Distributed Bio-Oil Reforming

2007 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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Project ID# PDP7

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

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

2012 Targets
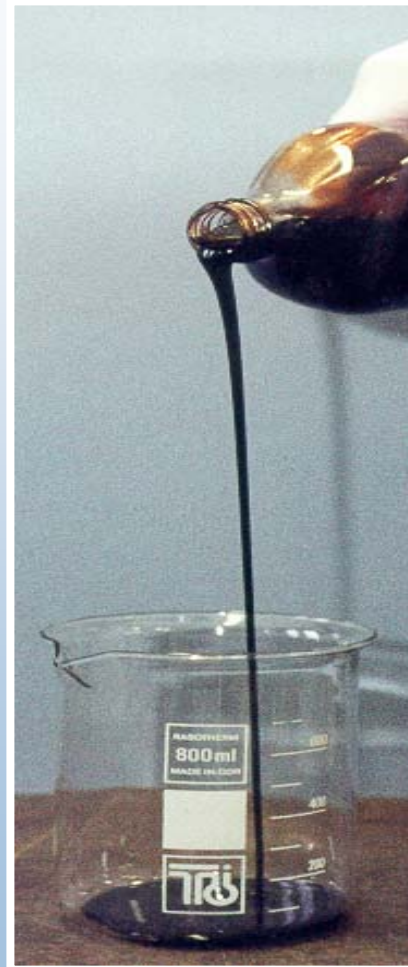- $3.80/gallon gasoline equivalent
- 72% energy efficiency

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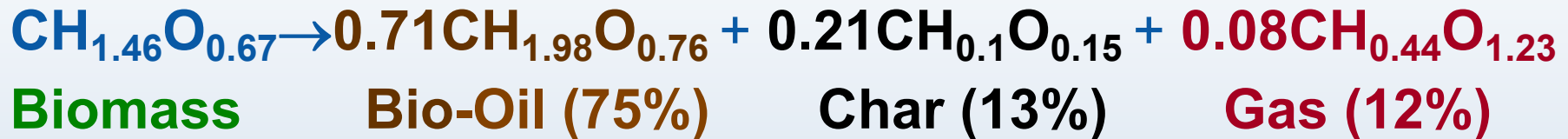- Chevron (FY 2006) – CRADA started in FY 2007

H$_2$ 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:

$$CH_{1.46}O_{0.67} \rightarrow 0.71CH_{1.98}O_{0.76} + 0.21CH_{0.1}O_{0.15} + 0.08CH_{0.44}O_{1.23}$$

Biomass   Bio-Oil (75%)   Char (13%)   Gas (12%)

Catalytic Steam Reforming of Bio-Oil:

