IN SITU LUNAR PRODUCTION OF MONOPROPELLANT HYDRAZINE

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Introduction: Monopropellant hydrazine (N_2H_4) represents one of the most widely used chemicals in the satellite propellant industry to produce the necessary thrust for spacecraft propulsion. The discovery of ammonia (NH_3) in cryogenic lunar polar soils by the LCROSS mission in 2009 introduced the concept of potential *in-situ* lunar hydrazine production. The presence of a lunar surface N_2H_4 production facility would give dramatic headway to the aerospace industry, allowing for lander and hopper refueling, higher distance capabilities for sortie and orbital missions, and aid exploring other realms of space. It could also extend the lifetime of orbital assets such as the Lunar Reconnaissance Orbiter - a spacecraft that is nearly out of fuel. We propose the design of a stand-alone integrated hydrazine production system that will utilize the peroxide process to synthesize hydrazine and hydrogen gas. With a target production rate on the scale of 1,000 kg/month of 98.5wt% hydrazine, unit operations include chemical reactions, phase separations, product separation and storage for process model development. Key challenges addressed are the mass and power budgets, thermal and vacuum related constraints, separation technologies, and calibration of an accurate process simulation.

Required Chemistry: On an industrial scale, hydrazine is typically produced using the peroxide process in a homogenous catalyzed gas-liquid-liquid reaction. In the peroxide process, the three reactants ammonia, hydrogen peroxide, and methyl-ethyl-ketone (MEK) are reacted to form ketazine. The hydrolysis of ketazine then produces hydrazine and water. The homogenous catalyst MEK is also regenerated in the hydroylsis. The main ketazine formation reaction is a series of five distinct reactions. First, MEK reacts with ammonia to form an imine intermediate. Hydrogen peroxide then reacts with acetamide to produce a peroxoic acid. These two intermediates react to form an oxaziridine and regenerate the acetamide. The oxaziridine then reacts with ammonia to form water and a ylidene-hydrazine. Finally, this reacts with another molecule of MEK to form the methyl-ethyl ketazine intermediate product. This is later hydrolyzed in a separate reactor to form hydrazine hydrate and MEK.

Process Description: The hydrazine process production operation utilizes multiple units including: photoelectrochemical water splitting reactor, continuously stirred tank reactor (CSTR), decanter, separation column, reactive separation column, and membranes. From the main CSTR reactor running the five step reaction described above, the ketazine product is fed through a decanter which separates the aqueous, organic, and gaseous phases. The organic product flows to a distillation column, and excess ammonia is recycled into the ammonia storage tank. The aqueous phase flows to a chitosan membrane. The membrane permeates water, moving to the reactive distillation column, and retains acetamide, which is recycled back to the CSTR. The distillation column separates MEK through the distillate and ketazine in the bottoms. The distillate of the column is recycled into the CSTR, and the bottoms is fed into the reactive distillation column. The reactive distillation column produces hydrazine and water from the hydrolysis reaction of ketazine. Water and hydrazine are the bottoms product. The distillate is recycled into the CSTR. The MEK formed during the reaction is separated and flows out as distillate and recycled to the CSTR. The bottoms are then separated through a polystyrene membrane where the produced hydrazine is stored. Water and some hydrazine are recycled back into the process. The operating conditions for each unit operation were determined considering safety concerns, kinetics, and separation propensities. Temperatures and pressures for the distillation columns, specifically the reactive distillation column, were chosen based on the azeotropes that form between water and hydrazine as well as the highly reactive nature of the chemicals being used. Separation was the most limiting factor in this design and the conditions needed for the operation of the membranes were important for ensuring their structure and full separation capability. This final design was chosen through refining initial designs with specific membranes, operating conditions, and kinetic information to ensure proper separation and purity of the hydrazine stream.

Orbital Refueling Market: Two missions are currently underway using spacecraft that will attach to retired GEO satellites and take over attitude control[2] and NASA is developing a spacecraft that will refuel (notably with hydrazine) and repair a legacy satellite to extend its lifetime.[3] These developments would be synergetic with the manufacturing of hydrazine in microgravity or on the lunar surface, provided a simple, robust method of chemical synthesis can be developed and proven. The system would utilize ammonia derived from lunar polar volatile resources. The value of hydrazine in GEO for refueling life extension of commercial and military satellites has been independently estimated to be as high as $350,000/kg.[1] Future customers could include near-term lunar landers and deep space missions that could be refueled before leaving cislunar space.

