VII.7 Florida Hydrogen Initiative*

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Contract Number: DE-FC36-04GO14225

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 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 Project

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Start Date: October 1, 2006
Projected End Date: December 31, 2008

Objectives

- Design, construct and demonstrate a 10 kW_{net} proton exchange membrane fuel cell (PEMFC) 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 the Hydrogen, Fuel Cells, and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

(C) Performance
(D) Feedstock Issues
(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 HFCIT Program MYRDDP:

- **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 approval for construction phase.
- Completed layout and design of construction site including selection of dual-wall methanol storage tank and fire suppression system.
- Identified and began working with potential citrus waste methanol supplier.
- Selected distiller to process citrus waste methanol mixture.

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Introduction

One of Florida's most important agricultural-based industries is citrus and using citrus waste as a source of fuel for the generation of electrical power would be significant benefit to the environment and provide additional feedstock for hydrogen fuel cells. The EnerFuel project aims to determine the effect of citrus-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 at the Florida Turpike's Turkey Lake Service Plaza to provide electrical power to the rest of the facilities, the project will demonstrate the value of the citrus waste as a viable source of fuel for the generation of electrical power.

Approach

EnerFuel is identifying sources of citrus-derived methanol, designing and demonstrating its transportation and storage, and the safety protocols required for the use of citrus-derived 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 citrus derived methanol on long-term power plant performance, and assess requirements for future commercialization.

Results

The project selected the demonstration site and secured the support of the Florida Turnpike Authority for the fuel cell power plant to provide the electrical power for the rest area facility. The locations of the power plant and the methanol storage container have been selected and the survey of the electrical interface requirements was begun. EnerFuel completed the trade study to compare the attributes of DMFC or IMFC approaches and determined that an IMFC is the best alternative for achieving the project's goals (Table 1). The fuel cell systems were purchased and are being currently tested at EnerFuel facility before installation at the Turnpike rest area (Figure1). Approval was obtained and permitting work started. The final set of plans is almost complete and will be submitted to Orange County for permitting. The fuel cell power plant demonstration site is shown in Figure 2. Although 6,500 gallons of citrus waste methanol mixture was secured the methanol content was measured to be too low for final processing. EnerFuel will continue to work with their primary supplier to obtain a viable citrus methanol mixture as well as looking into alternate bio-derived methanol sources.

Conclusions and Future Directions

- The project has selected the technical approach for using citrus waste derived methanol for the fuel cell power plant and has selected a function and location for the power plant.
- EnerFuel has started benchmarking of the fuel cell power plant and permitting for construction and installation.
- In the coming month EnerFuel will deliver and install the fuel cell power plant and analyze it under operation.

TABLE 1. DMFC vs. IMFC Trade Study Results

Performance Criteria	DMFC	IMFC	BASIS
Overall System cost		X	10 kW DMFC system is ~579% more expensive than IMFC system
Stack Cost		X	DMFC stack is an order of magnitude more expensive than an equivalent H-PEMFC stack
Stack size		X	10 kW DMFC stack will contain ~3 times as many cells as an equivalent H-PEMFC stack
System Complexity	X		DMFC system has nine major components. IMFC has at least 13
Overall System Efficiency		X	IMFC overall system efficiency is ~30%. DMFC is ~20%
Energy Density		X	Methanol/water tank is major contributor to lower DMFC power density. DMFC fuel tank is ~20 times larger than for an IMFC system with same energy storage
Emissions		X	Both systems are susceptible to emitting trace methanol amounts. Nonetheless, lower DMFC overall system efficiency means greater CO_2 emissions will be released from the DMFC system. Therefore, in this category IMFCs performed better

