NASA Hydrogen Research at Florida Universities

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ABSTRACT:

This paper presents a summary of the activities and results from 36 hydrogen research projects being conducted over a four-year period by Florida universities for the U. S. National Aeronautics and Space Administration (NASA). The program entitled "NASA Hydrogen Research at Florida Universities" is managed by the Florida Solar Energy Center (FSEC). FSEC has 22 years of experience in conducting research in areas related to hydrogen technologies and fuel cells. The R&D activities under this program cover technology areas related to production, cryogenics, sensors, storage, separation processes, fuel cells, resource assessments and education.

KEYWORDS: NASA, hydrogen, production, storage, cryogenics, sensors, fuel cells.

Introduction

The NASA Hydrogen Research at Florida Universities is a consortium of seven state universities as follows: Florida International University in Miami, Florida State University and Florida A&M University in Tallahassee, University of Central Florida in Orlando, University of South Florida in Tampa, University of West Florida in Pensacola, and University of Florida (UF) in Gainesville. The Florida Solar Energy Center (FSEC) of the University of Central Florida manages the research activities of all consortium member universities except UF (for a complete description of the NASA funded projects and publications at UF, see: http://www.mae.ufl.edu/NasaHydrogenResearch). Presently, the NASA Hydrogen Research at Florida Universities program funds a total of 36 individual university projects, more than 85 faculty/staff and over 100 graduate research students in seven member universities. To date, researchers involved in this program have filed for more than 20 patents in all hydrogen technology areas and put out well over 100 technical publications in the last year alone.

The objectives of the program are to support NASA's hydrogen-related activities by conducting research in the areas of cryogenics, storage, production, sensors, fuel cells, densified propellants, space power and education. The NASA Hydrogen Research at Florida Universities program activities and projects have resulted in the formation of a powerful partnership among the consortium member universities, NASA Glenn Research Center (GRC) - the nation's premier space research facility, and NASA Kennedy Space Center (KSC) - the nation's premier space launch facility. This program has positioned FSEC and the State of Florida to become major players in the future NASA and U.S. Department of Energy hydrogen and fuel cell program areas. Detailed information on each of the individual projects is available at: http://www.fsec.ucf.edu/hydrogen/new/research/funded_nasa.htm and http://www.hydrogenresearch.org.

The NASA Hydrogen Research at Florida Universities program has as its objective to generate significant cost savings to NASA's space and space launch efforts in five major areas as follows:

1. Using data from the past 21 years, the NASA Space Shuttle has been launched an average of five times per year (109 launches, in all), at a cost of more than $5 million annually for its hydrogen fuel. The annual cost for trucking the needed Shuttle liquid hydrogen from Louisiana to the Kennedy Space Center is about $2 million. Producing hydrogen locally, near KSC would eliminate these transportation costs.

2. For each launch, more than 50 semi-tractor-trailers must drive 640 miles from New Orleans to KSC to deliver the hydrogen. Local production will eliminate the infrastructure costs related to increased highway usage and the potential for accidents on the busy U.S. interstate highway system.

3. At the launch site, 400,000 gallons of liquid hydrogen are lost because of storage boil-off and transfer. Capturing boil-off and improving hydrogen transport technologies can save an additional $250,000 per year.

4. From past history, KSC has been able to launch the Shuttle, successfully, three out of every five attempts - or 60 percent of the time (109 times out of 191 attempts). The scrubbing of 82 shuttle launches has resulted in an average annual loss of about $2 million in hydrogen costs alone, which could have been saved if NASA had produced hydrogen locally, near KSC. These savings grow significantly when considering future flight schedules at the Cape Canaveral, which call for greatly expanded launch schedules of more than 50 per year – schedules that can only be met if liquid hydrogen is produced and liquefied locally near the Cape.

5. Densified propellants can lower payload-to-orbit costs because they enable more cryogenic propellant to be packed into a given volume and can save an estimated 10 percent in weight. Given that launching a payload costs about $4,000 to $10,000 per pound, this 10 percent weight savings equals an increased payload value of $20 to $50 million per launch.

Finally, another very important aspect of having local hydrogen production at KSC is that it provides valuable data for operating future automotive fueling stations. FSEC's analysis has shown that Shuttle operation at KSC launch closely mimics future vehicular hydrogen fueling stations in both fuel volume dispensed and energy content. Thus, local hydrogen production at KSC will present a model that can be replicated for the future hydrogen economy.

