Proceedings of the 2001 DOE Hydrogen Program Review
NREL/CP-570-30535

ENGINEERING SCALE UP OF RENEWABLE HYDROGEN PRODUCTION BY CATALYTIC STEAM REFORMING OF PEANUT SHELLS PYROLYSIS PRODUCTS

Robert Evans, Stefan Czernik, Esteban Chornet, Calvin Feik, Steven Phillips
National Renewable Energy Laboratory
Golden, CO 80401

Abstract

Renewable hydrogen may be produced in the near term at a cost competitive with natural gas reforming by integrating hydrogen production with existing industrial utilization of agricultural residues. Researchers at NREL are assisting a team of industrial and academic organizations from Georgia in adapting NREL's steam reforming process to a process for making activated carbon from densified peanut shells.

The thermochemical user's facility (TCUF) at NREL is the site for the initial shakedown of the scaled-up reactor. It will be interfaced with the 10-20 kg/hour fluidized-bed fast pyrolysis system and take advantage of NREL's process chemical analysis and computer control and monitoring capabilities. Working with the Georgia team, the scaled-up reactor was designed, built and shipped to TCUF for installation and initial operation before being shipped to the industrial site in Georgia for Phase 2 testing.

The hydrogen produced will be blended with CNG and used to power a bus in the nearby city of Albany, GA in Phase 3 of this project. This integrated strategy will demonstrate the potential impact of hydrogen and bioenergy on the economic development and diversification of rural areas.

Introduction

Near-term production of renewable hydrogen from biomass requires a co-product strategy to compete with conventional production of hydrogen from the steam reforming of natural gas (Chornet et al. 1994; Spath and Mann 1998). The production of hydrogen by the processing of pyrolysis products that are produced as a by-product of activated carbon is one path that is possible to demonstrate in the near term. NREL is supporting a team of organizations that are carrying on the demonstration of the NREL-developed technology. The research team includes:

- **Clark Atlanta University** – capabilities in steam reforming, combustion science, and environmental science.

- **Scientific Carbons Inc. –** a company developing innovative processes to make activated carbon from agricultural residues.

- **Enviro-Tech Enterprises, Inc**. - a technology transfer company whose goal it is to establish public/private partnerships to create jobs via sustainable technology.

- **Georgia Institute of Technology –** involving faculty with capabilities in systems analysis, and environmental and energy technologies.

Objectives

This project has these specific objectives in support of the subsequent demonstration of the reformer technology in Georgia.

- To lead the design of the 10 kg/hour fluid bed catalytic steam reformer system.

- To conduct the system shakedown at NREL by interfacing with the Thermochemical Process Development Unit (TCPDU) in the TCUF. NREL's experience with the development of the technology at the bench scale and the available analytical capabilities of the TCUF will allow the reactor to be characterized for the subsequent operation on a slipstream of the Scientific Carbons pyrolysis products.

- To participate in the design of the process modifications that will be necessary to integrate the reactor safely and efficiently in the existing Scientific Carbons process in Phase 2.

- To support the partnership development that will be necessary for the bus demonstration.

- To identify, with the Georgia Institute of Technology, other biomass resources in the region that could be used to produce hydrogen in conjunction with the Scientific Carbons process or by other integrated biomaterial processing technologies.

Catalytic Steam Reforming Development Status

NREL began the development of the catalytic steam reforming process in December 1993 (Chornet et al. 1994). The strategy is based on producing hydrogen from biomass pyrolysis oils in conjunction with other products that have greater value and can reduce the cost of hydrogen. The original concept was that the pyrolysis oil could be fractionated into two fractions based on water solubility. The water-soluble fraction is to be used for hydrogen production and the water insoluble fraction could be used in adhesive formulations (Kelley et al. 1997). Although this option remains viable, commercial deployment opportunities for hydrogen linked to the adhesives co-products are still not near-term. Hence, other opportunities had to be developed based on the co-product strategy.