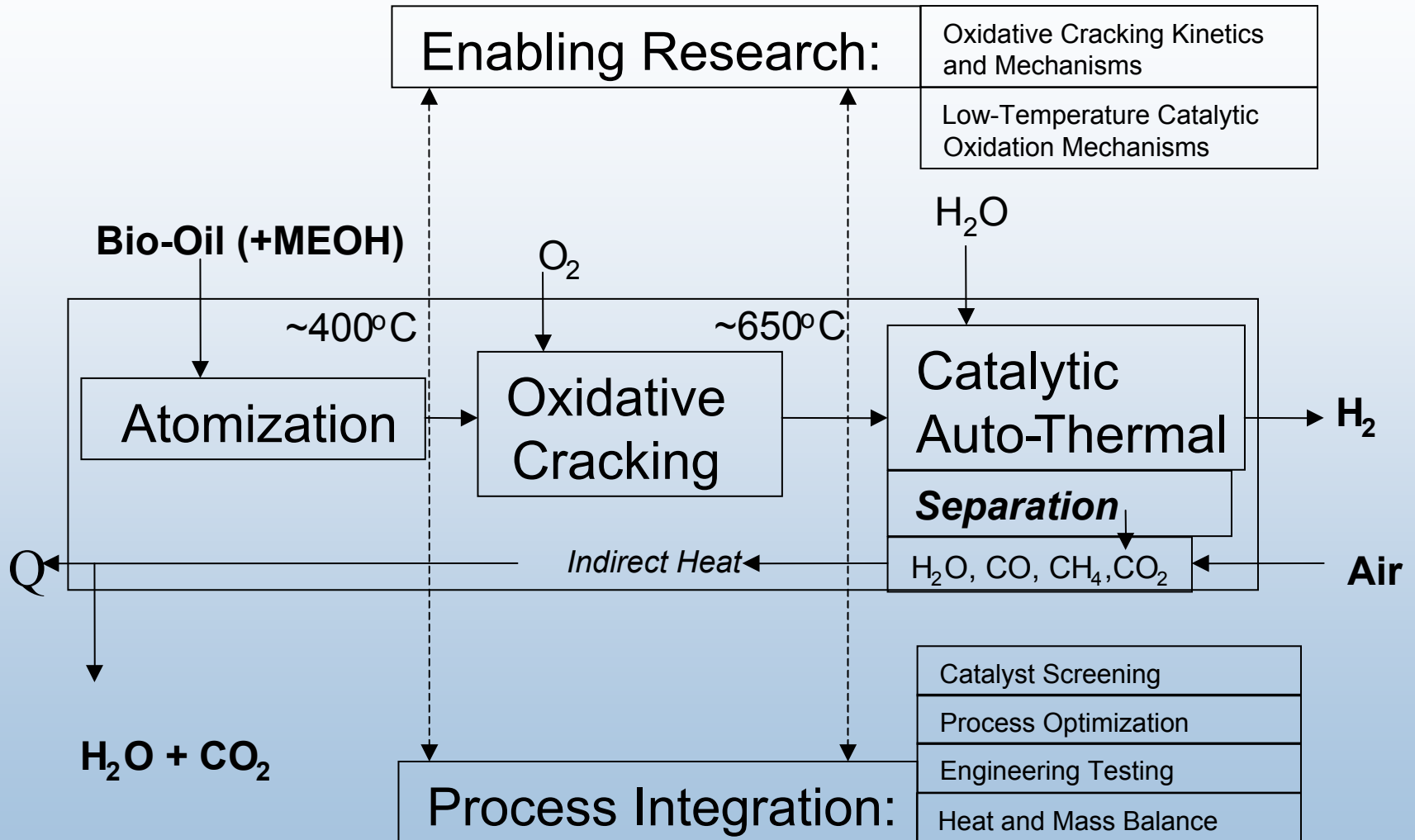$$CH_{1.98}O_{0.76} + 1.24\ H_2O \longrightarrow CO_2 + 2.23\ H_2$$

Practical Yield:

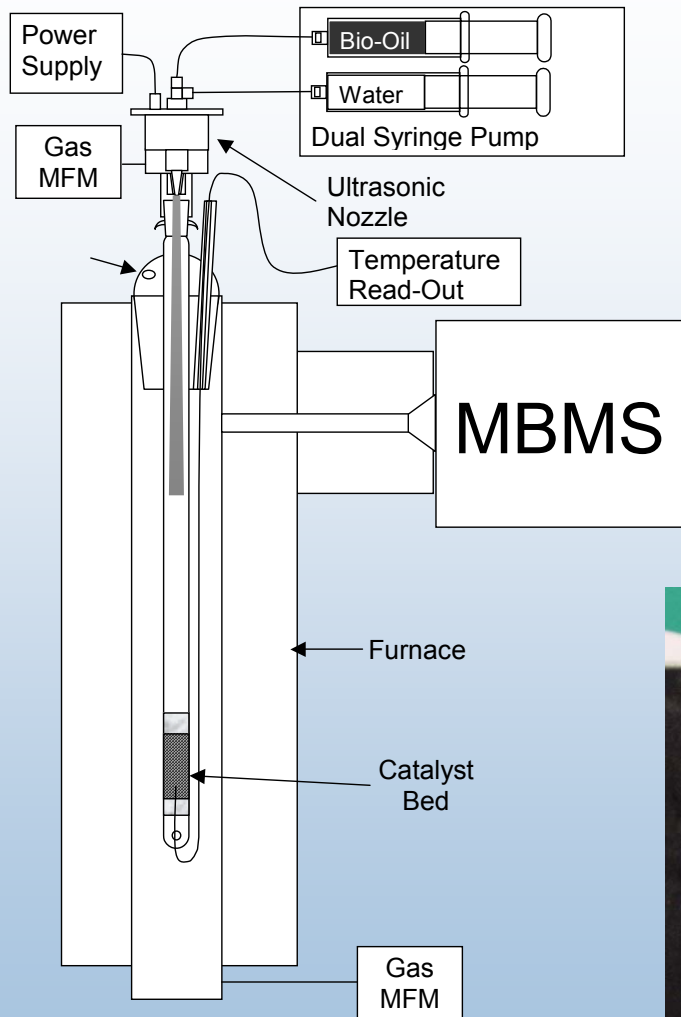10 wt%, 65% overall energy efficiency

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

Enabling Research:
- Oxidative Cracking Kinetics and Mechanisms
- Low-Temperature Catalytic Oxidation Mechanisms

Bio-Oil (+MEOH)

O_2

H_2O

~400°C

~650°C

| Atomization | Oxidative Cracking | Catalytic Auto-Thermal | H_2 |

Separation

Q

Indirect Heat

H_2O, CO, CH_4, CO_2

Air

$H_2O + CO_2$

Process Integration:
- Catalyst Screening
- Process Optimization
- Engineering Testing
- Heat and Mass Balance

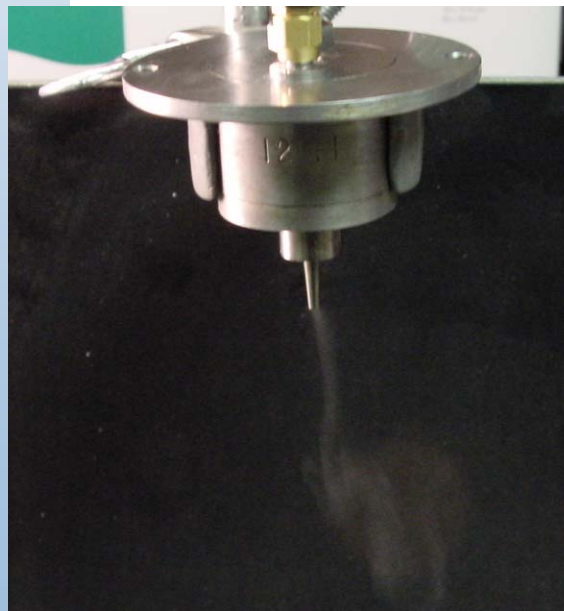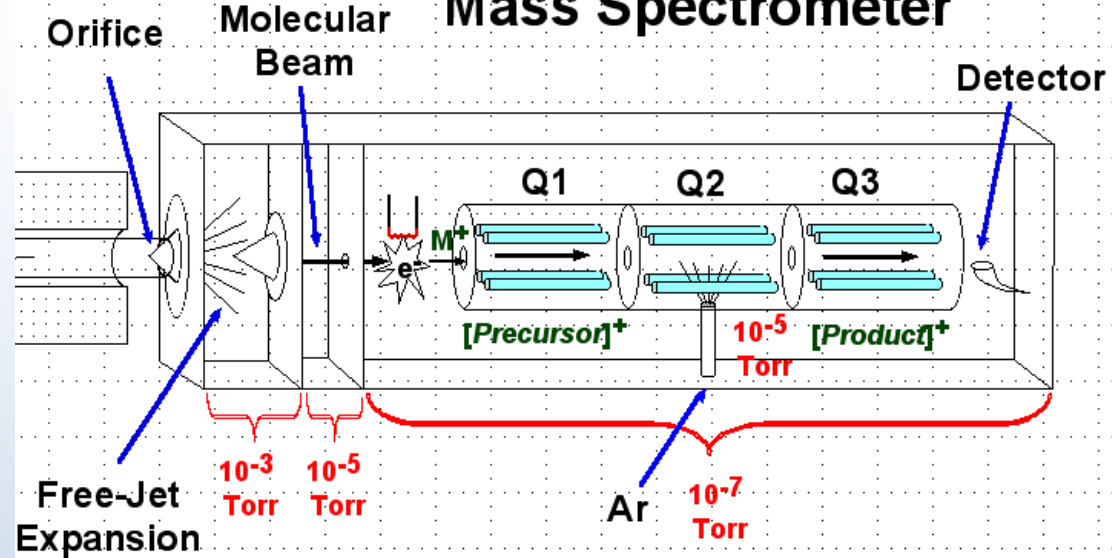NREL National Renewable Energy Laboratory

