Distributed Bio-Oil Reforming

2005 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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National Renewable Energy Laboratory

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This presentation does not contain any proprietary or confidential information

Project ID#PDP55

Overview

Timeline

- Project start 2005
- Project end 2010
- ~5% complete

Budget

- FY05 $100K

Partners

- CoorsTek

Production Barriers

A. Fuel Processor Capital
B. Fuel Processor Manufacturing
C. Operation & Maintenance
D. Feedstock Issues
F. Control & Safety

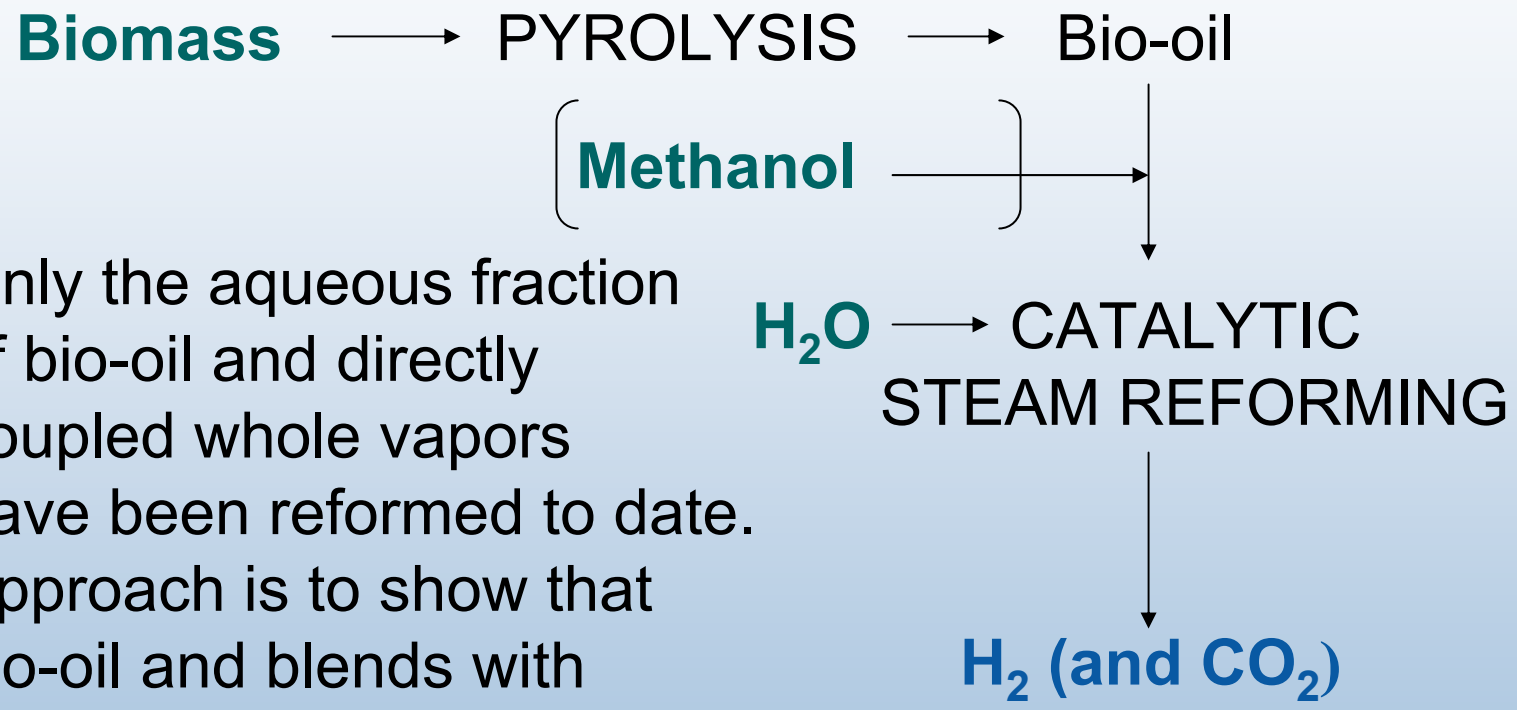
Target

Verify feasibility of achieving $3.60/gge for renewable liquids distributed reforming

Objectives

- Overall:
  - Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry and deactivation and regeneration strategy as a basis for process definition for automated distributed reforming
- FY05
  - Determine the process performance of the catalytic reforming of whole bio-oil

Approach

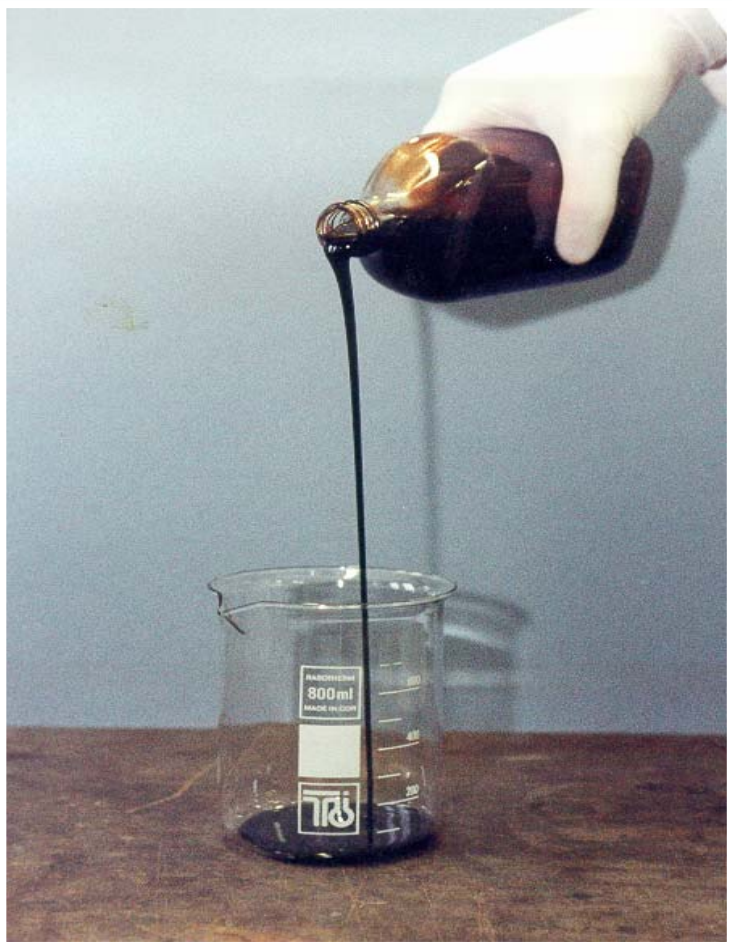


Only the aqueous fraction of bio-oil and directly coupled whole vapors have been reformed to date. Approach is to show that bio-oil and blends with Methanol can be fed without excessive coking and develop a process to meet cost objectives.

