

VIII.13 Florida Hydrogen Initiative*

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Project Start Date: July 1, 2006
Project End Date: November 15, 2010

*Congressionally directed project

Background

The Florida Hydrogen Initiative, Inc. (FHI) is a nonprofit corporation that uses its resources to aid the development of a robust Florida-based hydrogen industry. The FHI seeks to develop Florida's hydrogen infrastructure by:

- Brokering partnerships for applied technology demonstration projects throughout Florida;
- Sponsoring research in the production, storage, and use of hydrogen fuels; and
- Facilitating technology transfers between the public and private sectors to create, build, and strengthen high-growth potential, high technology companies.

The FHI is a grantee of the U.S. Department of Energy Hydrogen Program and in the past year has funded and administered three projects:

1. The Hy-Tech Rest Area project is being conducted by EnerFuel, Inc., which will demonstrate the use of hydrogen derived from citrus waste in a fuel cell located at a Florida Turnpike rest area.
2. Designing and building a museum exhibit to tour 18 Florida science museums to inform and educate the public about hydrogen's potential and use as an energy carrying medium and the future role of

hydrogen in energy distribution. This project is being conducted by the Orlando Science Center.

3. The On-site Reformation of Diesel Fuel for Hydrogen Fueling Station Application project is being conducted by the University of Central Florida, Florida Solar Energy Center in partnership with Chevron Technology Ventures. The goal of this research is to develop a cost-effective energy efficient fuel reformation process that can be used for the production of high-purity hydrogen from sulfurous liquid fuels. Once developed, this process will be used in hydrogen fueling stations and remote fuel cell-based electrical generation stations in areas with no access to natural gas.

Each of the three projects' annual reports is provided in the following.

I. Hydrogen Technology (Hy-Tech) Rest Area

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Start Date: October 1, 2006
Projected End Date: March 31, 2010

Objectives

- Design, construct and demonstrate a 10 kW_{net} proton exchange membrane fuel cell stationary power plant operating on citrus-derived methanol.
- Achieve an electrical energy efficiency >32%.
- Demonstrate transient response time <3 ms.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Performance
- (E) System Thermal and Water Management
- (G) Startup and Shut-down and Energy/Transient Operation

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE technology validation milestones from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 35: Validate \$1.60/gge hydrogen cost from biomass and \$3.10/kg for renewable/electrolysis at the plant gate.** This project will assess the sources and economics of bio-derived methanol in Florida.

Accomplishments

- Completed direct methanol fuel cell (DMFC) vs. indirect methanol fuel cell (IMFC) trade study.
- Selected the Florida's Turnpike Enterprise's Turkey Lake Service Plaza as demonstration site.
- Obtained four, 5 kW_{net} IMFC power plants.
- Completed benchmark testing of fuel cell power plants.
- Obtained National Environmental Policy Act (NEPA) approval for construction phase.
- Completed layout and design of construction site including selection of dual-wall methanol storage tank and fire suppression system.
- Completed first draft of civil and electrical construction plans.
- Identified commercial producer of bio-methanol able to supply entire amount of fuel necessary to complete demonstration phase.
- Completed inverter software upgrade to allow co-generation operation of fuel cell power plant with the Turkey Lake Service Plaza facility.



Introduction

The use of biomass waste or the waste stream from bio-fuel production as a source of fuel for the generation of electrical power would be a significant benefit to the environment and provide additional feedstock for hydrogen fuel cells. The EnerFuel project aims to determine the effect of bio-diesel waste derived methanol on long-term fuel cell power plant performance and assess requirements for future projects and commercialization. By designing, constructing, and operating a 10 kW_{net} stationary fuel cell power plant in a co-generation mode, at the Florida Turnpike's Turkey Lake Service Plaza, the project will demonstrate the value of bio-methanol produced from a low value waste stream as a viable source of fuel for the generation of electrical power.

Approach

EnerFuel will identify sources of bio-methanol, arrange for transportation and storage, and establish safety protocols for the use and handling of methanol. They will obtain all of the required permits and prepare the demonstration site for power plant installation, including the electrical interface and methanol storage. They will design, construct, test and benchmark the fuel cell power plant and install and operate it at the Florida Turnpike Turkey Lake Service Plaza. The analysis of the fuel cell power plant under operation will determine the overall electrical efficiency, document system transient response to load changes, determine the effects of bio-diesel waste derived methanol on long-term power plant performance, and assess requirements for future commercialization.

