, I used the raft adhesion support pieces from two PLA prints and infused them with $KMnO_4$ (Figure 1).

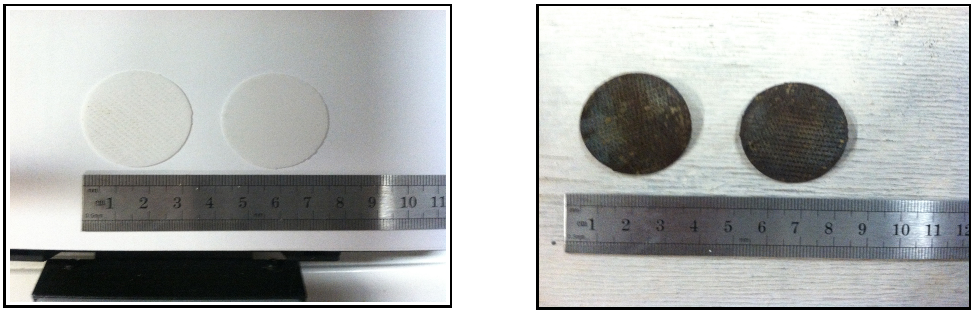


Figure 1. PLA/$KMnO_4$ Test Coupons

I dropped 85% HTP on the infused coupons to test decomposition and flammability (Figure 2). Eight to ten drops of HTP ignited the PLA which burned quickly as long as I continued to drop HTP onto the coupons. The speed of combustion was greater than expected, leaving me to surmise that PLA infused with $KMnO_4$ reduces the melt temperature of the PLA.

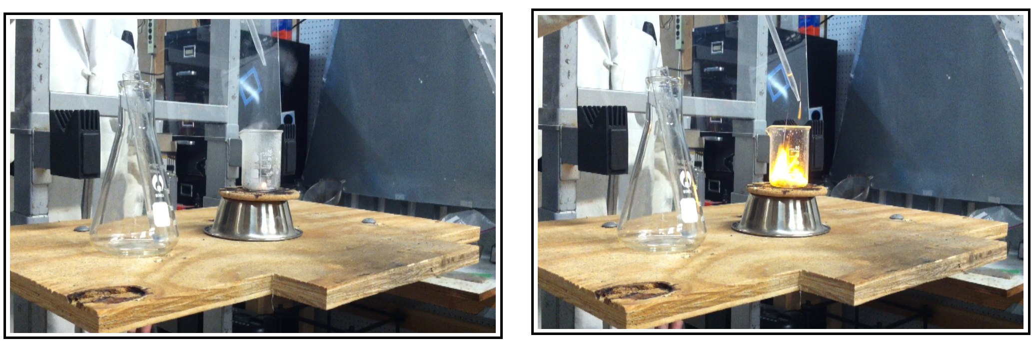


Figure 2. Drop Test of HTP on PLA/$KMnO_4$ Coupons

To test this hypothesis, I made a PLA filament with $KMnO_4$ and fed it through a 3D pen, which allowed me to control the temperature and speed of the extrusions. Starting at the PLA melt temperature, I could not lower the temperature of the pen fast enough to slow the flow of the PLA/$KMnO_4$ filament. Future research will determine the effect of lower melt temperature on regression rate and flame temperature. For now, I was encouraged to go to the next step, printing PLA fuel core segments and infusing the segments with $KMnO_4$.

2.2 PLA/$KMnO_4$ Fuel Core

The PLA fuel core consisted of seven segments (Figure 3) printed separately due to limited space, ease of infusion, and to verify that the hybrid fuel works just as well with small cracks, fissures, and segmentation as it does as a solid piece[10].

