

# Distributed Bio-Oil Reforming

2007 DOE Hydrogen, Fuel Cells & Infrastructure  
Technologies Program Review

R. J. Evans<sup>1</sup>, S. Czernik<sup>1</sup>,  
R. French<sup>1</sup>, M. Ratcliff<sup>1</sup>, J. Marda<sup>2</sup>, A. M. Dean<sup>2</sup>

<sup>1</sup>National Renewable Energy Laboratory

<sup>2</sup>Colorado School of Mines

May 15, 2007

This presentation does not contain any proprietary or confidential information

# Overview

## Timeline

- Project start: 2005
- Project end: 2012
- 20% completed

## Budget

- FY 2005: \$100K
- FY 2006: \$300K
- FY 2007: \$300K

## Partners

- Colorado School of Mines (FY 2006) - Oxidative cracking
- Chevron (FY 2006) – CRADA started in FY 2007

## Production Barriers

- A. Fuel processor capital
- C. Operation & maintenance
- D. Feedstock issues
- F. Control & safety

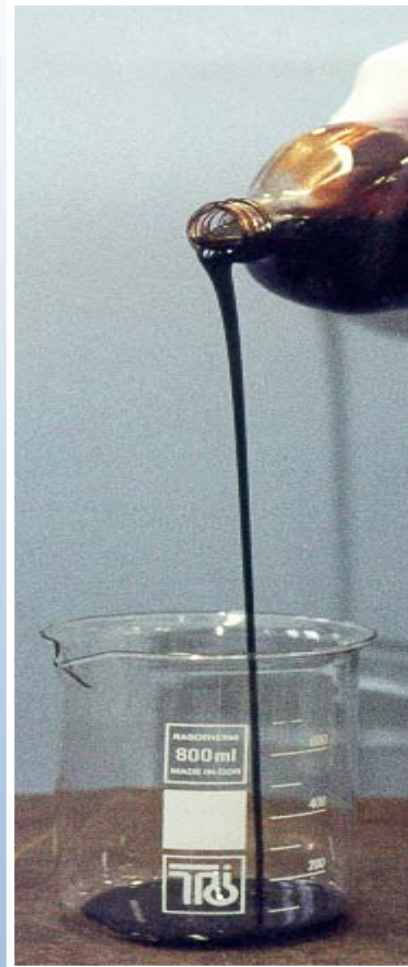
## 2012 Targets

- \$3.80/gallon gasoline equivalent
- 72% energy efficiency

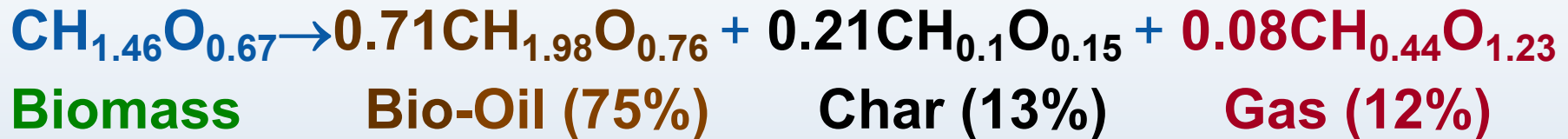
# H<sub>2</sub> Distributed Production via Biomass Pyrolysis

Biomass pyrolysis produces a liquid product, bio-oil, which contains a wide spectrum of components that can be efficiently produced, stored, and shipped to a site for renewable hydrogen production.

NREL is investigating the low-temperature, partial oxidation, and catalytic autothermal reforming of bio-oil for this application.



