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Paper Session II- B - Alternative Fuel Transport using semi volatile Ammonia

Dennis A. Lobmeyer
P .E., ASRC Aerospace

John E. Brandenburg
Ph.D., Florida Space Institute

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Dennis A. Lobmeyer, P.E., ASRC Aerospace;
John E. Brandenburg,Ph.D., Florida Space Institute

A major constraint to exploring space is the ability to carry the necessary fuel and oxidizer for a return trip. The aerospace community is continuously looking for methods to derive the fuel or oxidizer from "In-situ" resources. In the case of Mars, one option would be to derive the oxidizer from the CO2 rich atmosphere. This process relies on the ability to deliver hydrogen from earth to mars. The weight of the fuel is only 5%-10% of the overall system weight required to transport it. The Space Shuttle and some expendable launch vehicles utilize liquid hydrogen providing a "high" density storage technique. Alternative storage methods that would achieve hydrogen capacities greater than 10% are much sought after for both terrestrial and space based applications. This paper describes one method of transporting hydrogen to Mars by anhydrous ammonia. By chemically binding the hydrogen in the ammonia a storage capacity greater than 15% (mass of hydrogen to mass of total system) is theoretically possible. The ammonia is then dissociated into hydrogen and nitrogen using a patented microwave electro-thermal plasma reactor. The hydrogen is then available as a feedstock for processing or as a fuel for a fuel cell or propulsion system.

Alternative Fuel Transport using Semivolatile Ammonia

Dennis A. Lobmeyer, P.E., ASRC Aerospace;
John E. Brandenburg, Ph.D., Florida Space Institute

Abstract

A major constraint to exploring space is the ability to carry the necessary fuel and oxidizer for a return trip. The aerospace community is continuously looking for methods to derive the fuel or oxidizer from "In-situ" resources. In the case of Mars, one option would be to derive the oxidizer from the CO2 rich atmosphere. This process relies on the ability to deliver Hydrogen from earth to mars. The weight of the fuel is only 5%-10% of the overall system weight required to transport it. The Space Shuttle and some expendable launch vehicles utilize liquid Hydrogen providing a "high" density storage technique. Alternative storage methods that would achieve Hydrogen capacities greater than 10% are much sought after for both terrestrial and space based applications. This paper describes one method of transporting Hydrogen to Mars by anhydrous Ammonia. By chemically binding the Hydrogen in the Ammonia a storage capacity greater than 15% (mass of Hydrogen to mass of total system) is theoretically possible. The anhydrous Ammonia is then dissociated into Hydrogen and Nitrogen using a patented microwave electro-thermal plasma reactor. The Hydrogen is then available as a feedstock for processing or as a fuel for a fuel cell or propulsion system.

Introduction

Space Exploration requires the achievement of very high velocities relative to our position on earth so that we can escape the gravitational pull of our planet. The current "best" technology available to obtain such velocities is by using chemical propellants, more commonly referred to as Rocket Propulsion. Rocket propulsion includes a large number of different types of fuels and oxidizers. The fuel of choice for any given propulsion system is dependent upon several factors, however there are some general characteristics that are favorable for use. The primary fuel that we will be focused upon is Hydrogen. When combined with oxygen, Hydrogen can achieve the highest thrust to weight of any of the chemical propulsion systems. However, Hydrogen is a very lightweight material and is difficult to condense and contain in any storage system at high weight of fuel to weight of system ratios. For extraterrestrial explorations such as Mars we will need to take significant quantities of Hydrogen with us. Transporting the Hydrogen as a pure liquid or gas may not be the most economical or efficient method. Alternatives that store the Hydrogen in a different state or even within a chemical compound have great promise.

Fuel Characteristics

1. High specific Impulse

The choice of fuel should achieve a high specific impulse. The specific impulse (Isp) is a measure of the thrust developed to the weight of fuel consumed. Many factors play into this equation, but suffice it to say that the higher the velocity that can be achieved out of the nozzle the higher will be the specific impulse. The higher the Isp the more efficient the operation of the thrust engine. Hydrogen fueled vehicles typically have a specific impulse of between 300 and 500 seconds at sea level.

2. Compact/Low Mass

The size and weight of the fueling system which includes the fuel, storage vessel and all of the necessary piping and safety systems is extremely important. Current liquid Hydrogen fueled vehicles achieve a fuel to system weight ratio of approximately 10%. That is the fuel weighs 10% of the total fuel handling system. This means that we are "lifting" nine times more weight than the fuel and getting very little in return. The excess weight of the fuel storage and handling system do not increase the payload capacity. The current liquid Hydrogen systems are also fairly complex due to the insulation, pressure control and relief requirements as well as cleanliness and purging needs. The goal is to minimize these systems as well as minimize the maintenance requirements that are associated with complex systems.

