

V.A.3 Hydrogen from Biomass for Urban Transportation

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Subcontractors:

Eprida Scientific Carbons Inc, Atlanta, GA

Georgia Institute of Technology, Atlanta, GA

Enviro-Tech Enterprises Inc, Matthews, NC

Objectives

- Undertake the engineering research and pilot-scale process development studies to economically produce hydrogen from biomass such as peanut shells.
- Educate and train underrepresented minorities to enhance diversity in the nation's workforce in the energy area.

Technical Barriers

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

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technologies
- Z. Catalysts
- AB. Hydrogen Separation and Purification
- AD. Market and Delivery

Approach

- Develop feedstock supply, process economics and deployment strategies.
- Develop process based on biomass pyrolysis and steam reforming of pyrolysis vapors (bio-oils and gases).
- Design, construct, integrate and test pyrolysis-reformer pilot reaction unit.
- Conduct pyrolysis at temperature of 500°C, pressure of 10 psig, feed rate of 50-500 kg/hr pelletized peanut shells, gas and charcoal exit temperature of 425°C.
- Study reforming at temperature of 850°C, pressure of 6 psig, H₂O/C = 5, with nickel-based catalyst (300-500 microns).
- Undertake long-term (1,000 hours) testing of the performance of the catalytic steam reforming in a fluidized bed (25-250 kg/day H₂ production).

- Develop an environmental and technical evaluation method based on engine tests and analytical monitoring of the process streams.
- Develop partnerships, collaborations, and education and training programs.

Accomplishments

- Continued developing a network model of process steps to account for feedstock, location, process, and the uncertainties in these factors.
- Completed design, construction and testing of reformer (Phase 1).
- Completed integration and 100 hours of successful operation of pyrolysis-reformer pilot unit (Phase 2).
- Completed analysis of the data for the 100-hour long-term catalyst testing.
- Developed plans and completed modifications for the 1,000-hour long-term testing of the catalyst and process for Phase 3.
- The 1,000-hour run pilot operation of the pilot unit is in progress.
- Identified potential co-product options, including agricultural uses of the carbon product from pyrolysis.
- Developed partnerships and collaborations with companies and organizations including the University of Georgia (UGA), Athens. This resulted in the move of the pyrolysis-reformer pilot unit to UGA's Bioconversion Center in Athens, Georgia.
- Initiated evaluation of approaches to hydrogen separation and storage including pressure swing adsorption (PSA) and Quantum's technology for hydrogen storage.
- Educated and trained several underrepresented minorities on the project.

Future Directions

- Complete development of models and solutions.
- Complete extraction studies and the evaluation of phenolates as co-products for adhesives.
- Complete and analyze the 1,000-hour long-term study.
- Complete the engine tests for stationary applications.
- Complete all partnership arrangements.
- Prepare a final report on the project.

Introduction

Biomass can be converted to hydrogen by two distinct strategies: 1) gasification followed by shift conversion, and 2) pyrolysis of biomass to form a bio-oil that can be subsequently converted to hydrogen via catalytic steam reforming and shift conversion. This project uses the latter approach, which has the potential to be cost-competitive with current commercial processes for hydrogen production [1]. The process has been demonstrated at the bench scale at the National Renewable Energy Laboratory (NREL) using model compounds and the carbohydrate-derived fraction of bio-oil [2,3]. The concept has several advantages over the traditional gasification technology. Bio-oil is easily

transportable, so the second step (steam reforming) can be carried out at a different location, close to the existing infrastructure for hydrogen use or distribution. A second advantage is the potential for production and recovery of higher-value co-products from bio-oil that could significantly impact the economics of the entire process.

The project focuses on the use of agricultural residues such as peanut shells to produce hydrogen for urban transportation using the pyrolysis-reforming technology. Specifically, a pilot-scale reactor at Eprida Scientific Carbons Inc., a small company in Georgia, that produces activated carbon by pyrolysis of densified peanut shells is being used to test the concept. The primary focus of Phases 1

and 2 of the project was to undertake the process development studies in the use of the large quantities of peanut shells produced in Georgia as feedstock for the proposed pyrolysis-steam reforming process. The reformer unit was designed, constructed and tested in Phase 1. In Phase 2, Eprida Scientific Carbons' pilot-scale pyrolyzer, which has a feed rate of 50 kg/hour, was integrated with the Phase 1 reformer and used to perform a demonstration of the process to convert the off-gas of the peanut-shell carbonization process to hydrogen. The integrated pilot process was successfully tested for 100 hours. In Phase 3, further modifications were made and a 1,000-hour long-term performance test of the catalyst and pilot system is being conducted. The process could be modified and expanded to run a variety of other agricultural feedstocks and to make a range of alternative products.

