Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming

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NREL

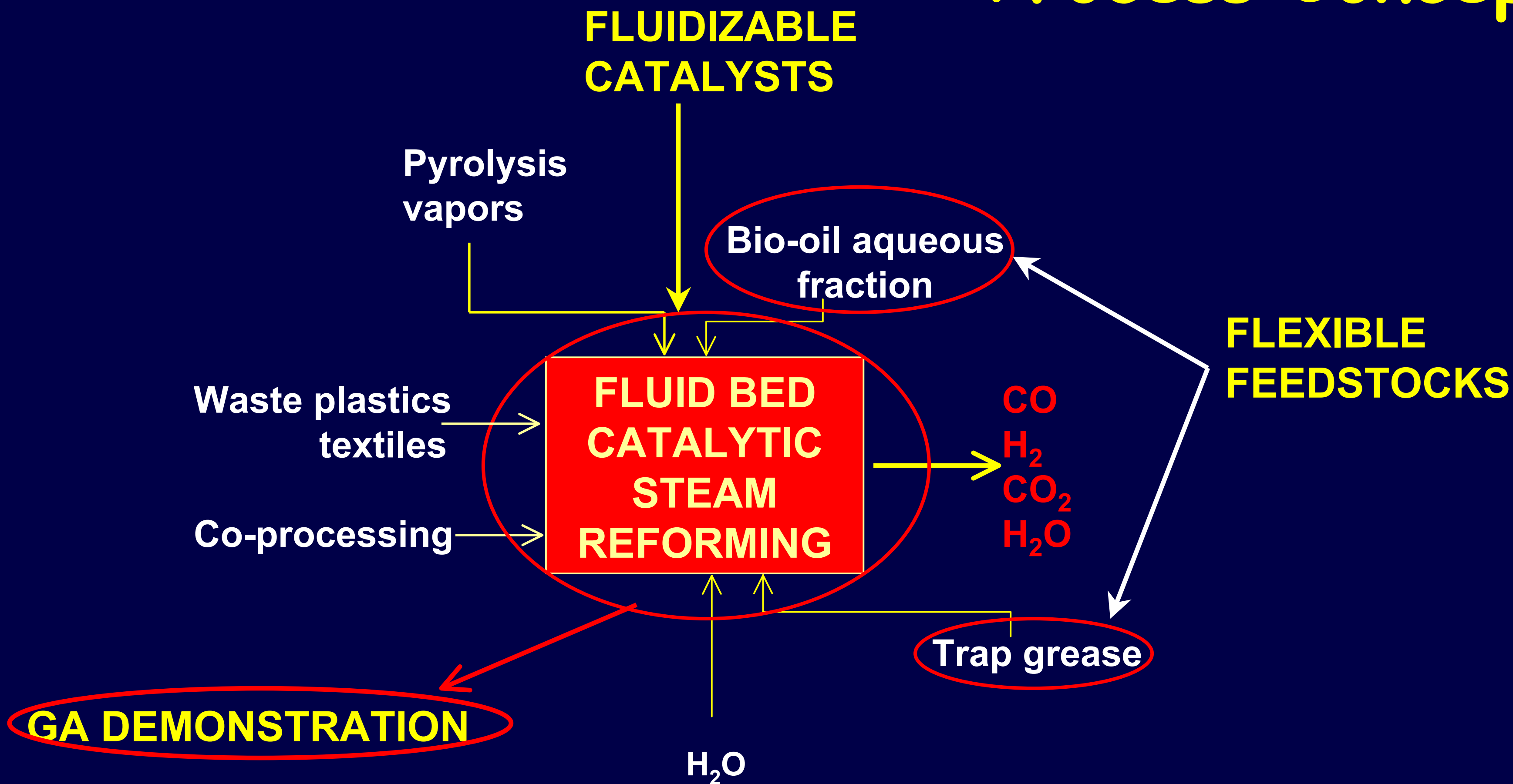
Relevance/Objective

Develop and demonstrate technology to produce hydrogen from biomass at $2.90/kg plant gate price based on 750 t/day by 2010. By 2015: be competitive with gasoline.

