Fluidizable Catalysts for Hydrogen Production from Complex Feedstocks

2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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Objectives and Challenges

- Relevance/Objectives
  - Develop and demonstrate technology to produce hydrogen from biomass at $2.90/kg plant gate by 2010. By 2015, be competitive with gasoline.
- Technical Challenges
  - Improve reforming catalysts
    - Accept flexible feedstocks
  - Improve catalyst regeneration
  - Understand deactivation

Budget

- Total FY01-FY04: $530 K
- Total FY04: $70 K
  - Planned: $400,000

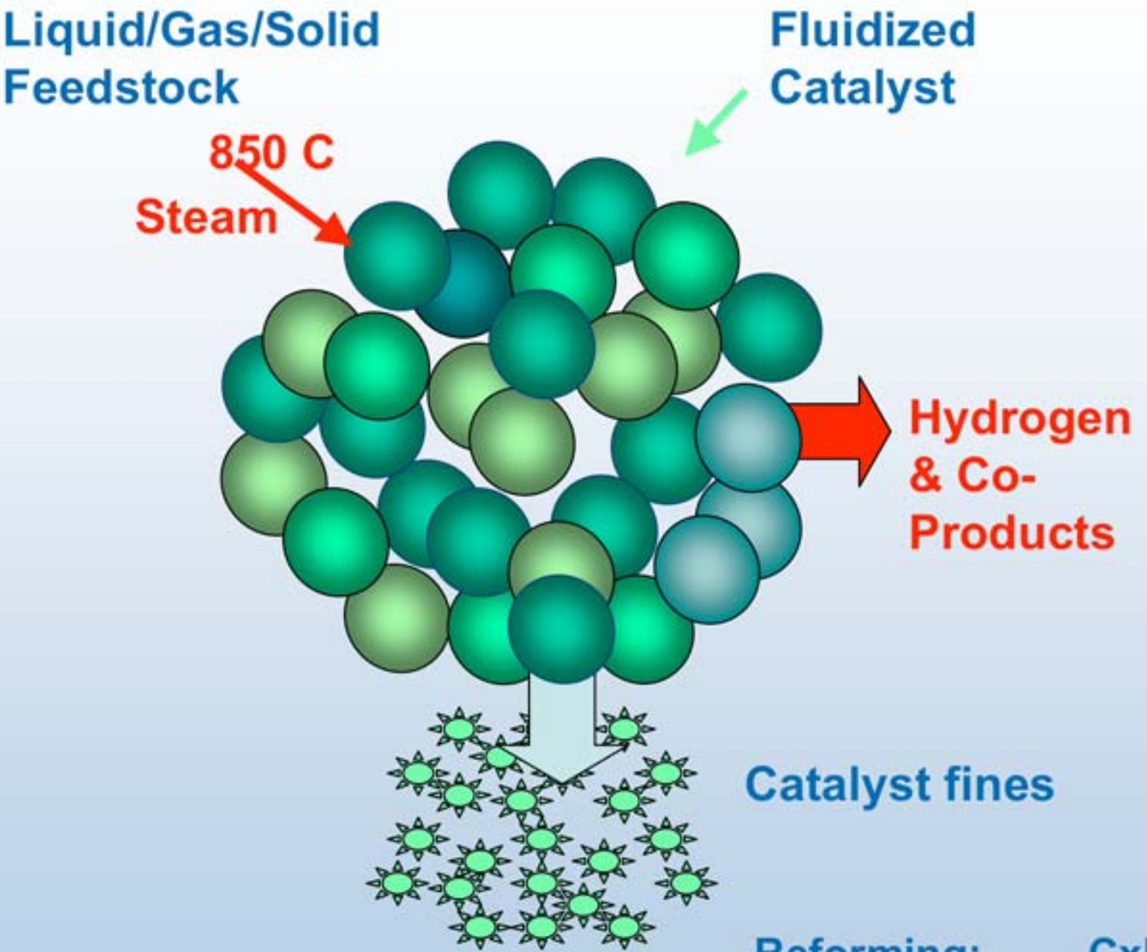
Technical Barriers and Targets

- Technical Barriers
  - C - Feedstock-flexible reformers are needed to mitigate and/or take advantage of price fluctuations and to address location-specific feedstock supply issues
  - G - Efficiency of reforming technologies: improved catalysts
- Technical Targets
  - $2.90/kg of purified hydrogen by 2010

Approach: Drivers and Impacts

- Feedstock complexity requires fluidized catalysts
- Industrial reforming catalysts exist for fixed bed processes. Industrial catalysts attrit when fluidized.
- Catalyst loss from fines causes significant performance, cost, and environmental impacts
- New markets for robust fluidizable catalysts
  - Lower Ni or non-Ni compositions
- New catalysts required for:
  - Flexible feedstock processing
  - Lower reforming temperatures

Problem: Catalyst Attrition



Reforming:	$CxHyOz + H_2O(g)$	$H_2 + xCO$
Water gas shift:	$H_2O + CO$	$CO_2 + H_2$
Gasification:	$C + H_2O(g)$	$COx + H_2$