FIGURE 1. 5 kW_{net} Indirect Methanol Fuel Cell Power Plant

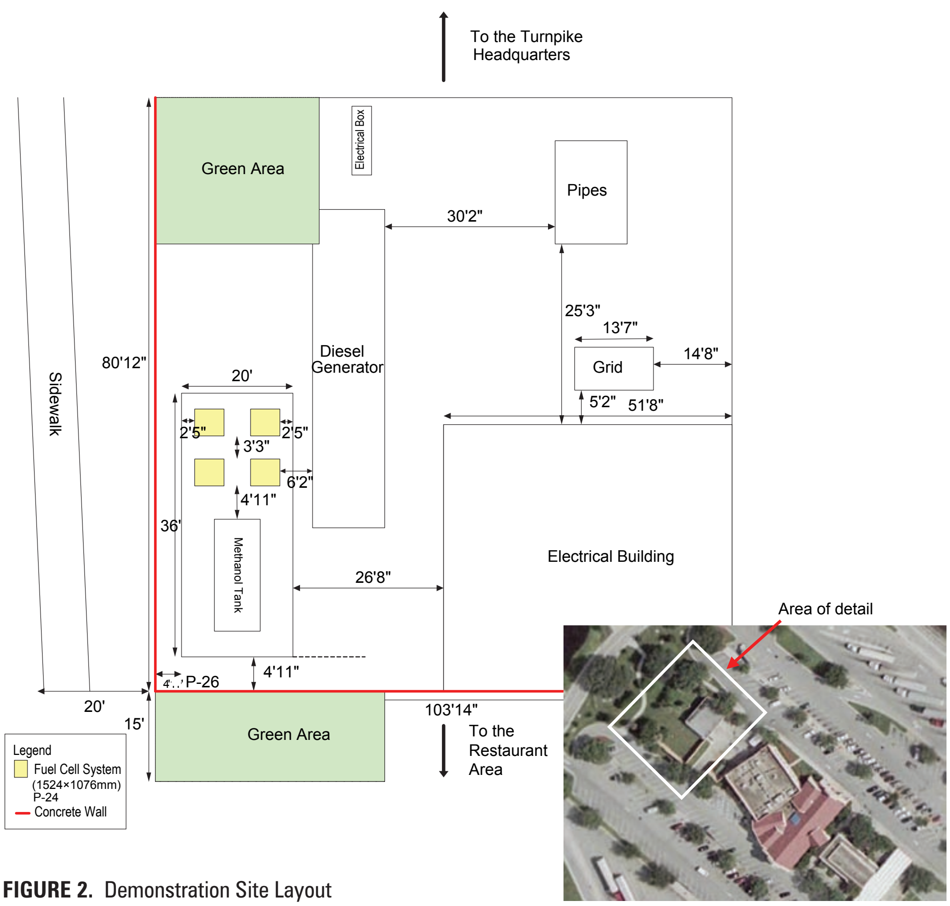

FIGURE 2. Demonstration Site Layout

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 HFCIT Program MYRDDP:

(A) Lack of Readily Available, Objective, and Technically Accurate Information
(B) Mixed Messages
(C) Disconnect between Hydrogen Information and Dissemination Networks
(D) 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 HFCIT Program MYRDDP:

- **Milestone 11 – Develop set of introductory materials suitable for a non-technical audience.** 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.
- **Milestone 32 – Evaluate knowledge and opinion of key target audiences and progress toward meeting objectives.** The projected has completed a survey of Florida teachers and students to determine content baseline knowledge and attitudes towards alternative energy sources in general and hydrogen in particular. The exhibit, slated to open August 1, 2008 will undergo visitor testing to determine both affective and cognitive effectiveness towards the learning goals of the exhibit.

Accomplishments

- Fabrication of interactive "city' Hydropolis, is complete and installed at OSC for critical analyses and visitor testing.
- H2Now charging stations have completed fabrication and will be installed July 28, 2008.
- Interactive software/visitor interface installed and undergoing critical analyses.
- H2Now: the Great Hydrogen Xchange opens to the public August 1, 2008.

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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 OSC set out to perform front end evaluation and subsequent design, fabrication, and installation of an interactive exhibition at 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 (Figure 3). 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 (Figure 4).

Results

Over the past year, designers at I.d.e.a.s incorporated survey findings of target audiences, mock-ups and prototypes for software/visitor interaction, and the affective and cognitive goals of the exhibit into the final design for H2Now's major components.

Both the H2Now charging stations and the interactive city of Hydropolis have completed fabrication; interactive software is finished and all are currently installed at OSC for critical analysis and subsequent visitor testing.

With the exhibition now installed at OSC, critical analysis is underway to ensure 'mechanical' effectiveness of both physical interactives and software/user interface. The next step is cognitive and affective remedial evaluation to ensure that the original educational goals have been met.