## *Pyrolysis:*



## *Catalytic Steam Reforming of Bio-Oil:*



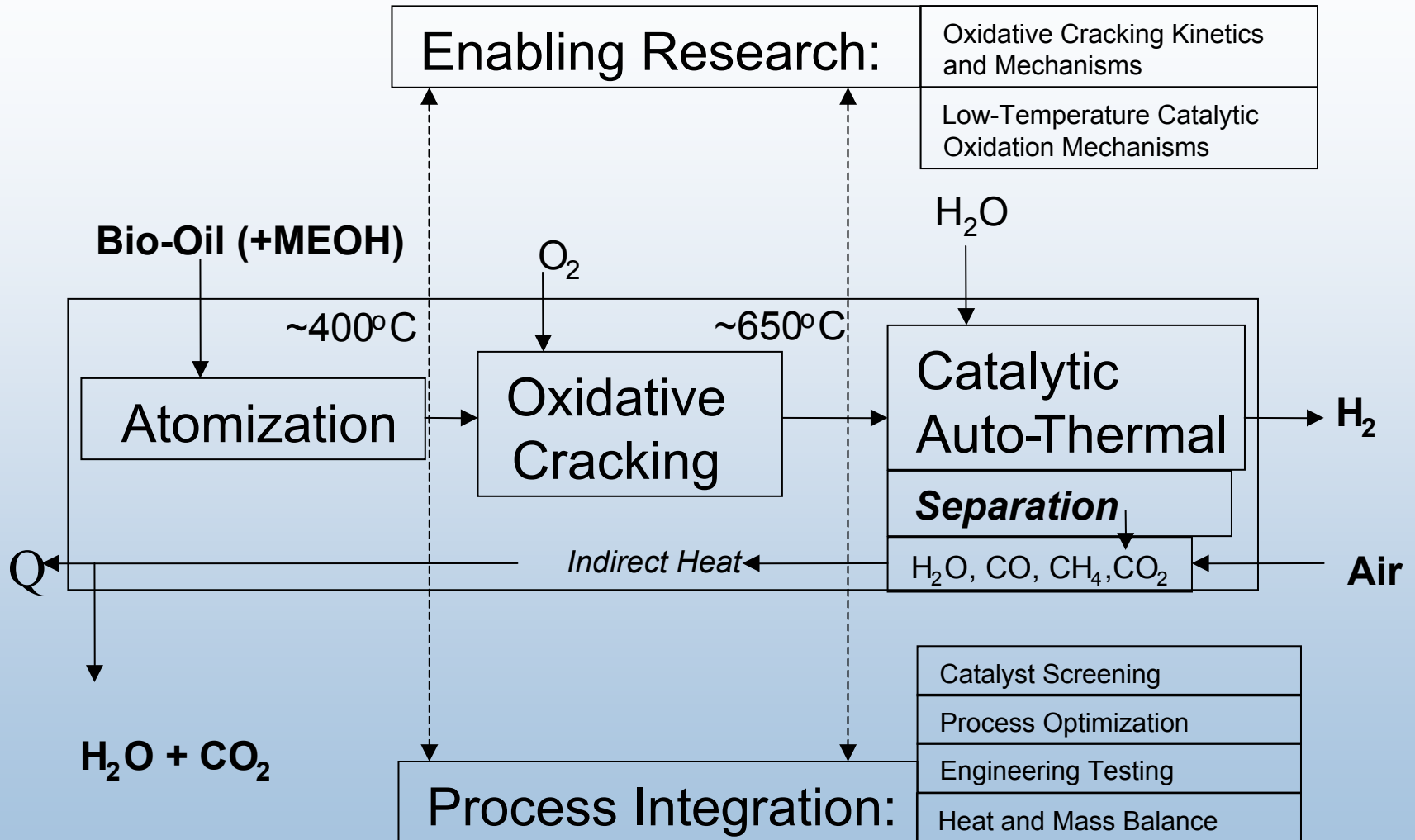
## *Practical Yield:*

10 wt%, 65% overall energy efficiency

# Objectives

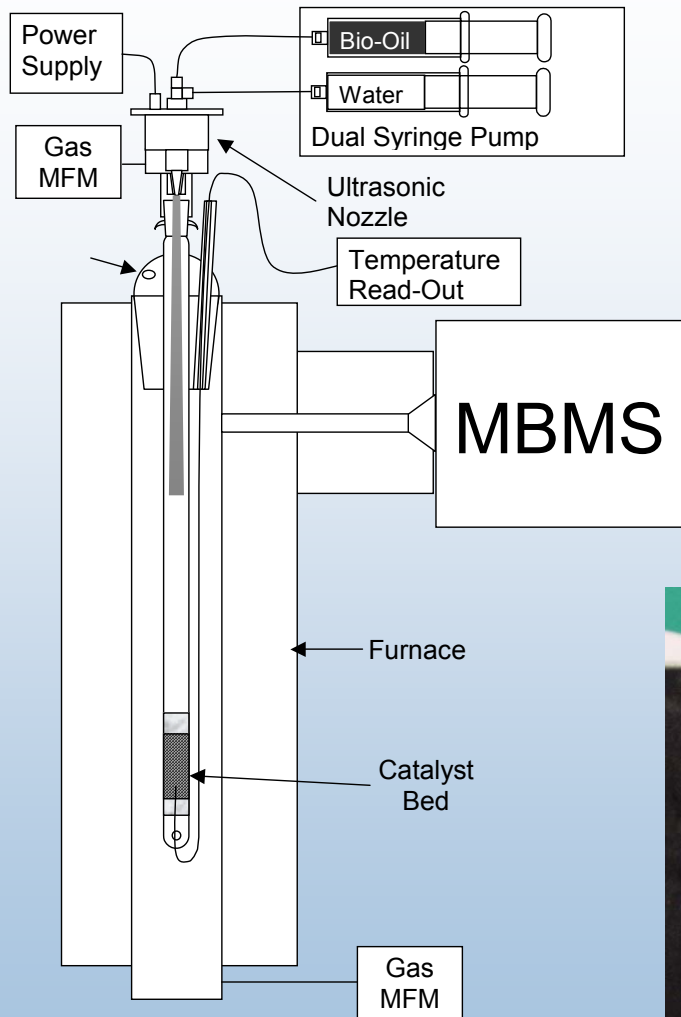
- Overall
  - Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry, deactivation, and regeneration strategy as a basis for process definition for automated distributed reforming; demonstrate the process
- FY 2007
  - Demonstrate integration of bio-oil atomization, partial oxidation, and catalytic conversion to obtain equilibrium syngas composition at 650°C

# Distributed Bio-Oil Reforming Approach

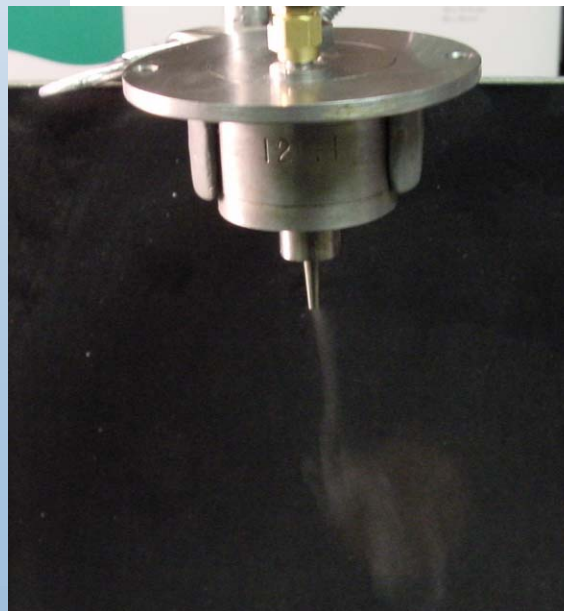
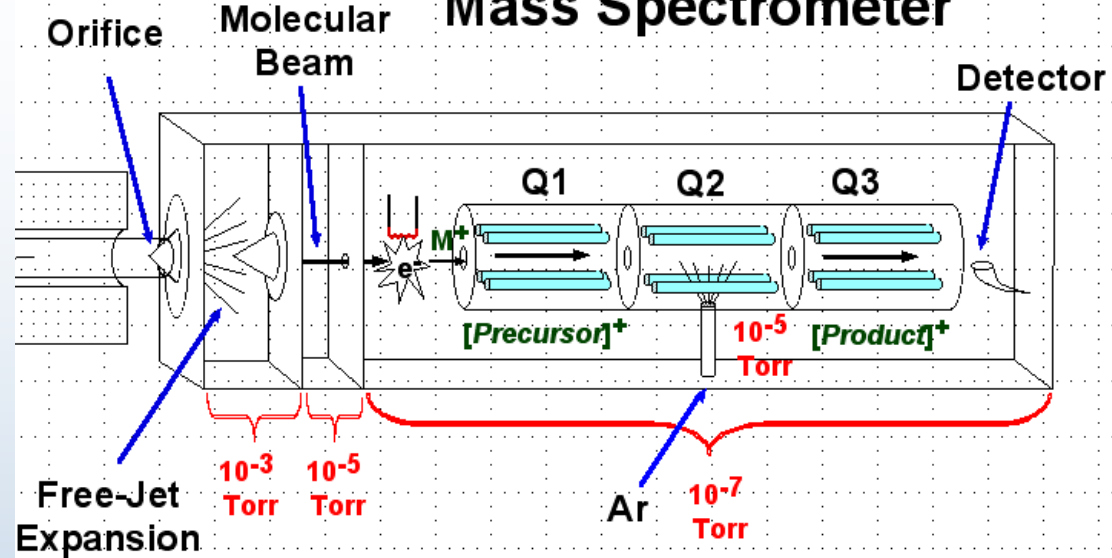


# Technical Accomplishments

- FY 2006
  - Bio-oil volatilization method developed
  - Oxidative cracking conversion to CO with minimal CO<sub>2</sub>
- FY 2007
  - Introduction of catalysts
  - Demonstrated equilibrium conversion to syngas at low temperature and low H<sub>2</sub>O/C
  - Improved bio-oil atomization
  - Methanol modeling studies
  - Parametric studies begun