Economic Impact of Catalyst Attrition

Catalyst	Wt. in Reactor (g)	Wt. out Reactor (g)	% Loss per hr	Loss Cost $/hr[2]
Best of the Industrial Catalysts				
Commercial Ni Cat. 1 (Sud Chemie C 11 NK)	292.7	208.7	0.6	19.20
Commercial Ni Cat. 2 (ICI 46-1 S)	250.2	167.1	0.7	22.40
Best ofthe Industrial Supports Tested				
90% Alumina	251.4	248.8	0.01	0.03
99% Alumina	298.9	299.6	0.0	0.00
NREL Catalysts				
Ni-Mg/90% Alumina[1]	250.1	250.1	0.005	0.015

Due to Catalyst Attrition

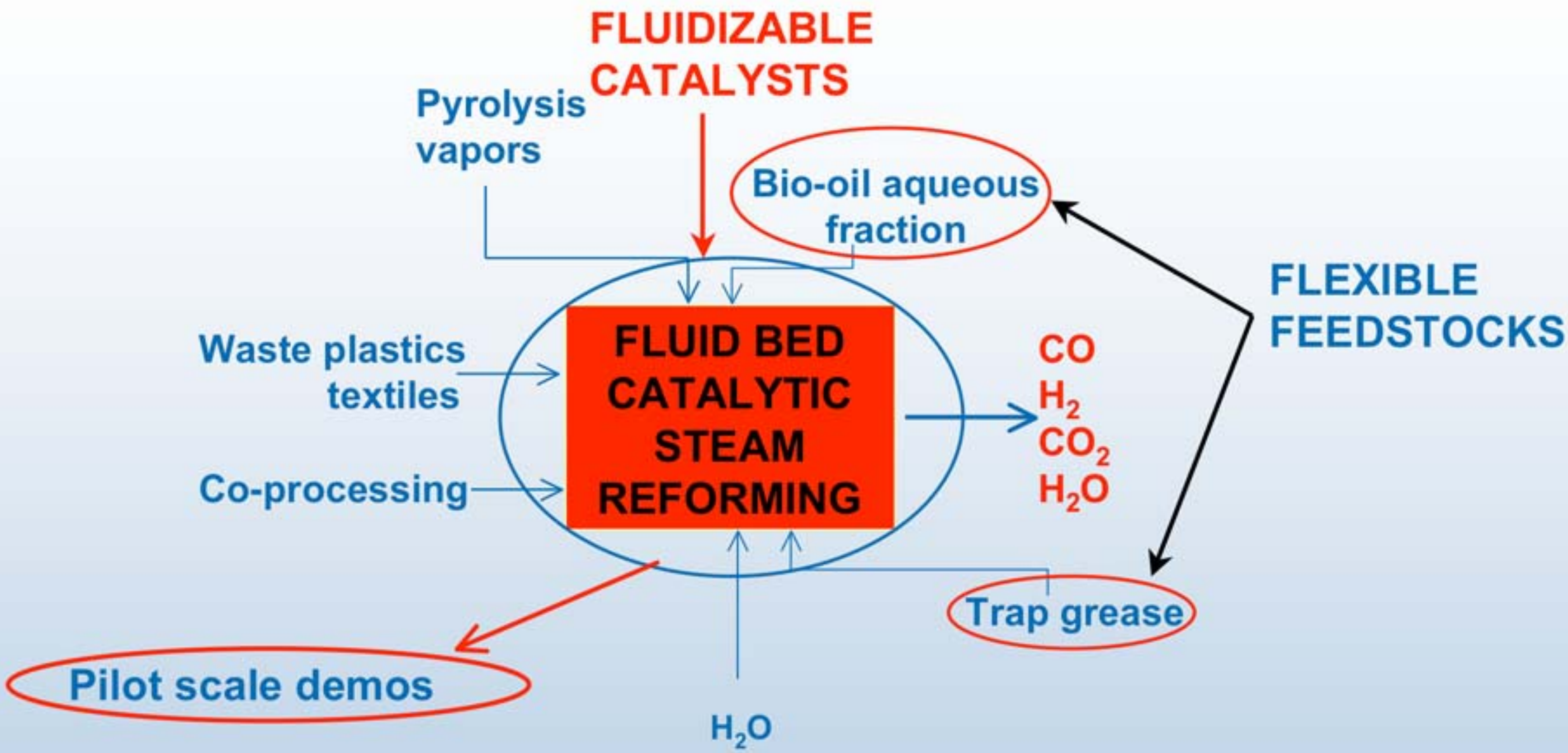
1 with Ni after methanol reforming

2 NREL and industrial catalyst costs are the same $32.00/lb. Cost per day calculated from amount of catalyst lost from reactor per hour of use.

