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Monopropellant Hydrogen Peroxide Rocket Systems: Optimum for Small Scale

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Increasingly military and commercial system applications seek smaller and smaller packaging. This in turn has a corresponding demand on energy and power requirements. This paper examines the available technologies which can be used to produce propulsion. The available technologies are examined using the criteria of: short duration power missions, millipound class and smaller thrust levels, performance and toxicity. It will be shown that for space, air, ground and sea applications monopropellant hydrogen peroxide based propulsion in general terms provides the best overall solution.

Nomenclature

CO2 = Carbon Dioxide
HAN = Hydroxyl Ammonium Nitrate
He = Helium
H2O2 = Hydrogen Peroxide
LC50 = Lethal Concentration Causing Death in 50% of the Subjects
LD50 = Lethal Dose Causing Death in 50% of the Subjects
MAV = Micro Air Vehicle
N2 = Nitrogen
N2O = Nitrous Oxide
N2H4 = Hydrazine
OSHA = Occupational Safety and Health Administration
PEL = Personal Exposure Limit
RTG = Radioisotope Thermoelectric Generator

I. Introduction

There are many existing types of technology from which energy and power can be produced for various system requirements. It is the goal of this paper to provide a cursory explanation of each of the technologies and provide a general measure when each of the technologies may find use. Further the provided technologies will be compared against system three general criteria:

1) Power based missions approximated as mission propulsive on times lasting less than 1 hr
2) Small scale systems approximated as propulsive thrust less than 0.1 lbf (0.445 N)
3) Performance and toxicity on a per unit mass basis.

These three criteria will be examined in the subsequent sections and used to reduce the available technology remaining in consideration. Figure 1 shows the general flow of the paper and technologies that will be discussed.

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II. Discussion of Energy Storage - State of the Art Technologies

For any system the ability to deliver power and energy is of paramount performance because it will dictate capability and endurance amongst other critical overall system level performance criteria. This is especially true for the more difficult mission associated with powered flight. In order to compare different technologies for deriving power and energy, terms such as specific power and energy density (how much can be performed per unit mass) are a useful discriminator to determine which technology would be best for given missions. Shown in figure 2 are most of the known state of the art technologies for producing power and energy. It should be noted that this is not a comparison of technology which does not necessarily produce propulsion directly but is the base power/energy source that then must be converted (with expected efficiencies) into propulsion or other desired system level performance. This type of comparison is known as a Ragone plot which shows specific energy density in the abscissa and specific power density on the ordinate. Also shown are approximate operating durations which appear as roughly 45 degree lines (because of the equal divisions of the log-log plot) in similar log spacing. Similar information could be provided wherein the specific energy and power would be compared on a per unit volume basis. However, preliminary design calculations have shown that for many mission and envelope requirements the mass is the more critical parameter and hence the information is provided on a per unit mass basis. Each of the particular technologies will be discussed in the subsequent sections.

The technologies examined fall into three basic groupings: Electrochemical Storage (e.g. batteries), Combustion (e.g. airbreathing engines) and Direct Energy Conversion (e.g. Fuel Cells). It should be noted that the technologies shown are rough order of magnitude comparisons since there are constant evolutions in economics and technology within each of these technology groups.

A. Electrochemical Storage

1. Primary Li, Lead-Acid, Ni-Cd, Ag-Zn[1]

Figure 2 shows that this technology increases in energy density from Lead-acid, Ni-Cd, Ag-Zn and then primary Lithium. Note that Lead-acid is approximately an order of magnitude less in energy density but actually has slightly higher power density for very short durations (starting a car is still dominated by lead-acid for short duration high power and probably economic reasons). Some of these technologies can be recharged with some upper limit on the amount of times and others are a bit of a one shot deal (e.g. primary lithium). Rechargeable Li technology has roughly the same maximum power density as Primary Lithium and approximately 50% of the energy density[3].

2. Thermal Batteries[1]

This particular technology is an excellent choice for single use short duration high power requirement systems. This is a bit of a hybrid technology in that it uses pyrotechnic material as the source and converts the “combustion” to electrical energy and power. These batteries have long shelf life and short activation periods compared to other batteries. They are of course intended for single usage and very short (< 1 minute) usage as the energy density falls of significantly.