Technical Challenges

- Improve reforming catalysts
  - Accept flexible feedstocks
- Improve catalyst regeneration

Process Concept

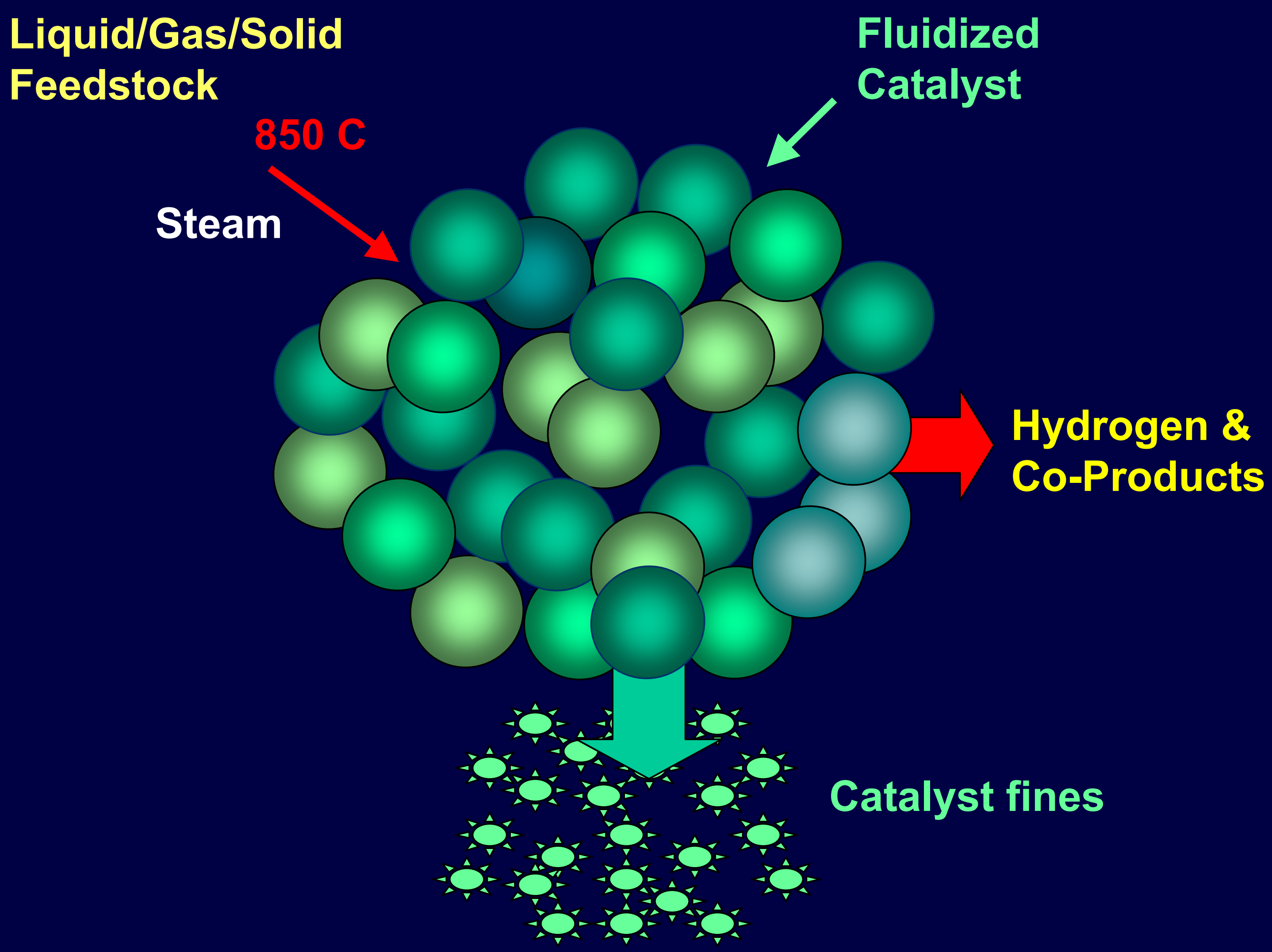


Reforming: $CxHyOz + H_2O(g) \rightarrow H_2 + xCO$

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

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

Problem: Catalyst Attrition

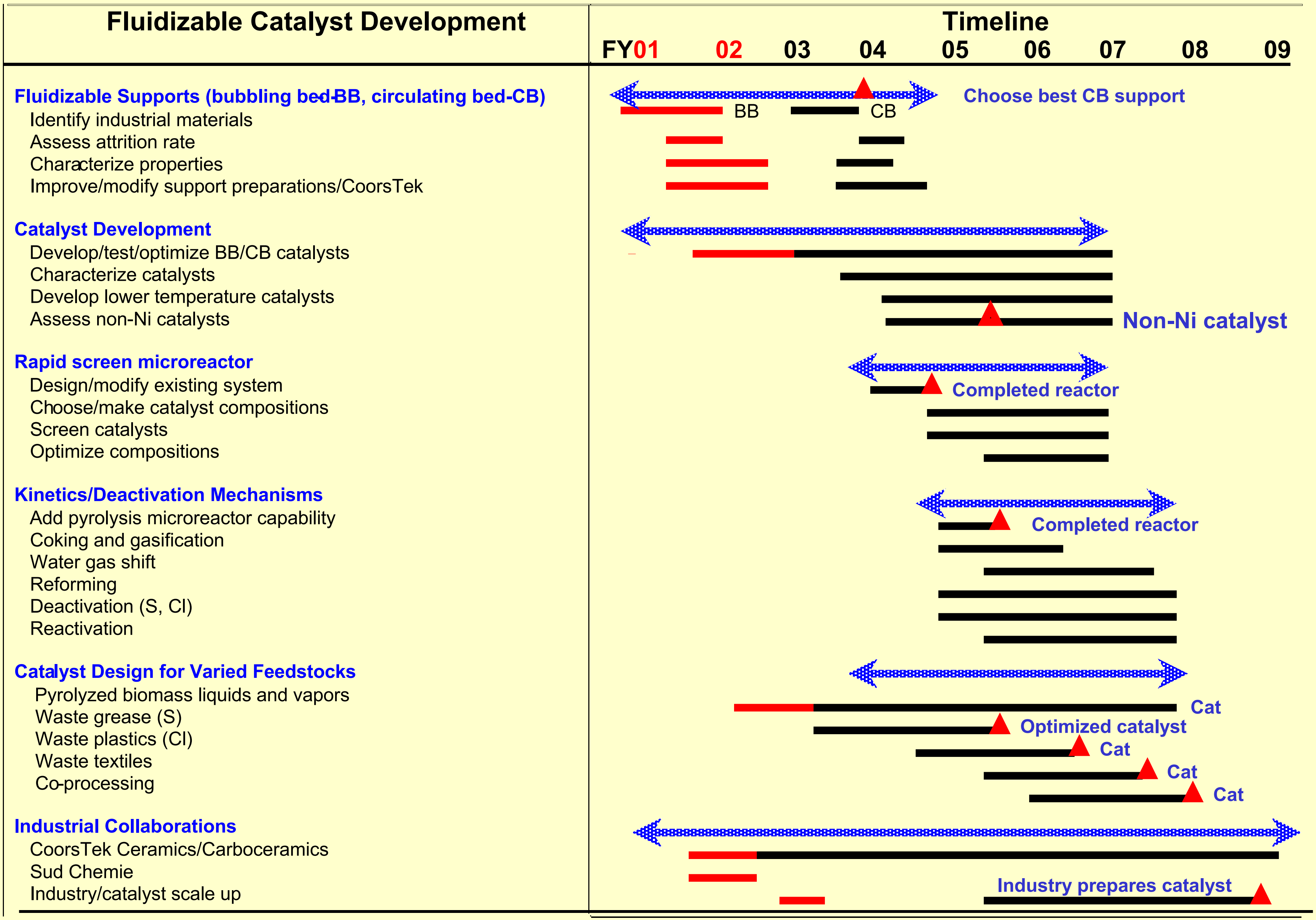


Approach: Drivers and Impacts

- 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

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 made from these supports
- Evaluate renewable feedstocks


Fluidizable Catalyst Development
Timeline
FY01 02 03 04 05 06 07 08 09
Fluidizable Supports (bubbling bed-BB, circulating bed-CB)
Identify industrial materials
Assess attrition rate
Characterize properties
Improve/modify support preparations/CoorsTek
BB
CB
Choose best CB support
Catalyst Development
Develop/test/optimize BB/CB catalysts
Characterize catalysts
Develop lower temperature catalysts
Assess non-Ni catalysts
Non-Ni catalyst
Rapid screen microreactor
Design/modify existing system
Choose/make catalyst compositions
Screen catalysts
Optimize compositions
Completed reactor
Kinetics/Deactivation Mechanisms
Add pyrolysis microreactor capability
Coking and gasification
Water gas shift
Reforming
Deactivation (S, Cl)
Reactivation
Completed reactor
Catalyst Design for Varied Feedstocks
Pyrolyzed biomass liquids and vapors
Waste grease (S)
Waste plastics (Cl)
Waste textiles
Co-processing
Cat
Optimized catalyst
Cat
Cat
Cat
Industrial Collaborations
CoorsTek Ceramics/Carboceramics
Sud Chemie
Industry/catalyst scale up
Industry prepares catalyst