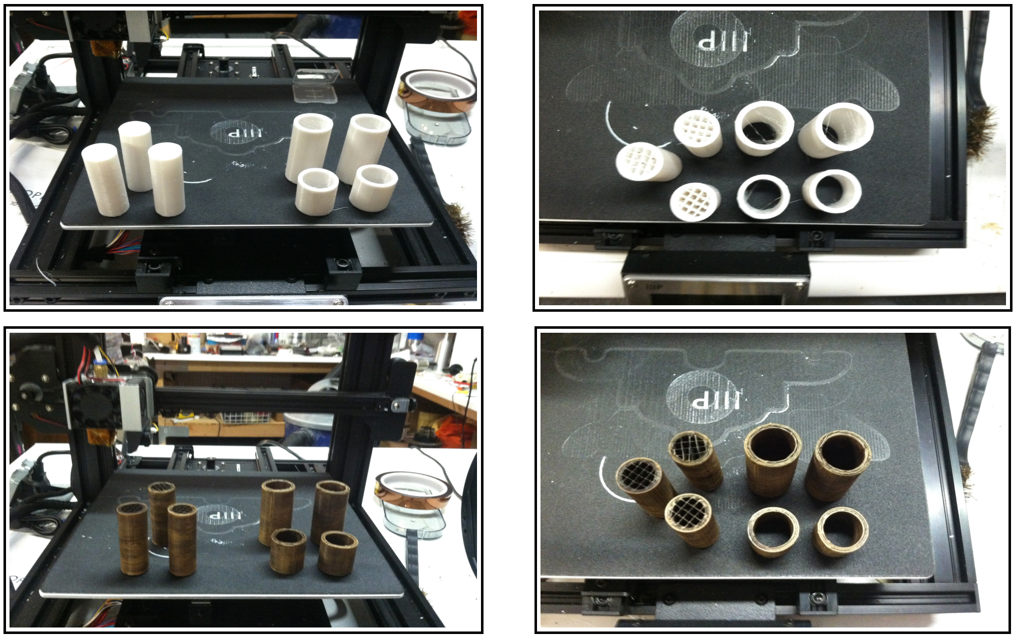


Figure 3. $PLA/KMnO_4$ Fuel Core Segments

The first three segments on the left are smaller in diameter and have a 20% infill. The infill, having a higher surface area than the core, melts quickly and aids in ignition. I've found that a higher percentage of infill melts too fast and plugs up the throat. This leads to an unpredictable ignition, as the $PLA/KMnO_4$ does not always clear the nozzle, once resulting in a small explosion. With no infill, ignition does not always occur. The first three segments are inserted into the larger diameter segments on the right. The result (Figure 4) is a 15 cm long $PLA/KMnO_4$ hybrid fuel core with an L/D of 12.5.

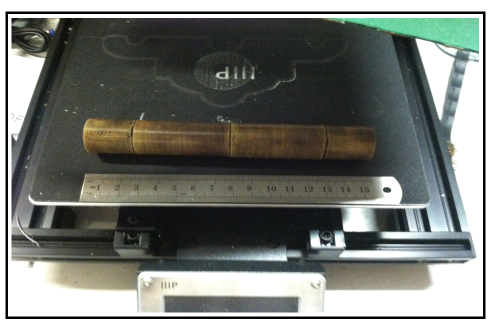
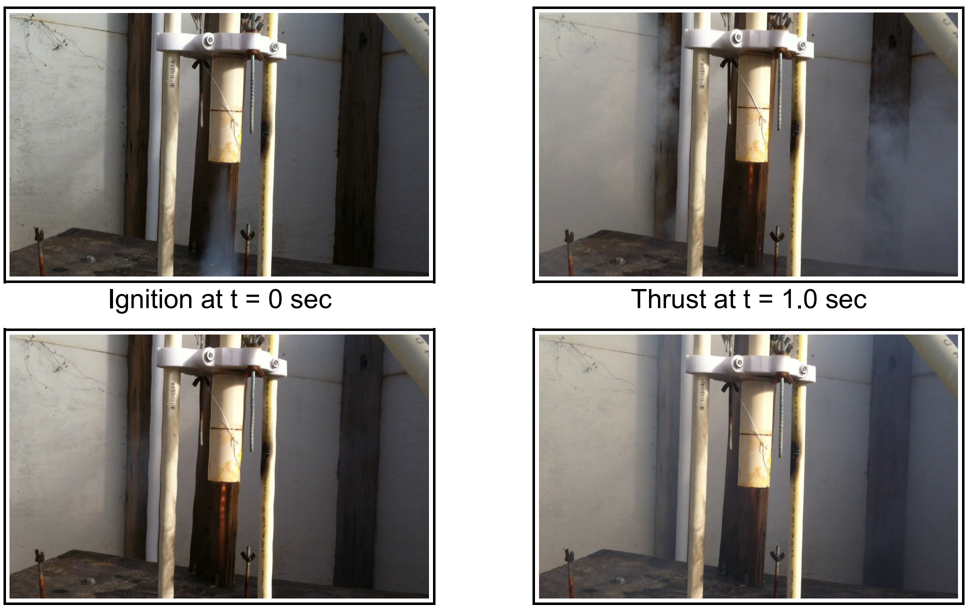