3. Capacitors & Supercapacitors[2]

Capacitors and their newer offspring, Supercapacitors, are very simplistic devices that hold a charge across a dielectric and as such this charge can be used in a very short period of time. Hence the capacitor has very high power density (actually much greater than indicated in figure 2) upwards of 10000000 W/kg. These devices have the advantage of being recharged a great many of times without loss in performance and in practical usage do not have lower temperature limits. Also these devices are not inherently voltage limited to chemistry like most batteries are. The supercapacitor differs from the capacitor in that the dielectric is an electrolyte as opposed to a dry material and as can be noted from figure 2 this corresponds to a reduction in specific power density for an increase in specific energy density.

B. Combustion

The technology in this section may also be considered as direct energy conversion but generally requires additional equipment for conversion to electrical energy. As such it is put in a separate section and split into two divisions: Airbreathing (requires oxygen from the atmosphere) and Rockets (Non-Airbreathing) which do not require mass inputs to combustion process.

1. Airbreathing Engines[1,3]

Typically these engines consume a hydrocarbon based fuel and combust it with oxygen from the atmosphere which is then exhausted. Because the oxygen does not need to be carried and is used in situ this makes for a very high energy density system. As can be noted from Figure 2 this technology is much higher in specific energy density than batteries and also in specific power density in the limiting case of no fuel usage at around 1000 W/kg. This technology is extremely versatile and has been effectively exploited in many different systems (e.g. gas turbine engines for aircraft, internal combustion engines for autos, etc) which is generally for durations of a few minutes or more. This technology has short comings in that it usually requires some other means to initiate the combustion reaction (usually a high power requirement).

2. Rockets[7, 8]

In figure 2 are shown three different classes of rockets: Cold Gas, Monopropellant and Bi-propellant. It should be noted that the rocket technology would also have an upper limit of specific power much like the airbreathing engines which would be somewhere around 10000 W/kg (Figure 2 upper specific power density range). This technology lives at the extreme upper limits of specific power density and specific energy density (hence its use in launch vehicles). This technology however, is almost an order of magnitude lower in specific energy density compared to airbreathing engines and hence is practically limited to systems where the duration is less than approximately one (1) hr. The rocket by definition does not need to interact with its environment and hence is fit for use in space and below the water. Within the rocket technology family the bipropellant thruster has the greatest specific power density and is typically characterized by combustion of a fuel and oxidizer (e.g. space shuttle main engines use liquid hydrogen and liquid oxygen). Solid rocket motors also fit this class in that the fuel and oxidizer are intimately mixed and stored in solid form with long shelf life (e.g. military air-to-air missiles). At approximately a 50-60% reduction in specific energy density is the monopropellant thruster. In this particular rocket there is generally a catalytic reaction which decomposes a molecule which releases energy in the catalytic reaction (e.g. liquid 98% hydrogen peroxide decomposition results in gaseous products at approximately 1800 F). At another 75% reduction in specific energy density is the cold gas thruster which is nothing more than venting a compressed gas (e.g. nitrogen). Complementary with the drop in performance between each of these rocket technologies is an approximate drop in complexity.

C. Direct Energy Conversion

1. Fuel Cell[3, 4]

Fuel cells are an exciting technology that promises to surpass airbreathing engines for specific power density (while maintaining specific energy density) because of the direct conversion to electrical from interaction of a fuel with oxygen at an electrode. The reason for the increase is reduction of the mass overhead and inefficiencies of a generator and mechanical linkages. Although this technology is very attractive to date specific energy and power densities an order of magnitude lower than airbreathing engines have been achieved. This general trend is shown in figure 2.

2. Radioisotope Thermoelectric Generator[3]

This technology is very attractive for its simplicity (no moving parts) and extreme duration (on the order of years). As figure 2 shows this technology (RTG) has one of the lowest specific power densities but it has the greatest specific energy density. This stems from the fact that the energy is derived from decaying radioactive materials which is then converted to electricity through thermoelectric means. Because of the extremely long mission possibilities this technology has found use on deep space probes (e.g. Pioneer 10 operated 30 yrs[9]).