Results to-Date

The premise of the NASA Hydrogen Research at Florida Universities program is that fundamental and applied research is required to create the "disruptive" technologies that will push hydrogen from being a "potential" solution to the U.S. transportation energy dilemma to that of dominating energy vector. Past experience has shown that new industries and investment capital follows those that successfully engineer the disruptive technologies of the future. In this program, each university partner has identified areas of expertise and interest while contributing to the overall success of the effort. The following presents a brief description of each project's accomplishments. Projects are grouped according to the technology areas.

Production

System Analysis of Hydrogen Production and Utilization at KSC – The objectives of this project were to systematically analyze various approaches for local hydrogen production at NASA/KSC. Hydrogen generation plants were modeled using Aspen Plus™ Chemical Process Simulator (CPS) and compared to a base case that was steam reformation of natural gas. The economics and financial viability of the plants were also investigated. The cost of gaseous H_2 produced was determined as a function of the number of Shuttle launches.[1]

Waste Oil to Hydrogen – A catalytic reformation process is being developed for generating hydrogen from used lubricating oils at a lower cost than what NASA presently pays for LH_2 ($4.50/kg). The research has shown that the quantity of waste oil generated in Florida is sufficient to supply hydrogen for more than 100 Shuttle launches per year.[2]

Local Hydrogen Production via Catalytic Reformation of Fossil and Renewable Feedstocks – This project has developed and demonstrated a novel catalytic hydrogen production process that produces solid carbon and hydrogen with a 80% efficiency and 99.9% purity by volume at significantly reduced greenhouse gas emissions (see Figure 1). The added value of the carbon by-product lowers the net H_2 cost below present NASA costs.[3]

Hydrogen Sulfide Methane Reforming – In this project, researchers developed a high-temperature thermochemical process to reform hydrogen sulfide and methane from ultra sour natural gas resources. The process converts a toxic feedstock, hydrogen sulfide, into useful commodity chemicals – hydrogen and carbon disulfide.[4]

Figure 1. Pilot plant at FSEC for the production of hydrogen by catalytic reformation of hydrocarbon fuels and renewable feedstock.

Photoelectrochemical Hydrogen Production – This project is based on the use of organic pigments deposited on wide band gap semiconductors to perform oxidative and reductive water-splitting to generate hydrogen from water. Its unique advantage compared to photovoltaic based water splitting methods is its lower capital cost for H_2 production.[5]

Photoelectrochemical Water Splitting Using a Multiple Bandgap Thin-Film Photovoltaic-Cells – In this project, laboratory scale PV cells and a photoanode container have been developed that show a calculated solar to hydrogen conversion efficiency of greater than 5% at one sun insolation.[6]

Citrus Peel Gasification – Researchers have designed and constructed a biomass gasification unit for hydrogen production that utilizes Florida citrus peel waste. The unit has successfully generated hydrogen with yields as high as 51%.[7]

Genetic Engineering of Escherichia Coli to Enhance Biological Hydrogen Production from Biomass-derived Sugars – Employing bacteria to produce hydrogen by catalyzing the reduction of protons with electrons using hydrogenases enzymes is being developed. Objectives are to genetically engineer metabolic pathways in bacteria and to enhance the hydrogen yield generated from oxidation of the sugars. Researchers first demonstrated that genetic engineering of metabolic pathways could enhance hydrogen production in the model system of *Escherichia coli.* Now, the research has moved on to organisms with similar hydrogenase enzyme systems that are efficient at hydrolysis of plant biomass. The research is presently focusing on engineering a closely related enteric bacterium, *Erwinia chrysanthemi*. This phytopathogen can efficiently break down plant biomass and expresses a number of pectate lyases and cellulases. Research is being done to transform plasmids carrying FhlA165 and another activator, HufR, to determine both hydrogen yield and their ability to upregulate FHL systems in this organism.[8]

Hydrogen Production via Methane Nonoxidative Aromatization – The objective of this project is to optimize the production of hydrogen from methane using a ZSM zeolite based catalyst. Modifications to produce ultra high purity hydrogen along with benzene and other hydrocarbons are considered. Catalytic and catalytic membrane reactors have been built and preliminary results reported for the zeolite supported catalyst.[9]

Rectenna – Researchers have developed innovative full rectification structures and a method to capture orthogonal polarizations with a single rod antenna and electromagnetic coupling in order to produce electricity from solar by a rectenna. H_2 is then produced by electrolysis.[10]

Development of a Solar Thermochemical Water Splitting Cycle for Hydrogen Production – Researchers at the Florida Solar Energy Center (FSEC) are developing a solar-driven thermochemical water splitting cycle (TCWSC) that utilizes both thermal (*i.e.* high temperature heat) and light (*i.e.* quantum energy) components of the solar resource, thus boosting the overall solar-to-hydrogen energy conversion efficiency compared to those with heat-only input. FSEC's cycle is a modification of the well-known Westinghouse hybrid cycle wherein the electrochemical step in the Westinghouse cycle is replaced by a photocatalytic process. [11]