Economic Impact of Catalyst Attrition

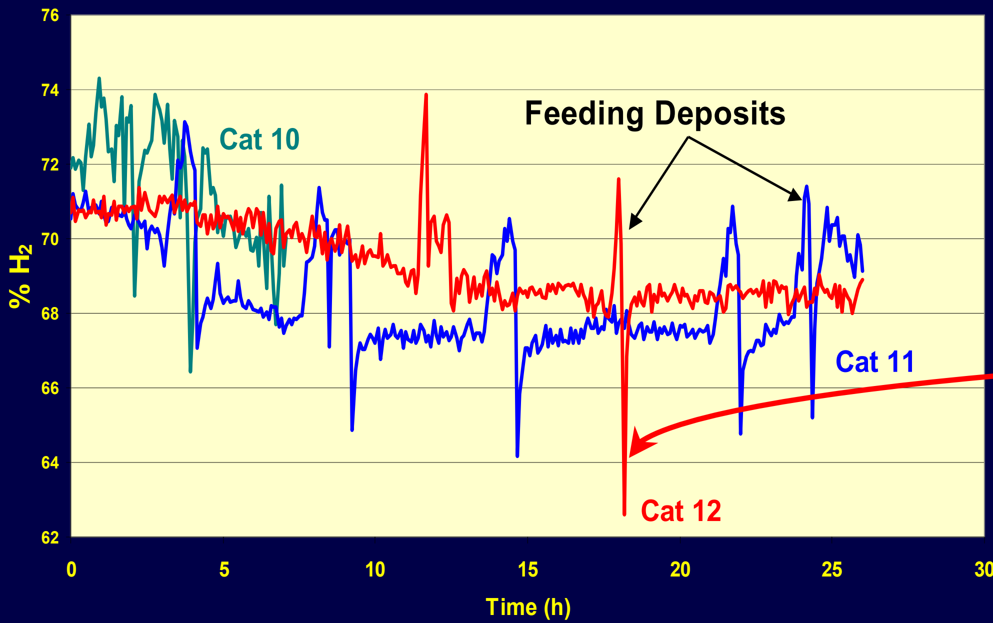
Catalyst	Wt. in Reactor (g)	Wt. out Reactor (g)	% Loss per hr	Loss Cost $/hr[2]
Best of the Industrial Catalysts				
Commercial Ni Cat. 1 (Sud Chemie C 11 NK)	292.7	208.7	0.6	19.20
Commercial Ni Cat. 2 (ICI 46-1 S)	250.2	167.1	0.7	22.40
Best of the Industrial Supports Tested				
90% Alumina	251.4	248.8	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

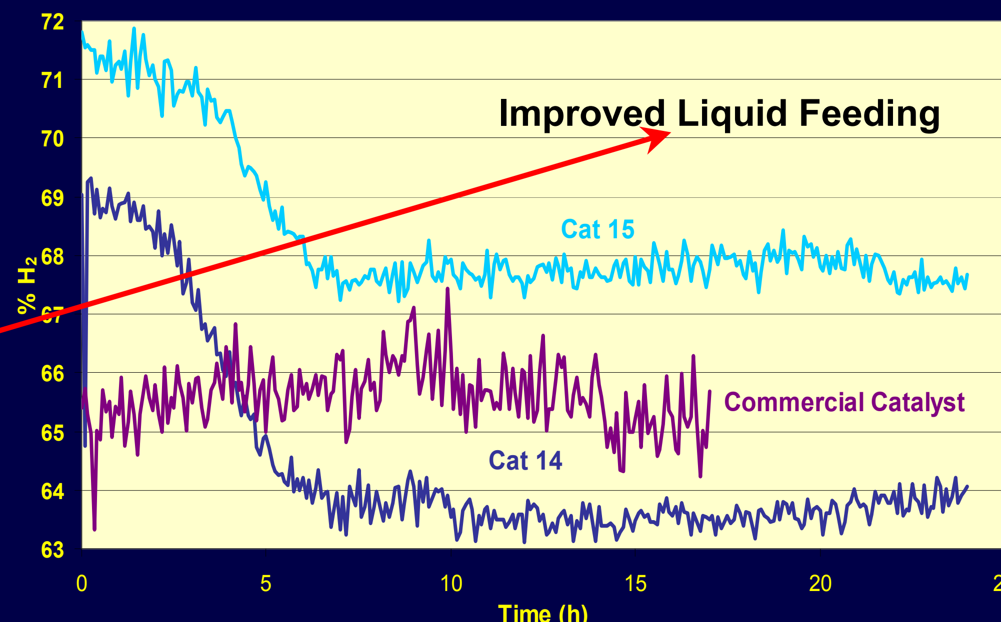
2 NREL and industrial catalyst costs are the same $32.00/lb. Cost per day calculated from amount of catalyst lost from reactor per hour of use.

