

II.1.3 Aqueous Phase Base-Facilitated Reforming (BFR) of Renewable Fuels

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- SENTECH, Bethesda, MD
- Energy Conversion Devices, Inc. (ECD), Rochester Hills, MI
- Western Michigan University (WMU), Kalamazoo, MI
- Sierra Marine Technologies (SMT), Ramona, CA

Project Start Date:

Phase 1: June 30, 2008, Phase 2: August 12, 2009

Project End Date: Phase 2: August 13, 2011

Technical Targets

This project is conducting pilot-scale system design, construction, and experimental testing for distributed hydrogen production from municipal solid waste. Insight gained from this effort will be applied toward a full-scale hydrogen production system that meets the DOE 2012 distributed hydrogen production targets listed in Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

Characteristics	Units	2012 Target	BFR Projection
Production Unit Energy Efficiency	%	72.0	79.0 ^a
Production Unit Capital Cost (Un-installed)	\$	1.0M	\$0.664 M – 1.59 M ^b
Total Hydrogen Cost	\$/gasoline gallon equivalent (gge)	3.80	\$2.27 - \$3.26 ^c

^a Preliminary.

^b Linearly scaled down from a 2 tons per day modular production system.

^c In 2005\$USD, includes only H₂ production costs, using H2A standard economic assumptions.

Objectives

- Experimentally demonstrate a continuous BFR reactor with similar performance to the Phase 1 batch system.
- Experimentally determine the appropriate operating parameters specific to our reactor design.
- Develop a system which allows for reuse of catalysts.
- Determine, through experiments, the appropriate operating parameters specific to our precipitator design.
- Validate process feasibility by correlating experimental results with economic analysis.

Technical Barriers

This project addresses the following technical barriers from Section 3.1 – Hydrogen Production of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (B) Reformer Manufacturing
- (D) Feedstock Issues
- (E) Greenhouse Gas Emissions

Accomplishments

- Developed continuous reactor concept with a fixed-bed catalyst design thereby eliminating the need for complicated particle separation subsystem.
- Achieved similar hydrogen yields on pre-dissolved feedstock thereby allowing a continuous reactor system design to be based on a liquid medium rather than a slurry.
- Experimentally validated that similar hydrogen yields are possible at higher reaction temperatures and lower NaOH concentration which will assist in the precipitation process.



Introduction

Approximately 100-150 million tons per year of municipal solid waste (MSW) are potentially available for hydrogen production [1]. This equates to ~14-22 million tons of hydrogen per year from a source that is normally considered a nuisance or, in some cases, even a hazard. The main advantages of using MSW as a feedstock are its low (or even negative) cost, its already established collection system, and its proximity to population centers which are also hydrogen demand

centers. Disadvantages include separation of the heating value constituents of MSW (paper, wood, grass, food) from the non-heating value constituents (rocks, plastic, metal, etc.).

One solution is to use a process not limited by feedstock type such as BFR. The chemical reaction within BFR has been found to produce hydrogen from most MSW materials. BFR allows one to produce highly pure hydrogen gas (>98% purity) in a simple one-step process with no need for water-gas shift systems and minimal, if any, additional gas purification. In Phase 1 of this Small Business Innovation Research project, we investigated process parameters, evaluated case studies of various commercial system scenarios, and performed system analysis using laboratory data to confirm economic feasibility. In Phase 2 we are addressing the hurdles associated with a continuous prototype system to better understand the operation and viability of a commercial product.

Approach

The continuous BFR system is being developed using an iterative test and design approach. As different operating conditions are tested, the results from those experiments influence the design of the feedstock preparation, BFR reactor, and causticizing reactor. Major subsystems are being designed and experimentally tested individually and will not be linked in a complete system as part of this project. Thus current work focuses

on developing a system design and defining operating conditions that will optimally work together when all subsystems are linked. This is particularly challenging as the reactor and precipitation subsystems optimum performance are at contradictory conditions.