Technical Accomplishments

- Review of past work completed
  - Report summarizes all aspects of producing hydrogen from biomass by pyrolysis/reforming studied in past projects
- Whole oil successfully run
  - With 10% MeOH addition, bio-oil processing was trouble free over short run durations (up to16 hrs)
- NREL catalysts shown to be effective
  - Four catalyst compared with commercial
  - Patents being filed

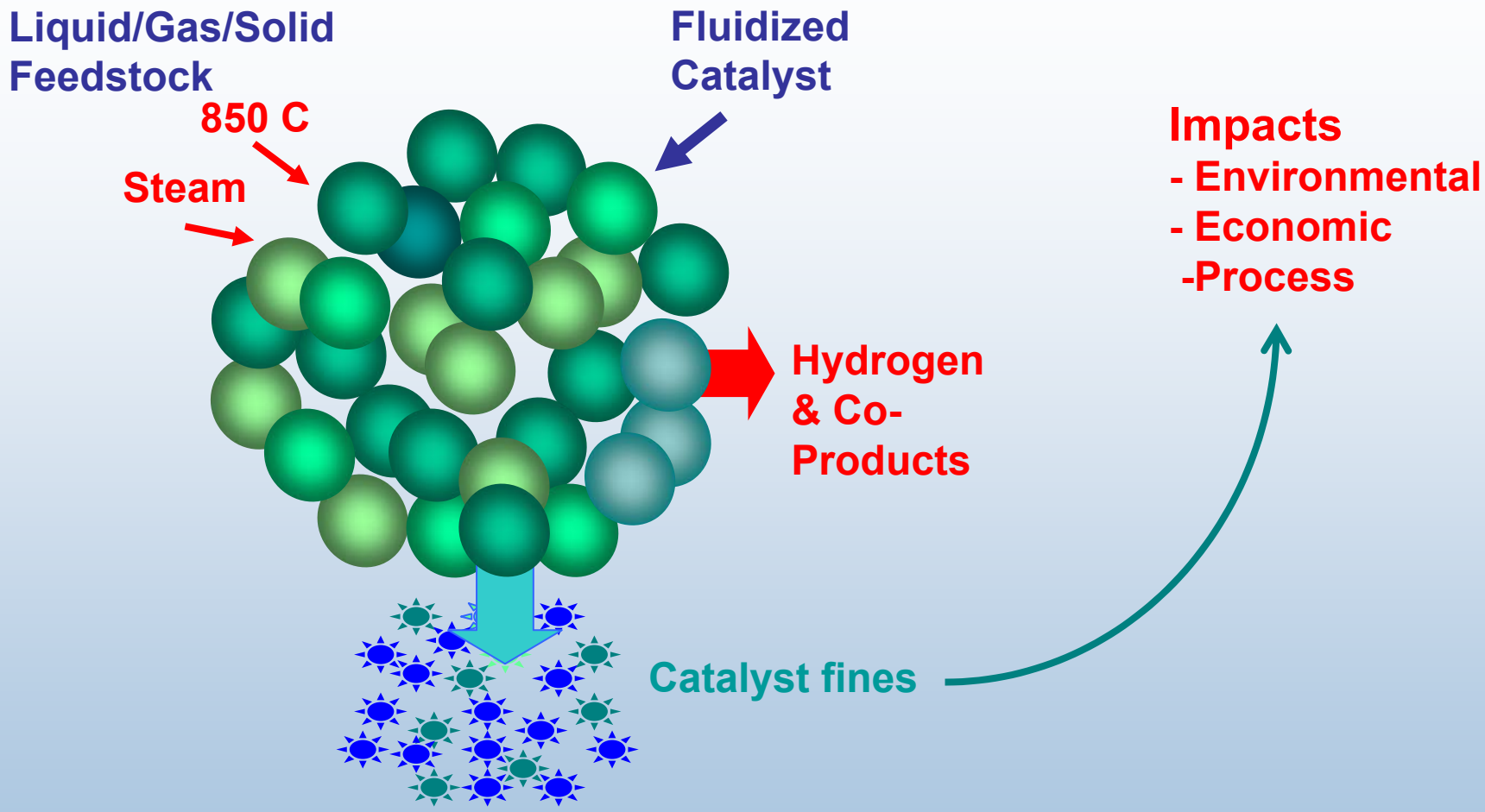
Bio-Oil



Bio-oil produced by fast pyrolysis of biomass with 75% yield is comprised of many oxygenated organic chemicals.

- Properties
  - Not miscible with hydrocarbons
  - Heating value ~ 17 MJ/kg
  - Density ~ 1.2 kg/l
  - Acid, pH ~ 2.5
  - Pungent odour
- Energy Density ~5 times green wood chips