Catalyst Improvements: K_2O Improves Gasification



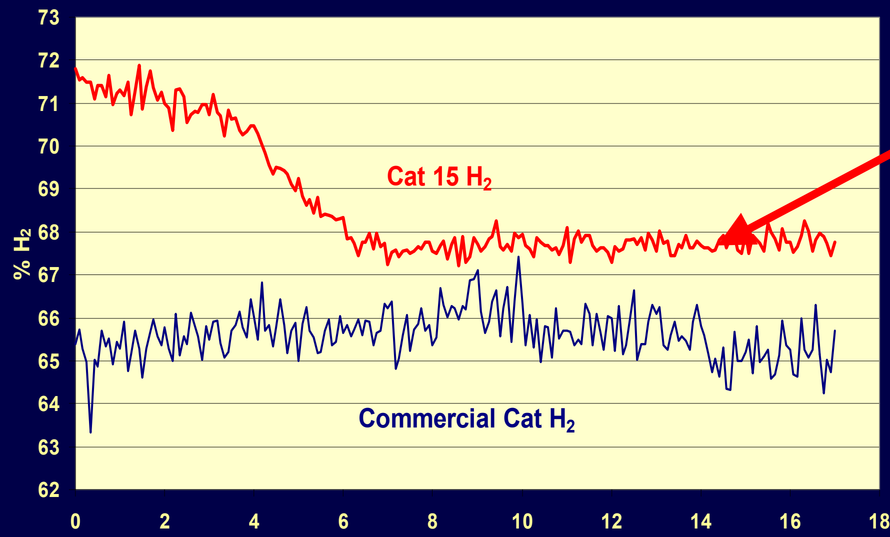
CATALYST	Wt % NiO	Wt % MgO	Wt % K_2O
CAT 10	2.0	0.2	0.07
CAT 11	2.0	1.0	0.08
CAT 12	4.0	2.0	0.09

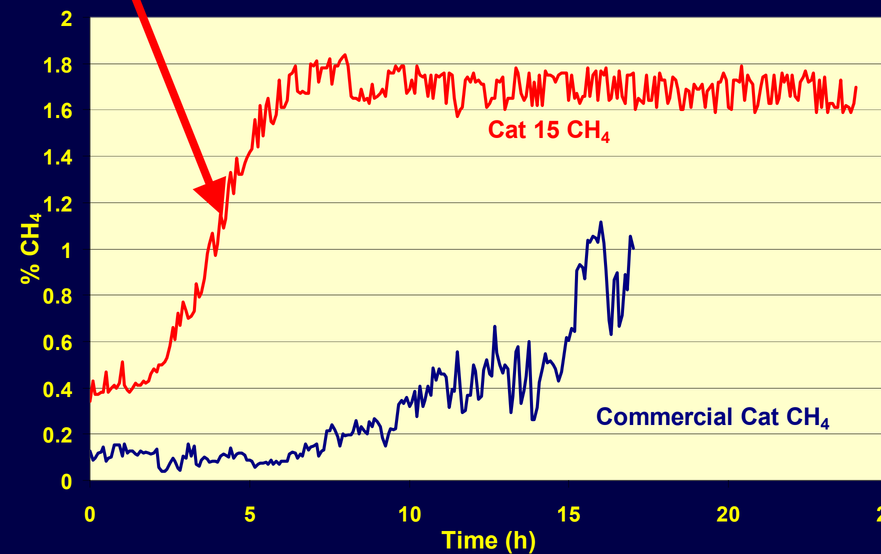
Milestone: Improve catalyst gasification performance for pyrolysis liquid reforming



