Hydrogen from Biomass-Catalytic Reforming of Pyrolysis Streams

Objectives

- Explore feasibility of producing hydrogen from low-cost, potentially high-hydrogen-yield renewable \bullet 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: \bullet biomass, post-consumer wastes, trap grease, and synthetic polymers.
- Develop attrition-resistant supports and multi-functional, multi-component fluidizable catalysts from these \bullet 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 \bullet and liquids.
- Develop and demonstrate technology for producing hydrogen from biomass at \$2.90/kg purified hydrogen \bullet 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 \bullet .
- F. Feedstock Cost and Availability $\pmb{\ast}$
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology \bullet

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 \bullet 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 ٠ run with high confidence of safety and reliability.

Accomplishments

- A conceptual design was completed for a 250 kg H_2 per day pyrolysis/reforming system that addresses the ٠ 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 \bullet 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 ٠ test run
- Novel fluidizable reforming catalysts were developed in collaboration with CoorsTek Ceramics that show \bullet 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 \bullet 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 ٠ 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 ٠ 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. \bullet

Future Directions

- Develop catalyst deactivation and poisoning model. $\pmb{\ast}$
- Develop strategy for handling the contaminants in the feedstocks gas clean-up, hetero-atom resistant $\pmb{\ast}$ catalyst.
- Demonstrate production of hydrogen by co-processing renewable (solid and liquid) and fossil (natural gas) ۰ feedstocks.
- Demonstrate pyrolysis/reforming process for complex feedstocks (textiles, mixed plastics). ٠

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

Figure 4. Simplified Process Flow Diagram

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.