3. Thermoelectric[5]

This technology functions on the basis of the Seebeck effect wherein when two dissimilar conducting materials are in contact with one another will product a current when exposed to a thermal gradient at that contact. This is attractive technology because of its solid state nature and hence has very long life. As can be seen from Figure 2 this technology has a specific power density in the battery range but does not produce electrical power on its own and requires a thermal source. As such it would be expected that the specific power density would drop by an order of magnitude if the thermal source were to be accounted for (much like the RTG which has an energy source). Hence this device may be useful for scavenging rejected heat from a rocket or air breathing engine.

4. Photovoltaic[3]

This again is a solid state technology which directly converts photonic (solar) energy into electricity through the photovoltaic effect which occurs at a p-n junction of semiconductor materials. This device has long life and requires a source of energy much like the RTG and hence is most useful for conversion of "free" solar energy when a mission may permit reliable access to solar energy (e.g. satellites). Additionally this technology has low conversion efficiencies.

5. Thermophotovoltaic[6]

This technology is a means of producing electricity from a thermal source that is adjusted to emit in the infrared spectrum and collected by a photovoltaic cell that is adjusted to be more optimum at this frequency. This technology is approximately three (3) times better than standard photovoltaic and again requires a thermal source. Because of the solid state nature of this technology long life is expected and has the greatest specific power density (Figure 2) of the thermal scavenging technologies but is still somewhat under development.

III. Power Missions for Propulsion

As noted previously the intent of this paper is to focus on technology that is useful for power missions. More specifically the term power mission is the technology which is better suited for short mission duration. Again in reference to figure 2 the technologies that are more suited to "energy" missions would have larger energy density (lower right hand) and those for "power" missions have larger power density (upper left hand side). Figure 2 hence provides a ready means of reducing the technology to those of interest in a power mission by the choice of missions in duration less than 1 hr. Further for the purposes of this paper the focus is on system propulsion and hence will only consider the top 5 technologies for further discussion. Hence the technologies for power mission consideration are:

1) Capacitors (including Super Capacitors)
2) Thermal Batteries
3) Rockets (Bipropellant, Monopropellant & Cold Gas)
4) Airbreathing Engines
5) Ni-Cd & Ag-Zn Batteries

IV. Small Scale Propulsion

For the purposes of this paper small scale shall be defined as a maximum being the propulsion required for micro air vehicles (MAV). Per this definition we will use the semi arbitrary value of 100 mlbf (0.445 N) which is roughly four (4) times the propulsion requirement of the "Black Widow" MAV[10]. This is also roughly the upper bound of propulsion being considered for nanosatellites[11].

The primary discriminator between each of these technologies at smaller scale is the phenomena commonly known as the cube-squared law. This relationship is a simple understanding of the fact that as dimensions shrink the volume will shrink as the cube of a characteristic length compared to the surface area shrinking as the square of the same characteristic length. As an example is the shrinking of a cube of which the length is halved then the surface area will reduce by factor of 4 (square power) and the volume will reduce by a factor of 8 (cube power). Hence this tends to advantage systems which rely on surface area (e.g. catalysis) but will be disadvantageous to thermal and mixing systems which rely on volume (e.g. combustion). Additionally the reduced scale is disadvantageous for mechanical systems where the increased area per unit volume producing work leads to more frictional losses (e.g. pistons) and hence greater conversion inefficiencies.

Discussions in the sections below provide the justification for the delivered maximum power density values shown in Table 1. As can be seen from the table the superior technologies for the small scale power mission are the monopropellant and cold gas rocket.

Table 1 Delivered Maximum Power Density at Typical vs. Small (e.g. MAV) Scale

Technology	**Typical Scale Max Power Density (W/kg)**	**Small Scale Maximum Power Density (W/kg)**
Ni-Cd & Ag-Zn Batteries	600	200

Thermal Battery	10000	1500
Super Capacitors	1000	300
Airbreathing	750	75
Rocket - Bipropellant	10000	1000
Rocket – Monopropellant	10000	9000
Rocket – Cold Gas	10000	10000

A. Batteries & Capacitors

Batteries are a very attractive option for producing thrust in that they tend to be "clean", fairly inert, in some cases can be recharged and somewhat "fool proof". That being said there are some penalties to be paid for their use as a power source for propulsion. The primarily penalty is to be found in the conversion from electrical device to propulsive device. As an example of this the "Black Widow" MAV uses NiCd batteries and uses the electrons to drive a small electric motor which in turn drives a gearbox which then drives a micro-propeller for propulsive thrust[10]. The overall propulsive energy conversion was found to be around 40-45% and the associated hardware added approximately 25% to the propulsive system mass[12]. Hence the system level power density compared to that of figure 2 is reduced by approximately 1/3 resulting in a top end technology of around 200 W/kg for Ni-Cd & Ag-Zn batteries. Similarly the thermal battery upper envelope would be reduced to 1500 W/kg.