Results

Due to recent economic shifts in the value of citrus waste and improvements in ethanol produced from citrus waste, the attractiveness of citrus derived methanol as an inexpensive fuel is no longer being considered. With increases in the price of cattle feed, citrus waste derived feed, once a low margin product, has become a product of higher value. In addition, ethanol producers that utilize citrus waste have improved their process resulting in the generation of significantly less methanol by-product. These factors diminished the viability of citrus-derived methanol as an inexpensive fuel. After a renewed search EnerFuel identified an alternate provider capable of producing commercial quantities of bio-methanol. BioMCN, a Netherlands company, is producing commercial quantities of bio-methanol from the glycerin by-product of bio-diesel production and selling it at competitive commercial methanol prices. EnerFuel will utilize this source of bio-methanol to demonstrate the feasibility of using low value renewable feedstocks to generate low cost electrical power.

The project selected the demonstration site and secured the support of the Florida Turnpike Enterprise for fuel cell co-generation of electrical power for the rest area facility. The inverters purchased to provide the necessary 208V, 3-phase power are being configured to provide the controllability and functionality necessary to allow the fuel cell systems to operate in a co-generation mode. An upgraded version of the manufacturer's firmware was installed in the inverters and its ability to allow co-generation operation verified on an in-house test rig (Figure 1). The entire power plant including IdaTech fuel cells (Figure1), inverters and batteries will be tested in-house prior to installation at the Turnpike rest area.

The locations of the power plant and the methanol storage container have been selected and the survey of

the electrical interface requirements has been completed. NEPA approval was obtained and permitting work started. A final review of the site layout and construction plans is underway to assure all mechanical and electrical requirements for the demonstration have been covered. The plans will then be submitted to the permitting office in Orange County, Florida as well as submitted to the Florida State Fire Marshal's office for approval.

The cost for purchasing and transporting the bio-methanol from BioMCN has been identified. Once site construction is underway the entire amount of methanol will be ordered and delivered directly to the demonstration site.



IdaTech 5kW_{net} indirect methanol fuel cell



Inverter test rig

FIGURE 1. IdaTech 5 kW_{net} IMFC System and Inverter Test Rig

Conclusions and Future Directions

- The project has selected the technical approach for using bio-diesel waste derived methanol for the fuel cell power plant and identified the cost and logistics for transporting the fuel to the demonstration site.
- EnerFuel is currently configuring the inverters, batteries and fuel cell system to properly function in a co-generation mode prior to installation at the Turnpike Turkey Lake Service Plaza site.
- A final review of the site layout and construction plans is underway prior to submission for county permitting and fire marshal approval.
- Construction of the demonstration site is estimated to commence in November of 2009 with operation of the fuel cell power plant expected to begin in mid-December 2009.

II. Assessment of Public Understanding of the Hydrogen Economy Through Science

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Project Start Date: July 31, 2006

Project End Date: September 30, 2008

Objectives

- Design and build an interactive exhibit "H2Now: the Great Hydrogen Xchange."
- Assess current public understanding about hydrogen science and engineering.
- Increase public understanding of hydrogen science and engineering.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect between Hydrogen Information and Dissemination Networks
- (E) Regional Differences

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section (3.9.7) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 11 – Develop set of introductory materials suitable for a non-technical audience.** (4Q, 2006) The interactive exhibit, titled “H2Now: the Great Hydrogen Xchange incorporates basic information about hydrogen and its use as an alternative energy source. Learning outcomes include:
 - Defining what hydrogen is, where it comes from, and many of its possible uses.
 - Determining fact from fiction that surrounds hydrogen as a renewable energy source.
 - Listing some benefits of using hydrogen as an alternative energy source.
 - Describing how hydrogen energy is created and how it can affect daily life.

Accomplishments

- Opening of H2Now: the Great Hydrogen Exchange at the Orlando Science Center on August 15, 2009.
- Extensive testing of mechanical and software effectiveness with periods of mechanical and software remediation between August, 2008 and February, 2009.
- Visitor testing to determine educational effectiveness against educational objectives completed April, 2009.