3. Fuel Types

For our purposes we will highlight the major chemical propulsion fuels and only briefly mention some of the alternatives.

a. Liquid Hydrogen (LH_2)

Liquid Hydrogen is one of the most popular fuels because it can achieve high mass ratios, it achieves a high Isp and it is very light. However, in order to use the Hydrogen we must first liquefy it. Hydrogen condenses at a temperature of 20 Kelvin (-423°F) which makes it the second coldest of the cryogenic fluids. There is a significant cost associated with liquefying Hydrogen and then keeping it cold. Additionally cryogenic liquids require well designed safety systems due to their capability to expand up to 800 times their volume and over pressurize the storage system.

b. Hydrocarbon

Hydrocarbon fuels such as RP-1 (Rocket Propellant-1) are based upon a derivative of the oil that we use to power our cars and homes. Hydrocarbon fuels deliver a tremendous amount of energy in a very compact volume. Hydrocarbons are relatively heavy and provide a lower specific impulse than does Hydrogen or anhydrous Ammonia, however they are able to achieve much better fuel to system weight ratios. Hydrocarbon fuels are usually higher molecular weight fuels and therefore deliver lower specific impulse, however most achieve Isp's in the low to mid 300's.

c. Anhydrous Ammonia (NH_3)

Anhydrous Ammonia is another liquid propellant that can used directly for rocket propulsion. Anhydrous Ammonia has been tested and shown to be capable of achieving Isp's in the same range of LOx/H2 when the anhydrous Ammonia can be vaporized at a high enough temperature. Anhydrous Ammonia can also be combusted similarly to Hydrogen and RP-1 and has been shown to achieve Isp's in the range of 250 to 400. Anhydrous Ammonia is a clear vapor at normal pressures and temperatures, however it can be liquefied much easier than Hydrogen and can be stored in uninsulated vessels. Ammonia when in contact with water becomes corrosive. Ammonia concentrations in air above 500 ppm are considered toxic to humans.

d. Hypergolics

One class of fuels that achieve good Isp's as well as allow for normal temperature storage are the hypergolic fuels. Hypergolics are fuels that ignite upon mixing, requiring no outside spark or ignition source. The down side to hypergolic fuels is that they are extremely toxic, highly corrosive and expensive. Additionally, there are exceedingly high environmental costs associated with using hypergolic fuels on earth. Due to their self ignition properties they are highly desirable in space and some military activities.

e. Ion/nuclear

Ion and nuclear propulsion use a number of different types of fluids as ejectants for propulsion. To date these types of engines have not been developed into large thrust devices for use in/on earth. Their application has primarily been for long duration and deep space exploration. These engines are outside the scope of this paper.

Mission Requirements

For the purposes of this paper we are only considering a Mars mission. This would be a manned or robotic mission with the need to return a "heavy" payload from Mars to Earth, such as a human crew. The mission would carry enough fuel for a return, however the oxidizer would be produced in-situ on Mars.

1. Fuel Sources/Choices

For our reference Mars mission we will need a variety of energy types so that we can accomplish the goals. The types of processes requiring fuel fall into two primary areas. The first is power generation for maintaining the habitat, controlling the operational systems and providing communications back to Earth. The second provides the propulsion for the return trip to earth.

a. Power generation can be accomplished by several different means, however we will focus on three primary generation schemes.
   i. Solar power generation provides electrical power without the need for fuel storage or chemical reaction. However on Mars the ability of solar panels to provide adequate power are severely limited. The distance from the sun reduces the solar incidence by 43% from earth levels. This reduces the power output from a panel by a similar amount requiring additional panel surfaces to be deployed. The constant dust and blowing sand on the surface of Mars also provide a physical blocking of the sun requiring a significant oversizing of the units or some mechanical cleaning process to be employed.
   ii. Fuel Cells are a very good source of power provided that the fuel and oxidizer are available for use. Current fuel cell designs require very pure Hydrogen (99.9+%) and a good source of oxygen. The exhaust water can then be recycled for use elsewhere or converted back into Hydrogen and oxygen by using solar, wind or some other source of local energy. Fuel cells in general do not deal well with Sulfur, Carbon or any of the heavier metals. Since most fuel cell designs use air as the source of oxygen, they are only minimally affected by Nitrogen.
   iii. Thermal Systems such as Radio Thermal Generators (RTG), Small Nuclear Reactors and Standard Thermal Power plant designs (i.e. gas turbines, steam turbines, etc.) are an additional possibility. RTG's and compact nuclear systems are politically "incorrect" at this time. The activist communities come out in force to protest small amounts of radionuclide being launched, and would no doubt be even more vocal should a small power plant be launched into space.

