

II.C Biomass Gasification/Pyrolysis

II.C.1 Hydrogen from Biomass – Catalytic Reforming of Pyrolysis Streams

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Objectives

- Explore feasibility of producing hydrogen from low-cost, potentially high-hydrogen-yield renewable feedstocks that could increase flexibility and improve economics of distributed and semi-central reforming processes.
- Demonstrate efficiency of pyrolysis/reforming technology in application to readily available feedstocks: biomass, post-consumer wastes, trap grease, and synthetic polymers.
- Develop attrition-resistant supports and multi-functional, multi-component fluidizable catalysts from these supports for efficiently reforming pyrolysis vapors and liquids derived from biomass and wastes.
- Develop the engineering basis for scale-up of the catalytic fluid bed reforming of biomass pyrolysis vapors and liquids.
- Develop and demonstrate technology for producing hydrogen from biomass at \$2.90/kg purified hydrogen by 2010. By 2015, produce biomass-based hydrogen that is competitive with gasoline.

Technical Barriers

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

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

Approach

- A robust reforming process capable of producing hydrogen from diverse, locally-available biomass feedstocks needs to be developed in order to minimize the impact of price fluctuations; feedstock collection, delivery and processing costs; and hydrogen delivery cost.

- Processing technologies, including pyrolysis, partial oxidation and catalytic steam reforming, are evaluated for a variety of complex feedstocks.
- Fluidizable reforming catalysts on attrition-resistant supports are developed and optimized to improve conversion rates, minimize catalyst losses, and improve catalyst lifetime.
- Support is provided to DOE-funded partners in order to demonstrate the integrated pyrolysis/reforming process using agricultural residues (peanut shells) as a feedstock; mass balance and catalyst performance in a long-duration test are documented.
- State-of-the-art chemical analysis and process control are employed so that the small-scale systems can be run with high confidence of safety and reliability.

Accomplishments

- A conceptual design was completed for a 250 kg H₂ per day pyrolysis/reforming system that addresses the following design challenges: reformer preheater, heat recovery and integration, compression, conditioning, co-product optimization, pyrolyzer heat optimization.
- System design improvements were provided to the Clark Atlanta team to increase the robustness and safety of their system in preparation for the 1000-hour run.
- A 100-pound batch of catalyst was prepared and provided to the Clark Atlanta team for their 1000-hour test run.
- Novel fluidizable reforming catalysts were developed in collaboration with CoorsTek Ceramics that show improved reforming activity and durability compared to commercial catalyst.
- The performance of 16 catalysts was evaluated for 24 hours with pyrolysis oil-derived feedstocks; the best catalysts were also evaluated with gasified biomass vapors and waste grease.
- An 80% yield (90% when followed by water-gas shift) was achieved for the pyrolysis/reforming of polypropylene. Autothermal reforming of polypropylene was also demonstrated.
- One-step (feedstock fed directly to the reformer) and two-step (pre-processing by pyrolysis) reforming of trap grease were demonstrated with yields of 65% and 56%, respectively; catalyst lifetime was greatly improved with pyrolytic pre-processing. Phosphorous from trap grease accumulated on the catalyst surface and likely reduced activity.
- The feasibility of co-reforming bio-oil with natural gas was demonstrated.

Future Directions

- Develop catalyst deactivation and poisoning model.
- Develop strategy for handling the contaminants in the feedstocks – gas clean-up, hetero-atom resistant catalyst.
- Demonstrate production of hydrogen by co-processing renewable (solid and liquid) and fossil (natural gas) feedstocks.
- Demonstrate pyrolysis/reforming process for complex feedstocks (textiles, mixed plastics).

Introduction

Approximately 95% of the hydrogen produced today comes from carbonaceous raw material, primarily fossil in origin. Renewable biomass is an attractive alternative because of essentially zero CO₂ impact. Although by 2050 biomass could

realistically supply 15% of the world's energy, to do so will necessitate the use of a variety of feedstocks, including agricultural and forest residues, municipal and industrial byproducts, and sustainable energy crops. The challenges for this variety of feedstocks include feedstock handling and drying, regional and seasonal availability and variability, and the potential

range of impurities that could be present; the conversion technology must be feedstock-flexible, and the approach must minimize costs for feedstock collection, transport and processing. Additionally, given the high cost of hydrogen storage and delivery, technologies that can be distributed at or near the point of use are attractive.

The National Renewable Energy Laboratory (NREL) has developed a two-step approach geared at addressing these challenges. Pyrolysis is used to convert the feedstock into a liquid that can more easily be transported. This so-called bio-oil can then be catalytically steam reformed to hydrogen and carbon dioxide. The bio-oil can also be co-processed with other biomass or fossil liquids and gases.