Figure 4. Assembled Fuel Core

2.3 $HTP/PLA/KMnO_4$ Static Engine Test

The major structural components of the rocket engine are made of CPVC; cleaned, primed, and glued together with CPVC cement. Combustion pressure was around 80 psi and as long as I didn't run over 10-15 seconds, the CPVC stayed intact. Using CPVC pipes, couplings, and adapters, I was able to test, change a parameter, and retest one to two engines a week, weather permitting.

After eight months of research and development on propellant tanks, plumbing, injectors, and valves, I finally achieved a working system. The PLA/$KMnO_4$ fuel auto ignited but it took ~10 sec, insufficient for my purposes. To shorten the ignition time, I added a small heating element at the nozzle inlet. By preheating for 10 to 15 seconds, ignition occurred in less than one second. A series of photos of one of the test is shown in Figure 5. There is a link on my web page (www.fisherspacesystems.com) for a video of the test.



Ignition at t = 0 sec

Thrust at t = 1.0 sec

Thrust at t = 2.8 sec

Shutdown at t = 5.9 sec

Figure 5. HTP/PLA/$KMnO_4$ Static Engine Test

The rocket engine had a positive thrust of over 10 N. I know this because the mass of the system is 1.1 kg. The rocket engine travels a centimeter until the top bracket hits a stop. There was a lot of vibration which I assumed was caused by combustion instabilities. The instabilities probably resulted from the type of injector I was using and a small pressure drop across the injector. I am in the process of testing different injectors to increase the pressure drop and reduce instability.

2.4 Distillation of Hydrogen Peroxide

As an oxidizer for a rocket engine, HTP is one of the least volatile, if you follow the safety precautions outlined in the Hydrogen Peroxide Handbook[1]. Despite its relative safety, HTP is still an explosive compound and mishandling can result in severe injury and property damage.

Disclaimer: Distill hydrogen peroxide at your own risk.

For small quantities (<500 ml), I use a partial vacuum distillation system (Figure 6) consisting of a boiling flask, condenser, receiving flask, and aspirator. The aspirator sets up the air flow and creates a partial vacuum. This setup is affordable and works well for bench top experiments.

I use food grade stabilized hydrogen peroxide in concentrations of 30-35% in a two step process. I start with approximately 750 ml of hydrogen peroxide and distill off 500 ml leaving 250 ml in the boiling flask. This takes the concentration from 30% to 70%. I save the 500 ml of distillate. It has a ~3% concentration of hydrogen peroxide and is great for passivation. I do this three times so that I end up with ~750 ml of 70% HTP.