Problem: Catalyst Attrition



Reforming: $C_xH_yO_z + H_2O(g) \rightarrow H_2 + xCO$

Water gas shift: $H_2O + CO \longrightarrow CO_2 + H_2$

Gasification: $C + H_2O(g) \longrightarrow COx + H_2$

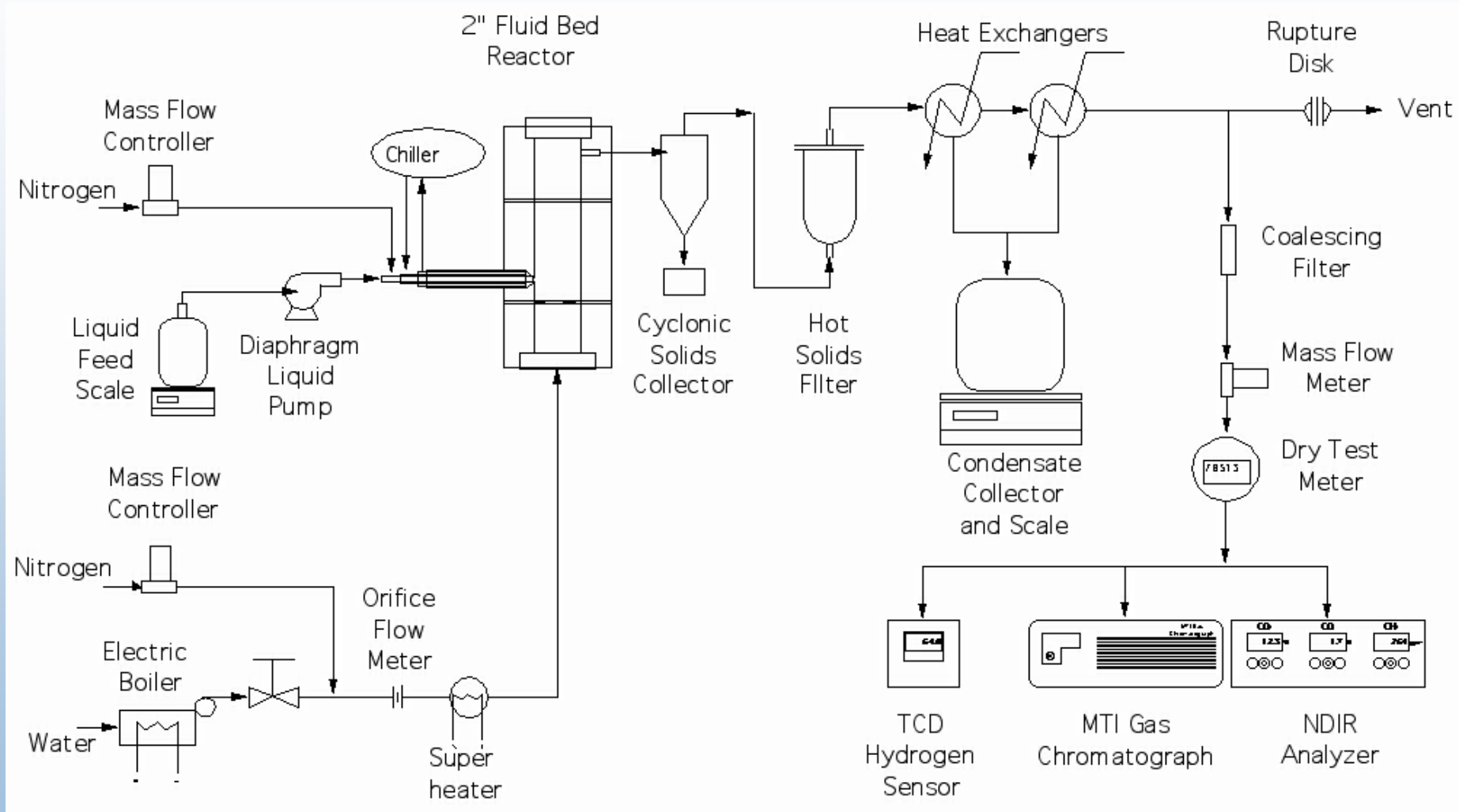
Catalysts

Whole Bio-oil on catalyst developed in prior work

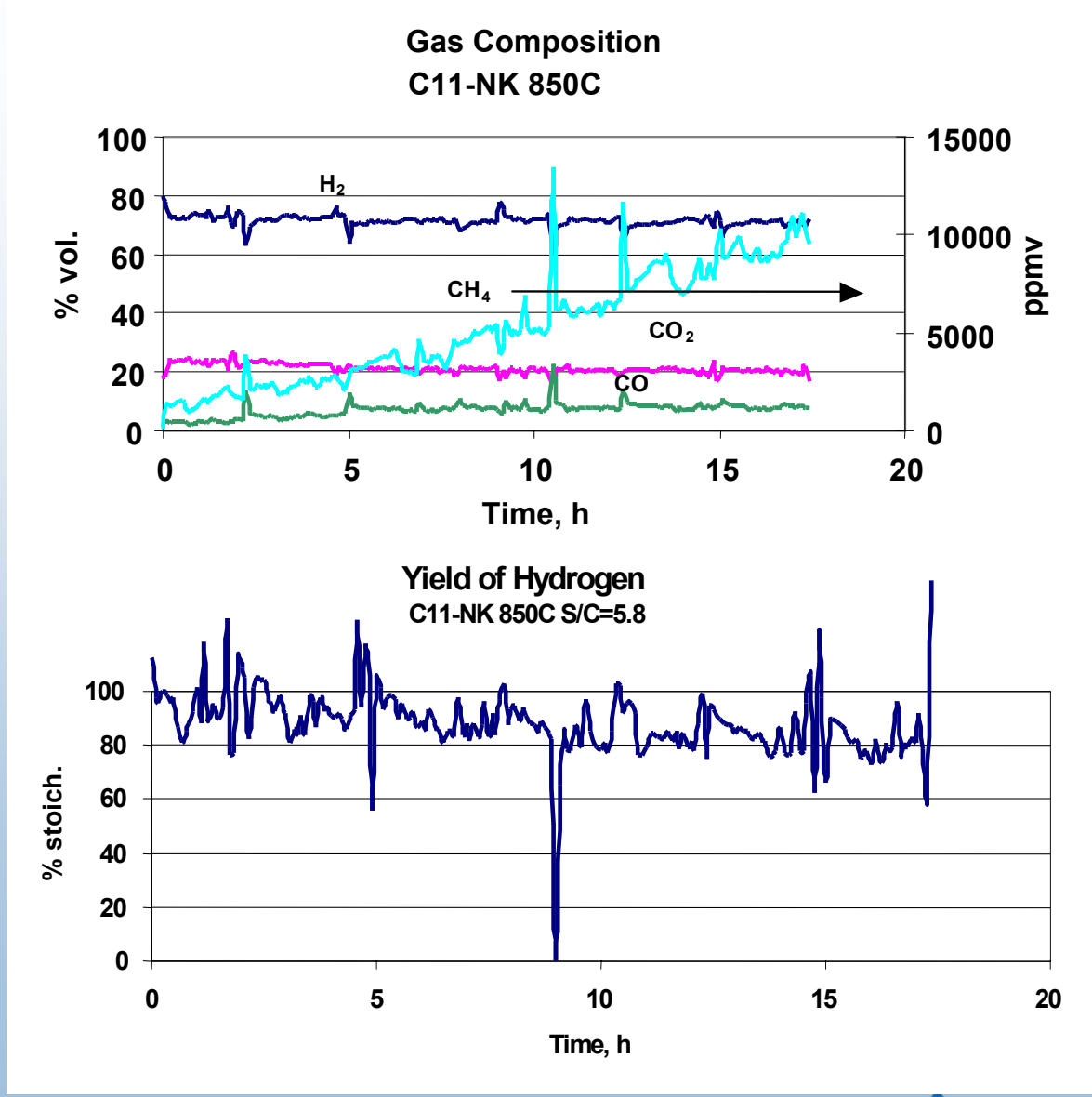
- Develop catalysts to reform *light and heavy organics*
- New supports now available with potential novel activity
- New catalyst rapid screening reactor available for whole oils – provides capability for combinatorial screening
- New catalyst characterization system available for determining catalyst deactivation, reactivation, and coking mechanisms
- Develop *low [Ni]* and bimetallic *(Ni, Cr)* reforming catalysts
- Lifetime tests (activity steady > 500 h)