Technical Accomplishments

- FY 2006
  - Bio-oil volatilization method developed
  - Oxidative cracking conversion to CO with minimal CO_2

- FY 2007
  - Introduction of catalysts
  - Demonstrated equilibrium conversion to syngas at low temperature and low H_2O/C
  - Improved bio-oil atomization
  - Methanol modeling studies
  - Parametric studies begun

Power Supply

Bio-Oil

Water

Dual Syringe Pump

Gas MFM

Ultrasonic Nozzle

Temperature Read-Out

MBMS

Furnace

Catalyst Bed

Gas MFM

Triple-Quadrupole Mass Spectrometer

Orifice

Molecular Beam

Detector

Q1   Q2   Q3

e⁻ M^+

$[Precursor]^+$ 10^{-5} Torr $[Product]^+$

Free-Jet Expansion

10^{-3} Torr 10^{-5} Torr

Ar 10^{-7} Torr

Ultrasonic Nozzle

- Generates a fine mist at 0.3g/min

- Enables steady liquid feed at low rates

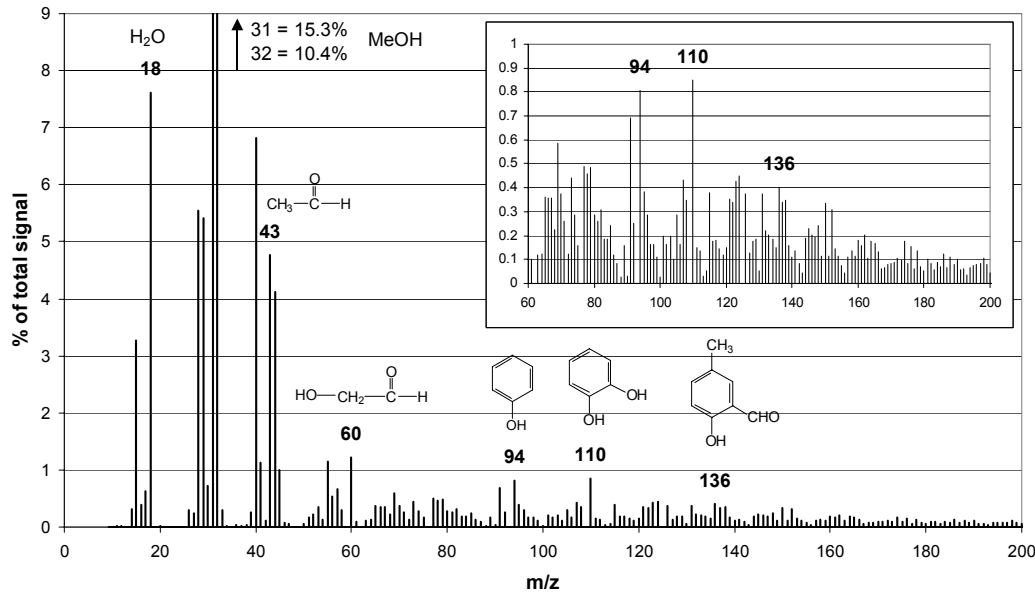NREL National Renewable Energy Laboratory