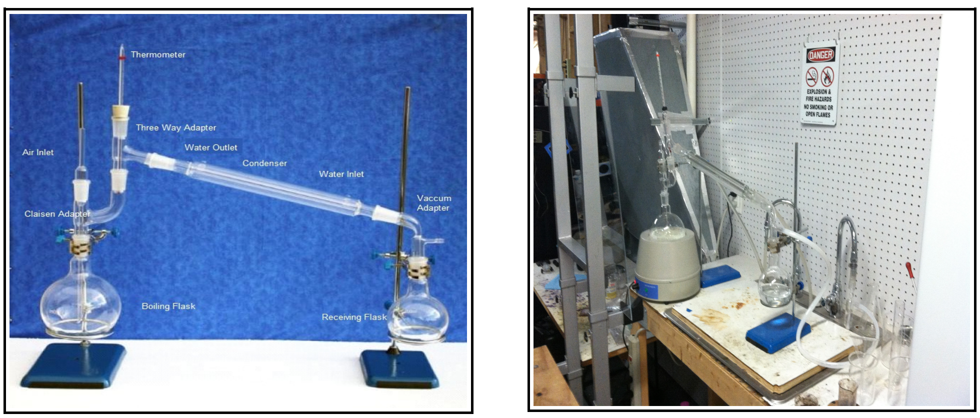


Figure 6. HTP Distillation

Next, I distill off ~250-300 ml of the 70% HTP leaving ~450 ml in the boiling flask. This step requires close monitoring. As the concentration increases, the pressure in the boiling flask increases. As the pressure increases, the air flow stops and HTP vapor collects in the boiling flask. If left unattended, it will lead to a small explosion. To prevent the vapor buildup, I increase the air flow by increasing the water flow through the aspirator.

This distillation process results in ~85-90% of highly stabilized HTP. The unstabilized distillate ends up around 30-35% concentration, which can be distilled to ~90%. Initial testing show that there is not much difference between stabilized and unstabilized HTP, but more quantitative testing is required to verify these results.

2.5 How Much Does it Cost?

It doesn't cost that much relative to larger rocket engine programs. The estimated startup cost is shown in Table I below. The basic lab equipment and 3D printer can cost between $400 and $1000. The PLA filament is used as the fuel core segments. I use the ABS filament to make an adapter for the graphite nozzle. The adapter is then glued into a 1" CPVC coupling. The miscellaneous cost are between $150 and $200 and include the CPVC plumbing, Soda Stream® bottle, 12V DC water valve, the check valve, $KMnO_4$, and other consumables. Of course, you'll need a place to test the engine. I went all out and build a below ground rocket engine test stand. I believe it cost me around $2000.

Table I. Estimated Startup Cost

Startup Cost	Low	High
3D Printer	$106.00	$500.00
Shaker Table	$90.00	$115.00
Pressure Cooker	$50.00	$100.00
One Burner Stove	$20.00	$25.00
Vacuum Distillation Kit	$50.00	$150.00
Heating Mantle	$55.00	$200.00
PLA & ABS Filament	$50.00	$50.00
Misc.	$150.00	$200.00
Total	$571.00	$1,340.00

3.0 Theory

I used the NASA Chemical Equilibrium with Applications (CEA) code[11]. The CEA code has HTP in its thermal library but does not have PLA or $KMnO_4$. For the code to run, I needed to find the energy of formation for PLA, so I derived it from first principles using the heat of combustion. The energy of formation can be obtained by Hess's Law; the enthalpy changes are additive. Thus the ΔH for a single reaction is,

$$\Delta H_{reaction} = \sum \Delta H_{f(products)} - \sum \Delta H_{f(reactants)}$$

where ΔH_f is the enthalpy of formation. Using the heat of reaction (combustion) for PLA, I get,

$C_3H_4O_2 + 3O_2 \rightarrow 3CO_2 + 2H_2O$ $\Delta H_r = -1361.9$ kJ

$3C_{(s)} + O_{2\,(g)} \rightarrow 3CO_{2\,(g)}$ $\Delta H_f = 3(-393.5$ kJ$) = -1180.5$ kJ

$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(g)}$ $\Delta H_f = 2(-241.8$ kJ$) = -483.6$ kJ

-1361.9 kJ $= -1180.5$ kJ $+ (-483.6$ kJ$) - (\Delta H_{f\,PLA} + 3(0))$

$\Delta H_{f\,PLA} = -302.2$ kJ

The enthalpy of formation for PLA is -302.2 kJ/mol. I added an estimated 5% $KMnO_4$ ($\Delta H_f = -813.4$ kJ/mol)[12] to the user-provided names and properties block and optimize for O/F ratio (Table II).