Approach/Fluidizable Catalysts

- Identify/test best industrial reforming catalysts (naptha)
- Identify/test "*off the shelf*" particulate aluminas for use as catalyst supports in fluidized bed reactors
- Formulate, evaluate and optimize *multifunctional, multicomponent* catalysts mad from these supports
- Evaluate renewable feedstocks reactors

Process Concept



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

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

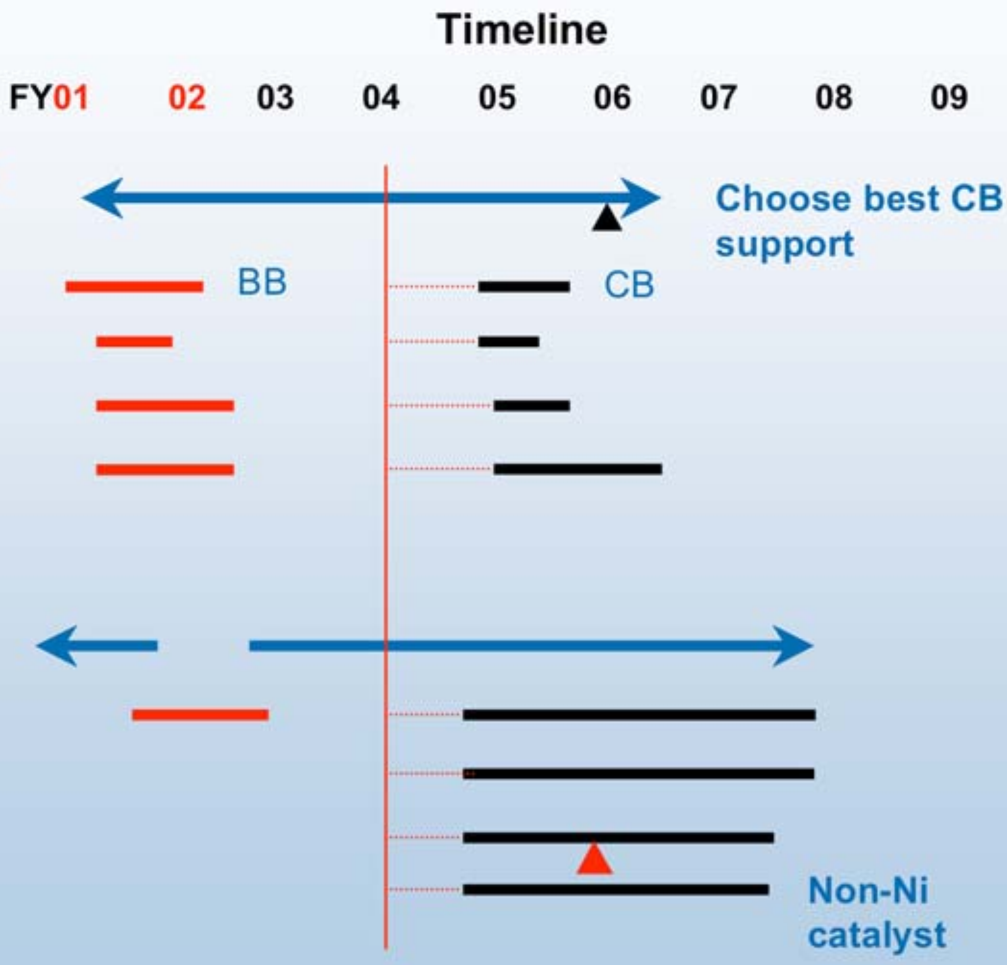
Gasification: $C + H_2O(g) \longrightarrow CO_x + H_2$

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)
  - All catalyst preparation and calcination is performed in fume hoods; catalyst is disposed of per hazardous waste guidelines.
- 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.