The conversion of biomass to activated carbon is an alterative route to hydrogen with a valuable co-product. Slow pyrolysis is used in the first step of the activated carbon process to maximize the yield of charcoal and organic vapors are produced as a by-product in 30 to 50% yield. Southwest Georgia was identified as an excellent opportunity because of the importance of agriculture, the forest product industry and the need for zero-emission transportation fuels in the Atlanta area. Scientific Carbons Inc. in Blakely GA uses pelletized peanut shells as the feed material for the production of activated carbon. They feed up to 1000 kg/hour of the densified peanut shells to a two-stage process producing charcoal that is further processed in a kiln to produce activated carbon. The vapor by-products are currently used for boiler feed. The team submitted a successful proposal to the U.S. DOE’s Hydrogen Program to demonstrate the steam reforming process over a three-year period. Scientific Carbons Inc. facility in Blakely, Georgia will be used as the development site. A slipstream of pyrolysis vapors produced in the 1000 kg of feed/h continuous pyrolysis unit will be used for the long-duration steam reforming tests.

Conversion Technology

Over the past four years, NREL has developed the technology for the generation of hydrogen from biomass and agricultural residue based on the pyrolysis of biomass to form a bio-oil that can be subsequently converted to hydrogen via catalytic steam reforming and shift conversion. The NREL approach has the potential to be cost-competitive with current commercial processes for hydrogen production. The process has been demonstrated at the bench scale using model compounds and the carbohydrate-derived fraction of bio-oil (see Chornet et al. 1994, 2001).

Recent laboratory work has demonstrated the feedstock flexibility with the processing of pyrolysis oil fractions from different feedstocks as well as other aqueous biomass streams such as glycerine from biodiesel production, trap grease, and wood hydrolysis effluents (Czernik et al. 2001).

Catalyst life is promising with run times in a two-inch fluid bed reactor of over 100 hours. Systematic studies of variation in catalyst composition have shown that commercial steam reforming catalysts perform optimally for the conversion (Garcia et al. 2000). However, physical attrition is a problem since these catalysts are not manufactured for fluid bed operation. The catalyst is prepared by grinding and sieving to the required particle size for fluidization. Losses of approximately 5% per day of operation have been reported in the small reactor (Chornet et al. 2001).

Results

Design and Construction of Catalytic Fluid Bed Steam Reforming Reactor

Based on the results from the 5-cm bench scale fluid bed catalytic steam reformer reactor, NREL researchers worked with the Clark Atlanta team (Abedi et al. 2001) to design a reactor that would process 10-20 kg/ hour of pyrolysis products. A schematic of the reactor is shown in Figure 1. The construction was completed in March 2001. The reactor will be operated with the NREL Thermochemical Users Facility (TCUF) pyrolysis unit in the summer of 2001. In Phase 2 of the project, the unit will be shipped to Blakely, Georgia and run on a slipstream of the Scientific Carbons process stream.

