Hydrogen from Biomass:
Process Research

U.S. DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Review

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Objectives of the Task

- 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 process.
- Demonstrate efficiency of pyrolysis/reforming technology in application to readily available feedstocks: post-consumer wastes, trap grease, mixed biomass and synthetic polymers.

Goal of the Project

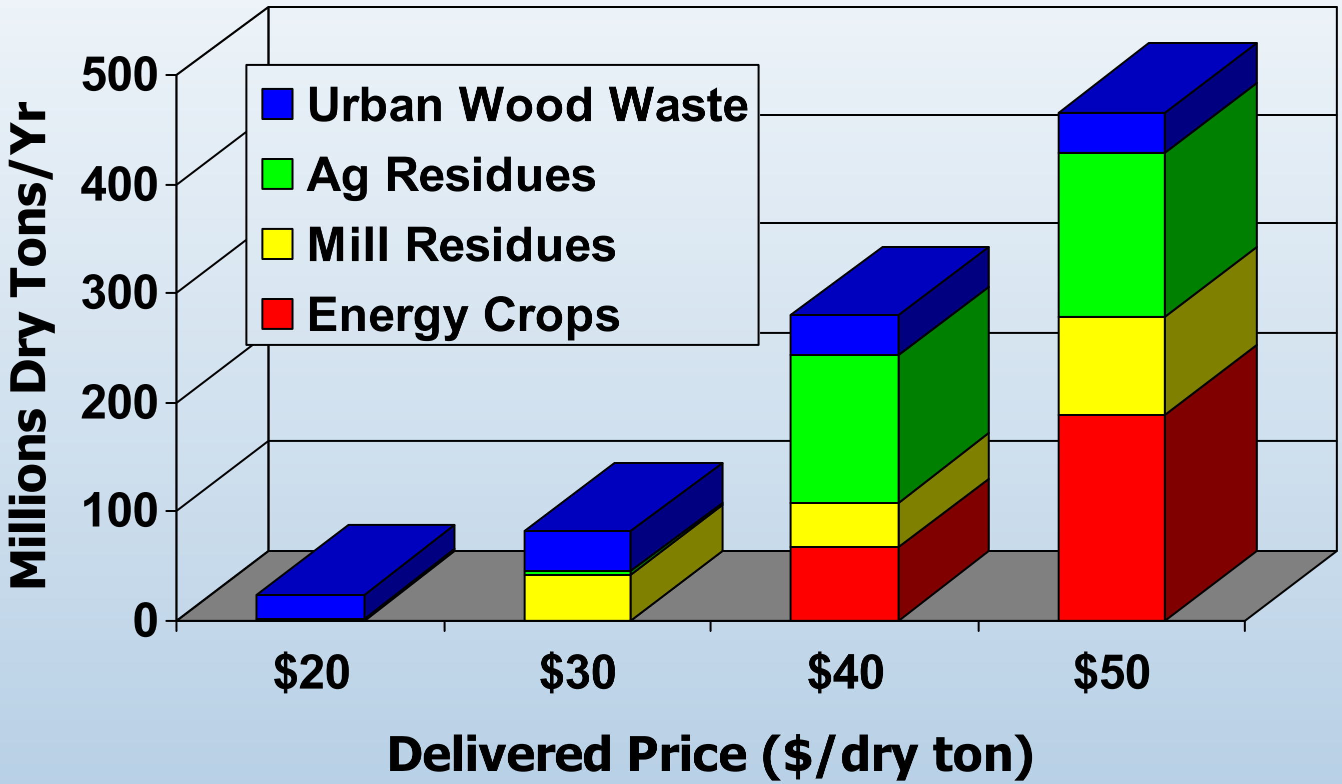
- Develop and demonstrate technology for producing hydrogen from biomass at \$2.90/kg purified hydrogen by 2010. By 2015, be competitive with gasoline.