Introduction

Finding sources of clean, renewable energy is one of today’s most pressing issues. However, there is much information – and misinformation – about renewable energy, particularly regarding the use of hydrogen as a new energy source. Increasing the basic knowledge and awareness among the public about hydrogen as a viable energy source, and correcting misconceptions of hydrogen and its properties, is necessary to create accurate and positive opinions about this substance as an important alternative to fossil fuels.

Key to this goal is the accurate and educationally effective translation of technical scientific and engineering concepts into a format that is easily understandable and accessible. In H2Now: the Great Hydrogen Xchange, visitors will be able to imagine a

community powered entirely by hydrogen, and discover that the renewable energy source is a viable alternative to other energy sources currently in use.

Approach

Working with I.d.e.a.s at Disney MGM Studios, the Orlando Science Center (OSC) set out to perform front end evaluation and subsequent design, fabrication, and installation of an interactive exhibition at the OSC. Beginning with the schematic design of concepts and educational objectives, the exhibit will undergo design and prototyping of both physical components and interactive software. This exhibition, H2Now, the Great Hydrogen Xchange, contains two main interactive areas. The first, the H2 Charging Stations, visitors will have the opportunity to express their opinions about alternative energy sources, and interact with increasing levels of content about hydrogen as a new source of fuel. As they answer questions correctly about hydrogen, they earn Hydrogen Energy Units (HEUs) that they can ‘spend’ at Hydropolis to power various interactive ‘city’ elements.

Results

From mid-August through December 2008, software developers at I.d.e.a.s, working with OSC staff, incorporated several changes to the software design and interface based on critical analysis of visitor usage to test for mechanical effectiveness. At the end of that time, it was determined that major modifications were needed to both software design and communication interface. OSC brought in a local multimedia design firm to complete this redesign at which time visitor evaluation to determine extent to which the affective and cognitive goals of the exhibit were met.

With the exhibition now installed and fully operational at OSC, additional exhibit enhancements have been made including a linear display on additional sources of renewable energy and plans are in the works for an interactive ‘video game’ on renewable energy to complement the messages of H2Now.

Conclusions and Future Directions

- The H2Now exhibit has completed software and hardware ‘shakedown’ that resulted in a streamlined interface and communication and is functioning at 100% in the OSC.
- Summative evaluation to determine the extent to which H2Now meets educational objectives revealed that:
 - 77% of the visitors surveyed either loved the exhibit or liked the exhibit.

- Nearly 64%, in the word choice section of the interview, indicated that they ‘learned something’ or found the exhibit ‘informative’.
- Nearly 32% found the exhibit ‘interesting’ indicates that both cognitive and affective learning has clearly taken place.
- Additionally, 65% indicated that they found out something they didn’t know before. This finding is a clear indication of both cognitive gain and a change of attitude i.e., compare this to the 44% who, when given the choice to select “I learned something new”.
- OSC has enhanced the experience with the short film produced by i.d.e.a.s called “I Am Hydrogen” and is exhibiting a linear display on additional information on renewable energy. OSC has received a grant from Progress Energy to produce an exhibit enhancement piece – a video game on renewable energy.

III. On-Site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications

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Project Start Date: January 21, 2008
 Project End Date: June 20, 2009

Objectives

- Develop efficient and stable catalysts for hydro-reforming of high-sulfur diesel and other liquid hydrocarbon fuels to sulfur-free light hydrocarbons (C₁-C₄) that can be readily reformed with steam to hydrogen.
- Develop, test and validate a viable desulfurization process suitable for on-site scrubbing of high sulfur gas for forecourt applications.
- Demonstrate continuous operation of an integrated process for pre-reformation of high sulfur diesel

coupled with a hydrogen sulfide scrubber for generating a mixed gas containing light molecular weight hydrocarbons and less than 10 ppmv H₂S impurity.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration:

- (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE Technology Validation milestones from the Technology Validation section of the HFC&IT Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 24:** Validate a hydrogen cost of \$3.00/gge (based on volume production). (4Q, 2009).

