Supercritical Water Partial Oxidation

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Objectives

- Develop a gasification technology that can convert biomass wastes of all types into hydrogen and other high-value products.
- Verify that high-pressure supercritical water is an ideal medium for gasification of biomass.
- Show that high hydrogen yields and gasification efficiencies can be reliably achieved with supercritical water partial oxidation (SWPO).
- Confirm competitive hydrogen production costs of ~$3/GJ (~$0.35/kg) can be achieved with small-size SWPO gasifiers.
- Demonstrate a 5-ton per day (tpd) reduced-scale gasifier at a small publicly-owned treatment works (POTW).
- Construct a 40-tpd commercial biomass gasifier at a large POTW.

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 R,D&D Plan:

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology

Approach

- Build on 20 years experience with supercritical water oxidation (SCWO) of hazardous wastes.
- Exploit the inherent characteristics of supercritical water (SCW) to convert wet biomass into hydrogen:
  - SCW quickly gasifies all organics with minimum char
  - Water-gas shift contributes significantly to hydrogen yields
  - SCW scrubs particulates and acids from hydrogen-rich gaseous products
  - High pressures aid in separation/storage of hydrogen
- Develop supercritical water gasification system in a four-step program:
  - Phase I: Pilot scale testing/feasibility studies (complete)
  - Phase II: Technology development (expect recompete/award in 2003)
  - Phase III: System integration and design
  - Phase IV: Reduced scale demonstration of 5-tpd system
  - Design and construct 40-tpd commercial demonstration system

Accomplishments

- Performed economic analysis showing that competitive hydrogen production costs of ~\$3/GJ (~\$0.35/kg) can be achieved with small-size SWPO gasifiers.
- Performed pilot-scale conceptual design of SWPO system for Phase II development.
- Prepared a SWPO development plan, including cost and schedule estimates.
- Prepared a business plan to identify SWPO market potential.
- Carried out SWPO market survey in collaboration with San Diego State University (SDSU).
- Defined follow-on activities from preliminary testing through pilot-scale demonstration of an integrated SWPO system.
- Identified improvements to reactor design.
- Submitted Phase I final report in December 2002.

Future Directions

Phase II: Technology Development: (2004)

- Design, fabricate and test advanced pilot-scale SWPO reactor.
- Optimize SWPO operating parameters and H_2 yields during extended-duration tests.
- Revise market, economic and life cycle cost assessments and define scale-up requirements.

Phase III: System Integration & Design: (2005)

- Perform safety, reliability and maintenance, and permitting studies.
- Perform process design and long-lead procurement for Phase IV.
- Update development plan for Phase IV.

Phase IV: Reduced-Scale Demonstration of 5-tpd System: (2006-2007)

- Implement requirements defined during Phase III studies.
- Match reduced-scale SWPO system to industrial H_2 separation and storage systems.

Introduction

General Atomics (GA) is developing supercritical water partial oxidation (SWPO) for the efficient and environmentally advantageous gasification and hydrogen production from low-grade fuels such as municipal wastes, biomass, and high-sulfur coal.

SWPO involves carrying out oxidative reactions in a supercritical water environment - akin to high-pressure steam - in the presence of limited quantities of oxidant, typically pure oxygen or air. Partial oxidation in-situ rapidly heats the gasification medium, resulting in less char formation and improved hydrogen yield. The high-pressure, high-density aqueous environment is ideal for reacting and gasifying organics. The high water content of the medium encourages formation of hydrogen and hydrogen-rich products and is compatible with high water content feeds such as sludges and biomass, and eliminates the need for feedstock drying. The high water content of the medium is also effective for gasification of hydrogen-poor materials such as coal.

Approach

Figure 1 provides a simplified process flow diagram (PFD) for the GA SWPO pilot plant. Pressurized slurry is fed to the preheater, where it is preheated to a temperature of 250°C or other suitable temperature depending on the feed material. It was found during testing that slurry preheating had to be limited to avoid char formation and plugging of the preheater. In addition, the pumpable concentration of biomass slurry was limited, for example to about 10-15 wt% for wood flour. To overcome these limitations, a high organic feed (designated auxiliary fuel in Figure 1) is coprocessed with the slurry. As shown in Figure 1, the high organic feed and oxygen are combined with the preheated slurry at the reactor inlet. The reactor has a volume of about 10 liters and provides a residence time of 60-75 seconds at an operating pressure of 3400 psi and operating temperatures of 650 to 800°C. In the reactor, the feed is converted primarily to CO_2, H_2O, H_2, CH_4 and CO. The gasifier products are cooled after leaving the gasifier and the liquid and gaseous products may then be separated at either high or low pressure. Figure 2 shows a photograph of the SWPO system gasifier skid.