Capacitors are expected to have similar reductions in power density due to the electric producing nature of the technology. Hence the upper right hand side of the technology envelope (figure 2) for supercapacitors is reduced to around 350 W/kg.

Further reductions in combined propulsive conversion efficiency should be expected for devices smaller than MAV and at least an order of magnitude reduction should be expected.

B. Airbreathing Engines

This excellent technology has a very great disadvantage for small scale systems related to large thermal losses and mixing inefficiencies. As an example of this is some rough knowledge that flame tubes less than 3 mm in diameter self extinguish from thermal losses[13]. Figure 3 shows that the best propulsive conversion efficiencies that should be expected at the small scale are around 10%. As such the delivered power density for a small device is around 75 W/kg.

C. Rockets

This class of energy conversion device is typically used to directly produce propulsive thrust and as such the mass associated with that system is accounted for in figure 2.

1. Bipropellant Rockets

This technology clearly has the advantage for power missions as may be noted in fig 2. There are many potential chemical combinations of which most of the higher power densities within this class suffer from either being cryogenic (liquid oxygen-liquid hydrogen) or volumetrically inefficient (gaseous oxygen-gaseous hydrogen). This is only an issue for systems requiring long term storability or those that are volume constrained. Additionally, solid rocket motors are an attractive option in that they package very well but suffer from not having true on/off capability if that should be a system level requirement. This may be compensated for with many smaller solid rockets but again the system complexity (multiple combustion chambers, ignition energy requirements and movement of thrust location) significantly reduces the utility. Other possible liquid based systems are those using storable fluids and hybrid motors (either fuel or oxidizer in solid form). However, the technology of the device still relies heavily on mixing and reduced thermal and should suffer from roughly the same losses as the airbreathing engine. Hence at MAV scale the conversion efficiency would be ~10% (fig 3) providing a maximum power density of around 1000 W/kg.

2. Monopropellant Rockets

This method is very simplistic and does somewhat benefit from the cube-square law in that the primary mechanism of producing power is surface catalysis. This technology system should result in propulsive conversion efficiencies greater than 90% at the MAV scale hence the delivered upper power density should be around 9000 W/kg. The conversion efficiency of 90% for a catalytic system is estimated from reference 11 for a hydrogen peroxide thruster approximately 0.4 lbf based upon measured decomposition temperatures for 87% H_2O_2.

3. Cold Gas

This technology is the most simplistic of the rocket family and although the performance will be modified for small scale due to changes in thermal interaction between the reservoir tank and the working fluid the change should not be significant.

V. Monopropellant Comparison

In the previous section it was shown that the preferred technologies on the basis of power density performance under the assumptions of small scale and "power" missions of less than 1 hr are the monopropellant and cold gas rocket. The cold gas rocket is a type of monopropellant rocket in that there typically only one fluid (non-reacting) and as such for the purposes of this section cold gas will be direct compared to the monopropellants. The monopropellants that will be considered are: Hydrogen Peroxide ($H2O2$), Hydroxyl Ammonium Nitrate (HAN), Hydrazine ($N2H4$), Carbon Dioxide ($CO2$), Helium (He) and Nitrogen (N). The later three being examples of cold gas with CO2 being an example of the liquefied gas family. CO2 is used for comparison purposes to generally represent the family of liquefied gases (See Ref. 24 for thorough examination of liquefied gases: ammonia, butane, propane, nitrous oxide, carbon dioxide and water).

The sections below provide a top level comparison of these propellants and it will be shown in general that hydrogen peroxide is the optimum selection. This conclusion is based primarily on performance with Hydrazine, H2O2 and HAN being the best. However, Hydrazine is less than optimum due to its toxicity and limited applications to that of space. It should be expected that Hydrazine will still find some niche uses where its toxicity can be tolerated. HAN still remains a highly developmental propellant and may find future uses, however for present day applications it should not be considered. Of the cold gases Carbon Dioxide looks to be an excellent selection for short duration (estimated to be 30 sec or less) terrestrial applications where its higher density impulse trades well against its heavier molecular mass.