Accomplishments

- A novel process has been developed for converting high-sulfur diesel to a mixture of light molecular weight hydrocarbons that can be readily reformed with steam to fuel cell grade hydrogen gas. The catalytic pre-reformer was coupled with a re-generable Fe²⁺/Fe³⁺ redox/electrolysis unit capable of scrubbing H₂S from the pre-reformer effluent in the form of hydrogen gas and elemental sulfur.
- An electrolytic process for oxidation of the acidic FeSO₄ aqueous solution has been developed having a columbic efficiency of 100% at a cell voltage of 1.0 V, and without using platinum as anode material.
- A robust bi-functional catalyst was developed for pre-reforming of high-sulfur fuels (sulfur content as high as 5,240 ppmw) to short chain hydrocarbons (C₁-C₄, mostly, propane) at an average yield of 97%.
- The combined Fe²⁺/Fe³⁺ redox/electrolyzer and high-sulfur fuel pre-reformer was operated successfully for 100 hours, continuously, achieving desulfurization efficiencies greater than 95% and removing sulfur down to less than 5 ppmv in the pre-reformate.



Introduction

One major challenge facing the future hydrogen economy is how to deliver H₂ fuel within the transportation sector. If hydrogen is to be derived from high energy feedstocks, it may be desirable to transport the feedstock itself to local fueling stations and convert the material on-site. Furthermore, it would be advantageous if the primary feedstock can be used as a fuel in the legacy vehicular power plants (e.g., internal combustion engines [ICEs], etc.). For example, diesel fuel could be delivered via tanker truck and converted in a small reformer on-site for generating and dispensing H₂ at the fueling station. There are many advantages to this approach including:

- Existing delivery infrastructure (highway to fueling station) could be utilized.
- More energy can be delivered per trip when the tanker is filled with diesel instead of liquid hydrogen.
- The fueling station would be able to service both ICE- and fuel cell-powered vehicles simultaneously.
- The fueling station operation would be flexible and easily change fuel availability in the form of hydrogen or diesel fuel to meet the customer demand.

Reforming high-sulfur hydrocarbon fuels (e.g., diesel fuel, JP-8, sub-quality natural gas, etc.) is particularly challenging due to rapid deactivation of conventional reforming catalysts by coke deposits and sulfurous compounds. Moreover, if sulfurous compounds (mostly, H₂S) are not removed from pre-reformate they deactivate the steam reforming catalyst used for hydrogen production. In a joint effort involving the Florida Solar Energy Center (FSEC) and Chevron Technology Ventures (CTV), a new on-demand hydrogen production process for the fueling station applications has been developed and validated. The objective of this work was to convert high-sulfur hydrocarbon fuels to an essentially sulfur-free gas suitable for steam reformation, while consuming only a small fraction of the hydrogen produced. The removal of sulfur from reformate is critical since most catalysts used for the steam reformation have limited sulfur tolerance. FSEC was tasked to build, operate and validate the performance of the pre-reformer as well as to develop and demonstrate a viable desulfurization unit capable of S-scrubbing of the pre-reformer effluent on-site at the filling stations. CTV provided a catalyst for the pre-reforming stage and assisted with the design of the pre-reformer.

Approach

The approach to meet the project objectives targeted at integrating a high-sulfur fuel pre-reformer with a desulfurization system. First, the high-S fuel is pre-reformed, catalytically, to short chain hydrocarbons (i.e.,

C₁-C₄) by hydrodesulfurization. In the pre-reformer, most sulfurous species present in the fuel convert to hydrogen sulfide (H₂S). This step is necessary in order to avoid deactivation of the Ni-based catalyst used in the steam reformer further downstream. Removing hydrogen sulfide from the pre-reformer effluent occurs in a special regenerative redox system that uses an iron-based scrubber paired with an electrolyzer. The sulfur-free gas emerging from the regenerative scrubber is fed to the main reformer, where it is mixed with steam and processed over a Ni-catalyst to syngas. This process precedes further treatment of the gas in a shift reactor followed by the pressure swing adsorption to separate H₂ for on-site storage and/or fueling vehicles. A rather small portion (10-15%) of the hydrogen produced in the process is returned to the pre-reformer and used to carry out hydrodesulfurization process in the pre-reformer.

Results

Pre-Reforming of High-Sulfur Hexadecane and Diesel Fuel

Figure 1 shows a simple block-diagram depicting the process used for the conversion of high-sulfur fuel to hydrogen gas.