b. Propulsion is the primary area of interest for fuel storage and transport to and from Mars. The propulsion system must provide for the Lift-off of the vehicle in order to get from the Surface to Orbit. This is a short duration, high thrust, high specific impulse desired capability. The power needed to achieve an orbital velocity is high even for Mars. Once in Orbit we then need to achieve an Escape Velocity of xxx so that we can begin the journey home to earth. Once away from Mars the propulsion needs change and lower power ionic drives can provide the long duration low g acceleration that will help get the vehicle back to Earth.

c. Specifications for fuel are different for the different uses. In a Fuel Cell the fuel must be much cleaner so that the fuel cell is not contaminated or plugged by unwanted reactions. For Propulsion the fuel must be sufficiently pure so that it does not cause problems from ice buildup in the delivery systems and/or contamination and plugging in the high temperature combustion zones. The availability of our chosen fuel is of paramount importance. Ideally, we would like to get the fuel from local sources, however at least in the beginning it is unknown whether we can efficiently extract these compounds there. In-Situ Production of oxygen on Mars is a straightforward process; however, it requires significant quantities of Hydrogen to convert the CO_2 in the atmosphere into Methane (CH_4) and Oxygen (O_2). We now have evidence that water once existed on Mars, but without the presence of free water somewhere within the planet we do not have the Hydrogen available for extracting and utilizing as a fuel. This leaves us with the need to transport the Hydrogen from either the Earth or the Moon. Transporting Hydrogen in a liquid cryogenic form is both expensive and difficult. Continual boil-off from the dewar or tank requires that we launch more Hydrogen than we actually need so that we can be sure to have what we need when we arrive at Mars. This is both expensive and wasteful. Our alternative is to transport the Hydrogen in a more stable format. One option is to utilize the Hydrogen that is chemically bound within the anhydrous Ammonia molecule. This can alleviate or minimize many of the issues we have with liquid Hydrogen.

2. Storage Requirements

The type of storage needed for transport and long duration storage on Mars is highly dependent upon the type of Hydrogen carrier or fuel that we choose.

Pressurized storage containers are good for some liquids and most gases. The requirements for meeting the design safety aspects are well understood and well documented. The weight of the storage system is a straightforward relationship to the pressure containment necessary. For example, the higher the pressure the stronger and heavier the vessels must be. Exotic materials can lessen the weight impact significantly with very little loss in functionality.

Cryogenic storage systems rely on sophisticated insulation schemes to minimize the heat transfer from the surrounding environment to the fluid inside. Most long duration and high efficiency insulation systems utilize a vacuum jacket or evacuated annular space between two separate vessels or tanks. The annular space is filled with an insulative material and must act as a radiation barrier. Most cryogenic storage systems are relatively low pressure (<300 PSI) so that the weight penalty of the outer tank and insulation can be offset by the lighter weight storage vessel inside.

A third option would be the transport of a solid material that contains the fuel within a chemical complex structure such as a Hydride or physically adsorbed to another material such as Carbon Nanotubes. These systems are typically low pressure and achieve low weight percentage storage (although new research is being performed at higher pressures to increase the loadings). Current state of the art is hovering between 6% and 10% by weight of the adsorbent or hydride material. This does not include the weight of the storage vessels. Additionally, the density of the hydride and adsorbent materials are quite high so that the entire system is very heavy.

The mass of the storage system and all of the ancillary components must be taken into account when considering the options. The tank and supports make up a significant portion of the launch vehicle structure and weight.

The stability of stored fuels can be addressed by two primary areas. When using Cryogenic fuels the primary issue is Boil-off of the liquid. Containing the gas (800 times the volume of the liquid) or reliquifying it so that it can be returned to the storage system is of significant cost and complexity such that it must be included in the storage system design. When using chemically or physically bound materials like anhydrous Ammonia or a hydride the chemical stability of the compounds becomes a serious concern. Does the chemical change with time and are there side reactions that can take place that reduce the effectiveness of the material once it arrives at the final destination? Adsorption processes are especially prone to catalyzing any side reactions due to the extreme surface areas that are available. Purity of the stored materials becomes of even greater concern.