A. Performance

The major comparative performance parameters of a given chemistry are the specific impulse and density impulse (specific impulse times the propellant density). Table 2 shows the values for the reduced set of monopropellants selected. For H2O2, HAN & Hydrazine performance is provided at a chamber pressure of 1000 psia and nozzle expansion ratio of 100 in vacuum conditions. The cold gas family is assumed to have the same specific impulse (at smaller expansion ratio) as Nitrogen for rough approximate purposes. The density used for the CO2 density impulse calculation is that of liquid assuming that it is stored at 1000 psia. As can be seen from the Table 2 Hydrazine has the best specific impulse by about 25% but lower density impulse by about 12% compared to HAN-Glycine-Water or 98% H2O2. The increased density impulse performance would be important for volume constrained systems. The cold gas family is clearly at a much lower performance level both from a specific impulse and density impulse perspective. It is noteworthy that CO2 storage at elevated pressure (as a liquid) has a clear advantage over He & Nitrogen and would be useful for terrestrial applications where the fluid mass is not as important.

Table 2 Comparison of Monopropellant Chemistry Performance

Monopropellant	**Vac Specific Impulse (lbf-sec/lbm)**	**Vac Density Impulse (lbf-sec/ft^3)**
Hydrogen Peroxide (98%)	192 (Ref. 8)	17140
HAN-Glycine-Water	200 (Ref. 15)	17729
Hydrazine (100%)	245 (Ref. 15)	15295
CO2 (Liquefied Gas)	65	4190
Helium	65	48
Nitrogen	65 (Ref. 16)	315

B. Storability & Toxicity

Table 3 shows the storability of the fluids of interest. As can be seen H2O2 and Hydrazine have about the same storability which for most aerospace applications would suffice. The cold gas systems have no real restriction on storage and in that case it may be more a mater of leak rates. The HAN propellant is still in development and as such its attractiveness would be considerably less than the other propellants listed.

Table 4 shows the exposure and toxic information for each of the propellants. The cold gases are merely asphyxiants and as such present no real concern. Hydrogen peroxide and Hydrazine both have Personal Exposure Limits (PEL) but the limits are established for different reasons. In the case of Hydrazine the limit is to prevent its absorption in the body. This limit is established because hydrazine is a mutagen and a carcinogen hence absorption in the body is undesired. In the case of hydrogen peroxide the limit is established as about 10% of the limit of irritation. For these reasons hydrazine *is* considered toxic and hydrogen peroxide is *not* considered toxic. The LD50 and LC50 values for Hydrazine and Hydrogen Peroxide inhalation and ingestion suggest that both are high energy chemicals which should come as no great surprise. HAN again is in development and nothing is really known about the toxicity. Hence HAN and Hydrazine are probably on the bottom of the list in terms of being non-toxic with the other propellants on the top with the cold gases having a slight advantage.

Table 3 Comparison of Monopropellant Chemistry Storability

Monopropellant	**Storability**
Hydrogen Peroxide (98%)	3+ yrs Sealed - 1965 Demonstrated 15 yrs Sealed – Estimated Modern Chemistry 17+ yrs Vented - Demonstrated (Ref. 17)
HAN-Glycine-Water	Unknown – In Development (Ref. 18)
Hydrazine (100%)	“Excellent if kept blanketed with inert gas” (Ref. 15) ~10 yrs Sealed (Ref. 19)
CO2 (Liquefied Gas)	Indefinite
Helium	Indefinite
Nitrogen	Indefinite