Cryogenic Systems

Long Term Liquid Hydrogen Storage Systems – Researchers have developed a cryogenic liquid hydrogen test facility. The facility is capable of liquefying and densifying hydrogen to a temperature of 16.5 K with zero boil-off. It uses a direct cooling process that utilizes a unique internal heat pipe design and a Gifford-McMahon cryocooler. The facility generates densified liquid hydrogen, which is 6% denser than normal boiling point liquid hydrogen meaning that more hydrogen fuel can be stored in the same tank volume. For zero boil-off, an on-board Joule-Thompson cryocooler has been employed to re-liquefy boil-off gas during flight. Various cryocooler designs have been investigated to optimize cooling system configuration while minimizing H_2 boil-off losses giving ZBO on-board liquid hydrogen storage. Analytical results on thermal stratification, pressurization and no-loss chilling processes have been verified by laboratory experiments.[12]

Measurement of Transport Properties of Densified LH_2 and LO_2 – Many new propulsion systems under development for future space exploration will utilize densified fuels such as slush hydrogen and subcooled LH_2 or LO_2. However, there are few experimental data points available on the properties of these fluids. The objective of this experimental project is to produce high-resolution density and transport property measurements for cryogenic propulsion fluids (mainly LO_2 and LH_2) in regions where data are either incomplete or unavailable. The region of primary interest for the measurements is subcooled liquid below the normal boiling point of 56 K to 93 K for LO_2 and 14 K to 20 K for LH_2 for pressures up to 0.7 MPa. A measurement precision of better than +/- 1% has been achieved and two specific precision instruments were built for this purpose. To date, measurements of density have been completed and the thermal conductivity measurements are underway. These measurements will be compared to available property databases and necessary models will be developed for anomalous behavior.[13]

Experimental and Numerical Investigations of Cryogenic Multiphase Flow – This project is focused on experimental and numerical simulation of multiphase flow for future space related propulsion cryogenic systems. Experimental effort has developed a multi-phase flow system of propulsion cryogens using a cryogenic flow visualization apparatus. Tests have utilized LN_2 and LHe as the model fluids for LO_2 and LH_2. The numerical simulation models are being developed for the multi-phase cryogenic flow system including liquid/vapor and solid particle/liquid media. The goal of the numerical work is to develop algorithms that can be compared to the experimental results and guide future experiments. The analysis has focused on simulating the solidification of H_2 particles in LHe and the associated slurry transport. [14]

Optical Mass Gauging – Researchers at FSU, in collaboration with Advanced Technology Group (ATG), are developing a fluid optical quality sensor. ATG has a bench top flow sensor that will be tested in conjunction with the multiphase flow experiments. Measurements include temperature, pressure and flow rate for various conditions. ATG will simultaneously measure the liquid and vapor velocities using their fluid optical quality sensor. [15]

Shape Memory Actuator Materials – In this project, researchers have developed a thermo-mechanical processing methodology for cryogenic shape memory actuator materials. These new materials are applicable to thermal conduction switching at cryogenic temperatures (see Figure 2). [16]

Reverse Turbo Brayton Cycle Cryocooler for Liquid Hydrogen Systems – In this project, researchers have designed and built a miniature and fully integrated helium compressor and motor which is capable of removing 20-30W of heat at 18K with a projected mass of 22 kg (10 times less than the state-of-the-art). The cryocooler will be required for future manned and robotic Mars missions and will find wide applications in distributed power generation fuel cells and microturbines.[17,18]

Magnetocaloric Liquefaction – Researchers are developing a process based on magneto-caloric materials with potential to double the efficiency of microcoolers for liquefaction of H_2. [19]

Figure 2. Shape memory actuator alloys under development at the University of Central Florida.

Sensors and Detectors

Research to develop cost effective hydrogen sensor and detection technologies is a critical need. Prospective sensors must deliver detection selectivity and sensitivity, dependability and durability, stability and reproducibility, applicability in the liquid hydrogen environment, ability to operate in air and oxygen-free environment, resistance to chemical degradation and real time response. In addition, enabling technologies that can monitor harmful contaminants in the liquid hydrogen flow stream are needed for increased safety. There are four on-going projects under this topical area.