# Triple-Quadrupole Mass Spectrometer



## Ultrasonic Nozzle

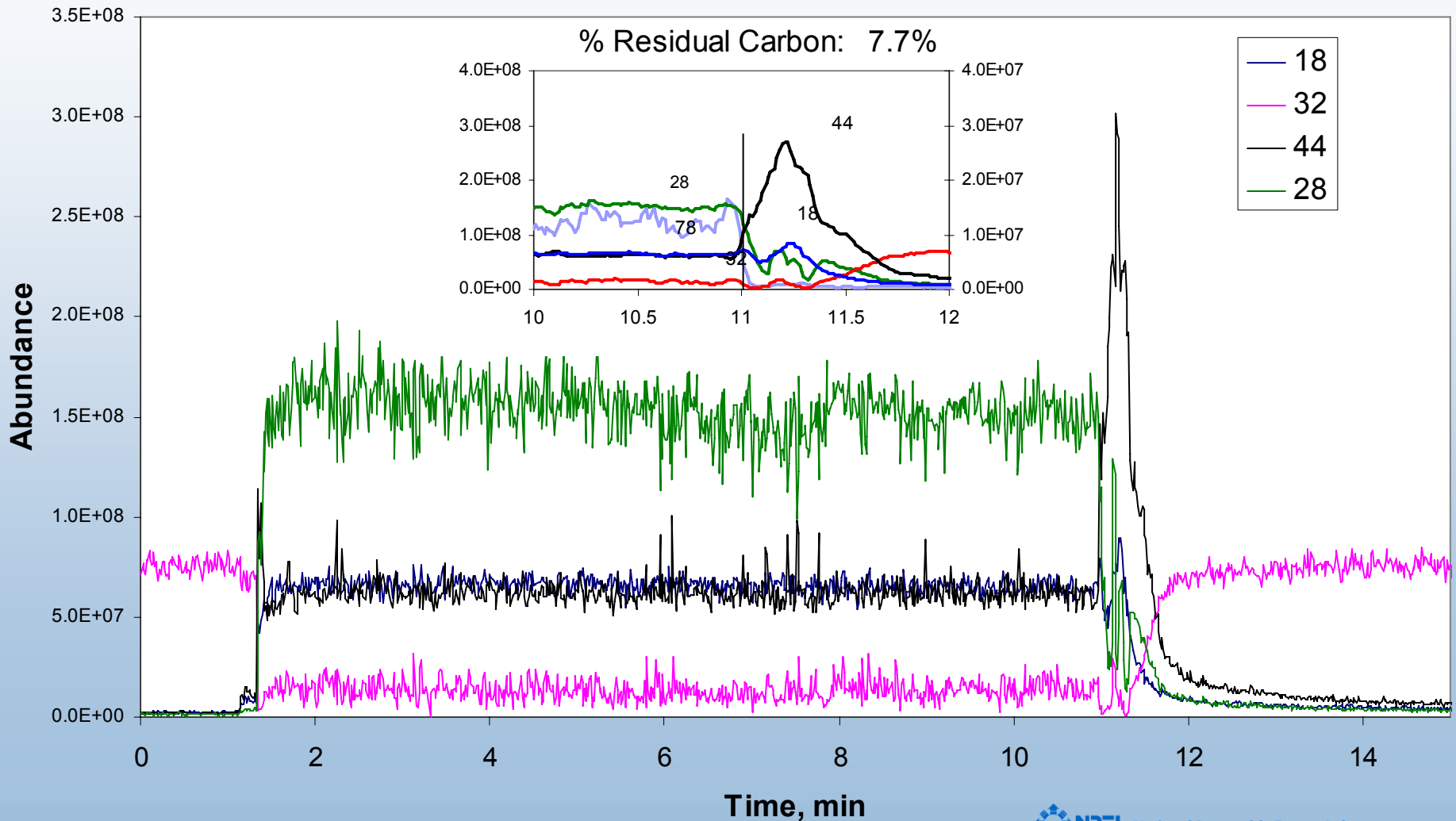
- Generates a fine mist at 0.3g/min
- Enables steady liquid feed at low rates