Approach

The approach used to conduct the project is based on six main tasks:

1. Feedstock supply, process economics, and deployment strategies (modeling, extraction and property estimation): Literature data and thermodynamic models were employed to evaluate a large number of organic solvents for the extraction of phenol from aqueous bio-oils. Several good solvents were identified, and extractions were carried out on bio-oil samples provided by NREL. Process models for feedstock supply and deployment strategies were developed.
2. Reactor modifications and shakedown: Modifications in the pyrolyzer and reformer were made and the entire system, including the pyrolyzer, reformer, and analytical instruments, was integrated and tested. The pyrolyzer unit achieves its heat requirements through the use of a rich-burning natural gas burner. A computer is used to track the temperature and pressure drops across the reactors.
3. Long-term catalyst testing: The pilot unit was operated in Phase 2 for 100 hours for long-term catalyst testing and is being operated for 1000 hours in Phase 3.

4. Hydrogen separation, storage and utilization: The effort in hydrogen separation initially focused on the use of pressure swing adsorption (PSA) for the separation of the hydrogen from carbon dioxide. After the baghouse and condenser, the reformer gas was to be dried and compressed before being sent to the PSA system. The current plans are to send the reformer gasses directly into an engine for performance testing.
5. Environmental and technical evaluation: A hydrogen analyzer and a gas chromatograph were set up to continuously monitor online the gas composition and the performance of the reformer bed and the engine run with the reformer gas.
6. Partnership building and outreach: The project team completed discussions with the University of Georgia (UGA) and moved the pilot unit from Blakely, Georgia to the UGA Bioconversion Center in Athens. All Phase 3 pilot experiments were conducted at the new facility in Athens, Georgia.

Results



Figure 1. Pictures of the Pilot Plant Unit Being Moved and Reinstalled at Athens, Georgia

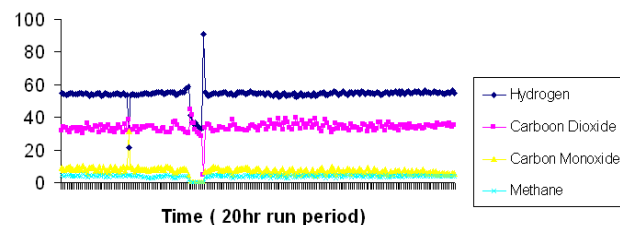


Figure 2. Typical Gas Composition over a 20-Hr Period during Long-Term Catalyst Testing

Table 1. Typical Yields and Gas Composition from the Pyrolysis and Reforming Units

Pyrolyzer (Yields %)		Reformer Gas Product Composition, (% Dry N ₂ -free basis)	
Char	32	Hydrogen	57
Water	32	Carbon Dioxide	26
Bio-Oils	31	Carbon Monoxide	12
Gases	5	Methane	5

Summary

- Demonstrated successfully pyrolysis-reformer concept for 100 hours operation in Phase 2.
- Discovered agricultural uses and carbon sequestration strategy via novel carbon slow-release sequestered fertilizer.
- Identified economical co-product options for bio-oils, e.g., adhesives.
- Successfully ran the product gas in an engine with significant reduction of NO_x.
- Currently in the middle of a successful demonstration of the pyrolysis-reformer concept in a 1000-hr operation during Phase 3.
- Additional research and development work could lead to an economically competitive and viable hydrogen and integrated bioconversion process.

References

1. Mann, M.K, 1995, "Technical and Economic Analyses of Hydrogen Production via Indirectly Heated Gasification and Pyrolysis," in Proceedings of the 1995 Hydrogen Program Review, Vol. 1, NREL/CP-430-20036-Vol. 1, pp. 205-236.

2. Wang, D., S. Czernik, D. Montané, M. Mann, and E. Chornet, 1997, I&EC Research, 36, 1507-1518.
3. Wang, D., S. Czernik, and E. Chornet, 1998, "Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oil," *Energy & Fuels*, 12, 19-24.

FY 2004 Publications/Presentations

1. Annual Project Review Presentation made at the Hydrogen, Fuel Cells and Infrastructure Technologies Review Meeting in Philadelphia, PA, May 2004
2. Semiannual report on project submitted to the Department of Energy in April 2004
3. Evans, R., E. Chornet, S. Czernik, C. Feik, R. French, S. Philips, J. Abedi, Y. Yeboah, D. Day, J. Howard, D. McGee and M. Realff (2002), *Renewable hydrogen production by catalytic steam reforming of peanut shells pyrolysis products*, American Chemical Society (ACS) Paper presented at the Annual ACS Meeting, Boston, MA