Highly Selective Nano-MEMS Hydrogen Sensors – The objective of this MEMS sensor project is to develop a cryogenic temperature device that is cheap, robust, highly responsive, selective, fast operating and can detect hydrogen at ppm levels. The device uses an advanced concept in hydrogen separation and gas sensing technologies to provide a sensor based on the porous, nano-clustered particulate/fiber/rod shaped doped tin oxide. The sensors under consideration are a unique integration of nanomaterials and MEMS devices.[20]

Smart Paints for Visual Hydrogen Leak Detection – The objective of this project has been to develop a special powder that can be applied onto any surface for the visual detection of minute hydrogen leaks. Researchers have developed special compounds that can be synthesized inexpensively and applied much like paint or deposited onto tapes that can be adhered to pipe and/or flange joints (see Figure 3). The color change is very prominent and easily detectable by naked eye. Another formulation developed involves the use of a powder that changes color upon exposure to hydrogen (minute quantities well below the levels that can pose safety risk) reverting to the original color once the H_2 flow stops. [21]

Figure 3. FSEC developed chemochromic hydrogen sensing and detection materials.

Novel Surface Acoustic Wave (SAW) Hydrogen Sensors Using Nanostructured Sensing Layers – Researchers have designed, fabricated and constructed prototypes of hydrogen sensors based on high frequency surface acoustic wave (SAW) devices and novel nanostructured sensing materials. Bilayer sensing materials used take advantage of the mass and electroacoustic perturbation mechanisms of the SAW sensor. Electronic structure and molecular dynamics calculations have been used to improve the nanomaterial sensing layer design. The project is developing new synthesis techniques for the nanowire metal and alloy sensing layers based on fabricated alumina templates and electrodeposition techniques. Results have demonstrated sensitivity improvements of 50-100 fold for organic vapors, faster response times and capability to operate in a wide temperature range. [22]

Wireless Passive Sensors and Systems – Researchers have developed wireless passive surface acoustic wave (SAW) multi-sensor systems. Currently, there are very few available wireless tagging systems and even fewer wireless SAW sensor systems. The goal of this work is to develop materials that act as the SAW sensor material, antenna designs for the proposed application, the interconnection apparatus and the device testing.[23]

Storage

Hydrogen Storage in Amine Boranes – Researchers have developed several amine boranes (AB) adducts for high gravimetric hydrogen storage applications. One member of the AB family is ammonia borane, which stores 19.6% by weight hydrogen. For equal amounts of hydrogen contained, ammonia borane complex takes up 48% less volume than liquid hydrogen. Researchers have developed special catalysts for rapid dehydrogenation of the amine borane compounds.[24]

Hydrogen Storage Using Metal Organic Frameworks – Advances in the chemistry of microporous metal organic frameworks (MOFs) have provided a range of low-cost porous crystalline materials assembled from molecular building blocks that exhibit high stability and porosity, and tunable properties. Recent systematic studies of MOFs have indicated that increasing the number of benzene rings in the scaffold of a MOF greatly improves the amount of hydrogen uptake and storage. Furthermore, inelastic neutron scattering (INS) studies suggest that MOFs can contain several types of hydrogen binding sites ranging from organic components to the metal constituents of the framework. The objectives of this work are to synthesize and characterize viable MOFs, to develop a better understanding of the interactions between sorbed hydrogen with the organic and inorganic constituents of the sorbent MOF and to construct a made-to-order cost-effective MOF material that exhibits superior hydrogen storage capacity. [25]

Hydrogen Purification and Storage Using Lithium Borohydrides – Researchers have developed a complete hydrogen capture and purification system using lithium borohydride. The novel aspects of the system are its large storage capacity, low cost and the ability to regenerate the borohydride material.[26]

Liquid Hydrogen Storage at NASA/KSC – Researchers have developed a 3-D CFD simulation model that has been validated against measured data from NASA-KSC Pad A and B LH_2 storage tanks. Researchers have estimated the size of the Pad B void area and the extent of perlite insulation void volume. The results showed that external insulation will not be an effective solution to the void area boil-off problem.[27]

Hydrogen Storage Simulation – This project has developed a 2-D and 3-D numerical simulation models to predict fluid circulation and heat transfer in a liquid hydrogen storage vessel similar to the ones used by NASA. [28]

Separation and Purification

High Temperature Separation Membranes – Researchers have developed novel gas separation membranes with mixed ionic-electronic conductivity based on pervskite material structure. [29]

Hydrogen and Helium Separation, Recovery, and Purification – Researchers have shown that addition of aluminium to lanthanum nickel metal hydride increases the hydride storage capacity and kinetics yielding a significantly cheaper and more efficient hydrogen storage system. The project has also resulted in the development of a novel gas-phase reaction to remove residual amounts of H_2 from a helium stream.[30]