Potential for Hydrogen

- Biomass: Potential for producing 40 Mt/year (or more) of hydrogen – enough to fuel 150 million fuel cell vehicles
- Plastics wastes: Potential for producing 6 Mt/year of hydrogen – enough to fuel 15-20 million fuel cell vehicles
  - Requires development/expansion of collection programs and separation technologies.
  - Target streams: manufacturing residues (textiles), MRF tailings.
- Trap grease: 6 kg/year/person - 1.5 Mt/year; potential for 0.5 Mt/year hydrogen.
  - Assuming that processing costs will be comparable to those for residual oil ($0.7/kg H_2), trap grease presents a near-term market opportunity for the production of hydrogen.

Biomass Potential in the U.S.

source: Oak Ridge National Lab, http://bioenergy.ornl.gov/resourcedata/



Plastics: ~$80-100/ton; yield 3-4 time higher

Budget

- Total funding (from 2001): $850,000
- Funding in FY 2004: $120,000
  - Planned: $400,000
  - Scope Reduced: Focusing on catalyst deactivation studies using model compounds

Technical Barriers and Targets

- DOE Technical Barriers for Hydrogen Production:
  - C - Feedstock-flexible reformers are needed to mitigate and/or take advantage of price fluctuations and to address location-specific feedstock supply issues
  - F - Feedstock cost and availability: lower-cost collection and transport, improved feedstock preparation, and feedstock-flexible processes
  - G - Efficiency of gasification, pyrolysis, and reforming technologies: improved vapor conditioning, heat integration, reactor configuration, improved catalysts, and higher yield
- DOE Technical Targets for Hydrogen Production from Biomass:
  - $2.90/kg of purified hydrogen by 2010