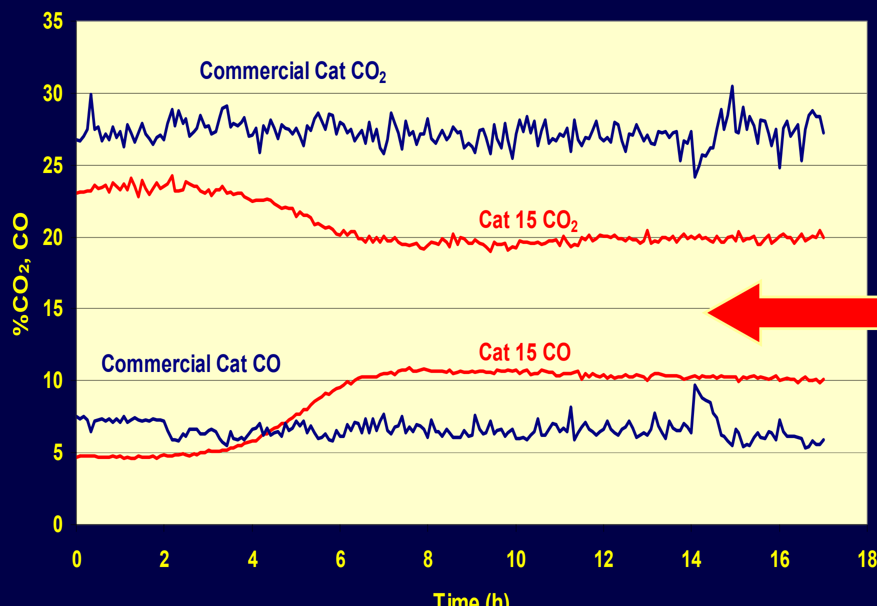
CATALYST	Wt % NiO	Wt % MgO	Wt % K_2O
C 11 NK	19.0	5.0	8.0
CAT 14	2.0	0.2	0.4
CAT 15	3.5	0.4	0.7

Catalyst Improvements (NREL vs. Commercial C 11)