Project Timeline

Fluidizable Catalyst Development

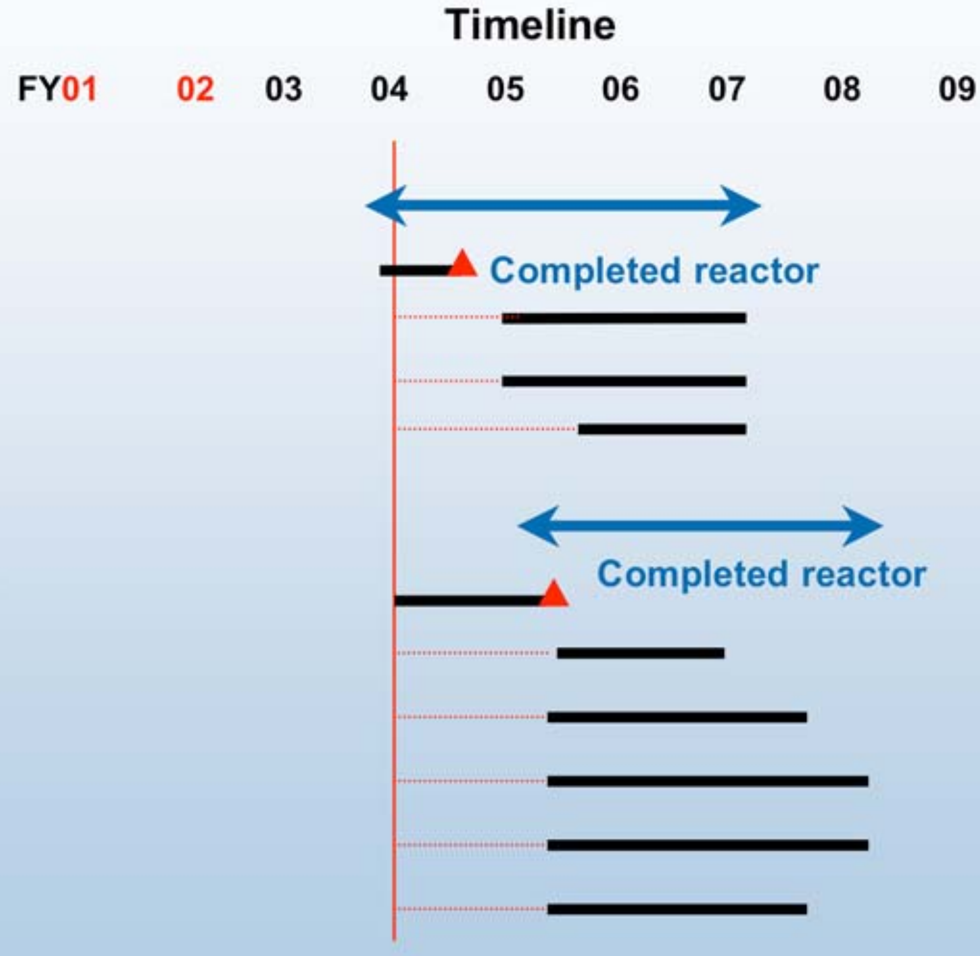


Fluidizable Supports (bubbling bed-BB, circulating bed-CB)
- -Identify industrial materials
- -Assess attrition rate
- -Characterize properties
- -Improve/modify support preparations (CoorsTek)

Catalyst Development
- -Develop/optimize BB/CB catalysts
- -Characterize catalysts
- -Develop lower temperature catalysts
- -Assess non-Ni catalysts

Project Timeline (cont.)

Fluidizable Catalyst Development



Rapid Screen Microreactor
- Design/modify existing system
- Choose/make catalyst compositions
- Screen catalysts
- Optimize compositions

Kinetics/Deactivation Mechanisms
- Add pyrolysis microreactor capability
- Coking and gasification
- Water gas shift
- Reforming
- Deactivation (S, Cl)
- Reactivation

Project Timeline (cont.)