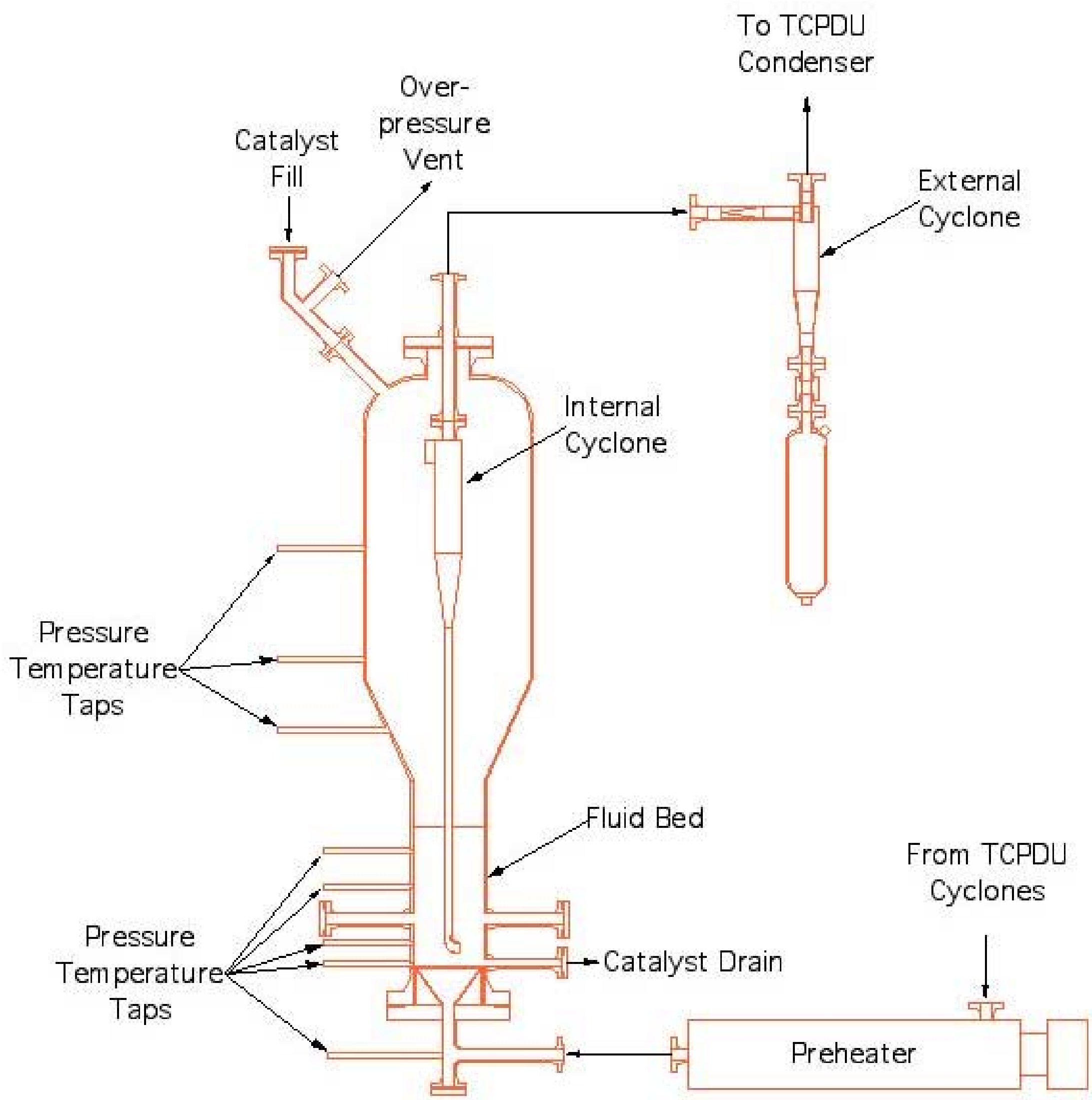

Figure 1. The Catalytic Fluid Bed Steam Reforming Reactor. Installation and Shakedown of the Reactor at NREL

The TCUF at NREL is designed to assist bioenergy technology developers in the testing of thermochemical process concepts by interfacing key unit operations in the existing TCUF facility. This approach minimizes risk and disruption by taking advantage of NREL's process control systems and analytical capabilities, which would not be available for shakedown or proof of concept in an industrial environment. By performing the initial system tests at NREL, the expertise of the NREL researchers and the state-of-the-art analytical equipment of TCUF can be used to monitor and optimize the system performance. The 20-kg/hr fluid bed pyrolysis unit at TCUF will be used to feed the steam reforming unit for the shakedown. A photo of the fluid bed unit is shown in Figure 2.

Figure 2. The Fluid Bed Pyrolysis Reactor.

A schematic of the unit operations that will be used is shown in Figure 3. Preheated steam is used to fluidize the sand bed and ground peanut shell pellets are metered into the bed with a screw feeder. An internal cyclone (not shown in Figure 3) removes most of the sand and large char particles before the gases are transported through a thermal cracker, which can be used for two-stage gasification. In this work the thermal cracker and all down stream operations before the reformer will be kept at 400°C to prevent physical condensation of the vapor and minimize thermal cracking. However, some tests will be done in the reforming work to determine how vapor-phase composition affects steam reforming efficiency. Char is separated in the two cyclones. The steam/vapor stream then enters a preheater that raises the temperature to the desired reforming temperature. The reformer is equipped with external electrical heaters to maintain the reactor at temperature during the endothermic steam reforming operation. The reformer also has an internal cyclone as well as an external cyclone. The reformed products are next passed to the spray scrubbers and a cold wall condenser before passing through a coalescing filter to remove aerosols. The condensable effluents will be analyzed and related to operating conditions and time on stream. This will be important in determining the operating procedures that will be used in Phase 2 operation.