Catalyst Microactivity Test System

Bio-Oil Reformer System



Reforming Whole Bio-oil



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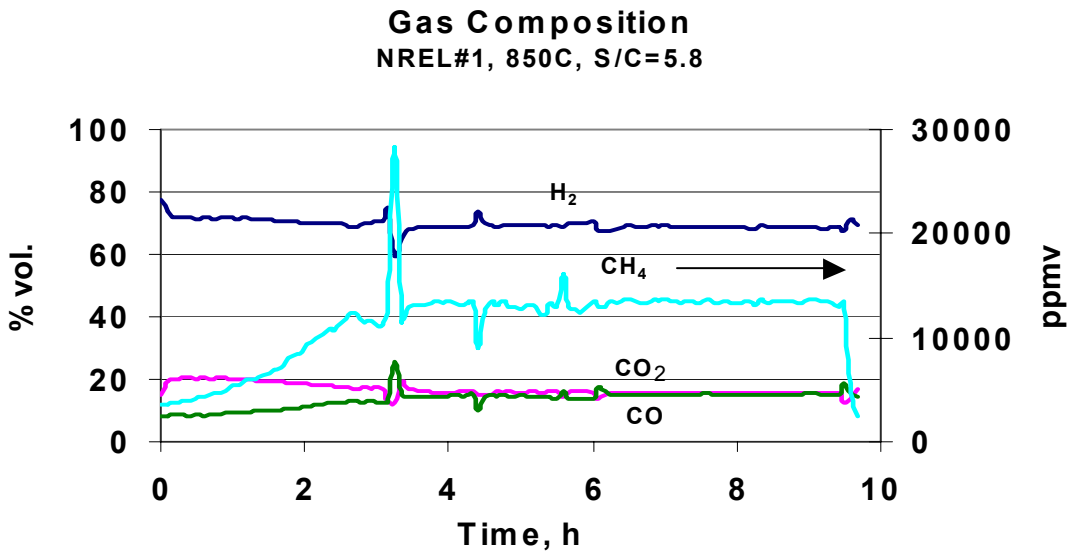