Table II. HTP/PLA/$KMnO_4$ Combustion (Frozen)

Pressure(psi)	Optimum O/F Ratio	c* (m/sec)
100	2.5	1496
1000	2.75	1518

To compare the characteristic velocity (c*) at different combustion chamber pressures, I ran the code at 100 psi and 1000 psi, optimizing the O/F ratio each time. The c* increased by only a few percent at the higher pressure. An increase of 22 m/sec is not enough, in my opinion, to justify an increase in the overall system mass. A chamber pressure of 1000 psi will require a propellant tank pressure of 1100 to 1200 psi. This increase in pressure increases the mass of every related component.

At 100 psi chamber pressure (120-150 psi tank pressure), I can use a plastic Soda Stream® bottle for the oxidizer tank, CPVC plumbing glued together with cement, a lightweight normally closed solenoid valve, and a low pressure check valve. As such, I can run one to two rocket test a week adjusting parameters as I go.

4.0 Plans

My immediate objective is to develop a class I hybrid rocket with an impulse of ~200 N-s (20 N for 10 sec) with a thrust to mass ratio of ~1.3. As such, the hybrid rocket will need a guidance and control subsystem and parachute recovery. In accordance with FAA guidelines, the system mass must be less than 1.5 kg (100 gm of which is propellants), difficult but achievable. With my class I hybrid rocket, I can garner a lot of system level experience with launch and recovery in my backyard and without a launch wavier from the FAA.

Going forward to a class II engine, I need to;

- measure the thrust with a load cell,
- measure the chamber pressure and temperature,
- measure the oxidizer flow rate,
- develop a fuel regression model, and
- fully characterize the system.

It will take one to two years of study and experimentation to completely characterize a class II engine. I have published this paper under the creative commons share alike copyright in hopes of future collaboration with like-minded individuals who are intrigued by the HTP/PLA/$KMnO_4$ rocket engine and wish to learn some basic rocket science or have some experience in basic rocket science.

5.0 Conclusion

To date, I have infused PLA with $KMnO_4$ and used it as a hybrid fuel in a pressure feed rocket engine with HTP as the oxidizer. I have demonstrated the rapid burn of test coupons and ignition (after preheating) of the PLA/$KMnO_4$ in less than one second. I surmise that the infused $KMnO_4$ reduces the melt temperature of the PLA. Pending further testing, this may show to effect the regression rate and flame temperature of the PLA. The reduction in melt temperature makes for the possibility of additional oxidizers besides HTP, such as oxygen or nitrous oxide. The HTP/PLA/$KMnO_4$ hybrid rocket engine needs further development but the initial results are very encouraging.

I have shown in theory, that characteristic velocity is independent of chamber pressure. As such, lightweight materials can be used for the oxidizer tank, plumbing, opening valve, check valve, injectors, fuel core casings, and combustion chamber. This reduces overall system mass and makes for quick turnaround when testing.

My immediate objective is to develop a class I hybrid rocket using HTP as the oxidizer and PLA infused with $KMnO_4$ as the fuel. The hybrid rocket will need a guidance and control subsystem and parachute recovery. With a class I hybrid rocket, I can garner experience with launch and recovery in my own back yard and without a launch wavier from the FAA. The experience gained will ease the transition to larger class rocket engines and systems.

The main reason for publishing this paper under the creative commons share alike copyright is to change the paradigm for manned spaceflight. My goal is to develop a cadre of owner, operators, and maintainers of privately owned rocket ships. To own a rocket ship, it needs to be affordable and cost effective. To operate a rocket ship you will need a pilot license with an instrument rating. And to maintain a rocket ship it has to be relatively simple and you need to have a basic knowledge of rocket science. I believe that the HTP/PLA/$KMnO_4$ hybrid rocket engine is the first step in this goal.

As a final note, HTP/PLA/$KMnO_4$ is a nontoxic and green propellant. According to theory, the major combustion products are water and carbon dioxide with a smaller percentage of carbon monoxide and hydrogen.

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