Ammonia as Fuel Carrier

Anhydrous Ammonia can be stored at low pressures (<250 psi) as a liquid at room temperatures. Anhydrous Ammonia has a Critical Pressure of 11.333 MPa (1643.7 PSI) and a critical temperature of 405.4 K (270.05 °F). Above either of these values anhydrous Ammonia exists as a dense fluid, neither a gas or a liquid. At 310 K (100 °F) anhydrous Ammonia has a vapor pressure of 1.424 MPa (206.5 PSI) which means that as long as the vessel that the anhydrous Ammonia is being contained in can withstand an internal pressure of 210 PSI the anhydrous Ammonia will remain in a liquid state. The specific gravity of anhydrous Ammonia at 210 PSI is 0.8. This leads to a hydrogen density of 119 kg H_2 per cubic meter. By comparison, liquid hydrogen has a hydrogen density of 71 kg H_2 per cubic meter, and water has a hydrogen density of 111 kg H_2 per cubic meter. Anhydrous Ammonia has an energy content per unit mass of 82 kJ/kg. Liquid Hydrogen by contrast has an energy content of 119,929 kJ/kg. However the liquid Hydrogen must be maintained at 20 K (-423 °F) in order to keep the volume and pressures at a reasonable value. If we look at the energy available from the Hydrogen (gaseous form) once we have arrived at our destination, the numbers do a complete reversal. The Hydrogen gas generated from one liter of liquid cryogenic Hydrogen has an energy value of 8,490 kJ while the Hydrogen liberated from one liter of anhydrous Ammonia has an energy value of 14,264 kJ.

1. Stability

Useful storage times for all of the storable propellants plays a major role in what propellant or fuel is going to be used for which part of the journey. Liquid Hydrogen is quite stable from a chemical point of view, however it is expensive and long term storage can be a problem. Maintaining the liquid at the extreme temperature of 20 K either requires allowing some boil-off to occur or providing refrigeration to maintain the liquid. Anhydrous Ammonia is not quite as stable chemically when in the presence of water, or iron catalysts. However by utilizing clean systems the storage of anhydrous Ammonia is common, well understood and relatively easy. The low vapor pressure of the anhydrous Ammonia at normal temperatures allows the material to be stored in low pressure vessels without the requirement of insulation or vacuum jacketing.

2. Transportation

Anhydrous Ammonia is toxic to humans when encountered in high enough concentrations. Required analysis and instrumentation for storing, handling and transporting anhydrous Ammonia are well understood and available as COTS technology.

The pressures necessary to store and transport anhydrous Ammonia are considered low pressure within the aerospace community. Vessel designs for 250 PSI maximum allowable working pressures are readily available and can easily be transferred to new materials and requirements that extraterrestrial transportation would require. Composite materials would minimize the weight while providing sufficient safety margins in the process. The safety systems necessary for long duration storage and transport can easily be incorporated into the vehicle designs such that should an issue arise the safety system could respond without creating any adverse reactions on the spacecraft.

3. Conversion to Hydrogen Fuel

Anhydrous Ammonia easily dissociates into Nitrogen and Hydrogen. The chemical bonds within anhydrous Ammonia are easily broken using either thermal energy or catalytic processes. A new thermal process called Plasmonia uses plasma generated by a small microwave device to thermally decompose the anhydrous Ammonia into Hydrogen and Nitrogen. The temperature and stability of the Plasma Processing design are simple, robust and can be scaled to any desired size. Plasmonia is a patented process originally developed for space based propulsion, however it has shown to be useful for generating Hydrogen and Nitrogen from anhydrous Ammonia.

For the Mars mission envisioned the Plasmonia reactor could be the size of a small loaf of bread and would need only 1500 watts of power. The Nitrogen gas could be separated from the Hydrogen and then reused in the Plasmonia reactor to help stabilize the plasma zone. The system would generate only Hydrogen and Nitrogen without the detrimental effects of side reactions and other products. The Plasmonia process requires three operations to produce the Hydrogen. The heat transfer and reactor itself are efficiently designed into a single apparatus while the separation module could be a commercially available system. The simplicity of the design and the minimization of parts and systems make this process a natural for extra-terrestrial applications.

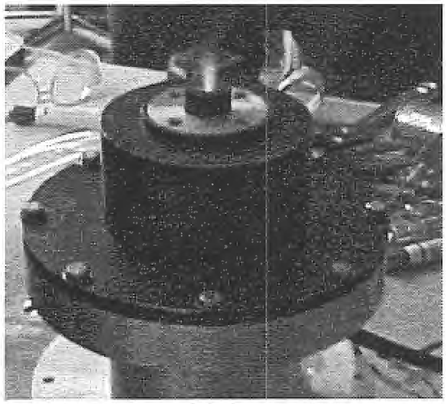

Fig. 1
Plasmonia Microwave Thermal Reactor

Summary

As can be seen, the use of a less volatile material that can carry a significant amount of Hydrogen is highly desirable. The use of anhydrous Ammonia as a chemical carrier for the Hydrogen is ideal in many ways. It is well understood and the safety and handling of the material are easily accommodated. Anhydrous Ammonia has a high density and relatively low vapor pressure so that it can be stored at reasonable pressures and temperatures. Anhydrous Ammonia carries a significant amount of Hydrogen within its chemical structure and it can be easily dissociated. The anhydrous Ammonia can also be used directly as a propellant in several different types of propulsion systems. The Plasmonia process allows the use of simple hardware and processing to recover the Hydrogen from the anhydrous Ammonia without creating a complex chemical reactor system.