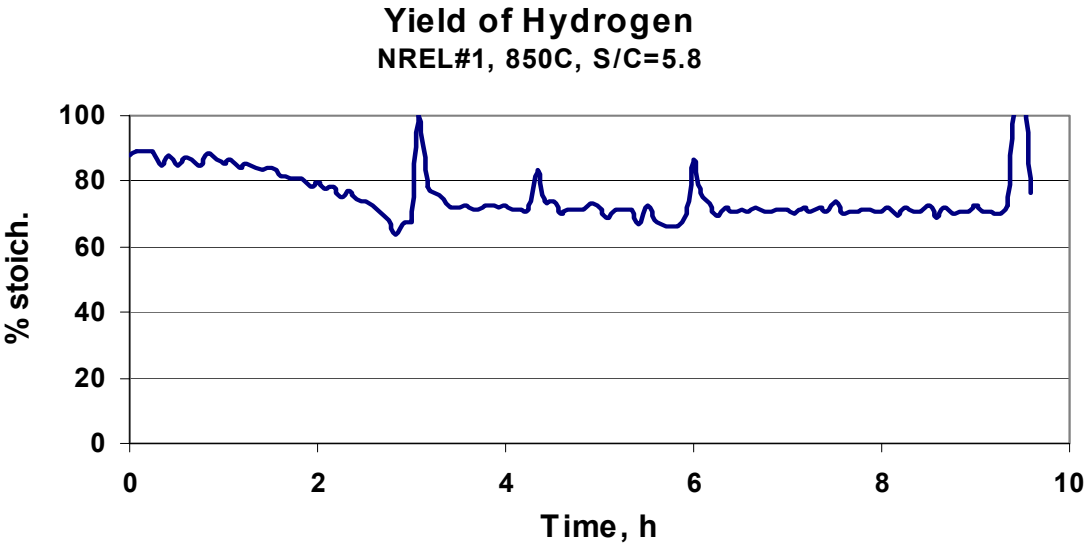

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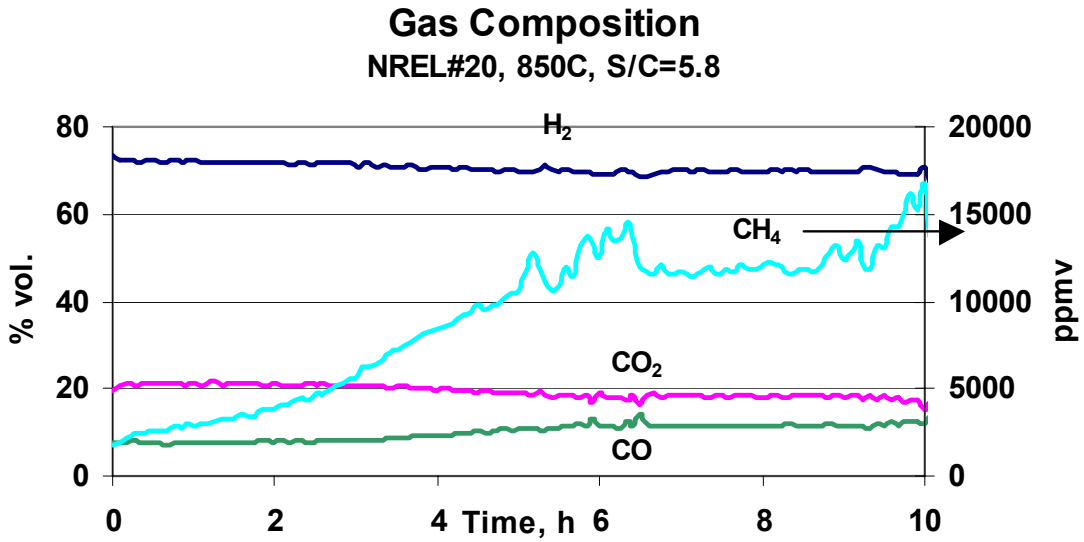
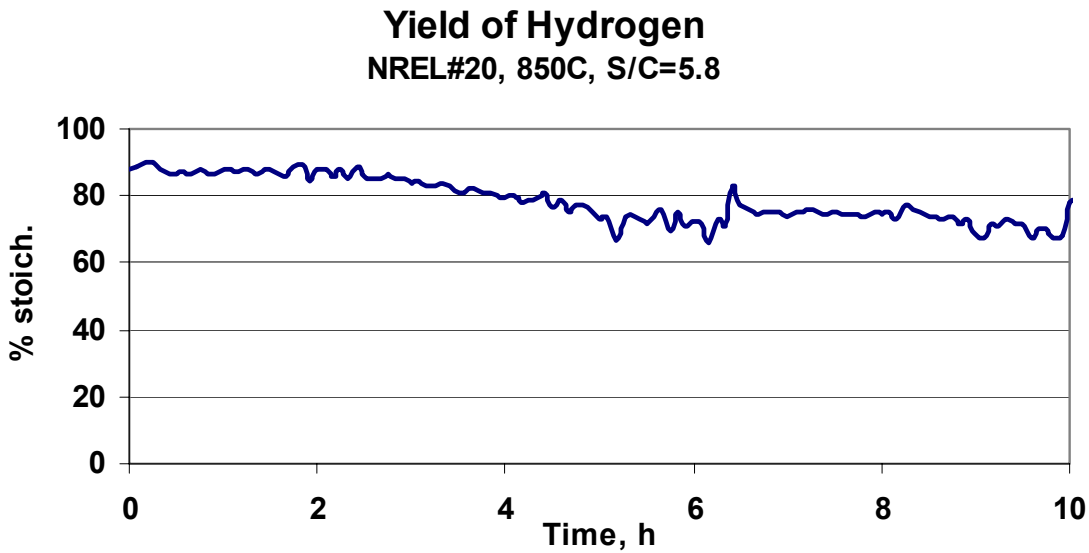
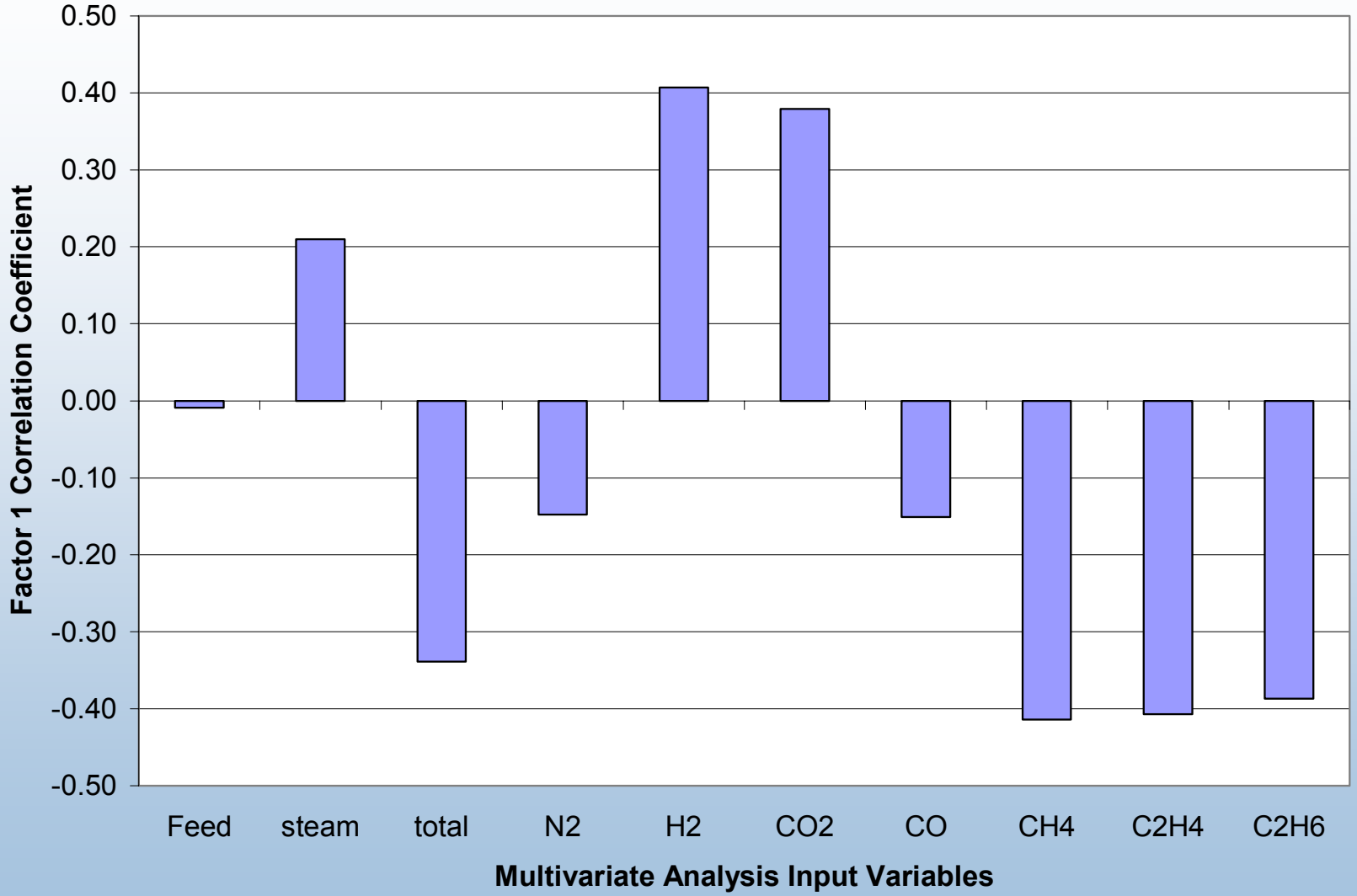