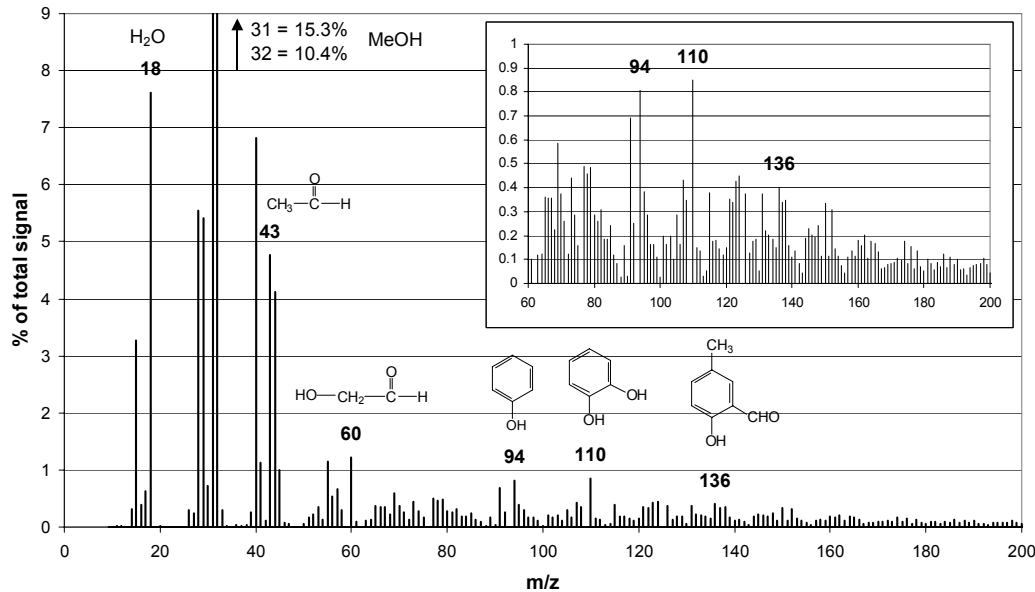
# Ultrasonic Nebulizer

## Oxidative Cracking 0.3 s @ 650 °C

### MeOH-Bio-Oil (50:50 mixture)

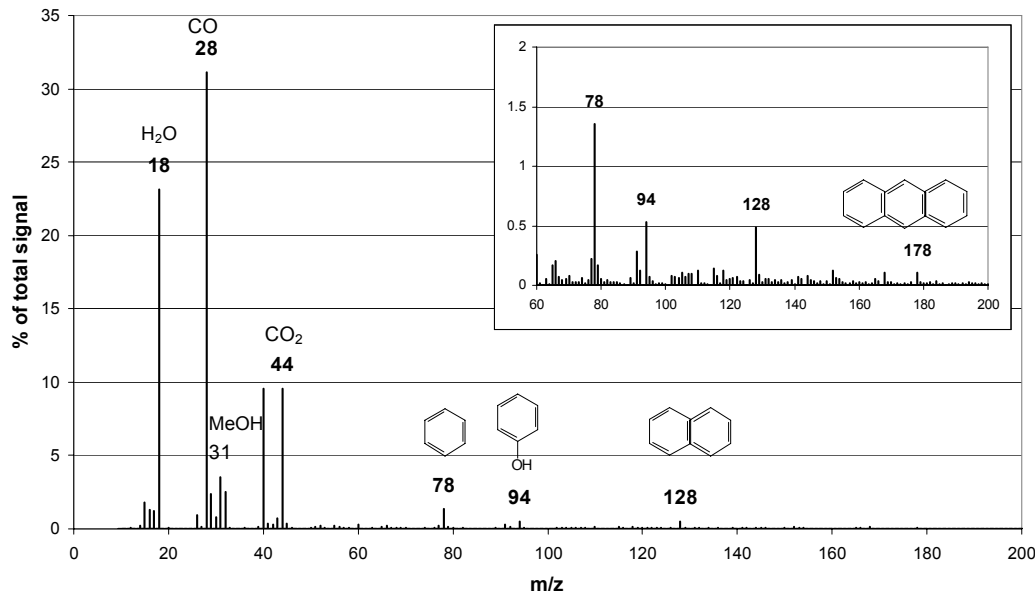


## Thermal Cracking at 650 °C (0.3 s;O:C 0.81)

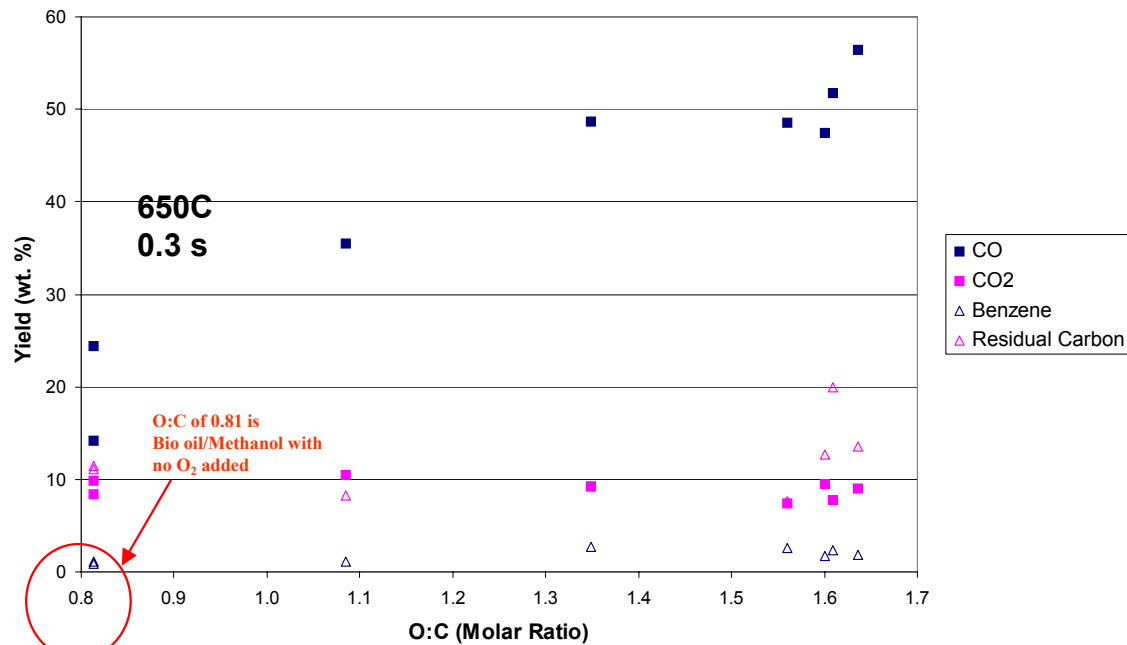


Under thermal cracking conditions, unconverted methanol and secondary products from the bio-oil predominate.

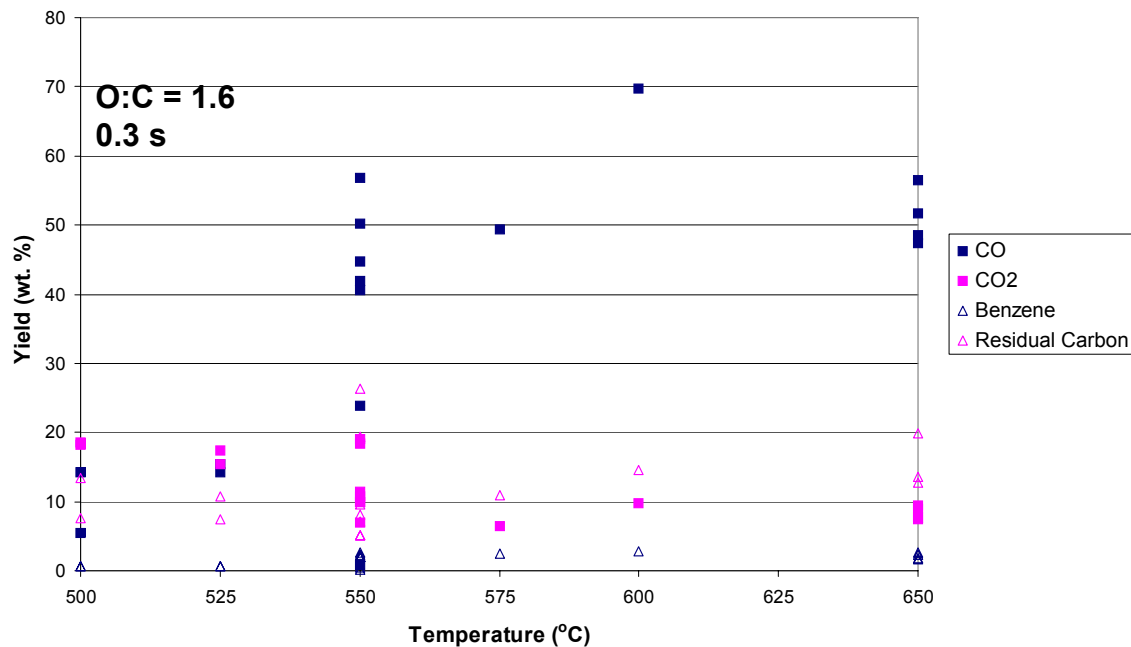
## Oxidative Cracking at 650 °C (0.3 s;O:C 1.6)



Under oxidative cracking conditions, H<sub>2</sub> (not shown), water, CO, and CO<sub>2</sub> predominate. Hence the role of the catalyst to be added is to finish the conversion and catalyze the water-gas shift.



Gas-phase partial oxidation leads to high CO yields with low CO<sub>2</sub>.



Byproduct yields surprisingly insensitive to O:C or temperature variations.

# Model Development

- Use model compounds to understand the complex system that undergoes low-temperature partial oxidation
  - Begin with methanol and other small oxygenates
- Next steps
  - Improved model for molecular weight growth
    - Recombination of resonantly stabilized radicals
  - Extend gas-phase models to account for partial oxidation of higher hydrocarbons
  - Improve catalytic mechanisms
  - Catalytic models to higher hydrocarbons
  - Apply to biomass kinetics for hydrogen production

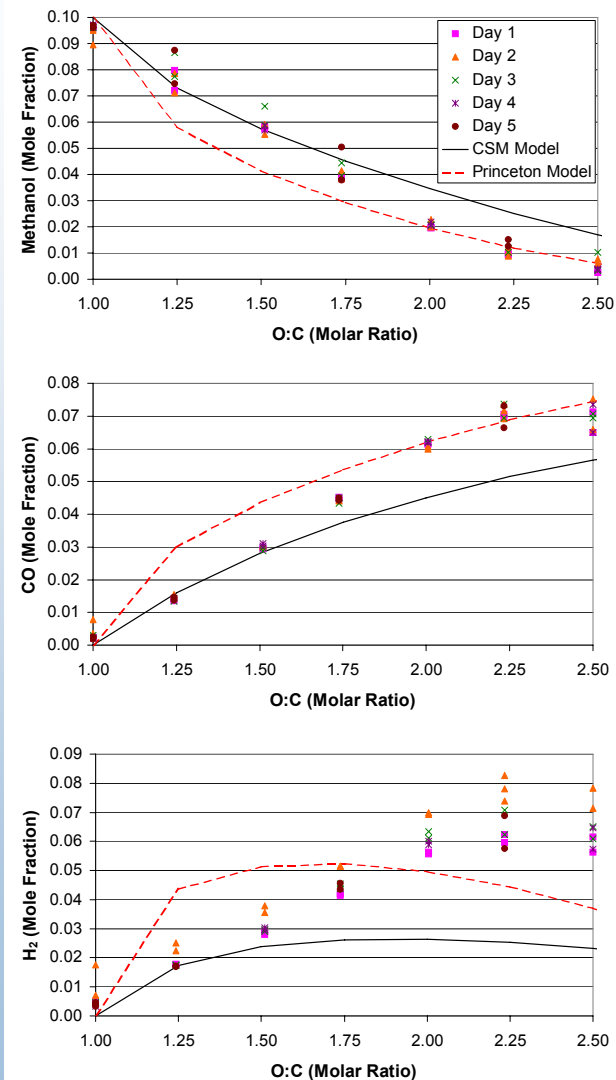
# Modeling Methanol Pyrolysis and Partial Oxidation

## Model Development

- **CSM model**
  - Rule based model originally developed to predict hydrocarbon pyrolysis and oxidation
    - Extended to methanol
  - Three types of reaction used to describe system
    - Dissociation, hydrogen abstraction, and -scission
  - 360 species and nearly 3550 reactions
- **Princeton model\***
  - Based on methanol pyrolysis and oxidation experiments
  - 22 species and 97 reactions

\*Held and Dryer, Int. J. Chem. Kin., 32, 805-830 (1998)