Fuel Cells

Compact, Lightweight and Optimized PEM Fuel Cells for Space Power – This project addresses several innovative proton exchange membrane (PEM) fuel cell technologies that can provide greater than 1 kW/kg stack power output, a 40,000-hour life cycle and operate at up to 70,000 feet altitude. The project objective is to develop high performance membrane electrode assemblies (MEAs) that will operate under no external humidification. This objective is accomplished by improving the MEAs conductivity with new and long lasting catalysts that reduce the need for high water content. Thin composite membranes, Nafion®-Teflon®-phosphotungstic acid are examples of approaches developed to address this objective. These new composite MEAs will use hydrophilic diffusion substrates with high gas permeability to help retain the water. Tests have shown that at 60°C and under non-humidified conditions, the new MEAs performance were close to conventional membranes in the fully hydrated state. In addition, the project investigates bipolar plate design and manufacturing, control systems schemes and hardware and heat transfer improvements. [31]

Fuel Cell Weight Reduction by New Solid Electrolytes Materials – The objective of this project is to improve the performance of solid polymer electrolytes in terms of chemical stability and proton conductivity while reducing the membrane costs. These new solid electrolyte materials have the goal of achieving high performance in terms of temperature stability (in excess of 125ºC), increased proton conductivity (exceeding 0.1 Siemens/cm), and reduced dependence on water-saturating conditions (less than 25% relative humidity). These performance goals are achieved by using high-density sulfonation and strategic fluorination membranes. The fluorination membranes are composed of proton-donating sulfonic acids of highly aromatic polymers such as polyarylimides, polybenzimidazoles, polyphenylquinoxalines, and polybenzoxazoles. In order to act as a transport chain, the fluorination is done in combination with polymeric inorganic media found in various oxide, nitride, sulfate, and phosphate families that possess a high density of hydrogen-bonding sites. [32]

Integrated Fuel Cell Test Bed Facility (IFCT) – This project has developed a permanent test facility where the performance of fuel cell components and systems can be tested and evaluated. The fully integrated test bed facility (IFCT) can determine fuel cell figures of merit and performance metrics to include round trip efficiency, specific power (kW/kg), reliability for long duration operation (approximately 1 year), redundancy path development, waste heat/cooling/heating management, turn down effects, transients, and the development of 'expert' systems for the process control. The IFCT is an integrated facility with instrumentation and data acquisition equipment designed to be flexible and accommodating to the needs of any user. The IFCT will focus on fuel cell development in terms of electrochemistry, polymer science and nano-materials. The facility gives researchers the ability to perform hands on research in membrane and electrode fabrication, electrochemical testing, materials analyses and cell and device operation. [33]

Analysis of Fuel Cell Power Systems – This research project is aimed at increasing the level of confidence and the design know-how for the integration of fuel cells on aircrafts. The project applies a systems analysis to the integration of fuel cells with aircraft power systems that include modelling of fuel cells in tandem with conventional turbines, optimization of on-board fuel cell systems for aircraft, optimization of fuel cell architecture, and implementation of fuel cell models in conjunction with power network simulators. [34]

Resource Assessment and Software Development

Florida Biomass Resources – This project produced a map of the Florida based on the availability of the major biomass resources using geographical information system (GIS).[35]

Launch, Fueling and Processing Software Agents – This research advanced the state of the art for space shuttle fueling and launch processing by applying automated real-time monitoring of complex process conditions and imposing dynamic user-defined limits and alarm conditions. [36,37]

Education and Outreach

An important part of the NASA Hydrogen Research at Florida Universities program is the educational and outreach activities that are conducted by all of the participating universities. The activities include the education of students at all levels, a goal that is important to NASA and one, which is critical for the nation's future aerospace industry. This activity also involves graduate student research projects, the development of K-12 education materials, dissemination of the results of the research, support of internet outreach activities and the conducting of training seminars and workshops.

Conclusions

This paper has given a brief summary of the projects being conducted as part of a four year NASA funded grant to the Florida Solar Energy Center that began in 2002. Under the NASA Hydrogen Research at Florida Universities program, FSEC has been managing 36 research projects at seven universities within the Florida State University system. The program has generated numerous publications and patents, and provided opportunities for education and training of more than 100 students in all areas of hydrogen and fuel cell technologies. In addition, the NASA Hydrogen Research at Florida Universities program has been leveraged by the University faculty to generate considerable additional hydrogen related funding received from the industry and other U.S. agencies including DOE, DOD and NSF.

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