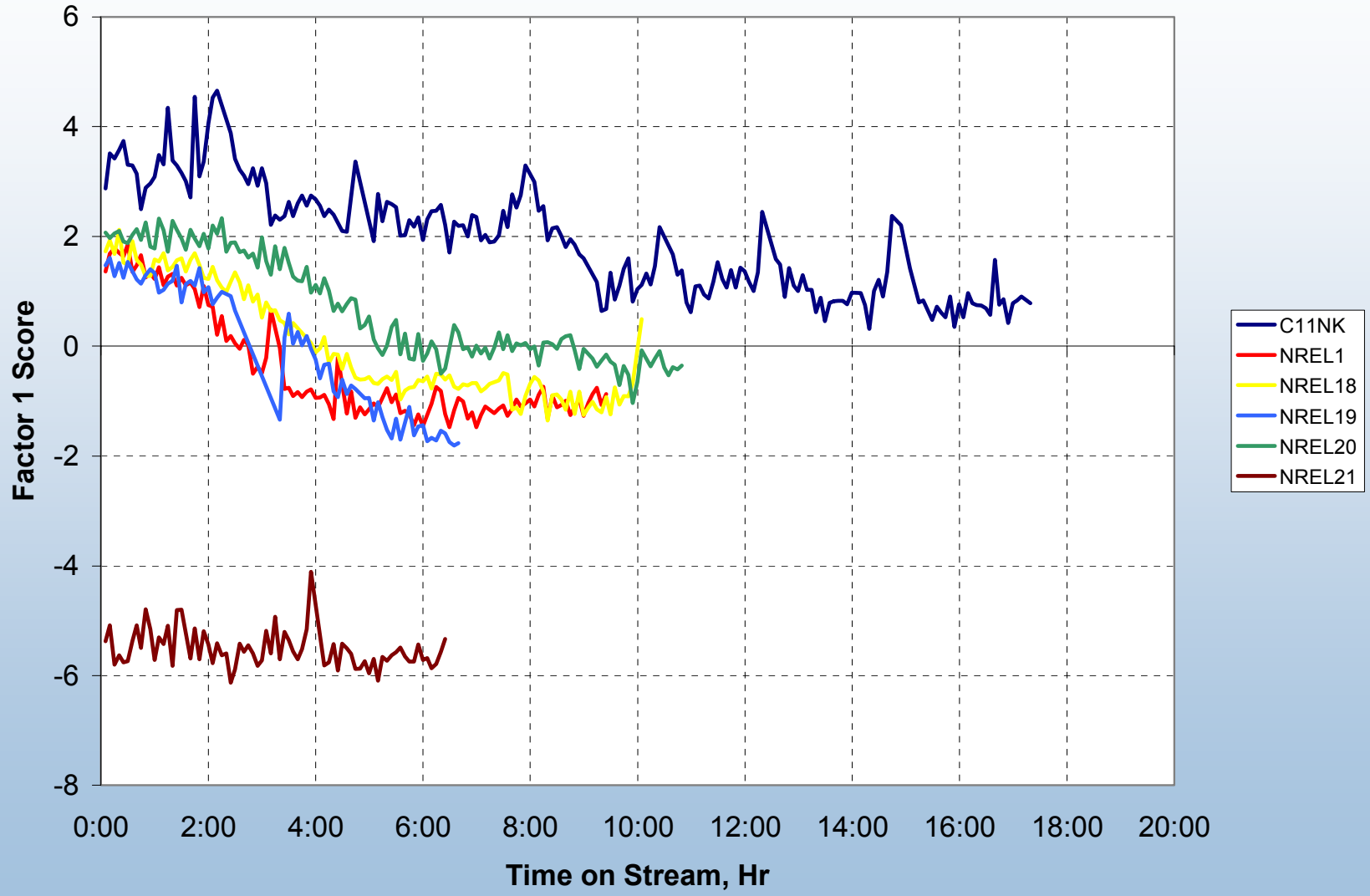
Multivariate Data Analysis

- Objective: develop a sensitive metric for catalyst performance to compare experiments
- Factor analysis used to determine correlated behavior among both independent (e.g., conditions) and dependent (e.g., products) variables
- Factor 1 represents 45% of variance in data set
  - 6 experiments = 10 variables x 700 readings