Approach

NREL has developed bench-scale reactors for both the pyrolysis and reforming steps, and tests have been run up to 200 hours. Additionally, tests have been performed in NREL's process development unit at a 25 kg H₂ per hour scale. A variety of feedstocks have been screened, including biomass-derived liquids and vapors, polypropylene and trap grease. In these tests, commercial catalysts showed a slow decrease in activity with time. Although this activity can be restored through regeneration, increasing the catalyst lifetime is a priority. Additionally, the mechanical strength of the catalyst is an issue with major impact on process economics. Commercial reforming catalysts are currently designed and used only for fixed-bed applications. The particles obtained by grinding these pelletized catalysts tend to disaggregate during the fluidization process, with losses of 5% per day. Over the last two years, the development of an attrition-resistant fluidizable catalyst has been conducted, with promising performance results.

Results

Process Research

This year, NREL focused its efforts on increasing the understanding of the process chemistry and on novel catalyst/support formulations with the goal of controlling coke deposition on the catalytic surface. Catalyst

deactivation was studied using furfural as a representative model compound for biomass pyrolysis vapors. NREL catalyst formulation #15, which performed the best in last year's bio-oil aqueous fraction reforming tests, was selected for these studies. At 800°C and a molar steam to carbon ratio 2.5, the catalyst performed very well with 100% feed carbon to gas conversion. The yield of hydrogen was almost 80% of the stoichiometric potential as shown in Figure 1. This yield would be close to 100% if CO in the product gas were further converted by water-gas shift. At 750°C, the catalyst initially also performed very well. However, after less than four hours on stream, the activity of the catalyst started deteriorating as shown in Figure 2. The catalyst after regeneration by burn off performed at almost the same level as the fresh (Figure3), but again loss activity about 4 hours on stream.

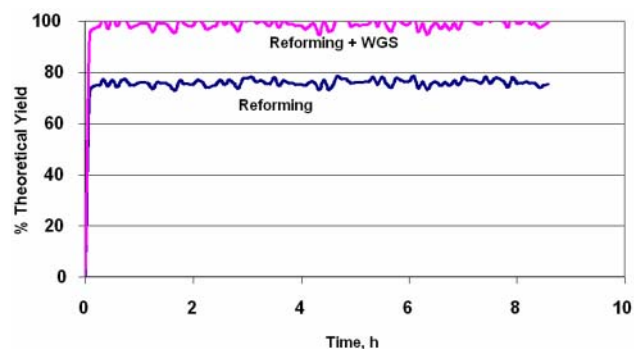


Figure 1. Yield of Hydrogen from Reforming Furfural at 800°C and S/C = 2.5 using NREL#15 Catalyst

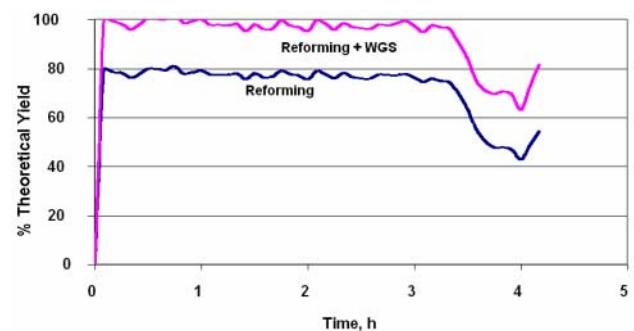


Figure 2. Yield of Hydrogen from Reforming Furfural at 750°C and S/C = 3 using NREL#15 Catalyst

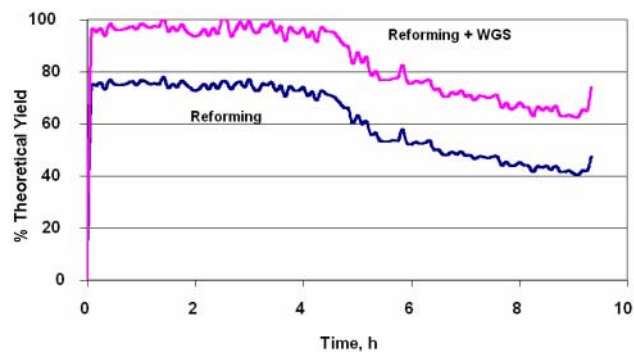


Figure 3. Yield of Hydrogen from Reforming Furfural at 750 C and S/C = 3 using Regenerated NREL#15 Catalyst

Systems Engineering

With the overall systems requirements in mind, NREL designed a scaled-up reformer system to produce 250 kg H₂/day. An overview of the system is shown in Figure 4. A bubbling fluid bed system has been the reactor of choice for the reformer since the decision to move away from packed beds for this process. Although work to date at both bench scale and the current engineering scale has been promising, there are two key aspects that need to be considered for scale-up: heat management and catalyst management.