Ultrasonic Nebulizer
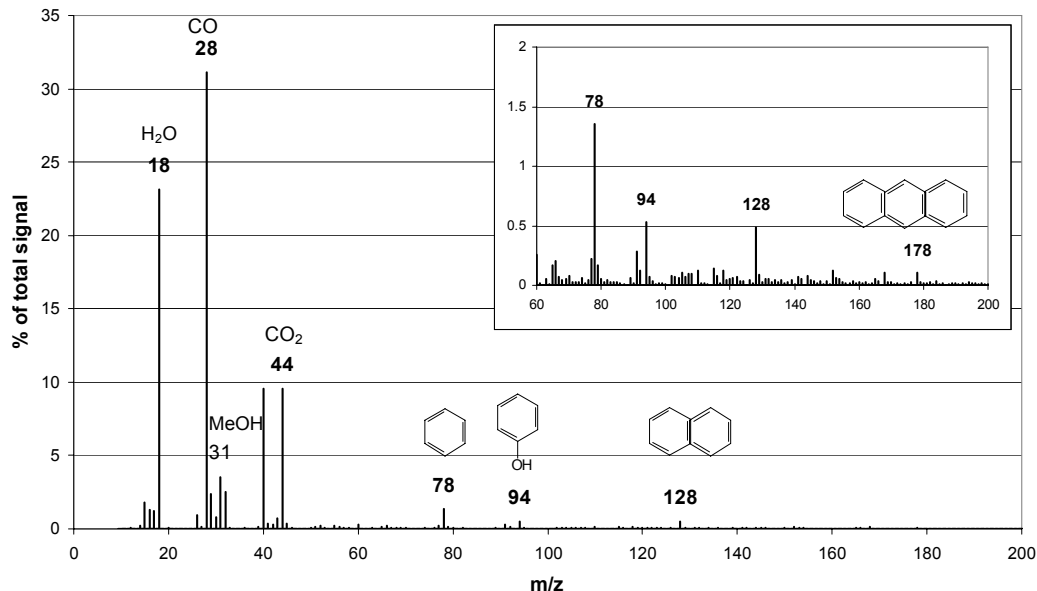## Oxidative Cracking 0.3 s @ 650 °C
MeOH-Bio-Oil (50:50 mixture)
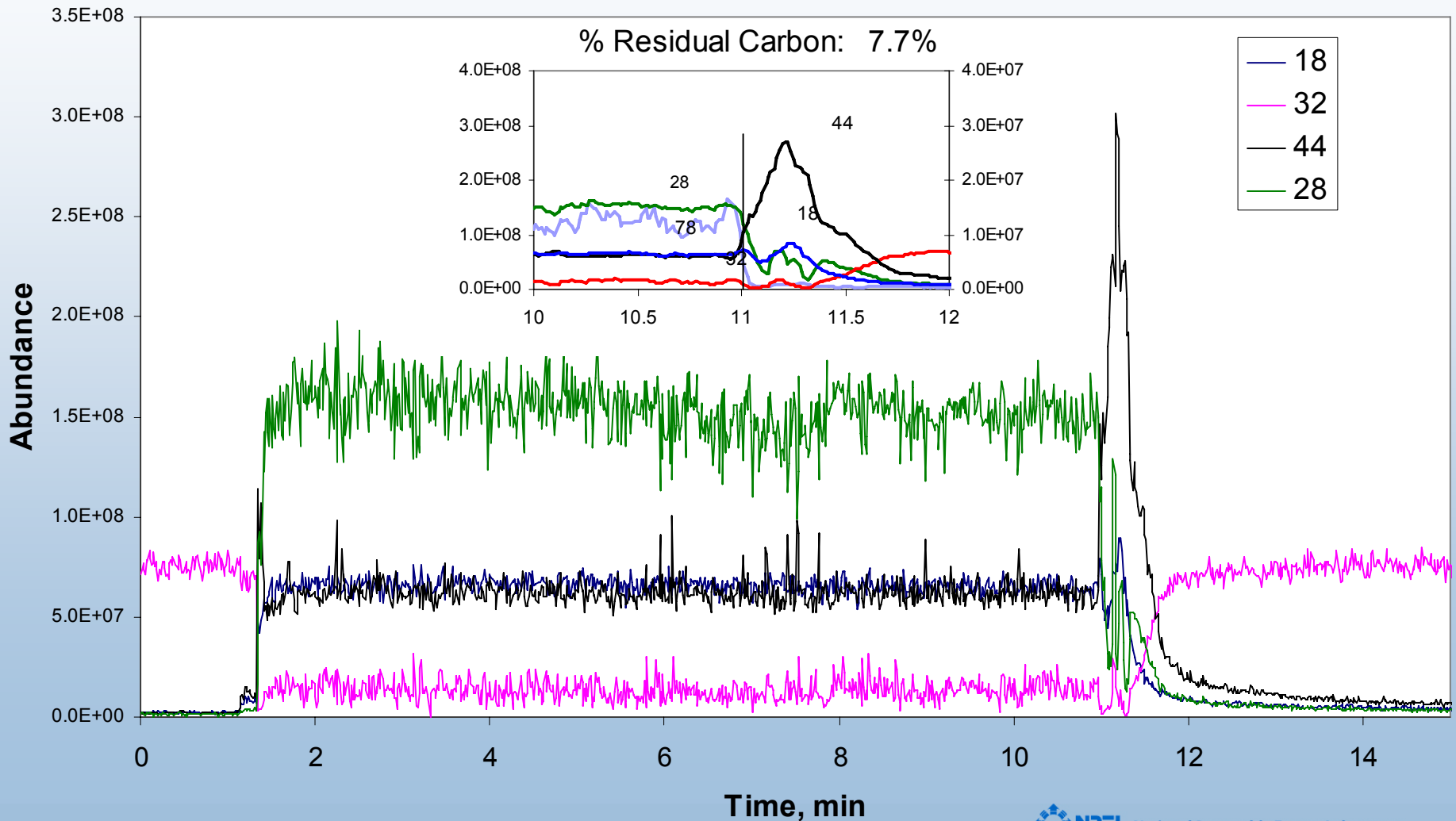