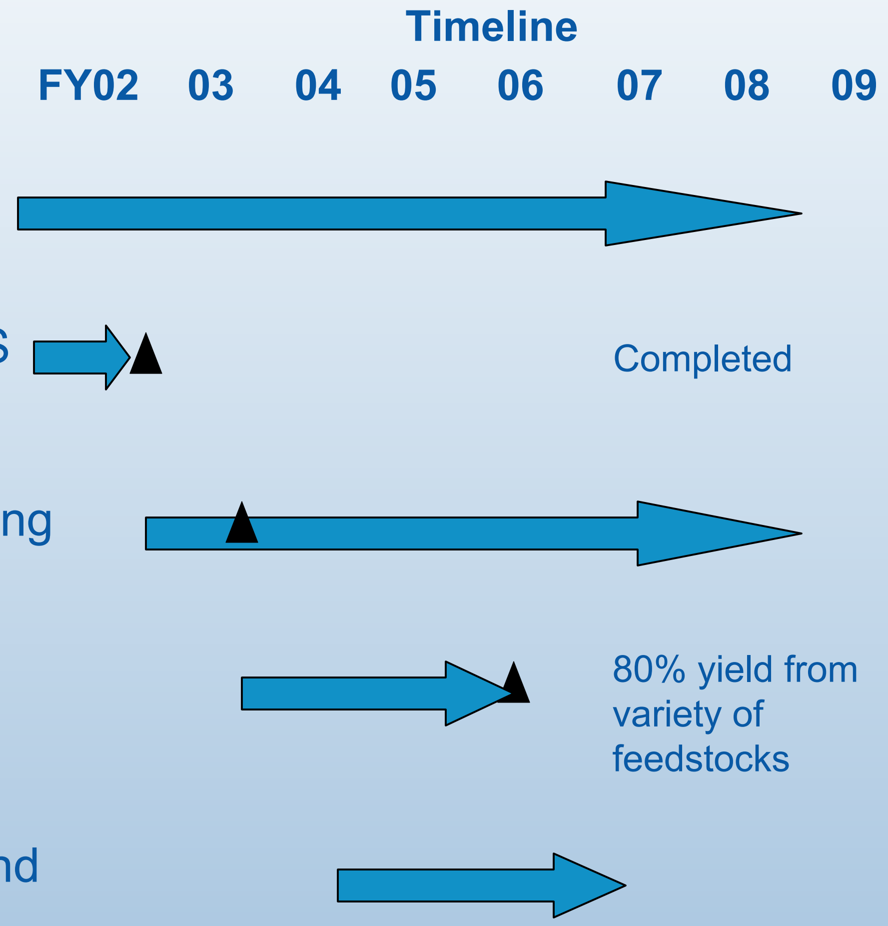
Project Timeline

Hydrogen from Mixed Biomass and Post-Consumer Residues

	Timeline: FY02 03 04 05 06 07 08 09	
Production of Hydrogen by Catalytic Steam Reforming of Trap Grease		
Reforming tests using commercial catalysts		80% yield, 150 hours on stream, catalyst attrition losses.
Reforming tests using NREL fluidizable catalysts		80% yield, low attrition of catalyst
Feedstock clean-up strategy and long-term catalyst performance demonstration		
Co-process trap grease with other biomass-derived liquids		80% yield, low catalyst attrition, long-duration activity

Project Timeline (cont.)

Hydrogen from Mixed Biomass and Post-Consumer Residues



Production of Hydrogen by Integrated Pyrolysis/Reforming of Plastics

Proof of Concept at Micro-Reactor/MBMS Scale

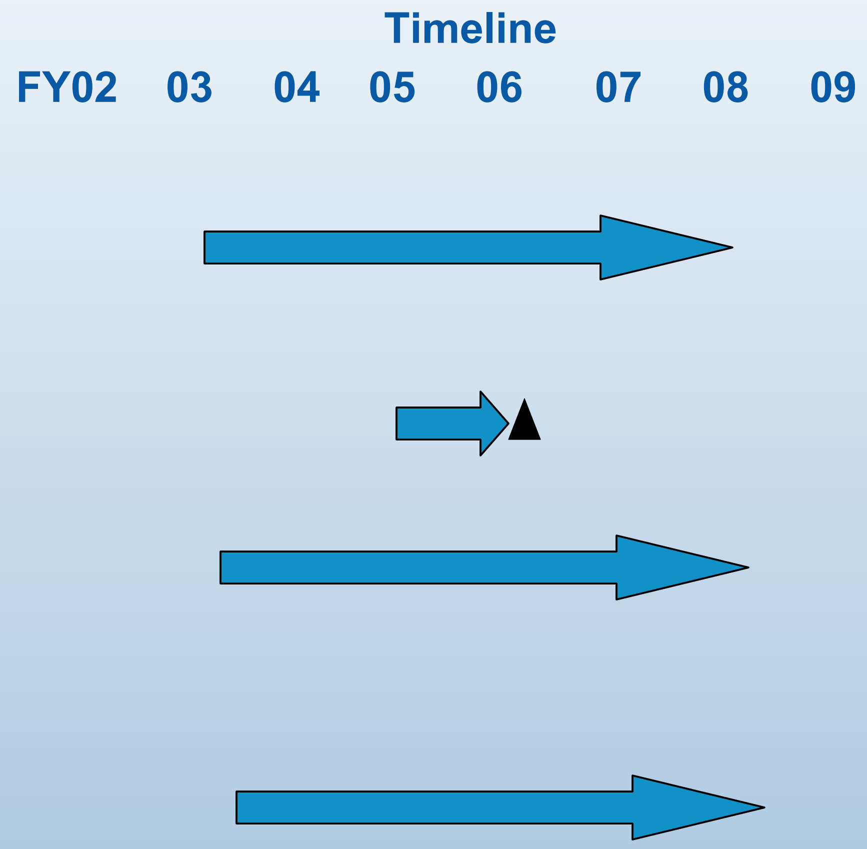
Bench-scale tests using integrated bubbling bed reactor system

Bench-scale tests using plastic mixtures (gas clean up)

Bench-scale co-processing of biomass and other feedstocks

Project Timeline (cont.)