A high-S hydrocarbon fuel (e.g., diesel) is heated and vaporized in a pre-heater (1) before entering a catalytic pre-reformer (2) wherein the fuel is hydro-reformed to shorter chain hydrocarbons (i.e., C₁-C₄). In the pre-reformer all sulfur organics are converted to H₂S gas. Hydrogen sulfide removal from the pre-reformate is accomplished in a special regenerative system having a sulfur scrubber (4) coupled with an electrolytic regenerator (5). The sulfur-free gas from the desulfurization unit (4+5) is fed to the steam reformer (6), where it is processed over a Ni-catalyst to syngas that is mostly H₂, CO and CO₂. The syngas is further treated in a shift reactor and purified (via pressure swing adsorption process) (7) to high-purity hydrogen gas. Figure 2 depicts the bench-scale experimental unit built and used at FSEC to conduct the desulfurization of high-sulfur diesel fuel.

The pre-reformer consisted of: 1) fuel metering and delivery section, 2) pre-reforming reactor, 3) products separation unit, and 4) products metering and analysis section. In the fuel delivery section, a high performance liquid chromatography pump was used to pump the liquid fuel (diesel or hexadecane) into the reactor at flow rates in the range of 0.2-0.4 mL/min. Hydrogen gas entered the pre-reformer via a high-pressure mass flow controller set at flow rates in the range of 0.72-3.50 L/min. The 316 stainless steel pre-reforming reactor used in this work was a tube reactor having an inside diameter of 25 mm, wall thickness of 2 mm, and a length of 45 cm. Three quarters of the reactor was filled with catalyst. Hydrogen entered at the bottom of

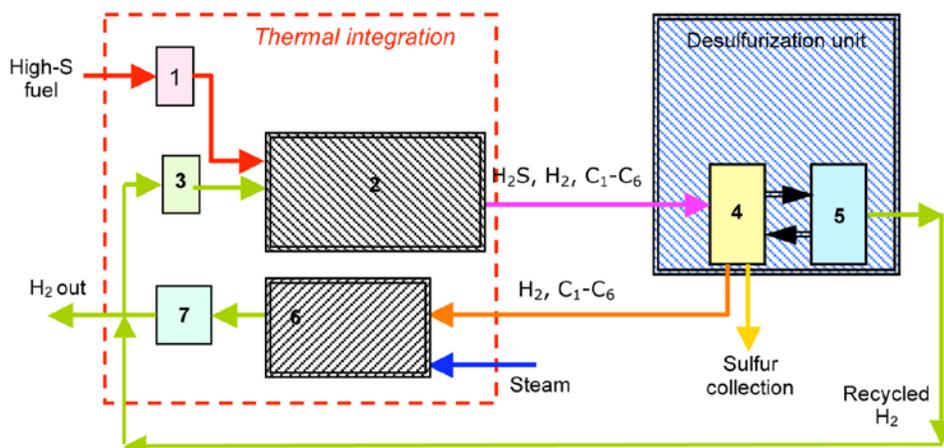


FIGURE 1. A simple block-diagram depicting the process used for the conversion of high-S fuels to hydrogen gas.

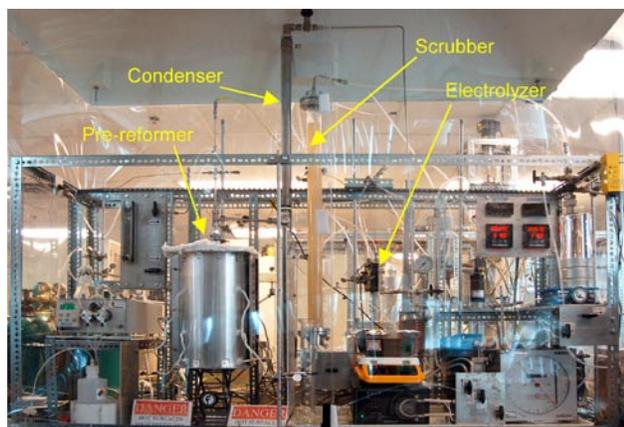


FIGURE 2. Bench-scale diesel pre-reforming reactor coupled with a desulfurization unit.

the reactor and the reformat counter flowed from the top. The temperature in the upper section of the reactor was maintained at 400-450°C and in the lower part (where the fuel entered the reaction zone) at 450-500°C. In the products separation section, the effluent passed through a shell-and-tube type condenser (maintained at 15-20°C) where most of C₆+ hydrocarbons condensed and refluxed back into the reactor and the gaseous hydrocarbons (mostly, C₁-C₄), H₂S and excess H₂ allowed to exit and flow into a knock-out chamber where the fugitive heavier hydrocarbons were trapped and collected. The product gas then flowed through in-line filters, passing through a back-pressure regulator and into a gas metering and analysis section.