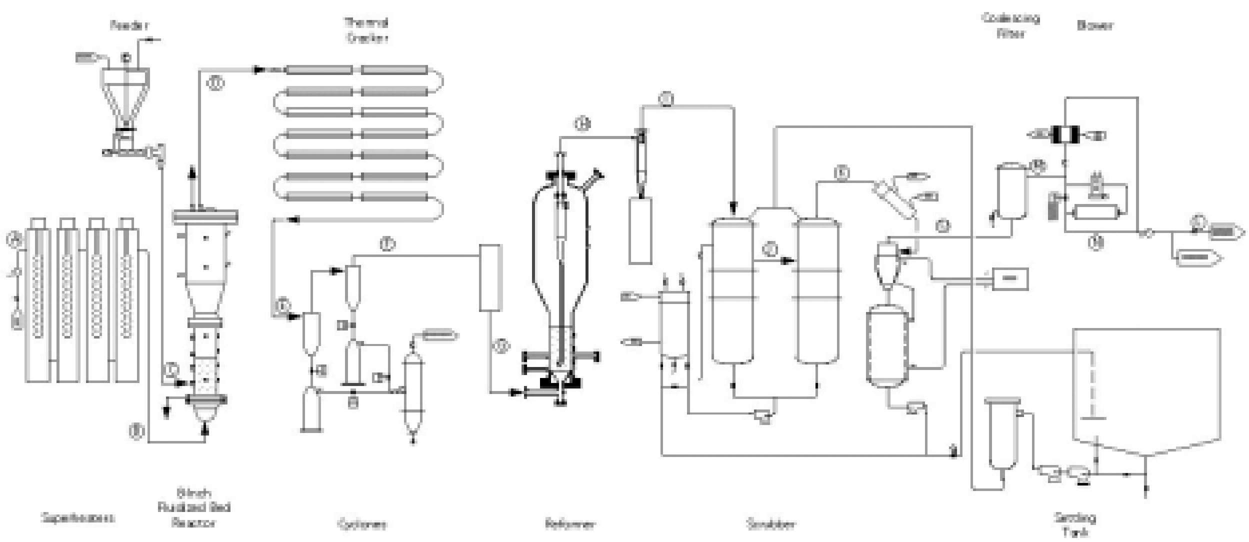

Figure 3. Process Flow Sheet for the Shakedown of the Steam Reforming Reactor in the Thermochemical Process Development Unit.

The system will be run in three modes: catalyst activation, reforming, and catalyst regeneration. In the initial activation mode, hydrogen and steam will be used to reduce the catalyst. The catalyst will then be first tested with methane to verify activity and to shake down the physical operation of the bed.

The estimated process conditions and compositions are shown for four key positions (refer to Figure 3) in the reforming mode in Table 1: D, after the pyrolysis unit; G, after the preheater and before the reformer; H, after the reformer; and M, after the scrubbing system. The molar gas composition is also shown for position M.

Table 1. Process Mass Flows at Several Key Positions in the Reforming Process. (Refer to Figure 3)

Process Site	D	G	H	M	M
Temperature, C	500	800	850	12	12
Pressure, psig	10	8.25	7	5.5	5.5
Flow Rate	Kg/hr	Kg/hr	Kg/hr	Kg/hr	Mol/hr
Biomass	0	0	0	0	0.0
Steam or water	30.9	30.9	27.2	0.0	0.0
Nitrogen	0.1	0.1	0.1	0.1	0.0
Hydrogen	0.0	0.0	0.7	0.7	0.4
Carbon Monoxide	0.3	0.3	0.8	0.8	0.0
Carbon Dioxide	0.7	0.7	6.2	6.2	0.1
Methane	0.0	0.0	0.5	0.5	0.0
Pyrolysis Vapors	3.4	3.4	0.0	0.0	0.0
Char/Ash	1.8	0.1	0.1	0.0	0.0
Total	37.2	35.5	35.6	8.3	0.6

The catalyst is not commercially available in a form suitable for a fluid bed, so it was commissioned from Süd-Chemie (formerly United Catalysts) who prepared the required size fraction by grinding a catalyst used for packed bed methane steam reforming.