Hydrogen from Post-Consumer Residues



Production of Hydrogen from Different Feedstocks in Support of the Scale-up Effort

Construction of bench-scale circulating fluid bed reformer

Co-reforming of biomass and post-consumer feedstocks with natural gas

Bubbling and circulating bed tests on flexible feedstocks

Approach

- A robust reforming process capable of producing hydrogen from diverse, locally-available feedstocks will minimize:
  - Impact of price fluctuations
  - Feedstock collection, delivery and processing costs
  - Hydrogen delivery cost
- Process technology:
  - Pyrolysis or partial oxidation of biomass, plastics, and other solid organic residues
  - Catalytic steam reforming of the resulting pyrolysis gases and vapors
  - Catalytic steam reforming of biomass-derived liquid streams
  - Co-reforming of renewable and fossil (natural gas or liquids) fuels

Process Reactions

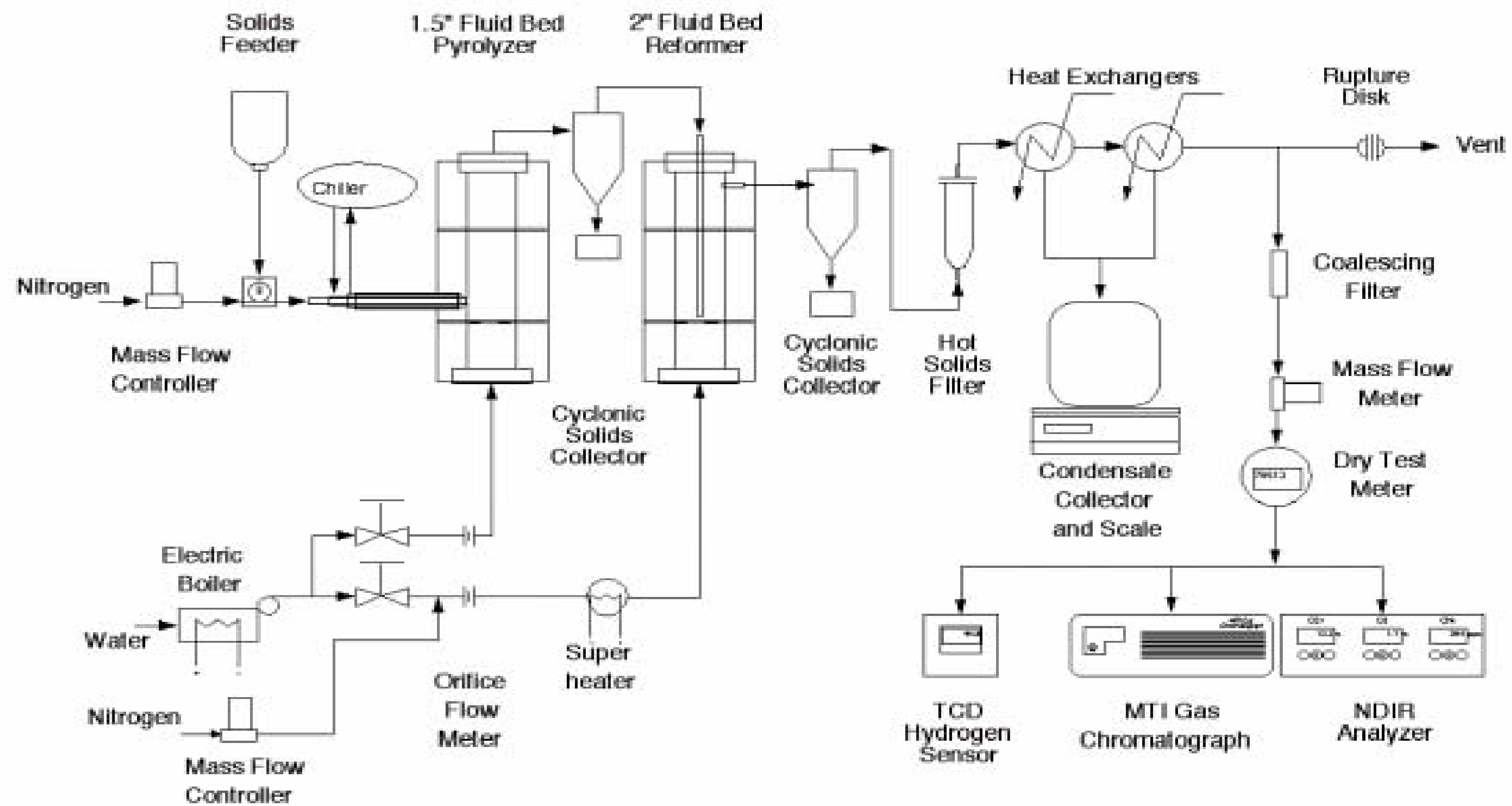
$$\text{Polymers} \xrightarrow{\textit{500-800ºC}} \text{Monomers and other volatile compounds}$$

$$C_nH_mO_k + (n\text{-}k)\ H_2O \xrightarrow{\textit{800ºC, cat.}} n\ CO + (m/2 + n\text{-}k)\ H_2$$