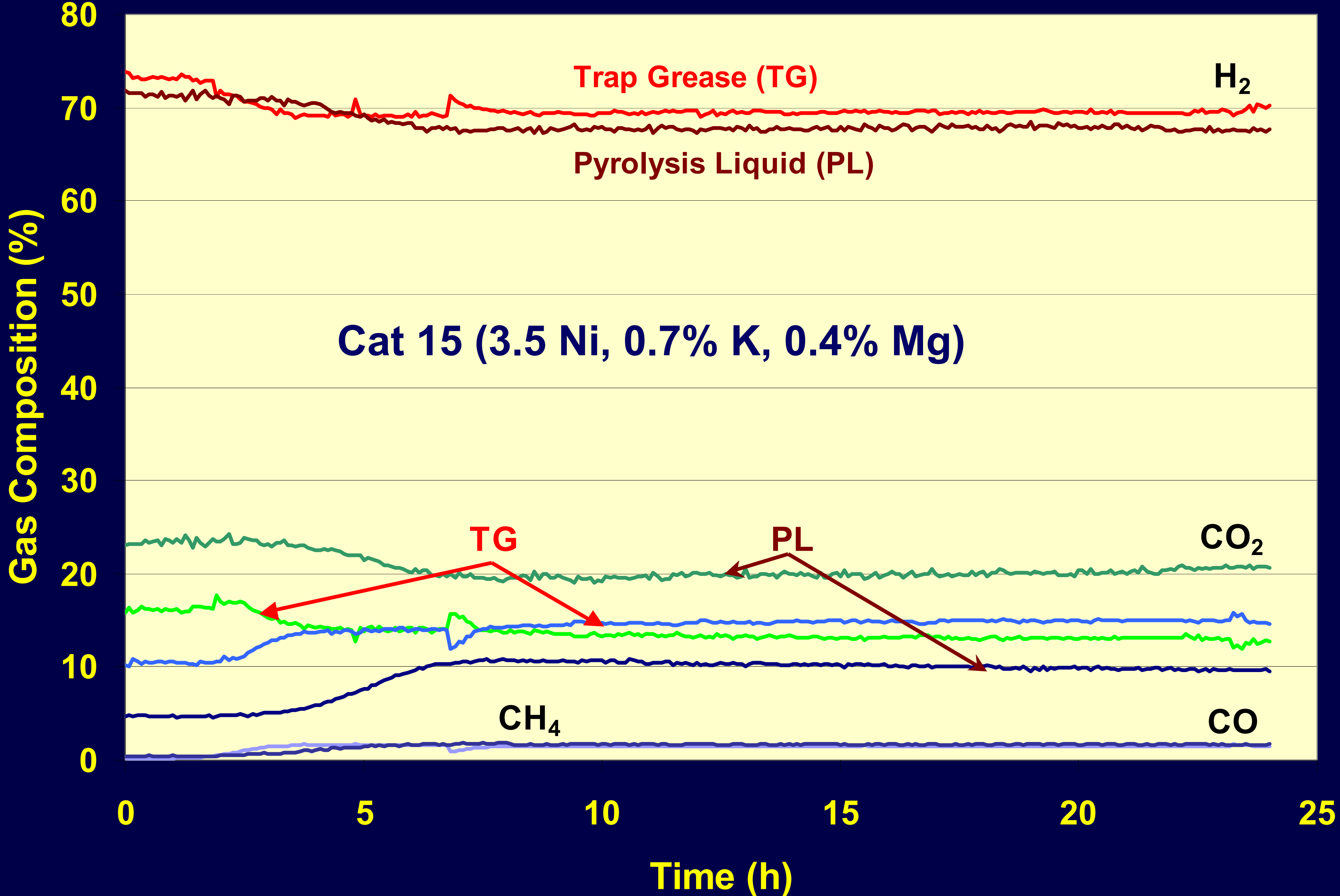


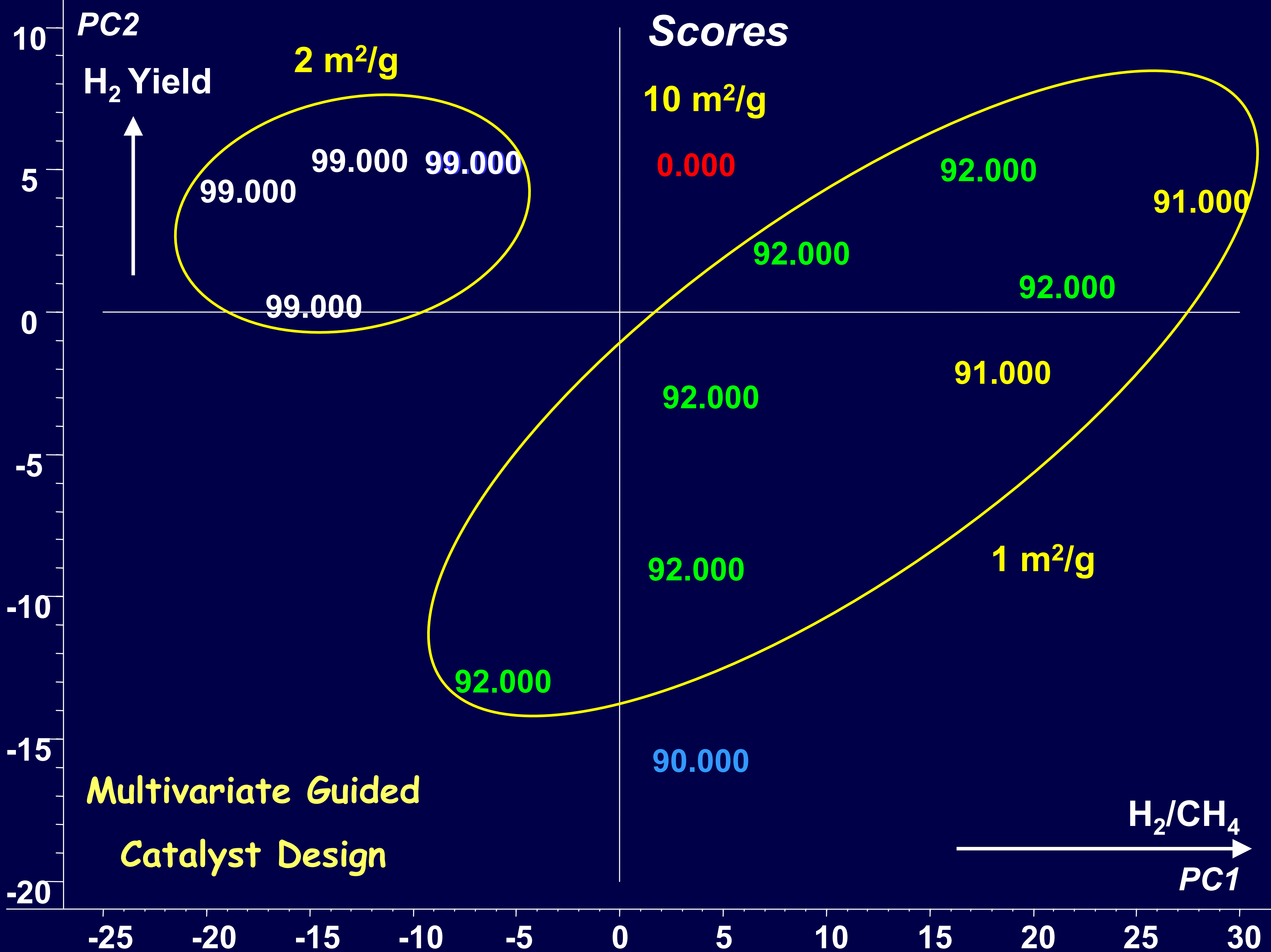
More hydrogen and methane
Need to reduce methane