Results for the SWPO pilot-scale testing were reported last year. In the latter half of 2002, the Phase I results were analyzed and used to identify favorable applications for the SWPO technology. An economic analysis was carried out, supported by a market survey of municipal sewage treatment plants in the U.S. All results were then documented in the Phase I Final Report issued in December, 2002.

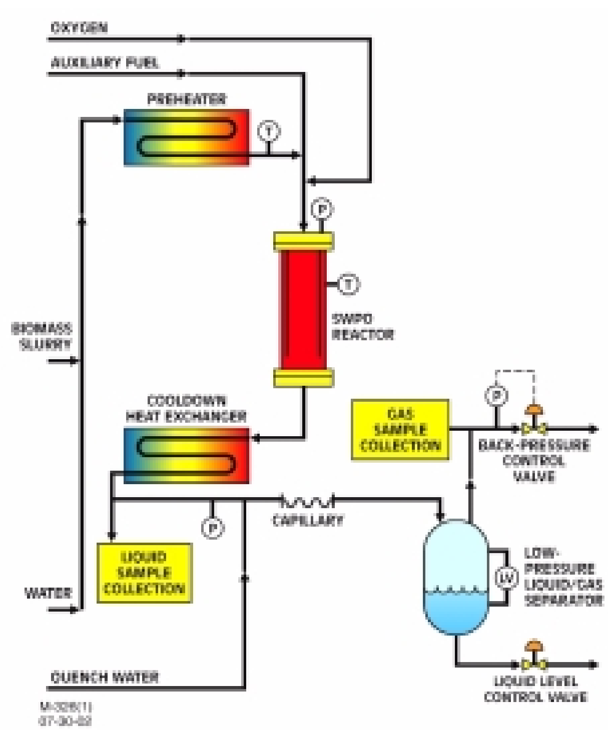

Figure 1. Process Flow Diagram for the SWPO System

Results

The major results for Phase I are as follows:

1. Based on successful Phase I testing, the SWPO pilot-scale conceptual design for Phase II development shall be based on the following:
   - Pumping tests indicate that a biomass slurry feed concentration of about 12 wt% solids is a practical maximum.
   - Feed preheat is typically limited to 260°C to avoid char formation and plugging.
   - A high heating value waste is coprocessed with biomass in order to attain the desired gasifier temperature and still have sufficient feedstock for gasification. Suitable high heating value wastes are trap grease, plastics, rubber, or coal.
   - A vessel-type gasifier rather than a pipe-type gasifier is used to achieve higher gasifier operating temperatures and minimize heat losses.
   - A catalyst-free gasifier is used to enable long-term operation with dirty feed materials without plugging.
   - A high-energy nozzle is used for high dispersion of the incoming feed to improve mixing and attain high gasification yields.
   - A methane-steam reformer is used on the clean SWPO product gas to reform the methane-rich gas to hydrogen.

Figure 2. SWPO System Gasifier Skid

- Due to the low level of CO produced in the gasifier, water-gas shift reactors are not necessary.

2. A nationwide web-based survey of municipal sewage treatment plants received over 100 responses. The survey indicates that sludge solids disposal costs are usually above \$100 per dry ton and range up to \$500 per dry ton.

3. An economic analysis for coprocessing of sewage sludge and waste grease was performed. Results show that competitive hydrogen production costs of ~\$3/GJ (~\$0.35/kg) can be achieved with small-size SWPO gasifiers. Table 1 shows the key parameters of the analysis. Figure 3 shows how the hydrogen production cost varies with financing terms and revenue received for accepting sludge solids.

Conclusions

The Phase I results indicate that a practical means to overcome limitations on biomass slurry feed concentration and preheat temperature is to coprocess an auxiliary high- heating value material. SWPO coprocessing of two high-water content wastes, partially dewatered sewage sludge and trap grease, yields a scenario for the production of hydrogen at highly competitive prices. It is estimated that there are hundreds if not thousands of potential sites for this technology across the U.S. and worldwide.

The economics for 40 tpd sewage sludge plants augmented with grease trap waste are favorable over a significant range of cost parameters such as sludge revenue and capital financing. Hydrogen production costs for SWPO plants of this size are projected to be about \$3/GJ (~\$0.35/kg) or less. Economics may be further improved by future developments such as pumping of higher solids content sludges and improved gasifier nozzle designs to reduce char and improve hydrogen yields. The easiest market entry for SWPO is expected to be sales to municipal wastewater treatment plants for use with sewage sludge in conjunction with trap grease, as both of these wastes are ubiquitous and have reasonably well-defined negative value (i.e., the process will receive revenue to accept the feed). Additionally, waste grease is frequently recovered at municipal wastewater treatment plants where it is already contaminated with sewage.