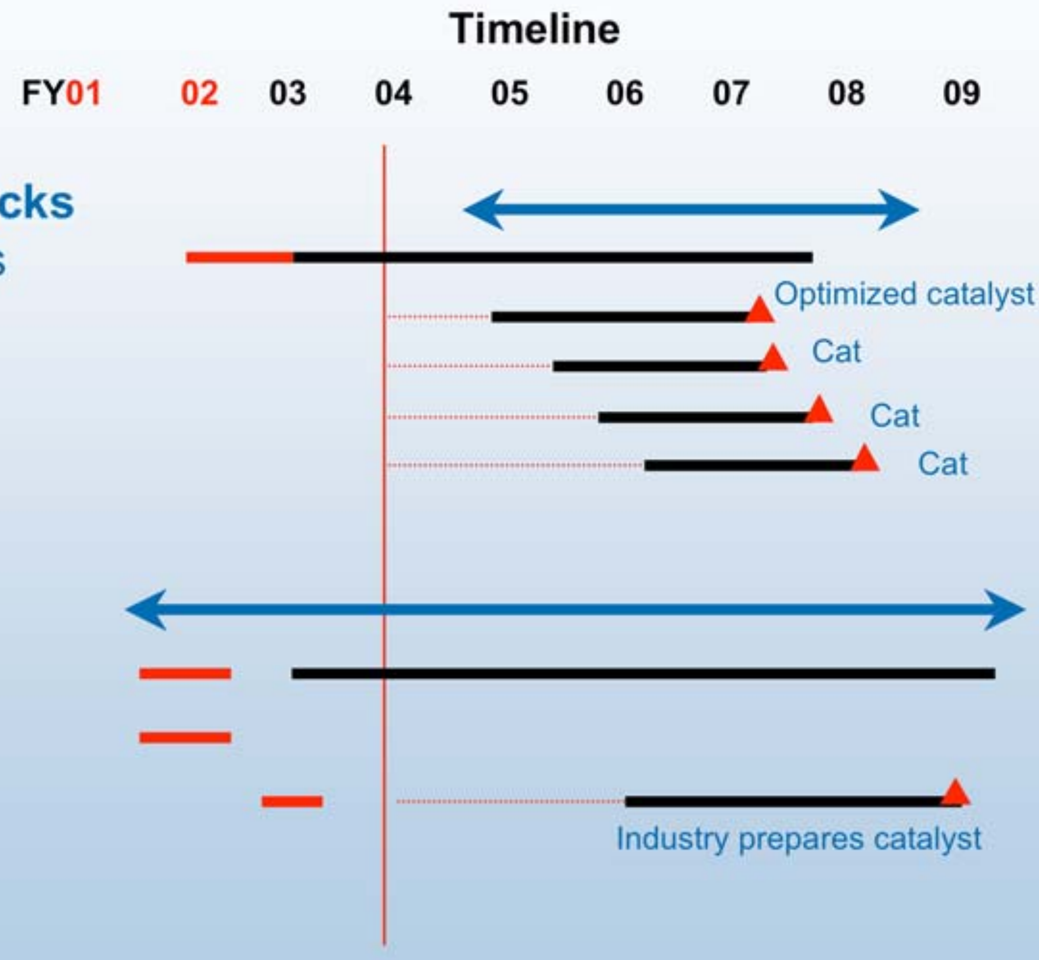
Fluidizable Catalyst Development

Catalyst Design for Varied Feedstocks

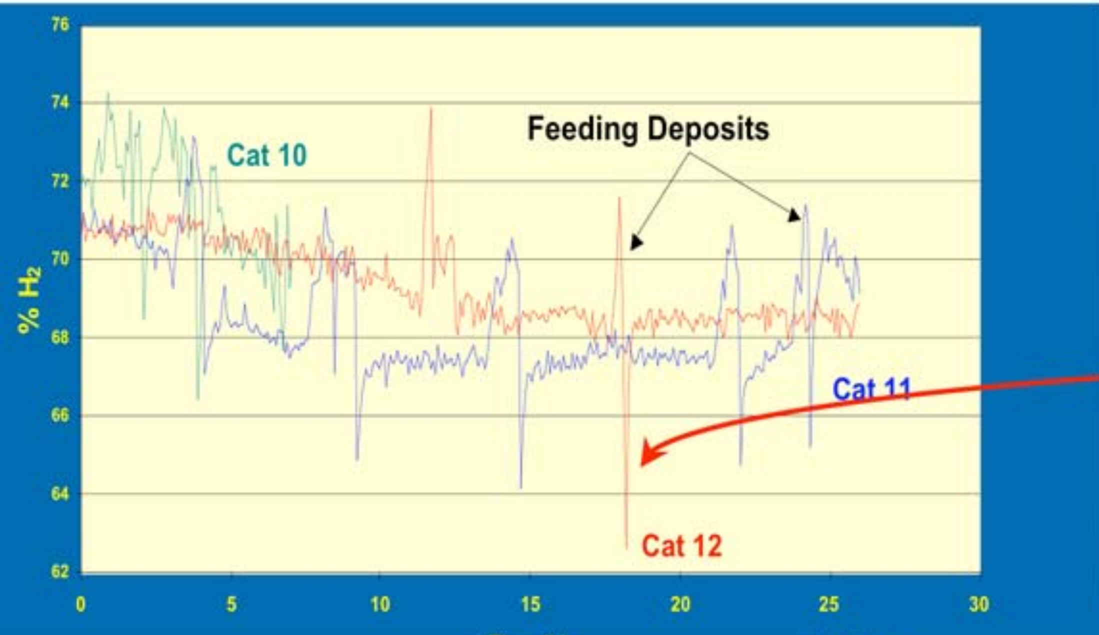
-Pyrolyzed biomass liquids and vapors
-Waste grease (S)
-Waste plastics (Cl)
-Waste textiles
-Co-processing

Industrial Collaborations

-CoorsTek Ceramics/Carboceramics
-Sud Chemie
-Industry/catalyst scale-up



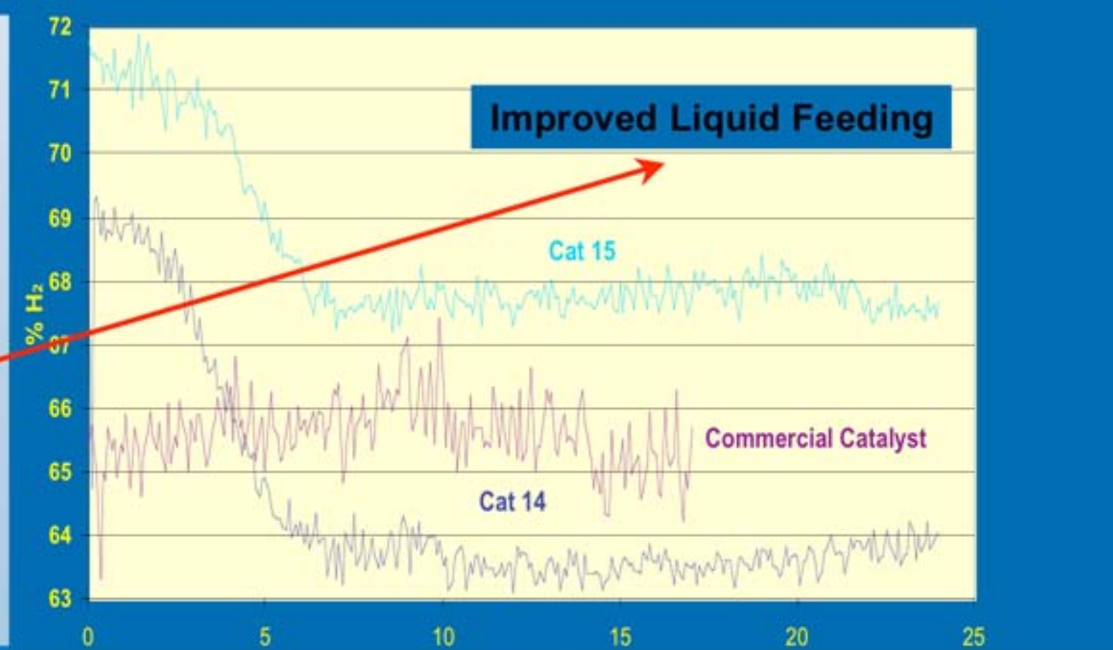
Progress FY03 Catalyst Improvement: K_2O Improves Gasification