More CO_2, less CO
Need to improve WGS

Comparing Feedstocks




Scores
PC2
H2 Yield
2 m2/g
10 m2/g
1 m2/g
99.000
99.000
99.000
99.000
99.000
0.000
92.000
91.000
92.000
92.000
91.000
92.000
92.000
92.000
90.000
H2/CH4
PC1
Multivariate Guided
Catalyst Design
10
5
0
-5
-10
-15
-20
-25
-20
-15
-10
-5
0
5
10
15
20
25
30

Accomplishments/Progress

- 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
- Evaluating S-tolerant catalysts with waste grease

Collaborations/Technology Transfer

- CoorsTek Ceramics
  Developing fluidizable supports
- Sud Chemie
  Reforming catalyst composition
- GE Power Systems
  Fluidizable catalysts

- Article
- Record of Invention

Plans/Future Milestones

Goal: Design efficient fluidizable catalysts to produce H_2 from varied feedstocks

- Improve catalyst gasification and WGS activity
  - Develop lower temperature reforming catalysts
- Evaluate different feedstocks (pyrolysis vapors, waste grease, plastics)
  - 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

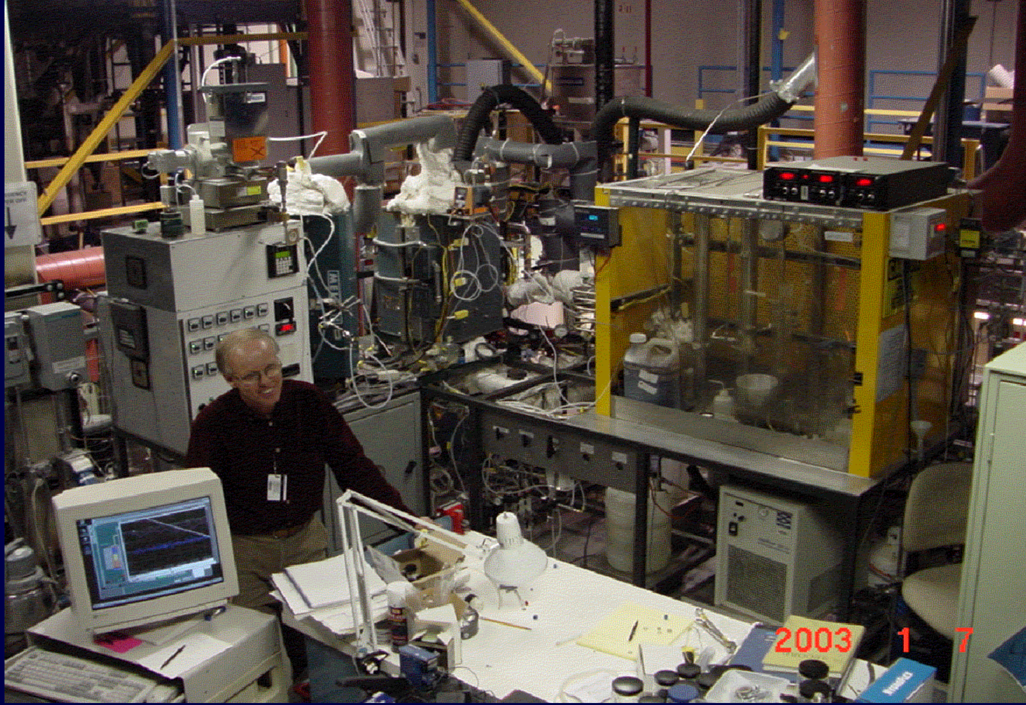
Responses to FY02 Review

- Commercial reforming catalysts attrit **(fall apart)** when fluidized
  - 3 of the best naptha reforming catalysts suffered losses > 10 wt% per day (need < 0.5 wt%/day)

- NREL catalyst composition based on commercial naptha reforming catalyst composition (Sud Chemie)

- Industrial reforming catalysts are for fixed bed use. New market is driving CoorsTek participation. IP in progress (composition of matter)

Challenges



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