Table 1. SWPO Economic Analysis Basis

Description	Assumption	Reference
Plant size	40 tpd total solids, 30 tpd organic sludge solids (not grease)	Numerous plants of this size in the US and worldwide
Sludge solids revenue	\$0-300 per dry ton	SDSU survey
Gasifier residence time	20 seconds	15 seconds for UHM, 1998
Trap grease revenue	\$0.08 per gallon	Darling/Al Max telecons
Steam revenue	\$3.50 per MMBtu (? 1000 lb)	Yeboah et al., 2002
Cost of liquid oxygen (LOX)	\$0.04 per pound	Vendor discussions
Hydrogen purity	99.99%	Typical purity level with pressure swing adsorption
Financing rate	6 to 12%	Current prime interest rate is below 5%
Financing period	Up to 20 years	City of San Diego methane contract is a 20-yr term

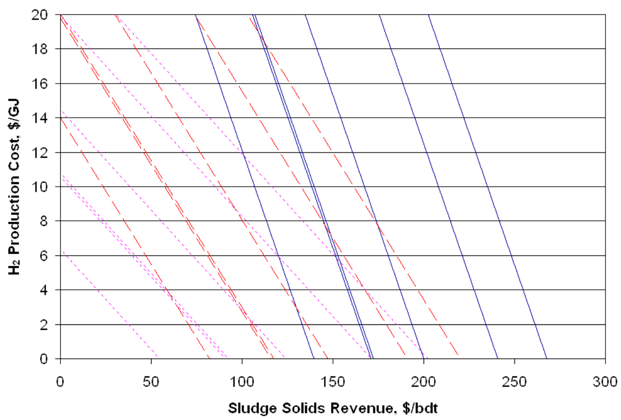

Figure 3. Hydrogen production cost for sewage sludge with trap grease. Solid lines show cases where the amount of grease supplied equals the amount necessary to raise the combined feeds to the final gasifier temperature of 650°C and all of the grease or its equivalent is completely oxidized to H_2O and CO_2. The dashed lines show cases where the amount of grease has been doubled. The dotted lines show cases where the amount of grease has been tripled. For each grease ratio, six different financing arrangements are shown. From left to right, these are 20 years at 6%, 20 years at 12%, 10 years at 6%, 10 years at 12%, 5 years at 6%, and 5 years at 12%.

SWPO should also be favorable to other market applications in which low or negative value, high water content biomass is available in conjunction with a low or negative value fuel material. For biomass slurries, primary candidates are sewage sludge, manure sludge, and shredded and/or composted organic municipal solid waste (MSW) slurries. For the high heating value stream, primary candidates are trap grease, waste plastic or rubber slurries, and coal or coke slurries.

The next phase of the SWPO program will be focused on verifying process improvements identified during the preliminary pilot-scale testing, and then performing extended duration testing with the GA pilot plant. Tests of at least 100 hours duration using sewage sludge and trap grease as simultaneous feedstocks are a primary objective. Follow-on Phases III and IV of the SWPO program will develop and demonstrate a dedicated 5-tpd reduced-scale SWPO facility at a location such as the Encina municipal wastewater treatment plant. Subsequent to this demonstration, the technology will be ready for a commercial-scale demonstration.

While there are clearly technical challenges that must still be addressed, such as demonstration and scale-up of the technology, SWPO represents an outstanding opportunity to further the dual goals of developing a hydrogen economy and practicing environmentally friendly waste disposal. It may well represent one of the few scenarios in which hydrogen may be produced economically from biomass at a relatively small scale. SWPO could thus play a pivotal role in the proliferation of distributed hydrogen generation. As an additional benefit, the high operating pressure of the process presents opportunities for the recovery of high pressure hydrogen product without the high cost of compression.

References

1. University of Hawaii at Manoa, "Hydrogen Production from High Moisture Content Biomass in Supercritical Water", M.J. Antal Jr. and X. Xu, Proceedings of the U.S. DOE Hydrogen Program Review, Alexandria, VA, April 28-30, 1998a.

2. Yeboah, Y.D. et al., "Hydrogen from Biomass for Urban Transportation", Proceedings of the U.S. DOE Hydrogen Program Review, Golden, CO, May 6-8, 2002.

FY 2003 Publications/Presentations

1. Spritzer , M.H. and G.T. Hong, "Supercritical Water Partial Oxidation", poster paper at the Annual Peer Review Meeting, U.S. DOE Hydrogen Program, Berkeley, CA, May 2003.