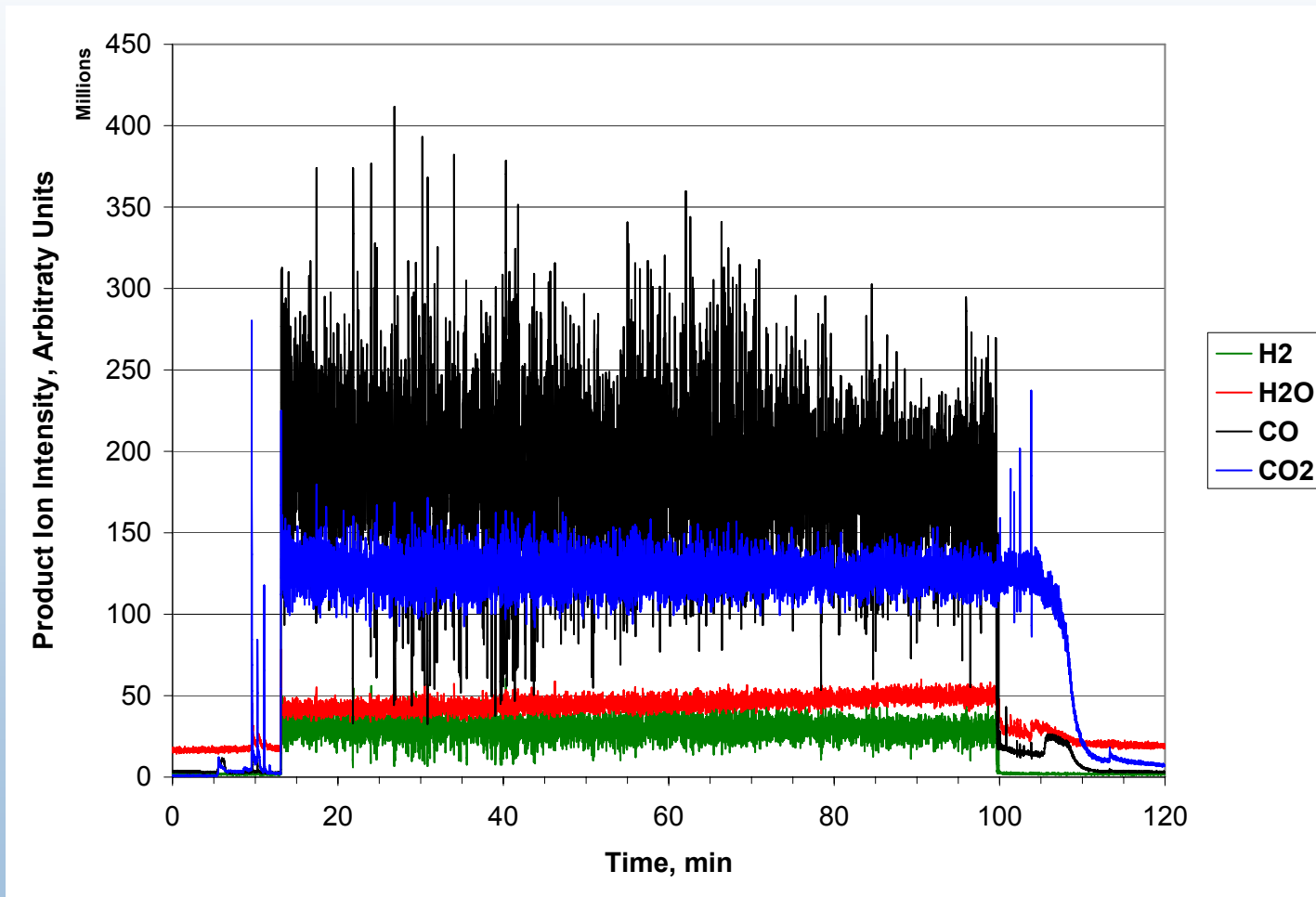
Issue: Need to account for potential temperature change.