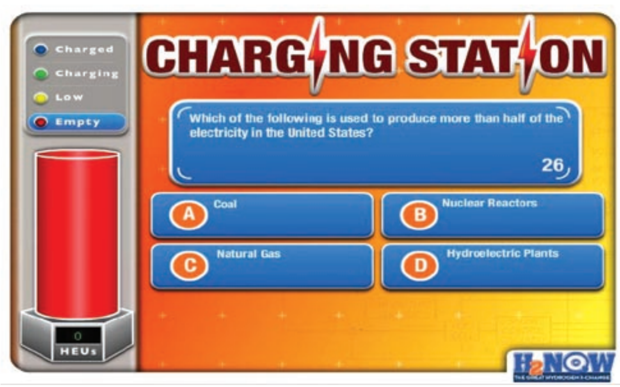

FIGURE 3. A Sample Screen for the H2Now Charging Stations

FIGURE 4. Photograph of the Interactive City of Hydropolis

Conclusions and Future Directions

- The OSC will test the exhibit with general visitors and school groups to test educational effectiveness.
- Following the initial testing phase, summative evaluation will continue on an on-going basis to measure the success rate of educational objectives.
- The interactive software program has the ability to be updated; OSC will combine results from periodic evaluation with new information as it comes available about hydrogen as a renewable energy source as that information becomes available. Thus, H2Now: the Great Hydrogen Xchange will be an effective dissemination tool for the latest information about hydrogen.

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

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Project Start Date: January 28, 2008
Project End Date: March 20, 2009

Objectives

- Design, fabrication and validation of a diesel pre-reformer. Demonstration of catalytic conversion of diesel to light gaseous hydrocarbons (primarily, C_1-C_6) and H_2S.
- Design, fabrication and validation of a compact desulfurization unit.
- Operation and evaluation of an integrated diesel pre-reformer/desulfurization unit.
- Techno-economic analysis of diesel-to-hydrogen refueling station.

Technical Barriers

This project addresses the following technical barriers from the 3.6.4 section of the HFCIT Program MYRDDP, Technology Validation – Distributed Hydrogen Production:

(B) Hydrogen Storage
(C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
(D) Maintenance and Training Facilities
(E) Codes and Standards

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE milestones from the Technology Validation section 3.6.6 of the HFCIT Program MYRDDP:

- **Task 2.2 – Milestone 31 (modified):** Technology validation of distributed high sulfur diesel-to-hydrogen refueling stations. (1Q, 2009)

Accomplishments

- FSEC, jointly with CTV, has designed, built and successfully operated a pre-reforming unit for catalytic conversion of diesel to light gaseous hydrocarbons (C_1-C_6) to be further treated in a special desulfurization unit designed and fabricated at FSEC.
- A compact desulfurization unit that relies on the ferrous/ferric (Fe^{2+}/Fe^{3+}) redox couple has been designed and tested at FSEC. The unit utilizes electrolytic iron recycled into a scrubber. Independent and combined testing of the scrubber and electrolyzer operation has shown that the optimum set point between the two modules is 0.1 M iron concentration at pH 1.7 (set by addition of sulfuric acid), and 50°C temperature. A 100 h life test has been completed.

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Introduction

The present infrastructure for production and distribution of hydrogen is far below what would be necessary to meet consumer demand for transportation fuels. One strategy that could rapidly expand the H_2 distribution network would be to deliver fuel to a filling station in the form of diesel and convert it to hydrogen on-site in a modest-scale reforming plant. Several advantages could be had with this approach. First, the existing delivery infrastructure (highway to filling station) could be utilized. Also, the volumetric energy density of diesel is such that more energy can be delivered per trip when the tanker is filled with diesel than with hydrogen. Finally, the filling station would be capable of servicing both internal combustion and fuel cell vehicles from adjacent dispensing tanks. CTV is supporting FSEC in its effort to bring the above distributed diesel-to-hydrogen production and delivery scheme to fruition.

Approach

Jointly, the CTV/FSEC team has developed a scheme where diesel is first pre-reformed to form shorter chain hydrocarbons (C_1-C_6) before continuing on to the main reformer unit. The removal of sulfur from this pre-reformate is a critical issue, as the reformer catalyst has limited sulfur tolerance. Accordingly, FSEC's effort has been to design, fabricate, and test a 1.0 kW_{th} pre-reforming plant, as well as design, fabricate, and test a desulfurization unit large enough to handle the resulting sulfur gases. A unique photochemical approach to performing desulfurization that had been developed at FSEC was evaluated for this application. After successful construction and testing of each unit separately, the two systems would be integrated and tested as a continuously operating system. Data collection and analysis would yield process parameters that could be used in a techno-economic analysis of a plant that would be able to supply a conventional filling station.