Variable Contributions



Factor Analysis Run Comparison



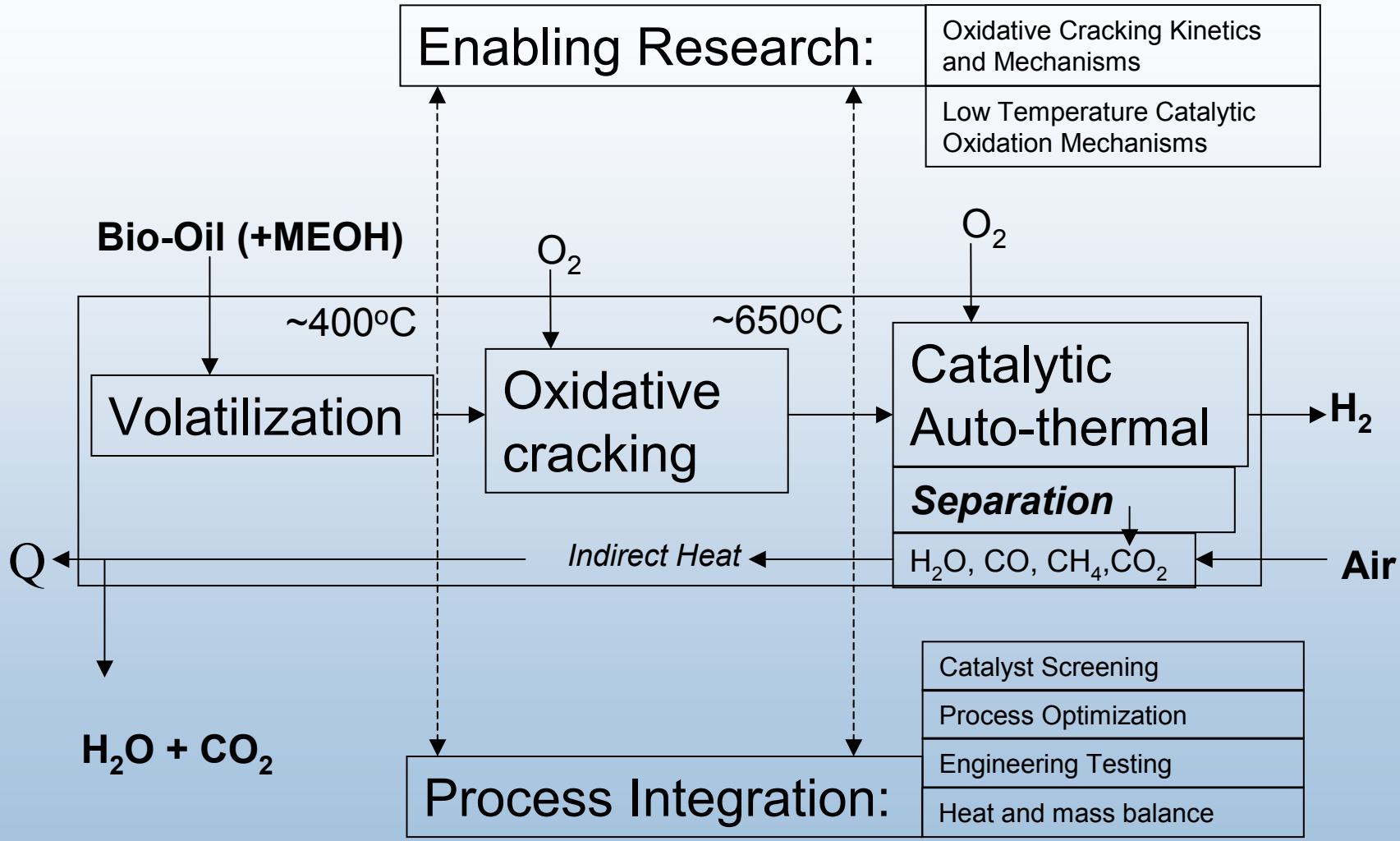
Response to Reviewers Comments

- ***Project should be combined with clearer focus on the program goals.***
  - Efforts combined in FY05. Historical approach based on co-products economics now switched to distributed reforming of bio-oil. New concepts in development to optimize this approach based on low temperature (650 °C) autothermal reforming.
- ***Limited progress made in FY04.***
  - Only limited progress was made in FY04 due to drastic budget cutbacks ($200K in FY04 and $100K in FY05).
  - The conceptual design completed in 2004 is highly relevant to the distributed reforming challenge since it addresses catalyst and heat management in scale up to 250 kg H2/day .

Future Work

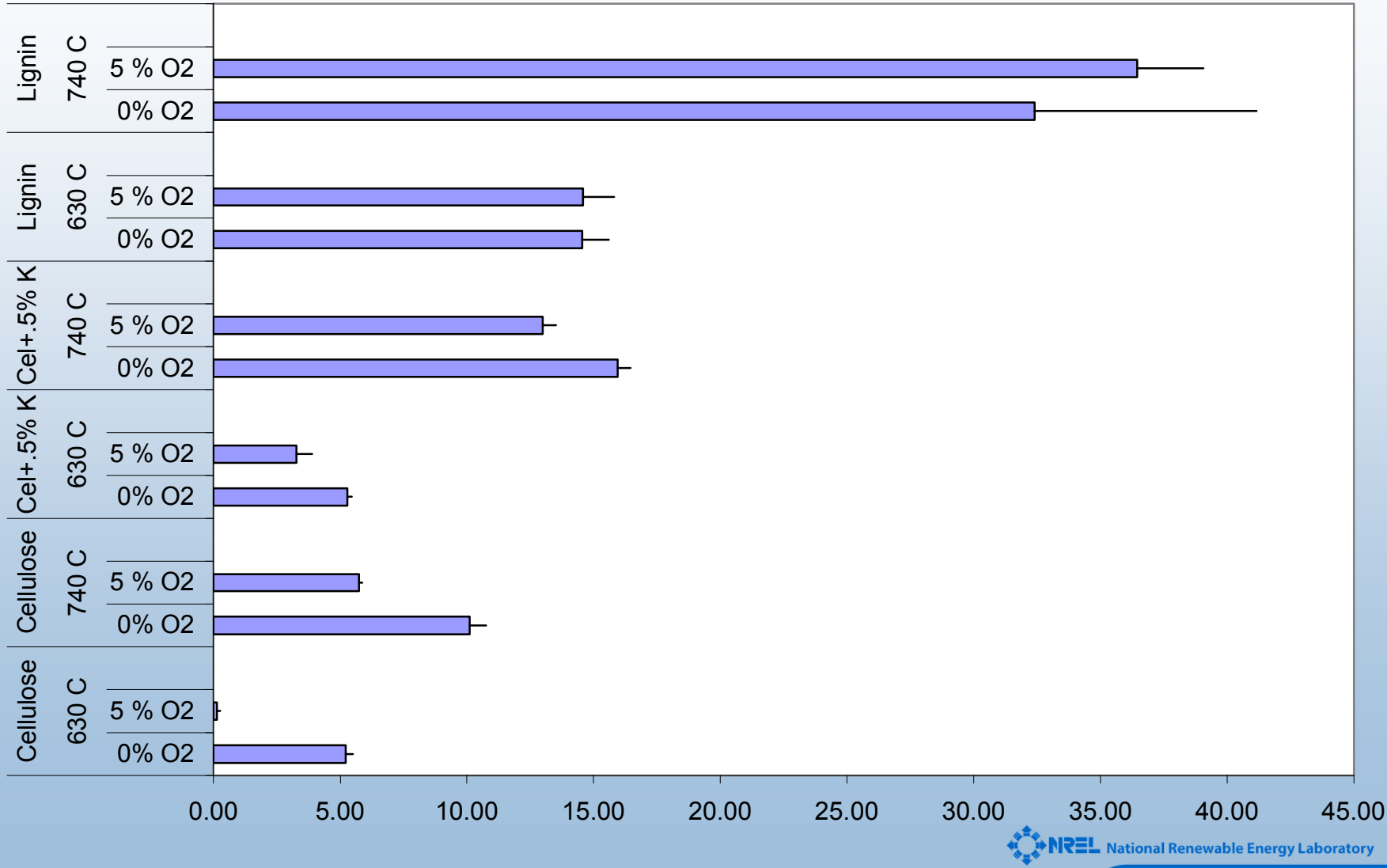
- FY06
  - Develop low-temperature staged autothermal reforming systems based on homogeneous and heterogeneous partial oxidation, appropriate for small-scale automated systems
  - New catalyst development for this new approach with emphasis on deactivation and poisoning
- FY07
  - New reforming process reactor configuration
  - Reaction Engineering
- 2008
  - Bench scale bio-oil reforming tests for long-term testing
- 2009
  - Scale up system development