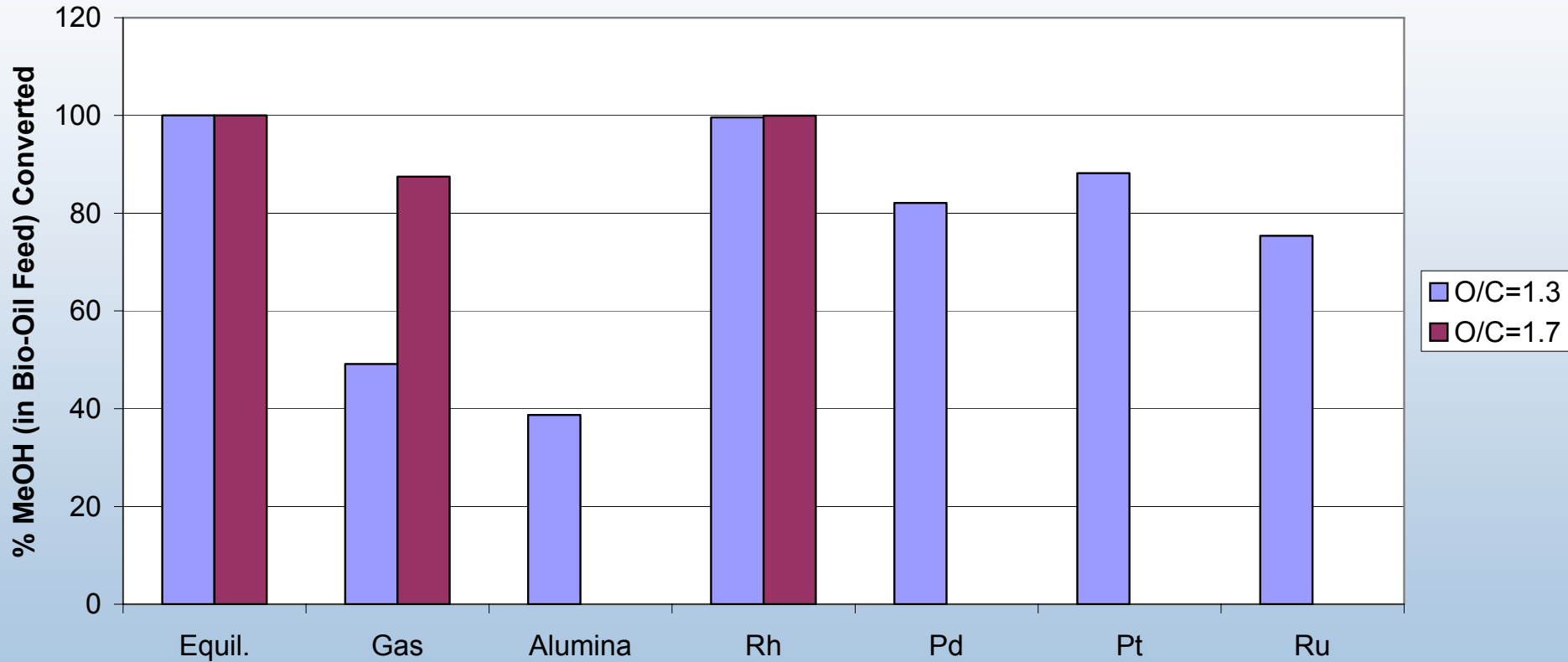
# Catalytic Conversion

Oxidative Cracking .3 s @ 650°C + .25% Rh on Al<sub>2</sub>O<sub>3</sub>

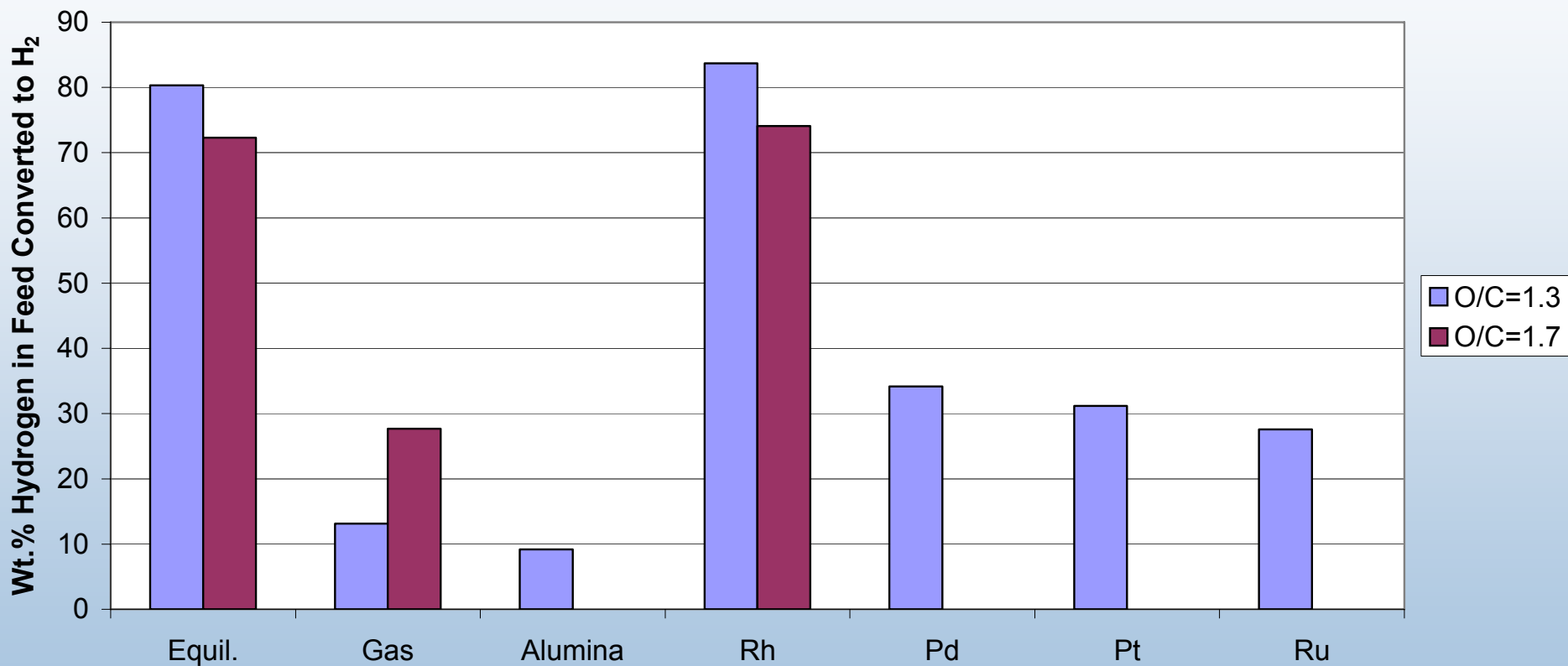
Bio-Oil:Methanol (50:50)