Preparation for Installation at the Scientific Carbons Site in Phase 2

NREL is supporting the work on the preparation for the testing that will occur in the second year at the industrial site. The existing pyrolysis facility owned and operated by Scientific Carbons, will be modified as follows:

- Design, construction, and addition of a slip stream system capable of withdrawing 10-20 kg/h of pyrolysis vapors

- Installation of instrumentation and on-line monitoring and data acquisition for the above system for product stream analysis, and process mass and energy balance.

In preparation for this task NREL researchers have designed a probe that will be installed on the Scientific Carbons pyrolysis reactor at the site for the interface to monitor product composition over time. Samples of condensate will be taken for chemical analysis and could be used for bench-scale steam reforming tests. The objective is to better understand the range of composition that will be experienced due to variation in process parameters, such as temperature and pressure. Installation and operation of the probe will occur during the next production run at the Blakely facility.

Cost Analysis for Hydrogen Production from Alternative Biomass Feedstocks

Feedstock issues, such as supply, cost, logistics and the value of coproducts, are major factors in the cost-effectiveness of the hydrogen production process. In this task, NREL is working with the project partners to develop decision models for selecting among feedstock, process, and deployment alternatives. Of particular interest are peanut shells supply and cost projections and the evaluation of other agricultural residue feedstocks available in the same geographical area.

In order for biomass-to-hydrogen to make a significant energy impact, multiple feedstocks will have to be used in combination with realistic markets for co-products. Activated carbon from peanuts is an excellent starting point. Approximately 750 million pounds of shells are produced in the United States with 45% of these produced in southwest Georgia. Using the yields for the activated carbon by-product scenario, this represents a hydrogen yield of approximately 5 trillion BTUs. If this were to be compared to the transportation use in the Atlanta area it would represent about 1% of the total. Therefore, for hydrogen from biomass to make a significant impact, other feedstocks will have to be developed in time. In the southwest Georgia region the list includes cotton gin trash, peach pits and pecan shells, all of which could be used for activated carbon production. Other feedstocks could be developed in other region of the state, such as wood wastes and residues from the textile industry. Ozyurt and Realff (1999) have addressed the logistics of deployment considering volume and distribution of feedstocks.

The development of new crops is an important part of the bioenergy and biomaterials initiative (Biomass R&D Board, 2001). The project team met with representatives from the Federation of Southern Cooperatives, Albany State University, Fort Valley State University, and the Albany Public Utility Commission to discuss the project and the participation of these local groups. The Federation represents 25,000 African-American farmers in the southern states. They are interested in developing new crops and new uses for crop residues. Fort Valley, a land grant HBCU (Historically Black College and University), is also interested in the same topic. Albany State will participate in the project by providing students and faculty to assist in the Phase 2 operation of the reformer in nearby Blakely and by hosting the utilization of the hydrogen in their campus transportation system. Albany Power will explore ways that they may participate in the demonstration. NREL is arranging to have students from Clark Atlanta, Fort Valley, and Albany State participate in the shakedown of the reactor at NREL this summer.

The economics of hydrogen and co-product production from fast pyrolysis liquids have been assessed for an adhesive co-product, resulting in a selling price of hydrogen in the range of $6-8/MBTU (Spath and Mann 1998). For this slow pyrolysis process used to produce charcoal for conversion to activated carbon, a preliminary economic analysis (Putcshe 1999) on the base case process assumes utilization of all of the pyrolysis vapors (225kg/hr) at the current scale of the Scientific Carbons process. The pyrolysis vapor was assumed to be available at $2.56/GJ, a value that is roughly 90% of its fuel value (assuming an energy equivalence to natural gas at $2.50/GJ). The analysis also assumed that steam would be produced in the reforming operation. A credit based on $3.50/1000 lbs. of steam was assumed. Using the above assumptions, the total capital investment for the additional equipment to modify the existing facility to produce hydrogen from the pyrolysis off-gas is estimated at $1.4 million. For an annual hydrogen production rate of 4.4 million Nm^3, the selling price of hydrogen is estimated to be $9.51/GJ.