New Distributed Bio-Oil Reforming Approach



Oxidative Cracking of Pyrolysis Products

M/z 128 = Naphthalene



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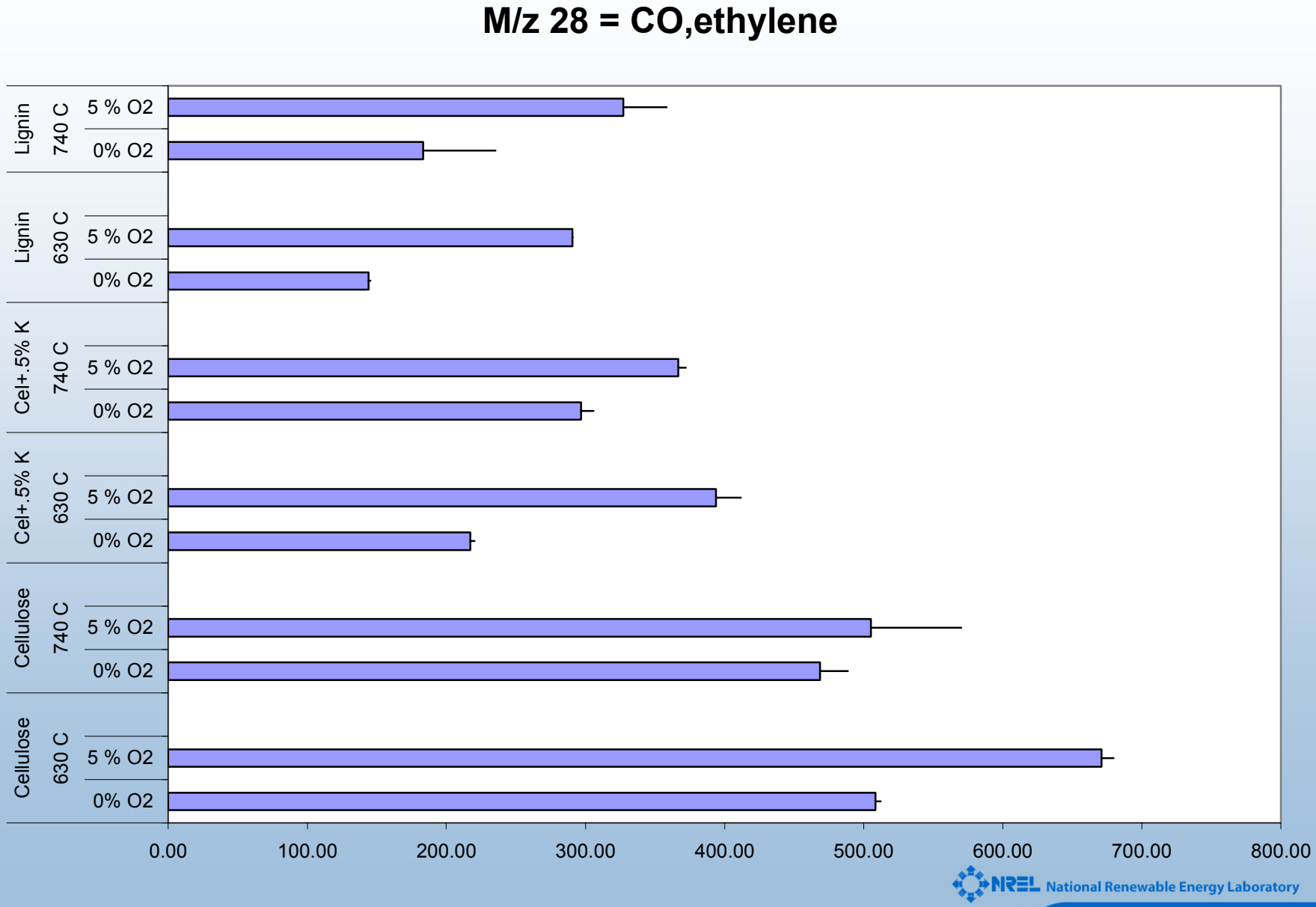
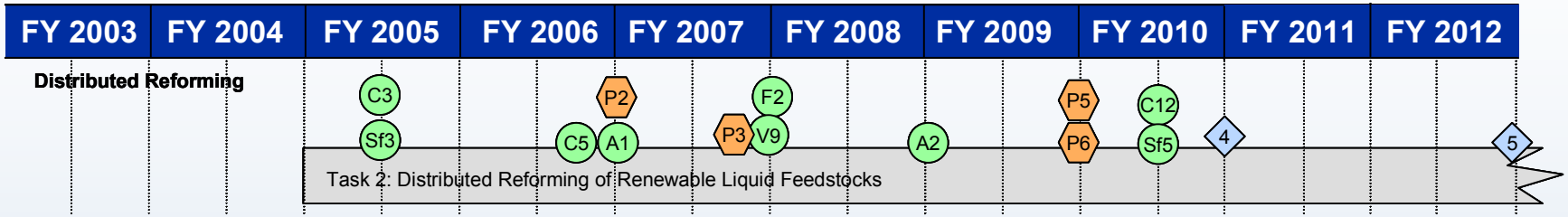


Project Time Line



Milestones

4 Verify feasibility of achieving $3.60/gge for renewable liquids distributed reforming.
5 Down-select research for distributed production from bio-derived renewable liquids.

Outputs

P2 Output to Delivery, Storage and Fuel Cells: Assessment of fuel contaminant composition.
P3 Output to Systems Analysis and Systems Integration: Impact of hydrogen purity on cost and performance.
P5 Output to Systems Analysis and Systems Integration: Impact of hydrogen purity on cost and performance.
P6 Output to Delivery, Storage and Fuel Cells: Assessment of fuel contaminant composition.

Inputs

C3 Input from Codes and Standards: Preliminary Assessment of Safety, Codes and Standards requirements for the hydrogen delivery infrastructure.
Sf3 Input from Safety: Safety requirements and protocols for refueling.
C5 Input from Codes and Standards: Completed hydrogen fuel quality standard as ISO Technical Specification.
A1 Input from Systems Analysis: Complete technoeconomic analysis on production and delivery technologies currently being researched to meet overall Program hydrogen fuel objective.
F2 Input from Fuel Cells: Research results of advanced reformer development.
V9 Input from Technology Validation: Final report on safety and O&M of three refueling stations.
A2 Input from Systems Analysis: Initial recommended hydrogen quality at each point in the system.
C12 Input from Codes and Standards: Final hydrogen fuel quality standard as ISO Standard.
Sf5 Input from Safety: Safety requirements and protocols for refueling.

Safety

- NREL's Thermochemical Users Facility as a Biomass Hydrogen Resource
  - Process Control Development
  - Best Practices Training Opportunities
  - Ten years of Biomass-to-Hydrogen Lab and Engineering Performance Data