Table 4 Comparison of Monopropellant Chemistry Exposure & Toxicity

Monopropellant	**Toxicity**
Hydrogen Peroxide (98%)	1 ppm OSHA – PEL (Ref. 20) OSHA Limit Actually ~10% of Irritation Limit (Ref. 21) 805 mg/kg (rat) Oral LD50 70%H_2O_2 (Ref. 20) 170 ppm (rat) Inhalation LC50 50% H_2O_2 (Ref. 20)
HAN-Glycine-Water	Unknown – In Development (Ref. 15)
Hydrazine (100%)	0.1 ppm OSHA – PEL (Ref. 22, pg 1053) 60 mg/kg (rat) Oral LD50 (Ref. 22) 570 ppm (rat) Inhalation LC50 (4 h) (Ref. 22) Mutagen (Ref. 22) Carcinogen (Ref. 22)
CO2 (Liquefied Gas)	Asphyxiant Other Liquefied Gases May be Oxidizers (e.g. N_2O) or Fuels (e.g. Butane) and Have Exposure Limits
Helium	Asphyxiant
Nitrogen	Asphyxiant

C. Special Considerations

It is noteworthy that the prior discussions and selection criteria have made no mention of system location use. In other words the conclusions are applicable to space, air, land and sea utilization. This section makes note of considerations which may be specific to location utilization. Table 5 makes an attempt to summarize some the know considerations. Hydrazine for example has several undesired characteristics which restrict its propulsive use to the space environment. HAN has been in development for the last 20+ yrs as a gun propellant and some effort to turn this fluid into a rocket monopropellant but finding a suitable catalyst has proved elusive. As such this propellant seems to stay restricted to the R&D lab.

Table 5 Comparison of Monopropellant Chemistry Special Considerations

Monopropellant	Consideration
Hydrogen Peroxide (98%)	Environmentally Friendly - Decomposes Into O2 & H2O
HAN-Glycine-Water	In Development from 1980 As Gun Propellant Catalyst Requires 400C Preheat (Ref. 23)
Hydrazine (100%)	Exhaust (H2) Will Afterburn in Atmosphere Exhaust and Propellant are Odorous (Ammonia) Flammability Hazard in Atmosphere Catalyst Bed Flux Levels 50-65% Less Than H2O2 (Ref. 14)
CO2 (Liquefied Gas)	Nitrous Oxide May Be Decomposed See Other Liquefied Gases (Ref. 24)
Helium	None
Nitrogen	None

VI. Conclusions

Available technology for storage and generation of power and energy was examined to determine the optimum for use in producing propulsive thrust at small scale and for mission durations of less than one hour. The reduced set of technologies was examined for performance, storability and toxicity. The following conclusions were reached:

- Selection Criteria
  - “Power Missions” – Lasting less than 1 hr in propulsive duration
  - “Small Scale” – Propulsive thrust less than 100 mlbf
  - Performance and toxicity

- 98% H2O2 systems provide the best overall general solution for space, air, land and sea applications.

- Hydrazine systems may find limited use in space based applications where its toxicity may be tolerated.

- CO2 systems may provide optimal solutions for terrestrial applications lasting less than 30 sec.

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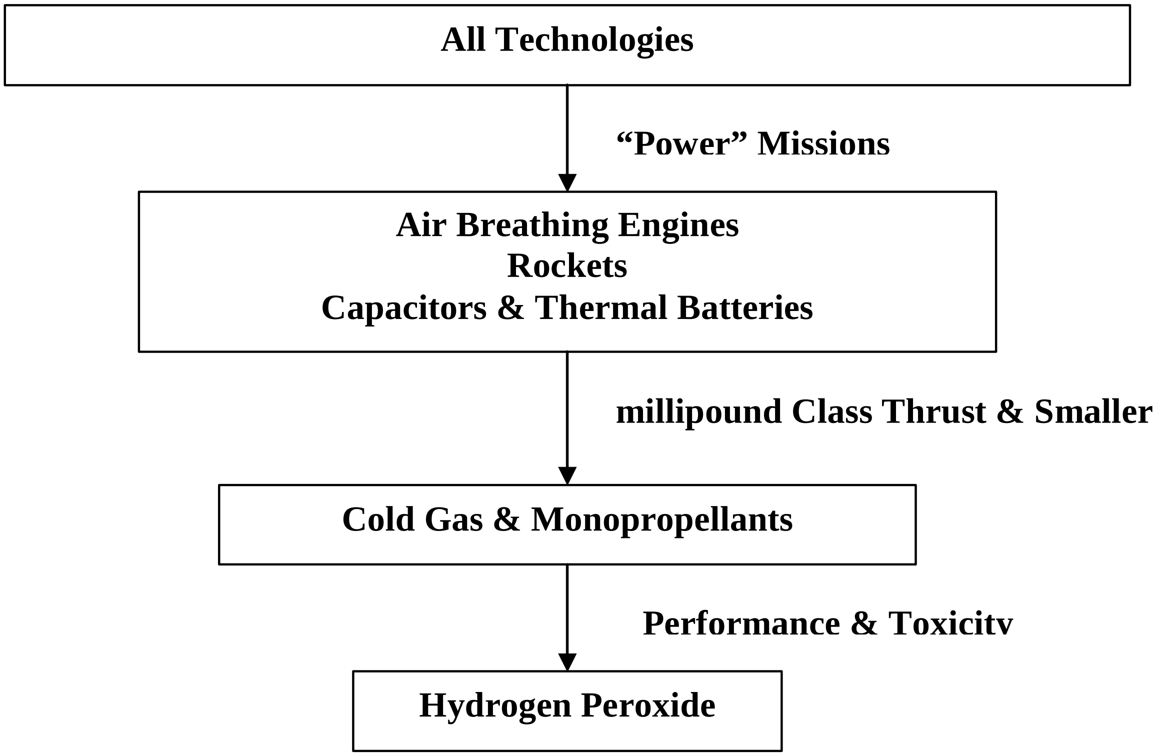