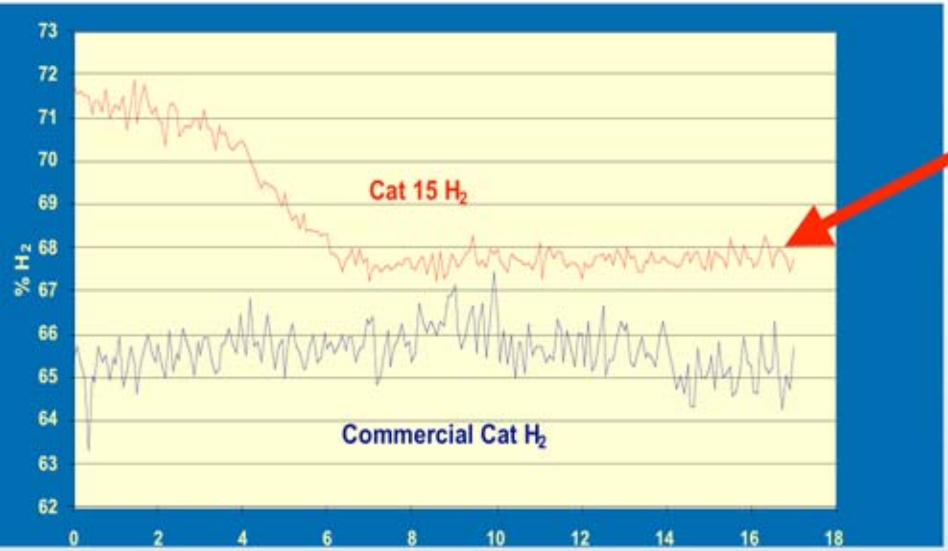
Milestone: Improve catalyst gasification performance for pyrolysis liquid reforming

CATALYST	Wt % NiO	Wt % MgO	Wt % K_2O
CAT 10	2.0	0.2	0.07
CAT 11	2.0	1.0	0.08
CAT 12	4.0	2.0	0.09

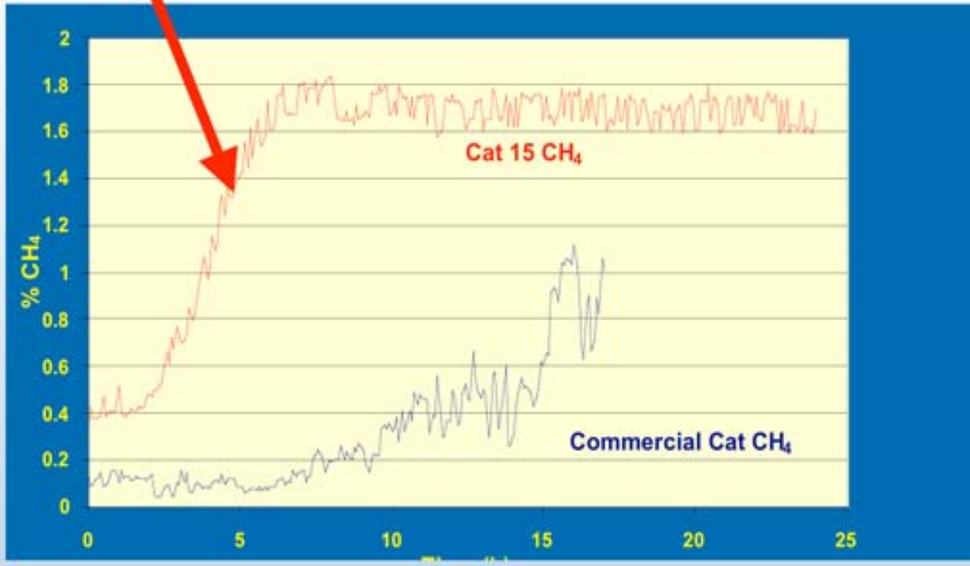
CATALYST	Wt % NO	Wt % MgO	Wt % K_2O
C 11 NK	19.0	5.0	8.0
CAT 14	2.0	0.2	0.4
CAT 15	3.5	0.4	0.7

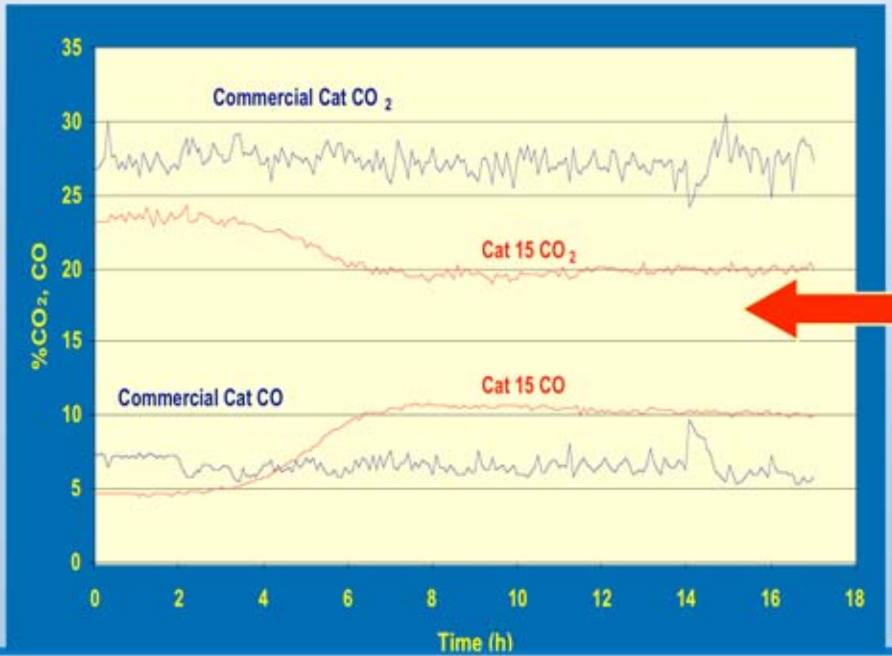


Progress FY03 Catalyst Improvement: (NREL vs. Commercial)