Several experiments were conducted employing zeolite catalyst, Ni-Mo/alumina catalyst and a mixture of zeolite and Ni-Mo/alumina catalyst. In these experiments, separate hydro-reformation of hexadecane and diesel over zeolite and Ni-Mo catalysts showed a gradual deactivation of the catalysts due to coke formation. However, a mixture of zeolite and Ni-Mo/

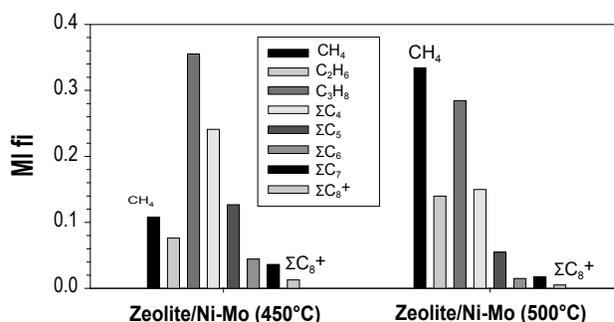


FIGURE 3. Product slate from the diesel hydro-reforming over zeolite/Ni-Mo catalyst at 450°C (left) and 500°C (right). (P = 13.7 atm)

alumina catalysts in the weight ratio of 2:1 performed very well. After about 16 hrs (through a 100-hr run), a steady-state condition was reached where the catalyst remained stable for the duration of the experimental run.

Figure 3 depicts the distribution of the high-sulfur diesel under two steady-state temperature regimes: 450°C and 500°C. Average conversions obtained in these experiments were in the range of 95-97%. The product distribution for the diesel and hexadecane hydro-reformation over the same catalyst and at the same temperature regime were similar. However, the diesel-derived gas contained slightly higher concentration of heavier hydrocarbons (C₆ - C₈+) compared to that derived from hexadecane. Figure 3 also shows that an increase in the pre-reformer temperature results in increased concentration of methane in the product.

Desulfurization of the Pre-Reformer Effluent

The analysis of the gas produced in the pre-reformer by the hydrogenation of the thiophene-laden hexadecane and diesel on zeolite/Ni-Mo catalyst indicated that

thiophene was almost quantitatively converted to H_2S . The pre-reformer effluent containing H_2 , H_2S and light hydrocarbons (mostly C_1 - C_4) flowed to the regenerative desulfurization unit. Figure 4 depicts a schematic diagram of the desulfurization sub-unit used for continuous removal of hydrogen sulfide in the pre-reformer effluent and its conversion to H_2 and sulfur. A gaseous mixture from the pre-reformer enters into the scrubbing unit having an absorption column filled with aqueous ferric sulfate solution, $Fe_2(SO_4)_3$. When H_2S dissolves in the aqueous solution, it oxidizes by ferric ion (Fe^{3+}) to elemental sulfur, and at the same time ferric sulfate is reduced into ferrous sulfate, $FeSO_4$. The elemental sulfur is removed from the flowing solution by a filter while the ferrous sulfate solution is fed to an electrolyzer. In the electrolyzer, ferrous sulfate is oxidized back to ferric state while, at the same time at the cathode, protons are reduced to hydrogen gas. The regenerated ferric sulfate solution is returned to the absorption column to scrub hydrogen sulfide – and thus, forming a closed cycle with the net reaction being hydrogen sulfide decomposition to elemental sulfur and hydrogen gas.