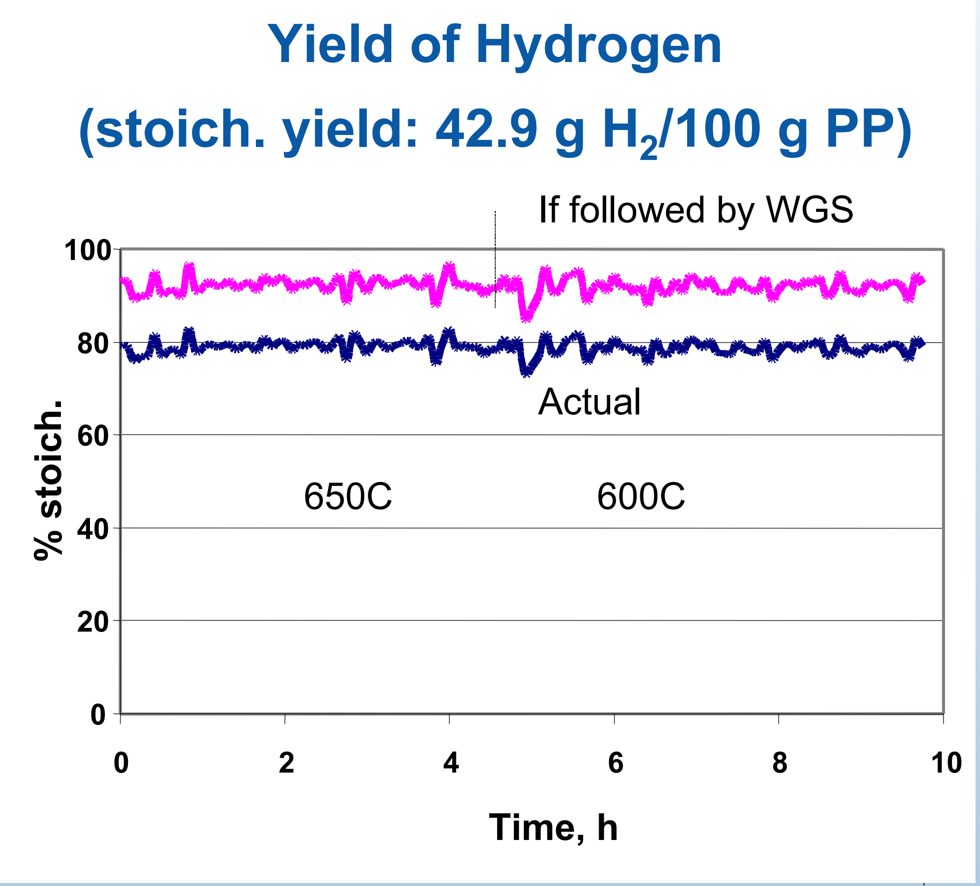
$$n\ CO + n\ H2O \longleftrightarrow n\ CO_2 + n\ H_2$$

$$C_nH_mO_k + (2n\text{-}k)\ H_2O \longrightarrow n\ CO_2 + (m/2 + 2n\text{-}k)\ H_2$$