# Methanol Conversion

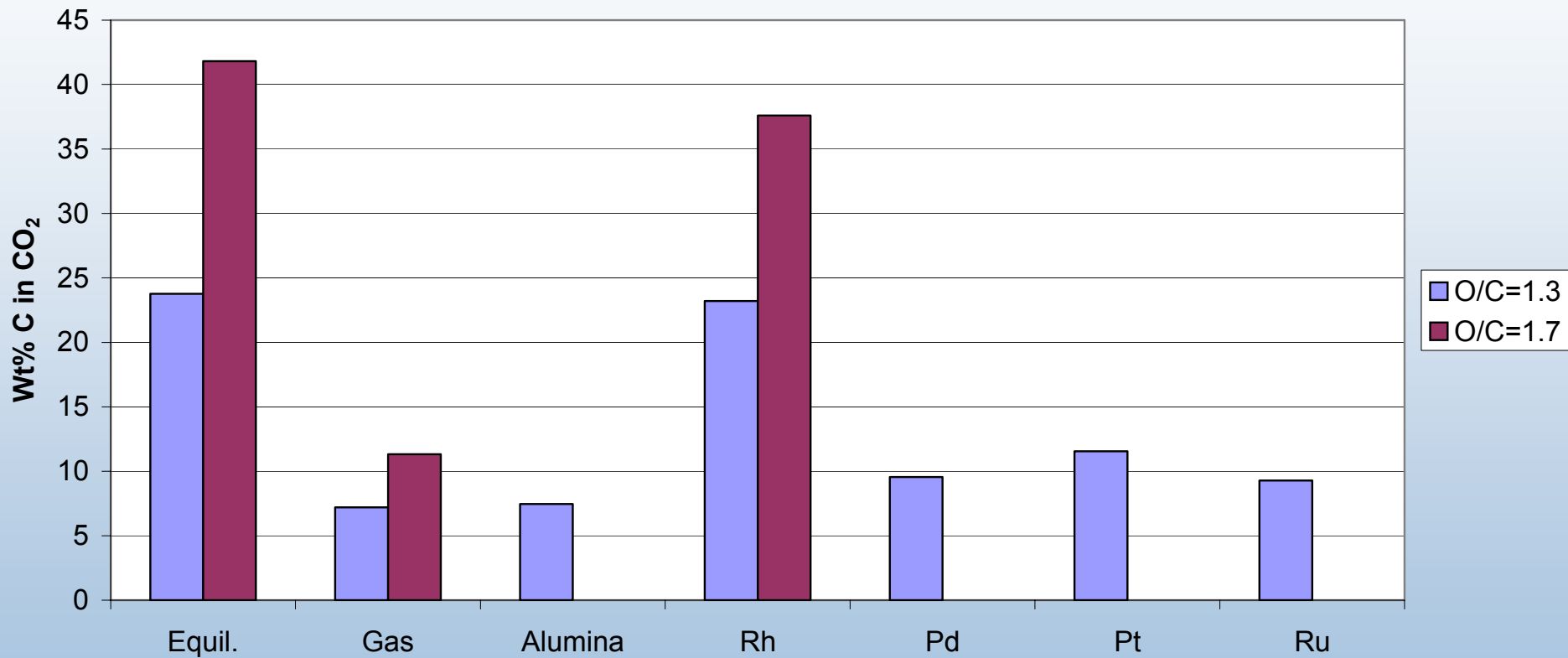


# Hydrogen Yield

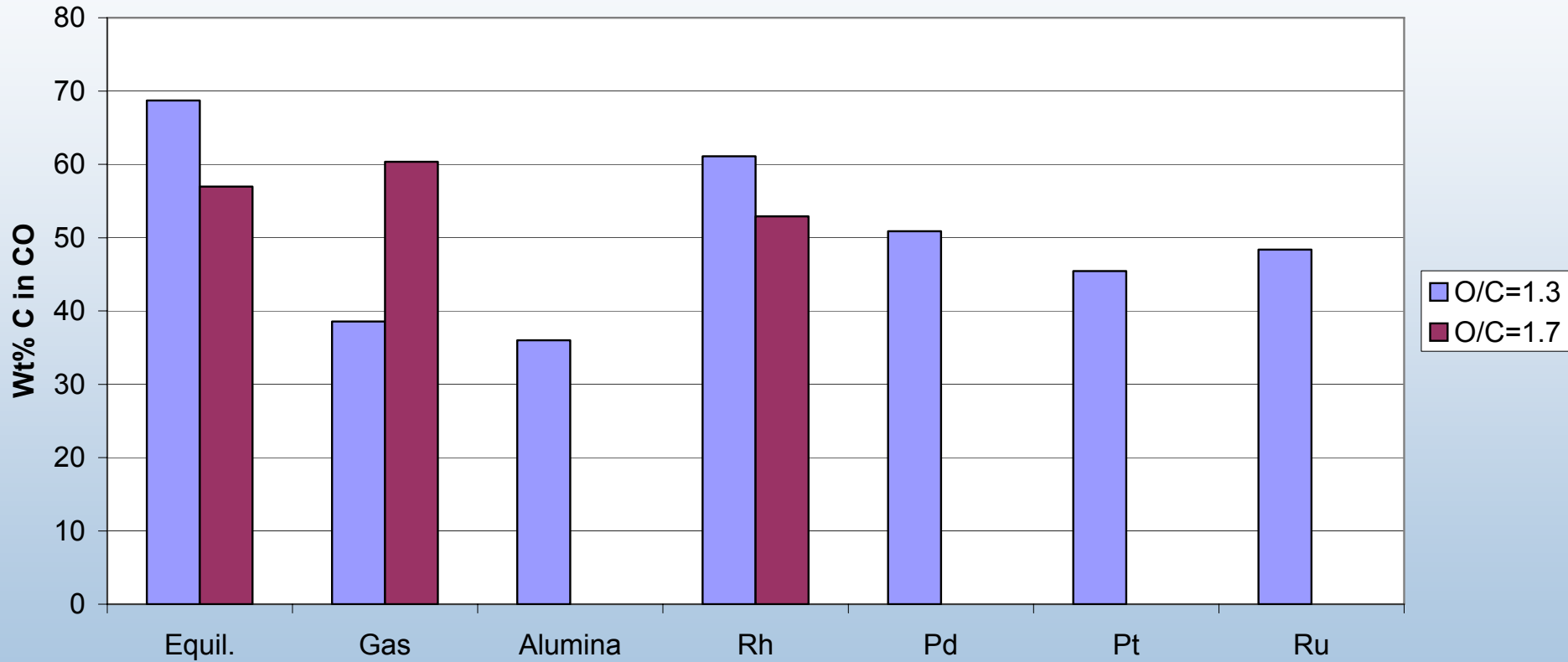




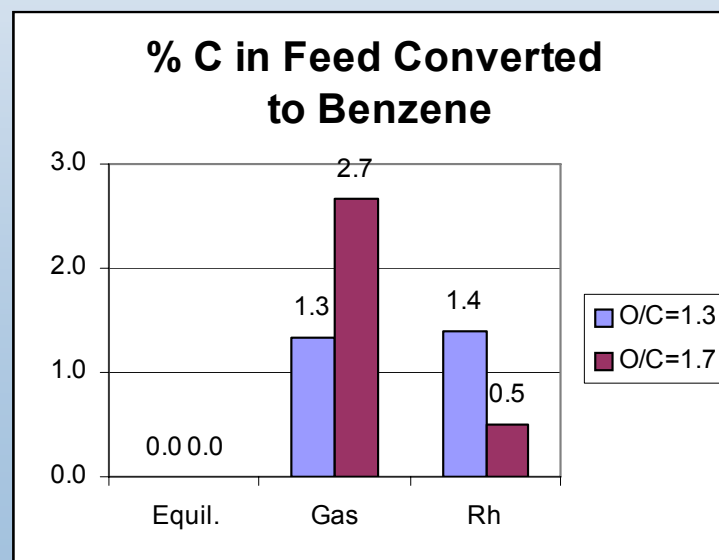
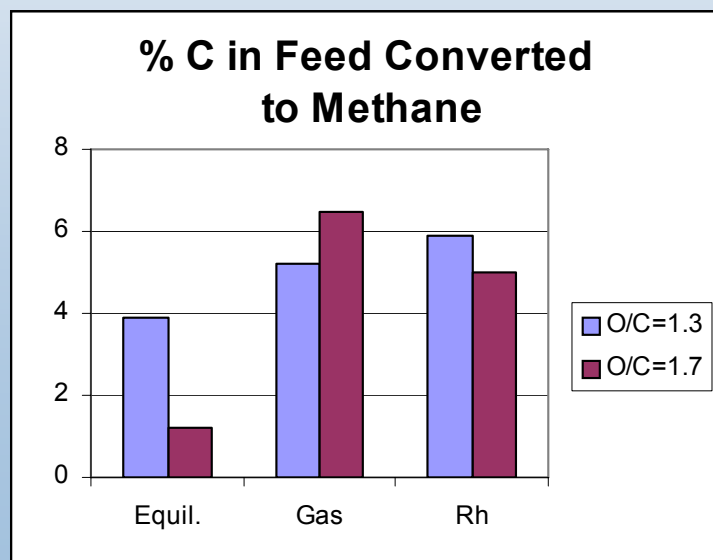
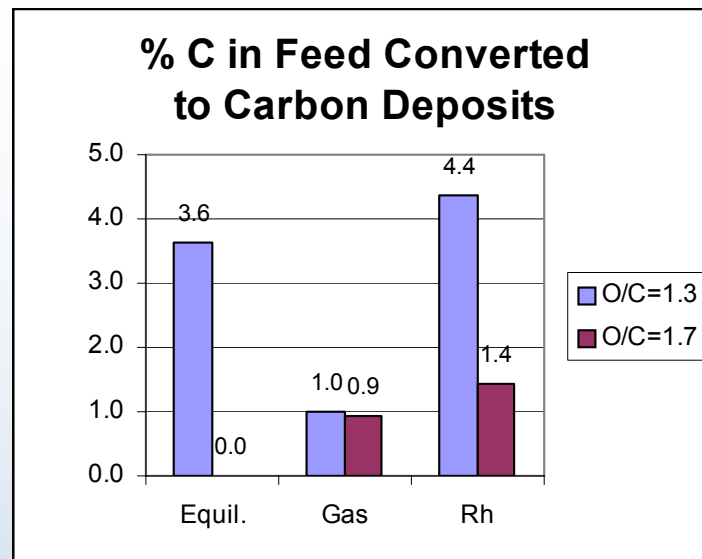
# CO<sub>2</sub> Yield



# CO Yield



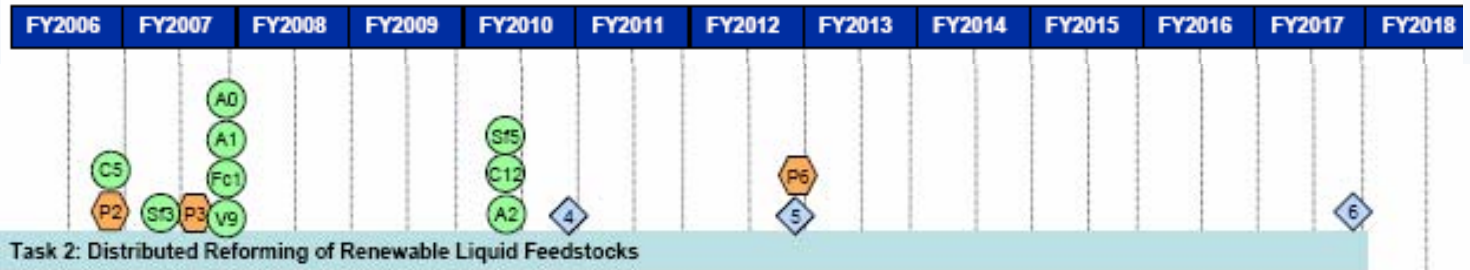
By-products are typically above equilibrium levels and thought to be generated from non-volatile species in aerosols and processes in the gas phase.