Electrolysis of acidic $FeSO_4$ aqueous solutions was carried out using a modified proton exchange membrane electrolyzer. The cathode section consisted of a stainless steel plate used as current collector in a contact with water for hydrogen evolution. This configuration eliminated the need for a carrier gas to sweep hydrogen from the cathode side of the electrolyzer. An electrolyzer potential of 0.80 to 1.03 volts was necessary for the electrochemical process to regenerate the scrubber solution at a rate sufficient to match the H_2S flow rate into the scrubber. The electrolytic system can be operated at the range of temperatures from ambient to $90^\circ C$. In our experiments, desulfurization of the pre-reformate gas occurred optimally at the following process

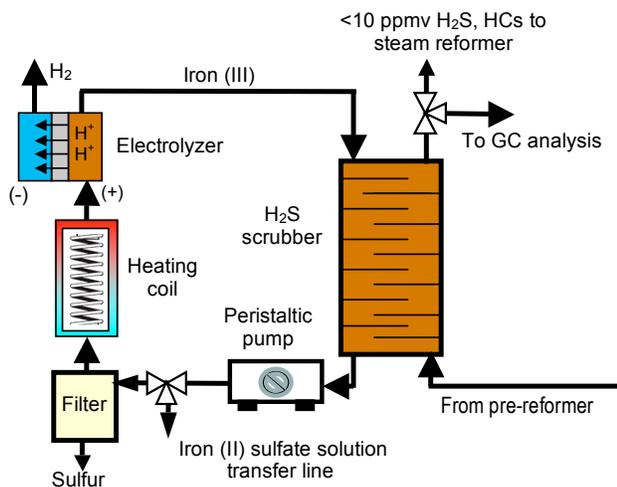


FIGURE 4. Schematic of a desulfurization unit including a scrubber and an electrolyzer.

conditions: iron sulfate (total) concentration of 0.1 M, pH of 1.7-1.8 (adjusted by addition of 5 N sulfuric acid), and electrolyte temperature of $50^\circ C$.

The hydrogen evolution rate in the regenerative electrolyzer is a linear function of H_2SO_4 concentration (within the range of $[H_2SO_4] = 0.25$ - 0.75 N), but not so with respect to the $FeSO_4$ concentration – for which it goes through a maximum corresponding to $[FeSO_4] \sim 0.15$ M. This can be attributed to the generation of polysulfate species at higher concentrations that are less active in transferring charge at the anode.

During initial testing of the scrubber-electrolyzer system, the desulfurization unit operated continuously for more than 300 hours using a surrogate gas mixture that contained 2,500 ppmv H_2S (remainder nitrogen) as an input. The system performed well and practically no H_2S could be detected at the scrubber outlet (which corresponded to several turnovers of the Fe^{2+}/Fe^{3+} -redox system). In the diesel pre-reforming experiment using the zeolite/Ni-Mo catalyst, diesel spiked with 3,180 ppmw of thiophene produced a product stream containing 185 ppmv of H_2S . The gas chromatograph analysis showed the presence of H_2S as the only product of hydrogenation of thiophene; no unreacted thiophene or other sulfurous compounds were present. On average, about 3 ppmv of H_2S was detected exiting the ferric sulfate scrubber during the run. A similar experiment using the zeolite-Ni-Mo mixed catalyst and hexadecane spiked with 5,240 ppmw thiophene produced largely desulfurized gas with the H_2S content of less than 5 ppmv.

The sulfur balance for the pre-reforming reaction and the degree of desulfurization was determined by comparing the molar mass of sulfur in the fuel entering the pre-reformer with the molar mass of H_2S detected in the scrubber exit gas. The sulfur balance for all tests conducted was closed within the margin of error of 6-8% using two independent methods for analyzing the H_2S gas (GC and gas-detection tubes). The fuel desulfurization yield was defined as:

$$\eta = \frac{(C_4H_8S)_{in} - (H_2S)_{out}}{(C_4H_8S)_{in}} \cdot 100\%$$

Where, η is fuel desulfurization yield, $(C_4H_8S)_{in}$ is number of thiophene moles in the fuel entering the pre-reformer, $(H_2S)_{out}$ is the number of H_2S moles leaving the sulfur scrubber.

Experimental data obtained from high-S diesel and hexadecane pre-reforming-desulfurization tests showed average desulfurization yields in the range of 96-98%.

Characterization of the Pre-Reforming Catalyst

Scanning electron microscope, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD)

analyses were employed to characterize zeolite/Ni-Mo catalyst before and after pre-reforming of high-sulfur diesel. The XPS spectrum of the $\text{Mo}3d_{5/2}$ and $\text{Mo}3d_{3/2}$ transitions for the oxidized form of Ni-Mo catalyst showed only Mo^{6+} species, corresponding to binding energies of 233 and 236 eV, respectively. After exposure of the catalyst to reducing and sulfiding environments, the reduced Mo^{4+} species appeared in the XPS spectrum with $\text{Mo}3d_{5/2}$ binding energy of about 229 eV. The peaks at 229-229.6 eV in the sulfided catalyst indicate the presence of MoS_2 . The spectrum showed that after hydro-reforming, a significant amount of Mo in the catalyst remained in its oxidized form implying that a strong interaction of oxidized Mo species with the alumina support did occur.