Results

The main activity conducted to date has been exploration of the integrated BFR system configuration and operating conditions. The complete BFR system consists of four main subsystems (Figure 1). The first subsystem is feedstock preparation which modifies the form of the feedstock so it is more easily handled and reacts best with the catalyst. The second subsystem is the hydrogen generation which takes place in the BFR reactor. The aqueous Na_2CO_3 waste stream from the BFR reactor is transferred to the third subsystem, the causticizing reactor, in order to reconstitute NaOH from the Na_2CO_3 . The NaOH is recycled to the feedstock preparation and the CaCO_3 precipitate is transferred to the final subsystem, the calcium carbonate recycle. Here, CaO is reconstituted from the CaCO_3 precipitate and recycled to the causticizing reactor for the slaking reaction. While hydrogen production takes place in the second subsystem, economic studies indicate that the recycling of the reaction components is necessary to lower the cost of hydrogen.

Major subsystems are being designed and individually tested. The optimum feedstock preparation

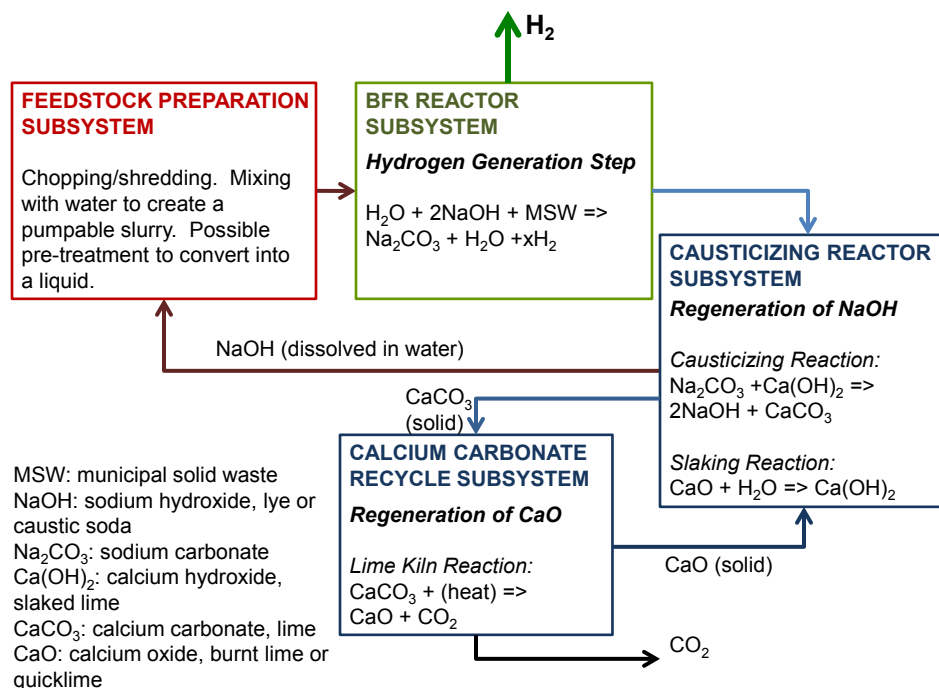


FIGURE 1. Complete BFR System Diagram

procedures are being refined. The hydrogen generation subsystem is being fabricated (Figure 2). The major components are a feedstock holding tank, a heating section to bring the fluid up to the reaction temperature, the BFR reactor which contains the catalyst, a hydrogen gas cooling and collection section, and a waste stream cooling and collection section. Using a pump and having sufficient storage at each end point makes this subsystem continuous over a period of time. Once assembled, test will be performed replicating batch BFR reactor conditions to validate hydrogen production capabilities on this subsystem. The reactor hardware will not be linked to the other subsystems previously identified as part of this project. This work's key results, rather, are the design of a continuous BFR reactor, its fabrication, and validation testing. Additionally, subsystem designs will be developed and tested at the component level. Upon project completion, the team will deliver a future system design, including all four subsystems, and the process parameters necessary for the optimal operation of the system.