Results

Jointly, the CTV/FSEC team has developed a process where diesel is pre-reformed to shorter chain hydrocarbons (C_1-C_6) and then fed into the main reforming unit. The removal of sulfur from the pre-reformate is a critical issue, as the reformer catalyst has low sulfur tolerance. FSEC had the responsibility to build and operate a pre-reformer and demonstrate desulfurization of its effluent. CTV provided a catalyst for the pre-reforming stage and guided the design of the pre-reformer. A block diagram schematic showing how diesel is converted to H_2 is shown in Figure 5.

Most of the sulfur exiting the pre-reformer is in the form of hydrogen sulfide, H_2S. Thus most of our effort has been directed toward scrubbing H_2S. FSEC's ultraviolet (UV) photolytic desulfurization process had already been successfully demonstrated with pure H_2S. The question was whether the nominal 1,300 ppmv H_2S from the pre-reformer could also precipitate sulfur and complete the chemical scrubbing cycle. As shown in Figure 6, at least five volume percent, or 50,000 ppmv, of H_2S would be required - well in excess of what would produced in the pre-reformer. Pressurization of dilute H_2S (2,500 ppmv) to >10 atm to force more gas into

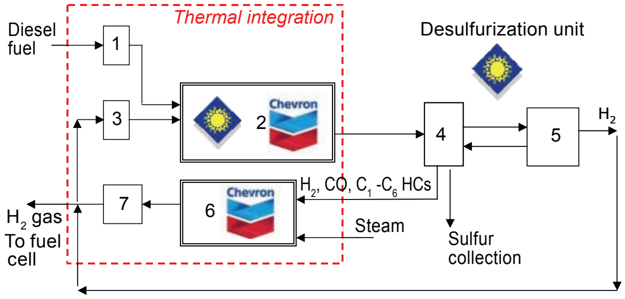

FIGURE 5. Schematic diagram of the process for hydrogen production via catalytic reforming of diesel: 1- fuel vaporizer, 2- catalytic pre-reformer, 3- H_2 compressor, 4- H_2S stripper, 5- H_2S capture, 6- catalytic reformer of pre-reformate, 7- H_2 separation and purification unit.

solution and shift the equilibrium toward the products was unsuccessful.

Having been unable to complete the cycle of chemical steps contained in the UV photolytic approach, it became necessary to investigate other approaches. A number of iron-based systems proved to be able to treat dilute H_2S. They all rely on the ferrous/ferric (Fe^{2+}/Fe^{3+}) redox couple, which can oxidize H_2S to elemental sulfur with little or no by-product:

$$4Fe^{3+}_{(aq)} + 2H_2S_{(g)} \rightarrow 4Fe^{2+}_{(aq)} + 2S_{(s)} + 4H^{+}_{(aq)}$$

The question then became how to recycle the ferrous ion back to the ferric state. Simple air oxidation would be unsuitable for this application. Use of UV light from the existing photoreactor could perform the oxidation, but there were other species in the solution that interfered with the reaction.

Finally, it was found that ferrous ion could be electrochemically oxidized back to the ferric state readily. The desulfurization work has since been directed toward incorporating electrolytic iron recycling into the scrubber. Independent and combined studies of scrubber and electrolyzer operation have shown that the optimum set point between the two modules is 0.1 M iron concentration, pH 1.7, set by addition of sulfuric acid, and 50°C. A 100 h life test was completed, identifying slow (>20 h) capacity loss that is currently under investigation.

Furthermore, collaboratively with CTV, FSEC has designed and fabricated a pre-reforming unit (see Figure 7) capable of producing light hydrocarbons (C_1-C_6) from diesel. To date, pre-reforming of dodecane and hexadecane, as model compounds for diesel, has been carried out using a proprietary catalyst provided by CTV. Both model compounds produced a pre-reformate rich in light hydrocarbons, predominantly, propane and butane. Also, at FSEC, we have conducted pre-reforming of a low-sulfur commercial diesel (max. sulfur content: 15 ppmv) in presence of hydrogen at 450°C and pressure.