Interpretation of the Ni2p region of the XPS spectra as it relates to oxidized and reduced forms of the Ni-Mo/alumina catalyst was challenging, because of proximity of Ni2p binding energies for different Ni species. Indeed, it is difficult to distinguish between different Ni species (e.g., NiO, Ni_2O_3 , NiAl_2O_4) in the XPS spectrum, as all may appear in the same region. The weak peak at the binding energy of 854 eV in the reduced/sulfided form of the catalyst may be attributed to NiS. The absence of a peak at a binding energy of 852.4 eV indicated that nickel was not reduced to its metallic state, and most likely, remained in its Ni^{2+} oxidation state.

The XRD pattern of the Ni-Mo/alumina catalyst after high-sulfur diesel pre-reforming showed two prominent diffraction peaks appearing at 2θ values of 46 and 67 degrees that were assigned to $\gamma\text{-Al}_2\text{O}_3$. The XRD pattern did not show XRD-observable Ni oxides; however, it is commonly observed that NiO and Ni_2O_3 may exist in amorphous or microcrystalline phases. Identification of the NiAl_2O_4 phase is rather difficult because of the proximity of its reflection to that of alumina. Peaks corresponding to Mo compounds were apparently too weak to be distinguishable on the XRD pattern of the catalyst used.

Conclusions and Future Directions

- A novel process has been developed for converting high-sulfur diesel to a mixture of light molecular weight hydrocarbons that can be readily reformed with steam to fuel cell grade hydrogen gas. The process employs a catalytic pre-reformer coupled

with a regenerable $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox/electrolyzer system for the scrubbing of H_2S from the pre-reformer effluent and its conversion to hydrogen gas and elemental sulfur. Electrolysis of acidic FeSO_4 aqueous solution was highly efficient with a coulombic efficiency of 100% at a cell voltage of 1.0 V. It was shown that the electrolytic process can be operated with a Pt-free anode to oxidize ferrous to ferric ions, thereby reducing the cost of the electrolytic system, considerably.

- A robust bi-functional catalyst was developed for accomplishing the pre-reformation of the high-sulfur fuels (sulfur content as high as 5,240 ppmw) to short chain hydrocarbons ($\text{C}_1\text{-C}_4$, mostly propane) at an average yield of about 97%.
- The integrated $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox/electrolyzer H_2S scrubber and pre-reformer was operated successfully for 100 hours, continuously, achieving desulfurization efficiencies greater than 95% and removing sulfur down to less than 5 ppmv in the pre-reformer effluent.

Special Recognitions & Awards/Patents Issued or Pending

- Cunping Huang, Franklyn Smith, Clovis Linkous, Karthikian Ramasami, Ali T-Raissi, Nazim Muradov, "Method and System for Hydrogen Sulfide Removal," U.S. Patent Application No. 61/023,755.

FY 2009 Publications/Presentations

- Nazim Muradov, Karthikeyan Ramasamy, Cunping Huang, Ibrahim Adebisi, Franklyn Smith, Clovis Linkous, Ali T-Raissi and James Stevens, "Combined Pre-Reforming-Desulfurization of High-Sulfur Diesel for Hydrogen Fueling Station Applications", submitted to *J. Fuel*.
- Nazim Muradov, Karthikeyan Ramasamy, Cunping Huang, Ibrahim Adebisi, Franklyn Smith, Clovis Linkous, Ali T-Raissi, James Stevens, "Combined Pre-Reforming-Desulfurization of High-Sulfur Diesel for Hydrogen Fueling Station Applications", Presented at the 2009 AIChE Spring Meeting, Tampa, Florida (2009).
- Nazim Muradov, Karthikeyan Ramasamy, Cunping Huang, Ali T-Raissi, James Stevens, "Catalytic Processing of High-Sulfur Fuels for Distributed Hydrogen Production", submitted to *18 World Hydrogen Energy Conference*, Essen, Germany, 2010.