Fluidized Bed Integrated Pyrolysis Reforming System



Technical Accomplishments: Pyrolysis/Reforming of Polypropylene



80% of theoretical yield obtained

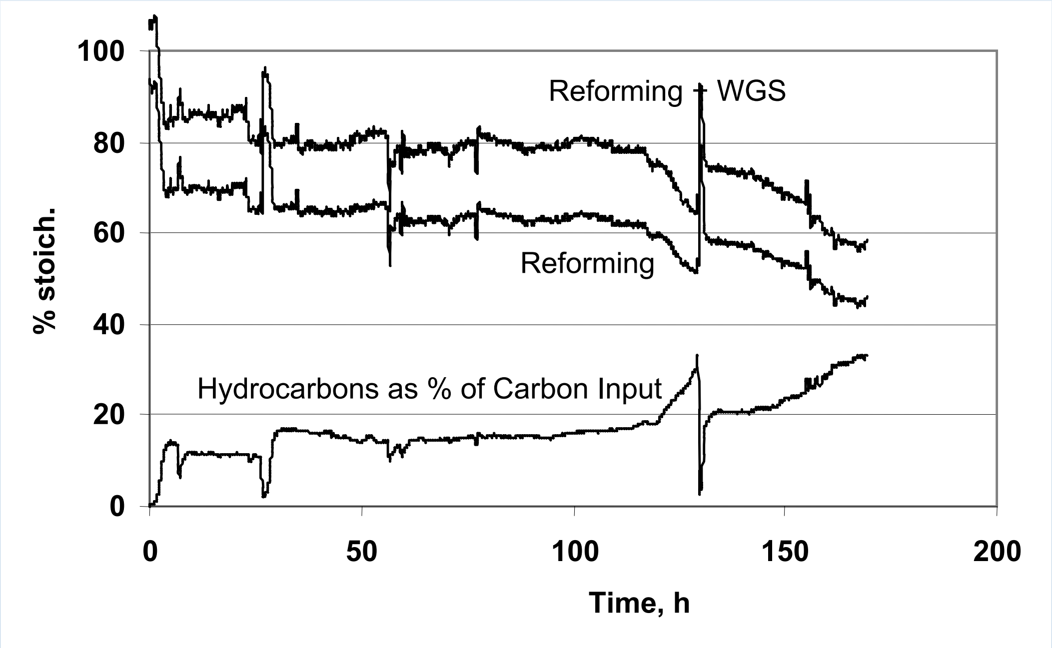
- >90% yield if followed by WGS
- Little temperature effect on yield or catalyst activity
- No coke deposits observed

Autothermal reforming also demonstrated

- Power demand reduced by 50% (power input still needed due to heat losses in small-scale reactor)
- <60% of theoretical yield (as expected)

Technical Accomplishments: Pyrolysis/Reforming of Trap Grease

Yield of Hydrogen
(stoich. yield of H_2: 35 g/100 g grease)



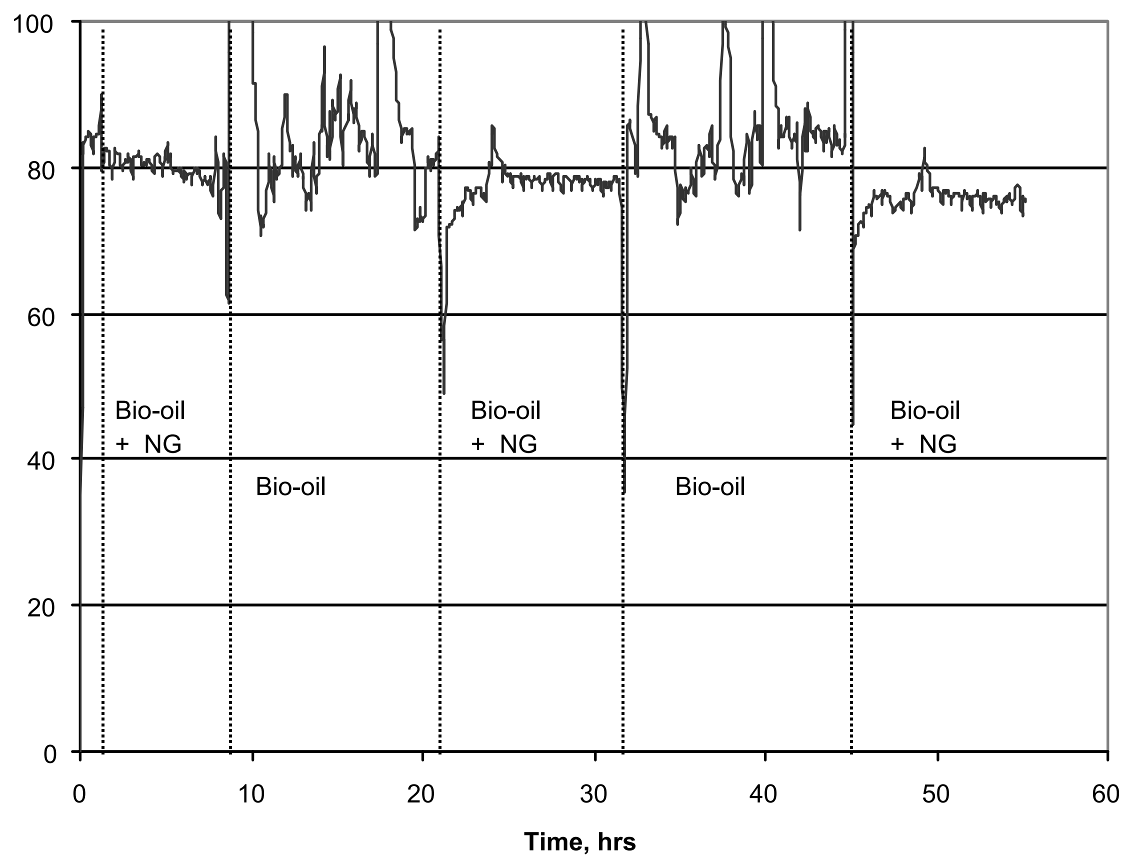
Two process options studied:

- One-step reforming of water-washed grease
  - 65% of stoich. yield; 80% with WGS
  - Decrease in catalytic activity after 115 hours; possibly due to phosphorus deposits
- Two-step: pyrolysis followed by reforming
  - 56% of stoich. yield
  - Two-step process protected catalyst from inorganic contaminants

NREL-developed reforming catalyst performed well:

- <1% attrition losses after 170 hours

Technical Accomplishments:
Co-Reforming of Bio-oil and Natural Gas



Feasibility of co-reforming demonstrated
- 25% H2 from bio-oil
- Non-optimized experiment

Test done using commercial reforming catalyst (C11-NK)
- Testing with NREL catalyst delayed due to funding

Future Work

- Develop catalyst deactivation and poisoning model
  - Coke formation kinetics
  - Extensive analysis of used catalyst
  - Regeneration studies
- 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) using commercial and NREL-developed catalysts
- Update techno-economic analysis of the process

Project Safety

- Safety Vulnerability Techniques
  - A hazard identification and control program is employed to identify possible failure modes and associated risks. Redundant engineering and procedural controls are used to ensure that acceptable levels of risk are not exceeded.
  - Hydrogen safety is addressed through redundant on-line process monitoring and control.
    - Hydrogen and toxic gas (CO) sensors
    - Built-in safety alarms and process shutdown (temperature, pressure, flow rates)
- Management of Change
  - All systems are extensively instrumented, with redundant engineering controls.
  - New feedstocks, catalysts, reforming conditions, etc., are first characterized at the milligram-scale, then at the bench scale.
  - Safety documentation is reviewed at least annually.
  - Hazards analysis is conducted whenever new equipment is added or there is a major change in feedstock characteristics.

Responses to FY03 Review

- No discussion of cost breakdown of $2.90/kg goal; not responsive to 2005 goals
  - 2005 Goal represents a $0.10 reduction in reforming cost over current status per MYRD&D plan
    - Improved Catalyst Durability: developing attrition resistant catalyst, optimizing conditions to minimize coke formation
  - 2010 Goal represents a $0.90 reduction over current status per MYRD&D plan
    - Biomass Feed: $0.10 reduction; accomplished through improved yield/efficiency and/or lower-cost feedstocks (compared to $42/dry ton)
    - Operations through Pyrolysis: $0.40 reduction; accomplished through improved heat integration, lower feedstock processing requirements, lower capital cost
    - Reforming: $0.30 reduction; accomplished through improved catalyst durability, low-cost manufacturing, improved heat integration
    - Purification: $0.03 reduction; assumes improvements in commercial technology