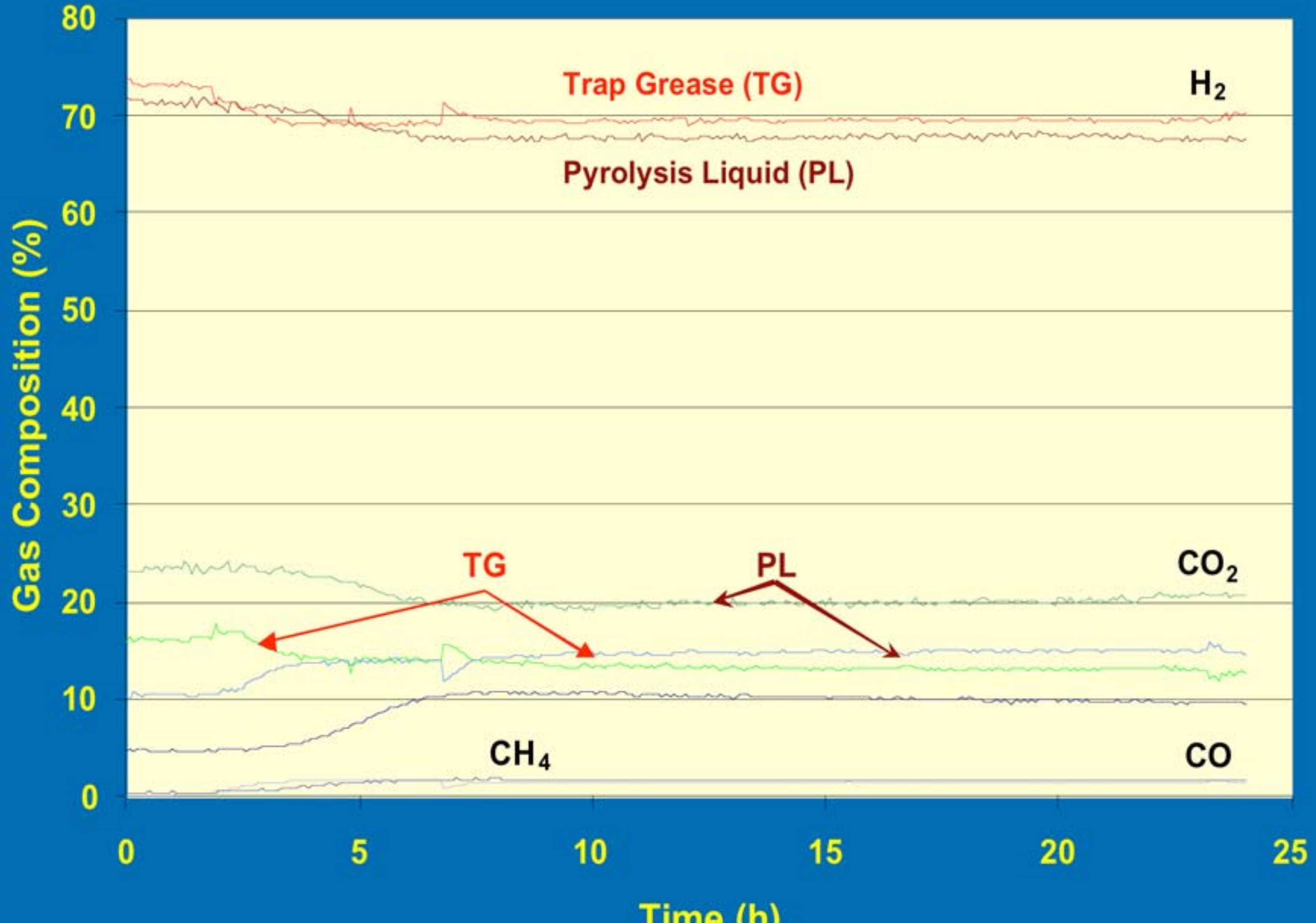
More hydrogen and methane
Need to reduce methane