# Process Comparison

	Fluid Bed	Staged
Bio-Oil Organics %	80	78
MeOH %	0	10
water,wt%	20	18
C	45	44.2
H	7.9	8.4
O	47.1	47.4
H/C	2.1	2.3
O/C	0.8	0.8
H2 production rate, kg/day	1500	1500
H2 Yield, wt%	11.9	11.9
Conversion efficiency,%	70	70
Bio-Oil Feed Rate, kg/hr	525	525
Feed C feed rate, kg/hr	236	232
O2 feed rate, kg/hr	0	246
Ratios with O2		
H/C(H2Ofree)	1.5	1.7
O/C(H2Ofree)	0.5	1.3
Starting H2O/C	0.30	0.27
H2O/C after Oxcrack	0.30	0.75
<b>Water addition, Kg/hr</b>	<b>1668</b>	<b>407</b>
<b>Catalyst load, kg</b>	<b>1734</b>	<b>430</b>
<b>Temperature, C</b>	<b>800</b>	<b>600</b>
Reactor diameter, M	1.03	0.31
Reactor height, M	6	5
Catalyst reactor volume, L	5029	372
Cracking reactor volume, L	0	130
Vaporizer, L	0	130
<b>Total reactor volume, L</b>	<b>5029</b>	<b>632</b>

# Program Timeline



- 4 Down-select research for distributed production from distributed renewable liquids. 4Q, 2010
- 5 Verify feasibility of achieving \$3.80/gge (delivered) from distributed renewable liquids. 4Q, 2012
- 6 Verify feasibility of achieving less than \$3.00/gge (delivered) from bio-derived renewable liquid fuels 4Q 2017

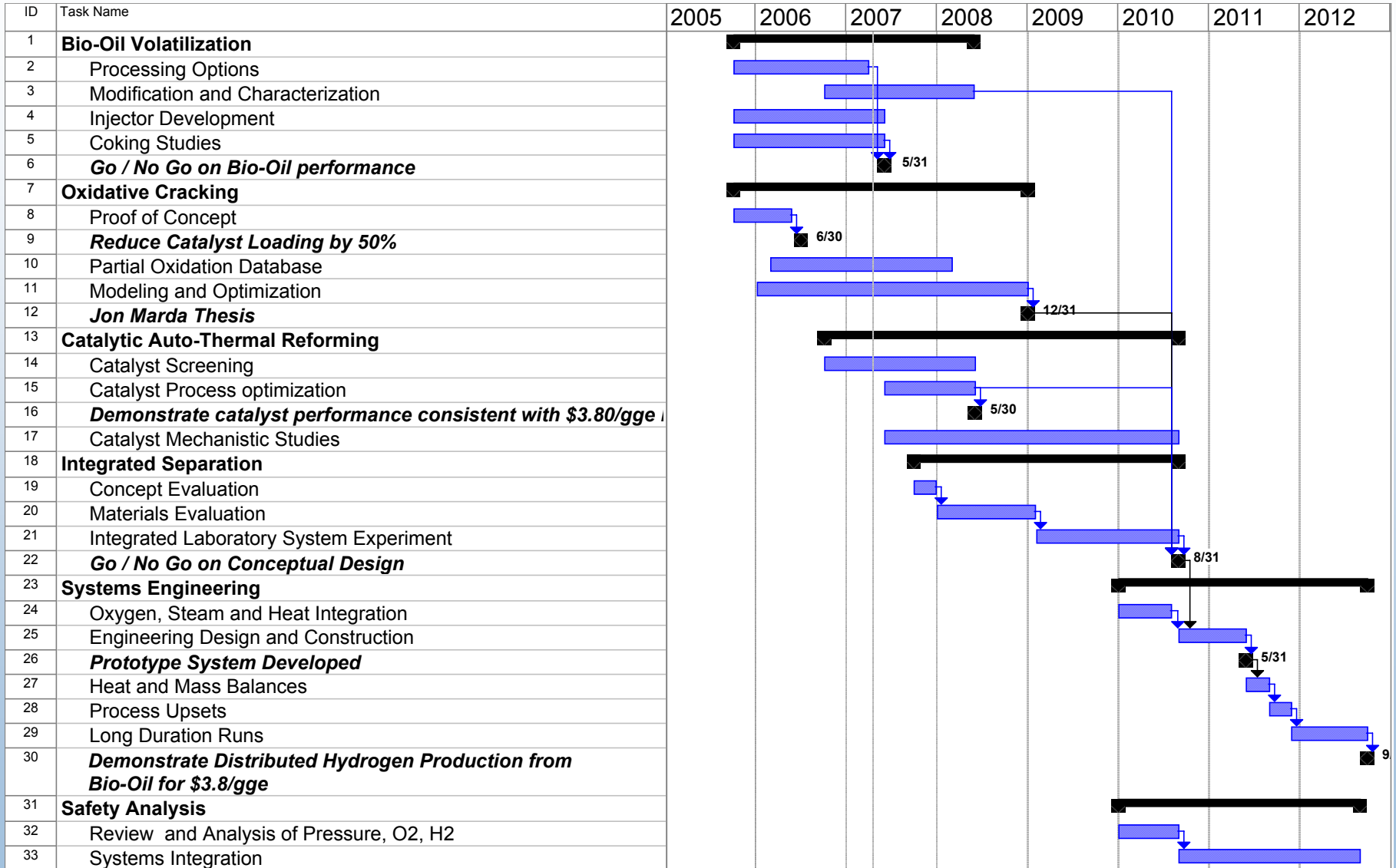
## Outputs

- P1 Output to Technology Validation: Hydrogen production technology for distributed systems using natural gas with projected cost of \$3.00/gge hydrogen at the pump, untaxed, assuming 500 units of production per year. 4Q, 2005
- P2 Output to Delivery, Storage, Fuel Cells, Tech Validation: Assessment of H2 quality cost and issues from production. 4Q, 2008
- P3 Output to Technology Validation, Systems Analysis and Systems Integration: Impact of hydrogen quality on cost and performance. 3Q, 2007
- P4 Output to Technology Validation: Hydrogen production technologies for distributed systems using natural gas with projected cost of \$2.50/gge hydrogen at the pump, untaxed, assuming 500 manufactured units per year. 4Q, 2010
- P5 Output to Technology Validation: Hydrogen production technologies for distributed systems using natural gas with projected cost of \$2.00/gge hydrogen at the pump, untaxed, assuming 500 manufactured units per year. 4Q, 2015

## Inputs

- C5 Input from Codes and Standards: Hydrogen fuel quality standard as ISO Technical Specification. 4Q, 2008
- Sf3 Input from Safety: Safety requirements and protocols for refueling. 2Q, 2007
- FC1 Input from Fuel Cells: Reformer results of advanced reformer development 4Q, 2007
- V9 Input from Technology Validation: Final report on safety and O&M of three refueling stations. 4Q, 2007
- A0 Input from Systems Analysis: Initial recommended hydrogen quality at each point in the system. 4Q, 2007
- A1 Input from Systems Analysis: Complete techno-economic analysis on production and delivery technologies currently being researched to meet overall program hydrogen fuel objective. 4Q, 2007
- A2 Input from Systems Analysis: Report on the infrastructure analysis for the transition 2Q, 2010
- C12 Input from Codes and Standards: Final hydrogen fuel quality standard as ISO Standard. 2Q, 2010
- Sf5 Input from Safety: Updated safety requirements and protocols for refueling. 2Q, 2010

# Project Timeline



# Future Work

- FY 2007
  - Continued catalyst testing and collaborative development with emphasis on deactivation and poisoning
  - Modeling and process optimization (continues in 2008)
- FY 2008
  - Reaction engineering
  - Bench-scale tests for long-term catalyst testing
- FY 2009
  - Integrated laboratory experiment
- FY 2010
  - “Go/no-go” on conceptual design
- FY 2011
  - Prototype system
- FY 2012
  - Long duration runs

# Summary

<i>Relevance</i>	Near-Term Renewable Feedstock for Distributed Reforming
<i>Approach</i>	<ul style="list-style-type: none"><li>• Bio-Oil Processed at Low Temp</li><li>• Homogeneous and Catalytic Auto-Thermal Reforming</li></ul>
<i>Accomplishments</i>	System for Bio-Oil Volatilization, Oxidative Cracking, and Catalysis
<i>Collaborations</i>	<ul style="list-style-type: none"><li>• Colorado School of Mines</li><li>• Chevron</li></ul>
<i>Future Work</i>	<ul style="list-style-type: none"><li>• Oxidative Cracking Mechanism and Catalysis in FY 2007</li><li>• System Development in FY 2008</li></ul>