In Phase 1 of the project all tests were performed in batch mode on solid feedstock using powder catalysts. While these conditions provided favorable results, a continuous flow system is desirable to allow convenient system scale-up and to achieve high thermal and pressure efficiency. However, the movement of solid feedstock through a continuous system creates complexity and fouling concerns. Consequently, a portion of Phase 2 testing has focused on investigating

if the feedstock can be completely liquefied prior to entering the BFR reactor.

Over 40 different tests were completed to determine the extent to which feedstock could be liquefied under various heating profiles. Testing reveals that ~97% (wt) of the wood feedstock dissolves to a liquid¹ at 220°C within 10 minutes when combined with NaOH and water (but no catalyst) in a pre-reactor (Figure 3). Pre-dissolving the feedstock in a pre-reactor enables multiple simplifying design elements. First, the liquid feedstock permits use of fixed-bed monolithic catalysts since the absence of solid particles ensures that the catalyst will not foul. This permits repeated use of the catalyst without costly separation equipment. Second, a liquid feedstock allows use of inexpensive, conventional liquid pumps as opposed to costly slurry pumps. Third, pre-liquefying the feedstock allows operating conditions to be easily varied between the pre-reactor and main BFR reactor. Last, hydrogen production can be located independently of the feedstock source and its processing.

Another portion of our experimental work has been focused on lowering the vapor pressure of the BFR solution so that we can operate at lower pressures for a given temperature. Batch testing in Phase 1 confirmed that hydrogen yield² is proportional

¹ Dissolves into liquid or liquid-like slurry strainable with a glass-fiber filter having 2.7 micron pore size.

² Hydrogen yield (%) = Volume of H₂ gas obtained / Theoretical maximum gas available