Figure 1. Shows the Reduction in Available Technologies after Considering the Three Sets of System Criteria

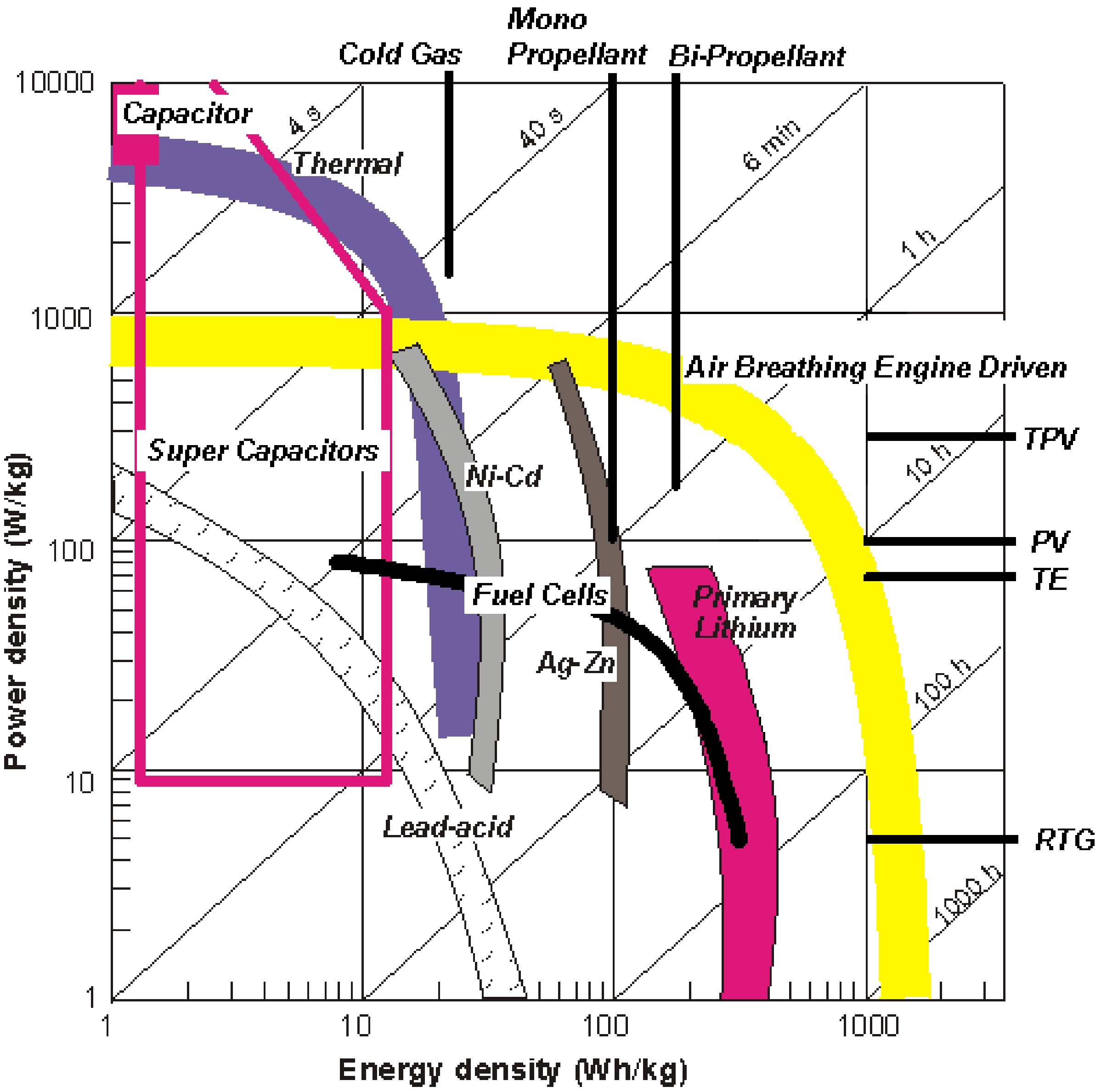

Figure 2. Comparison of State of the Art Technologies for System Power & Energy Showing Relative Value on the Basis of Specific