The hydrogen selling price for a fuel cost of $1.28/GJ (i.e., 45% fuel value) is $7.78/GJ. Using a no-cost bio-oil, the selling price for the hydrogen is $6.05/GJ. These price ranges are very promising considering that the economics were performed for a very small-scale operation.

Summary and Future Work

The Steam Reforming of Biomass Pyrolysis oil, when integrated with the production of high value products, is a promising near-term approach to the production of renewable hydrogen. Based on bench-scale work at NREL, a team from Georgia is utilizing the NREL TCUF and its staff to develop a 10-20 kg/hr scale reactor that will be operated at NREL this year before being run at the production site in Georgia on densified peanut shells. The application in Georgia is at a plant that makes activated carbon from peanut shells and has pyrolysis by-products available for conversion. The key technical goals for the shakedown at NREL are to ensure the safety of the reactor and obtain preliminary performance data on the catalyst, especially physical attrition and deactivation.

In Phase 2, the reactor will be tested on the pyrolysis vapors produced in the first step of the activated carbon process. An interface system is being designed this year for construction and operation in Phase 2. In Phase 3, the hydrogen produced will be purified by converting residual CO to H_2 over a shift catalyst and separating hydrogen from CO_2 using pressure swing adsorption. The purified hydrogen will be mixed with natural gas and used in a transportation demo. Working with the team from Georgia, other agricultural residues are being evaluated for cost and co-product potential.

References

Abedi, J., Y. D. Yeboah, M. Realff, D. McGee, J. Howard, and J. B. Bota, "An Integrated Approach to Hydrogen Production from Agricultural Residues for Use in Urban Transportation," *Proceedings of the 2001 DOE/NREL Hydrogen Program Review,* Baltimore, MD.

Biomass Research and Development Board, *Fostering the Bioeconomic Revolution in Biobased Products and Bioenergy.* See: http:/www.Bioproducts-bioenergy.gov.

Chornet, E, S. Czernik, D. Wang, C. Gregoire, and M. Mann, "Biomass to Hydrogen via Pyrolysis and Reforming," *Proceedings of the 1994 DOE/NREL Hydrogen Program Review,* 407-432. Livermore, California, NREL/CP-470-6431; CONF-9404194.

Chornet, E., S. Czernik, C. Feik, R. French, "Biomass-to Hydrogen via Fast Pyrolysis and Catalytic Steam Reforming," *Proceedings of the 2001 DOE/NREL Hydrogen Program Review,* Baltimore, MD.

Czernik, S., R. French, C. Feik, E. Chornet, "Hydrogen form Biomass-Derived Liquids," *Progress in Thermochemical Biomass Conversion,* A. V. Bridgwater, Ed. In press.

Kelley, S.S., X.-M. Wang, M. D. Myers, D. K. Johnson, and J. W. Scahill, "Use of Biomass Pyrolysis Oils for Preparation of Modified Phenol Formaldehyde Resins," *Developments in Thermochemical Biomass Conversion,* 557-572. A. V. Bridgwater and D. G. B. Boocock, Editors. London: Blackie Academic & Professional.

Ozyurt, B. D., M. J. Realff, "Synthesis of a Food Processing-Agriculture Based Industrial Complex," *AIChE National Meeting Special Symposium*, Dallas, TX.

Putsche, V., "Preliminary Analysis of Peanut Shell Pyrolysis/Activated Carbon Process," Personal Communications.

Spath, P. L., M. K. Mann, "Technoeconomic Assessment of Four Biomass-to-Hydrogen Conversion Technologies," *Hydrogen Energy Progress XII. Proceedings of the 12th World Hydrogen Energy Conference,* 2057-2067. Buenos Aires, Argentina. Eds. J. C. Bolcich and T. N. Veziroglu. Vol 3.