Heat Management: Heat management is essential because the reforming reaction is endothermic and the reaction kinetics require high temperatures. Heat can be added to the system either in a preheater between the pyrolyzer and the reformer or directly to the fluid bed. In the first case, the vapors enter the reformer at high temperature (> 900°C) from the preheater. In addition to the problems associated with carbon deposits from adding the vapors and steam through the distribution plate at > 900°C, the nozzles will become as hot as the incoming gases, which creates mechanical stresses. In short, the design of the distribution plate will be difficult. In the second case, the vapors enter at a moderate temperature (~700°C), and the increase in temperature is carried out in the reformer. Adding the vapors at 700°C permits the distribution plate and the nozzles to be maintained at less severe temperatures. In this case, the choice of materials and the design are not a problem; however, the bed must be maintained at 850°C. This is feasible via adequately positioned burners (in reactors having up

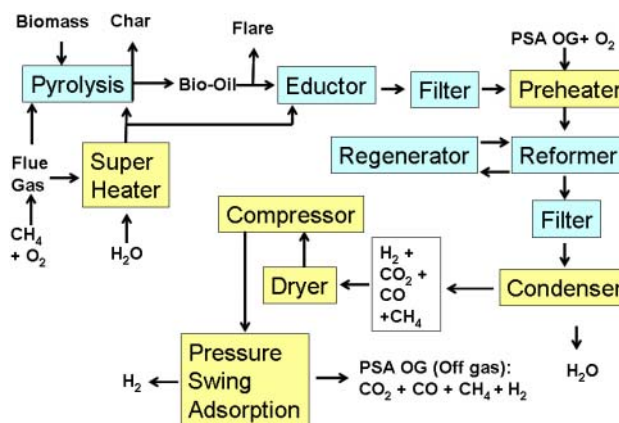


Figure 4. Simplified Process Flow Diagram

to 1 meter diameter, a single burner will likely be sufficient) and the use of pressure swing adsorber (PSA) off-gases and O₂-enriched air to provide the required heat to bring the incoming vapors to temperature and to account for endothermicity. Options for providing gas preheating (from the pyrolyzer outlet temperature of 450°C to the required reformer temperature of 850°C), the heat of reaction, and heat loss compensation include an external gas preheater, internal reformer fire tubes, and partial oxidation of the product gases. The best option is to use reformer internal “fire tubes” to provide the major portion of the necessary heating. Internal tubing is necessary for the reformer operation, and the additional amount of tubing reduces the overall system complexity by eliminating one unit operation. Approximately 70 meters of 2.5-cm diameter heat tubes will be required to provide the necessary energy input into the reformer. The reformer bed diameter must be increased to compensate for loss of bed area to the heating tubes and addition of internal supports for the tubing.

Catalyst Management: Catalyst management will be a function of the catalyst deactivation profiles. The synthesis of the data indicates that the catalyst progressively, yet slowly, loses its activity. The strategy, then, is to intermittently withdraw an amount of catalyst from the bed and replace it with fresh catalyst. Regeneration of the withdrawn catalyst will be done ad-hoc using steam and, if required, PSA off-gases that contain at least 5 vol% H₂. The exit gases from the regenerator could be sent to the preheater and be combined with the vapors being reformed or used to generate heat for the pyrolyzer. Integration will thus be achieved.

Conclusions

A conceptual design for a 250 kg H₂/day system was developed that addresses heat and catalyst management design issues. We were also able to demonstrate that by optimizing temperature and the steam-to-carbon ratio, catalyst activity can be maintained, indicating that carbon deposits are removed from the catalyst by steam gasification at the same rate as they are formed. Further work is needed to develop a robust catalyst deactivation and poisoning model and to develop a strategy, such as gas clean up and/or hetero-atom resistant catalysts, for handling the contaminants in the feedstocks.

FY 2004 Publications/Presentations

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2. French, R. J.; Czernik, S. (2003). Hydrogen Production by Steam Reforming of Waste Vegetable Oils. American Chemical Society. Preprints of Papers: Division of Fuels Chemistry. Washington, DC: American Chemical Society; Vol. 48, No. 2.
3. Evans, R. J.; Chornet, E.; Czernik, S.; Feik, C.; French, R.; Phillips, S.; Yeboah, Y. D.; Day, D.; Ellis, S.; McGee, D.; Realff, M. J. (2003). Renewable Hydrogen Production by Catalytic Steam Reforming of Peanut Shells Pyrolysis Products. American Chemical Society. Preprints of Papers: Division of Fuels Chemistry. Washington, DC: American Chemical Society; Vol. 48, No. 2.