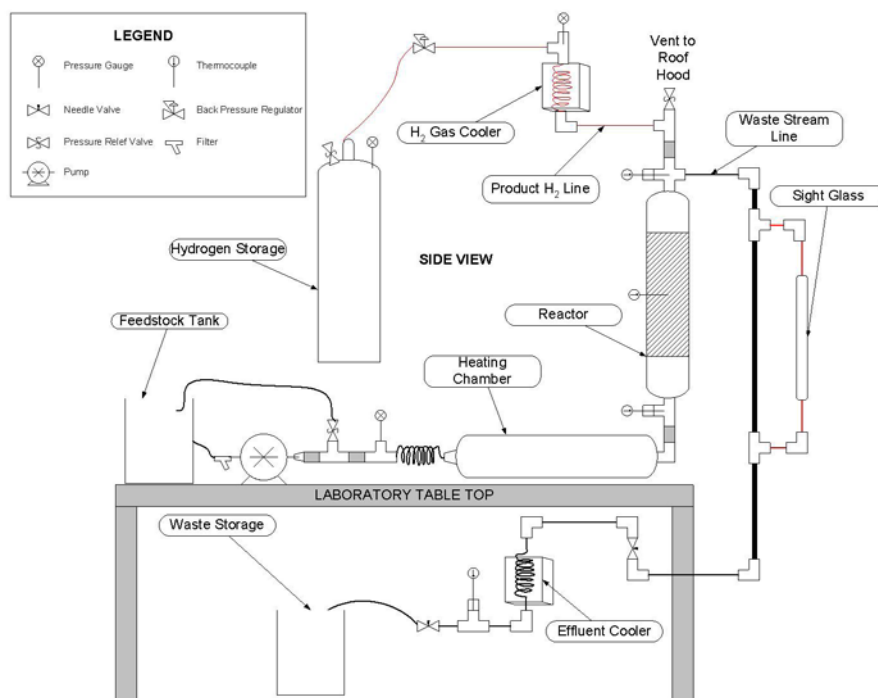


FIGURE 2. BFR Reactor Subsystem Design

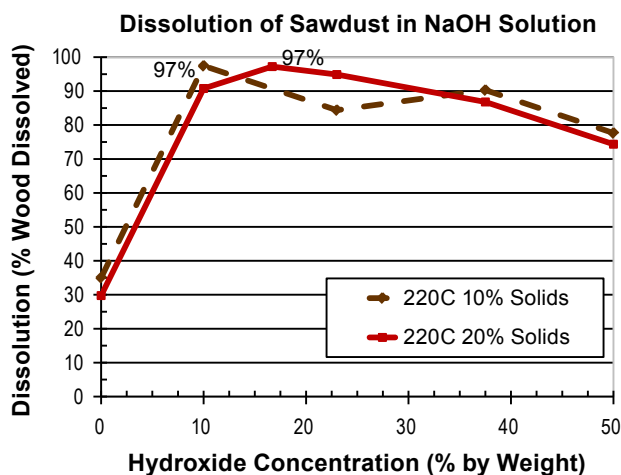


FIGURE 3. Feedstock Dissolution Potential as a Function of Sodium Hydroxide in Solution

to reaction temperature. In general, higher BFR reaction temperature leads to higher hydrogen yield. Consequently, a high temperature (~340°C) is desired. However, the necessary pressure to raise the boiling point and keep the water in liquid phase at elevated temperature can easily exceed 1,500 psi, a level undesirable for safe, low-cost industrial operation. In Phase 1 equipment was pressure-limited so high NaOH concentrations were used to keep reaction pressures low. However, the causticizer subsystem operates best at low NaOH concentrations which typically result in high operating pressures. Experiments have been conducted in Phase 2 to determine if additional solution constituents are able to suppress pressure while not increasing NaOH concentration. Testing reveals that these additives have a similar effect on vapor pressure as increasing the NaOH concentration. Most importantly though in our experimentation thus far it appears that these additives have no negative impact on the hydrogen production capabilities of the BFR process (Figure 4). These tests were performed in a batch reactor and thus heating and reaction time could not be decoupled. In the case of the Phase 2 continuous BFR reactor the heating section is separated from the catalyst bed and thus we expect lower catalyst residence time and the ability to compute reaction time with respect to hydrogen yield.

Conclusions and Future Directions

- In collaboration with our project team we are building a continuous reactor in which to test various operating conditions and validate batch-mode results.

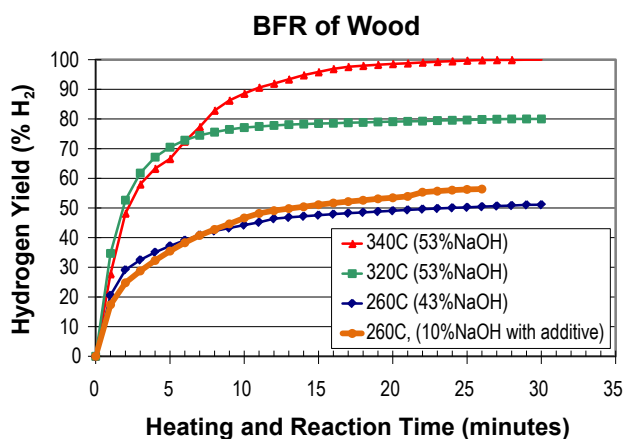


FIGURE 4. Hydrogen Yields Dependency on Temperature

- Best hydrogen yield potential is 99% in batch testing of wood at 53% NaOH, 340°C, and 500 psi. These conditions will be duplicated in the continuous reactor system.
- We will investigate further market synergies given the improvements made to the system design this year.

FY 2010 Publications/Presentations

- Aqueous Phase Base-Facilitated Reforming (BFR) of Renewable fuels, Brian James, Poster Presentation, DOE Annual Merit Review, June 2010.
- Aqueous Phase Base-Facilitated Reforming (BFR) of Renewable fuels, Brian James, Presentation, Hydrogen Production Tech Team, January 2010.
- Aqueous Phase Base-Facilitated Reforming (BFR) of Renewable fuels, Brian James, Presentation, Fuel Cell Technologies Program, October 2009.
- Low Temperature Hydrogen Production From Biomass Reformation, William Mays, Presentation, National Hydrogen Association Conference, May 2010.

References

- Municipal Solid Waste in the United States: 2007 Facts and Figures, Executive Summary, U.S. EPA, November 2008 (URL: <http://epa.gov/osw/nonhaz/municipal/pubs/msw07-rpt.pdf>).