Density (per Unit Mass). Does Not Include System Mass Required to Produce Thrust from Each of the Technologies

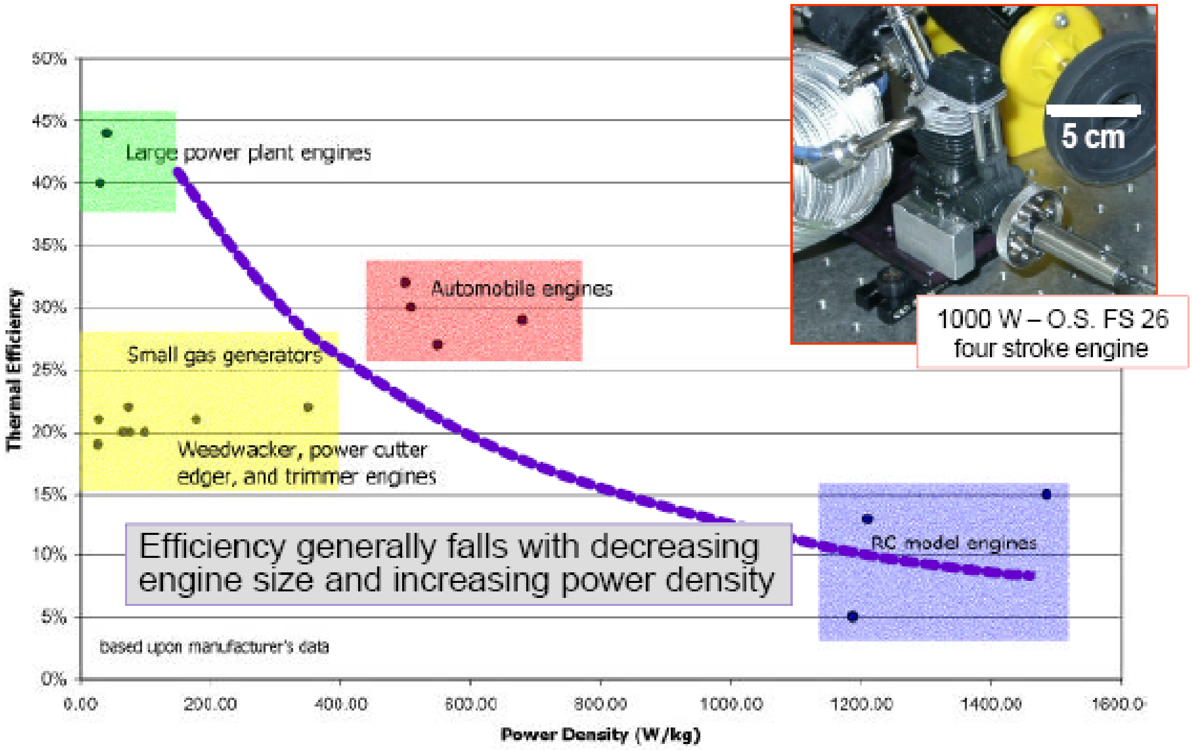

Figure 3. Comparison of Expected and Actual Efficiencies for Airbreathing Combustion Devices for Scale and Power Density[3]