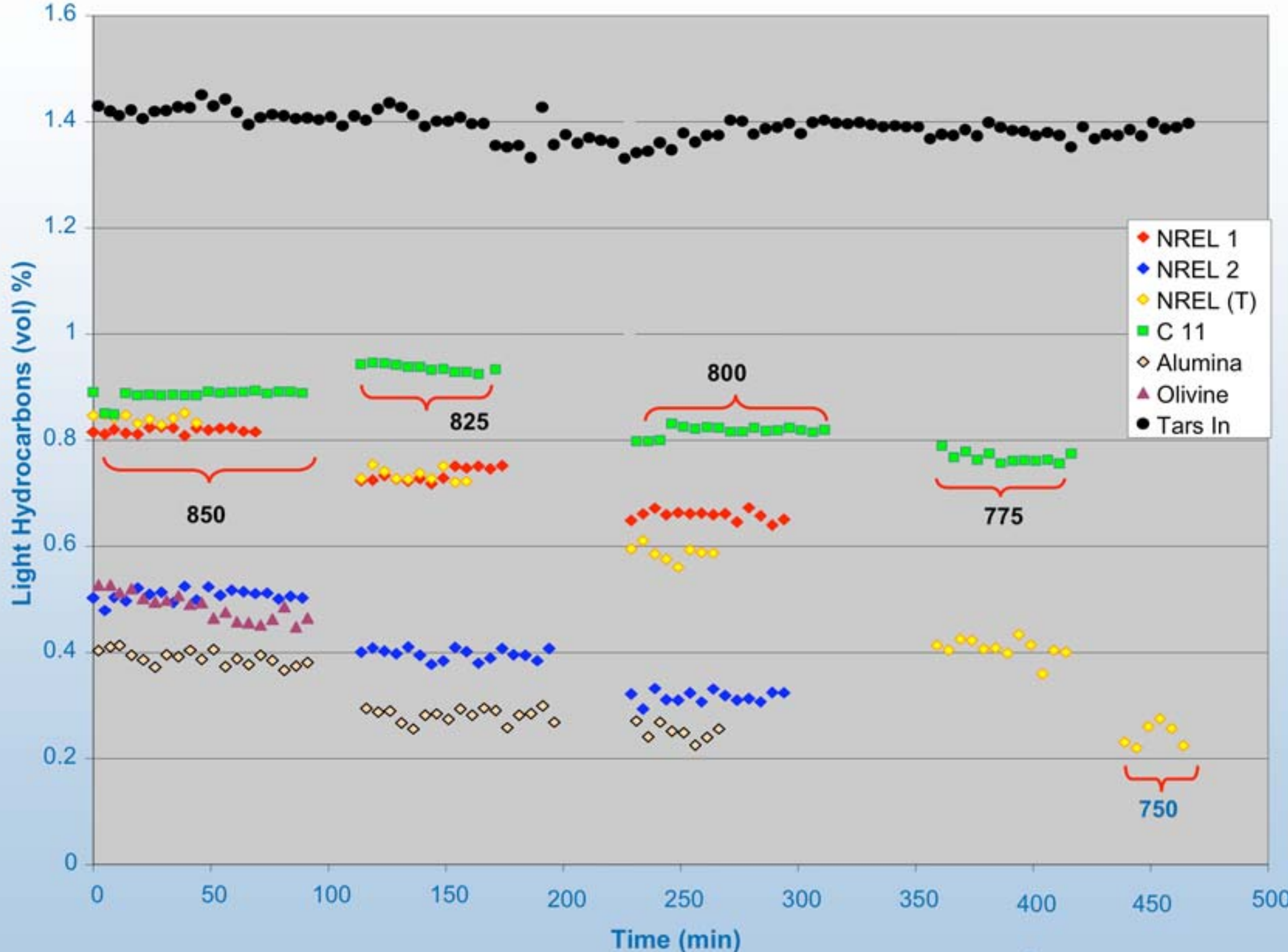


More CO_2, less CO
Need to improve WGS

Progress FY03: Comparing Feedstocks



Pyrolysis FY04 Vapor Tar Cracking - Gas Upgrading



Accomplishments/Progress

- FY03
  - Developed novel fluidizable reforming catalysts with CoorsTek Ceramics
  - Evaluated performance of 16 catalysts for 24 hrs with pyrolysis oil-derived feedstocks
  - Improved reforming activity (compared to commercial catalyst)
  - Prepared a 100 lb batch of catalyst for the GA demonstration project
  - Evaluated best catalysts with gasified biomass vapors and grease
- FY04
  - Prepared five new catalyst formulations for testing
  - Pursuing NREL patent on fluidizable catalysts
  - Awarded GPE funds for a micro-activity test system to improve catalyst screening
  - Completing 2nd catalyst screening reactor for liquid feedstocks

Interactions and Collaborations

- CoorsTek Ceramics
  - Developing Fluidizable Supports
- Sud Chemie and NCAR
  - Reforming Catalyst Compositions
- UOP
  - Alumina Supports
- Journal Article
- Patent Application
- Request for License (Enerkem)

Plans/Future Milestones

- Improve catalyst gasification and WGS activity
  - Understand coking mechanisms
- Evaluate different feedstocks (pyrolysis vapors, bio- and fossil-based liquids, waste grease, plastics, natural gas)
  - Understand deactivation mechanisms (S, Cl)
  - Develop poison tolerant catalysts per feedstock
- Prepare/evaluate non-nickel catalysts
- Evaluate new CoorsTek supports (Zr/Al_2O_3) for circulating/bubbling reactors
- Modify/use rapid catalyst screening reactor
- Expand industrial participation in support/catalyst development

Responses to FY03 Review

- Need to involve industrial catalyst suppliers for developing lower temperature reforming catalysts
  - We are in discussions with UOP, WR Grace and Sud Chemie to test their supports/catalysts in our systems
- Need to increase catalyst screening and understand deactivation
  - We have a MATS unit ordered for catalyst screening and are building a high throughput reactor for deactivation studies.

Challenges

- Real, complex feedstocks
- On-line comprehensive analysis
- Novel fluidizable catalysts
- Long term testing (>200 h)