Our patent-pending innovations are also anticipated to be adaptable for use at terrestrial worksites, providing a path to near-term economic returns. NASA and most terrestrial companies that utilize hydrazine have to ship it in but do not use it in large enough quantities to justify their own facility. Technology that could negate the need for shipping hydrazine fits the lean manufacturing technique of supply on-demand, minimizing safety hazards due to exposure.

Industrial analogs for individual hydrazine unit cell processes provide an incremental design path leading to an emergent space resource refining capability. Our goal is to build and test a stand-alone, integrated microreactor system that will utilize input power, water and ammonia to produce hydrazine and hydrogen gas for space propulsion customers anywhere ammonia and water are available in space. An additional application would be refueling of spacecraft designed to rendezvous with and deorbit space debris, then separate and reboost themselves to their next target. Such spacecraft could maneuver itself to a hydrazine depot in Earth orbit rather than requiring a tanker to rendezvous with it.

Our approach may also allow the salvaging of satellites presently in graveyard orbits or adrift. Since the beginning of the space age in 1957 with the launch of Sputnik, there have been over 5,000 rocket launches placing one or more satellites in orbit. It is estimated that there are also over 3,000 dead satellites in orbit with over 1,000 satellites in the GEO graveyard orbit. Many of these graveyard orbit satellites cost hundreds of millions of dollars to manufacture and launch into space. A restoration or recycling of even a small percentage of these legacy space assets could create tremendous value. The metals and electronics in these satellites could then provide additional space resource feedstocks.

One of the largest, most obvious and frequently discussed applications for refueling is satellite life extension in GEO. Recently, Northrop Grumman demonstrated its Mission Extension Vehicle by docking with an Intelsat satellite and taking over the station-keeping role. There are several other companies planning similar life extension capabilities. Satellites have generally been launched with enough station-keeping fuel for a 15-year mission life. Without an ability to keep a satellite in its licensed GEO orbital slot, revenue potential can be reduced by 80% to 100%. Giving a satellite owner/operator additional years of revenue potential can mean $50 million to $500 million per year of incremental revenue depending on the size and type of satellite and the markets it serves. As these satellites would typically be fully depreciated and operating margins can be 80% to 95%, most of this incremental revenue becomes operating cash flow and net income, greatly increasing the market value of the company and potentially allowing for significant expansion of satellite capacity and services to end users at reduced pricing.

Spinoff Analysis: A systems-level economic model was built for a terrestrial spinoff process that uses calculated cash flows, feedstock prices, utility prices, and labor costs. Assuming product hydrazine purity specifications are met, it can be sold terrestrially for $100/lb, and given the flowrate of 1000kg/month, this gives a total revenue of $2,645,000 per year. This of course assumes continuous operation year-round, but for the purposes of this estimation, that assumption will do. Methyl-ethyl ketone was found to cost roughly $1.04 /kg and the “flowrate” of MEK required to replace the circulating batch twice a year is roughly $1300kg/month. This results in the annual (quite conservative) cost of ketone to be $16,400. Next is acetamide, which also must be replaced twice yearly to ensure proper peroxide activation. This cost is higher at $5/kg, which results in an annual cost of $66,000. Ammonia is priced at $0.4/kg, and with the required feed to the reactor the annual price is $13,900. Utilities used include low, medium, and high-pressure steam, electricity, and hot oil. The prices for these utilities are based on the Aspen Plus simulation, and this value was calculated based on required flow rates to meet the heat duty requirements. The final operating cost considered was the replacement for the membrane units. The same price was applied twice yearly to account for fouling of the membranes and general repairs. This leads to an overall operating cost of $188,800/year and this number includes all utilities and feedstocks. operating costs including labor is estimated at $783,000 per year. This analysis was done over a period of 20 years, and the depreciation model used is the 12-year MACRS, which indicates how much capital will depreciate over time. A generous tax rate of 26% was used for calculation purposes. Using this method, the internal rate of return for this process was calculated to be 116%, and the net present value was found to be $2,870,000. This far exceeds the minimum rate of return necessary to recommend this project of 6.7% (accepted specialty chemicals minimum rate of return).

References: [1]Benedict, B., AIAA 2014-4445.
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