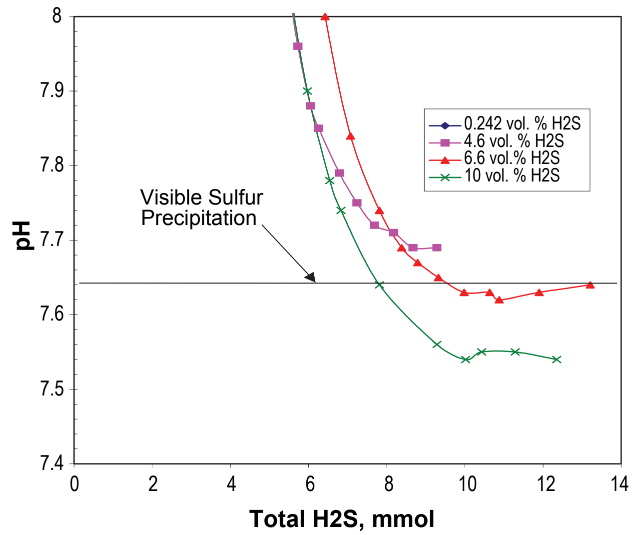

FIGURE 6. Determination of the minimum H_2S feed gas concentration to effect sulfur precipitation from 0.1 M Na_2S_2 solution.

FIGURE 7. Catalytic Pre-Reformer Unit at FSEC

As in the case of C_{12} and C_{16} feedstocks, the diesel fuel was converted to C_1-C_6 hydrocarbons (predominantly, propane, butane) (Figure 8). The effluent gas contained 2 ppmv of H_2S. The sulfur analysis indicated that most of the sulfur in the feedstock were converted into gaseous sulfur-organic compounds. The extent of coke formation on the catalyst surface during the pre-reforming tests was approximately 1.5 wt%.

Conclusions and Future Directions

- The UV photolytic process was unable to reduce the sulfur content of simulated pre-reformer effluent to the requisite 50 ppmv. The equilibrium constant for sulfur precipitation driven by H_2S is too small.
- Ferric iron redox systems were found to achieve the necessary level of desulfurization.

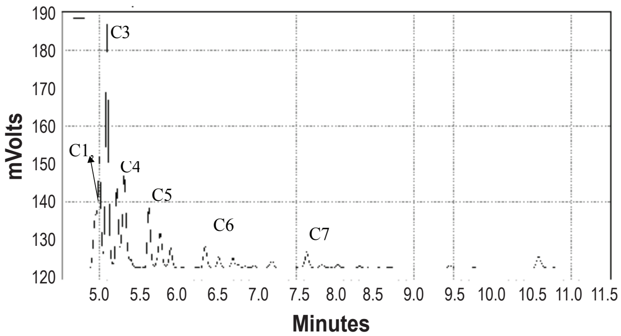

FIGURE 8. Gas Chromatogram of the Pre-Reformate from Diesel Reformation in the Presence of CTV-Supplied Catalyst

- Spectral interference and ligand decomposition discouraged photolytic recycling.
- Electrolytic recycling of acid sulfate ferric salts can be carried out at high efficiency.
- A 100 h endurance test of the scrubber/electrolyzer combination running 2,500 ppmv of H_2S was completed. Slow scrubber capacity loss issues were identified and are under further investigation.

Future activities include:

- Determining the effect of non-H_2S sources of sulfur, *i.e.*, mercaptans and thiophenes, on the scrubber efficiency.
- Identification and mitigation of the process responsible for slow scrubber capacity loss.
- Demonstration and performance validation of a 1.0 kW_{th} pre-reforming unit under construction at FSEC.
- Integration and operation of the pre-former and desulfurization unit.
- Operation of the pre-reforming unit using high-sulfur diesel (1,000-2,500 ppmv of sulfur).
- Evaluation of new and more robust catalysts for pre-reforming of high sulfur diesel.

Special Recognitions & Awards/Patents Issued or Pending

1. "Method and System for Hydrogen Sulfide Removal," Huang, C., Smith, F., Linkous, C.A., Ramasamy, K.K., T-Raissi, A., Muradov, N.Z. *Provisional Patent Application filed with the U.S. PTO, 2008.*

FY 2008 Publications/Presentations

1. "Hydrogen Production via Electrochemical Oxidation of Aqueous Ferrous Sulfite Solution," Huang, C., Linkous, C.A., Smith, F., Ramasamy, K.K., T-Raissi, A., Muradov, N.Z. *Proc. XVII World Hydrogen Energy Conference, Brisbane, Australia, June 2008.*