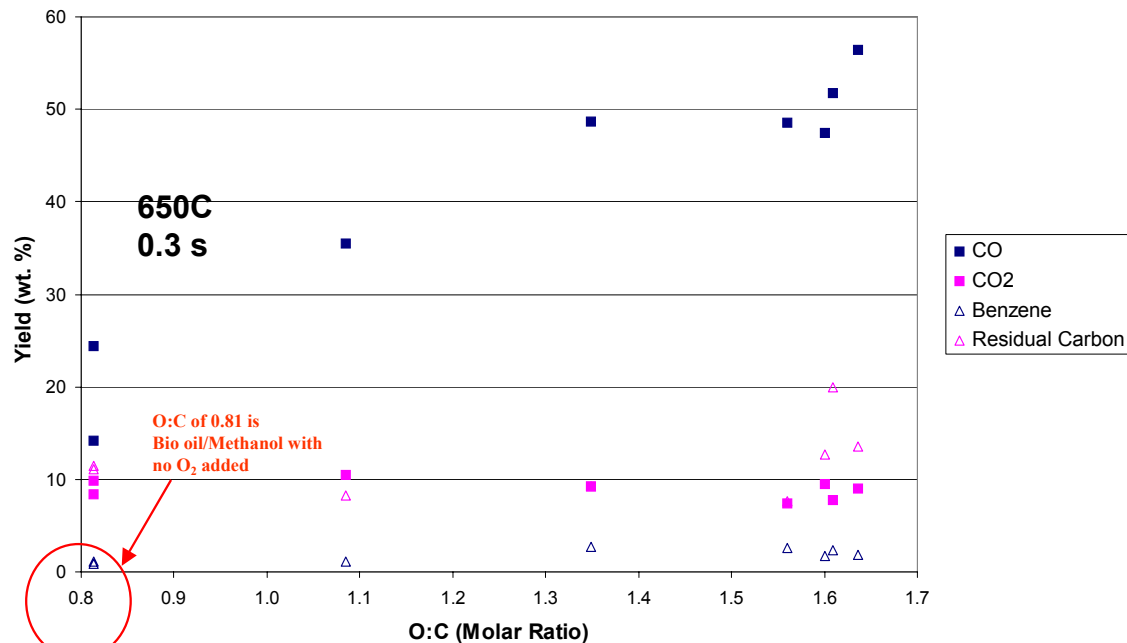**Thermal Cracking at 650 ºC (0.3 s;O:C 0.81)**

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

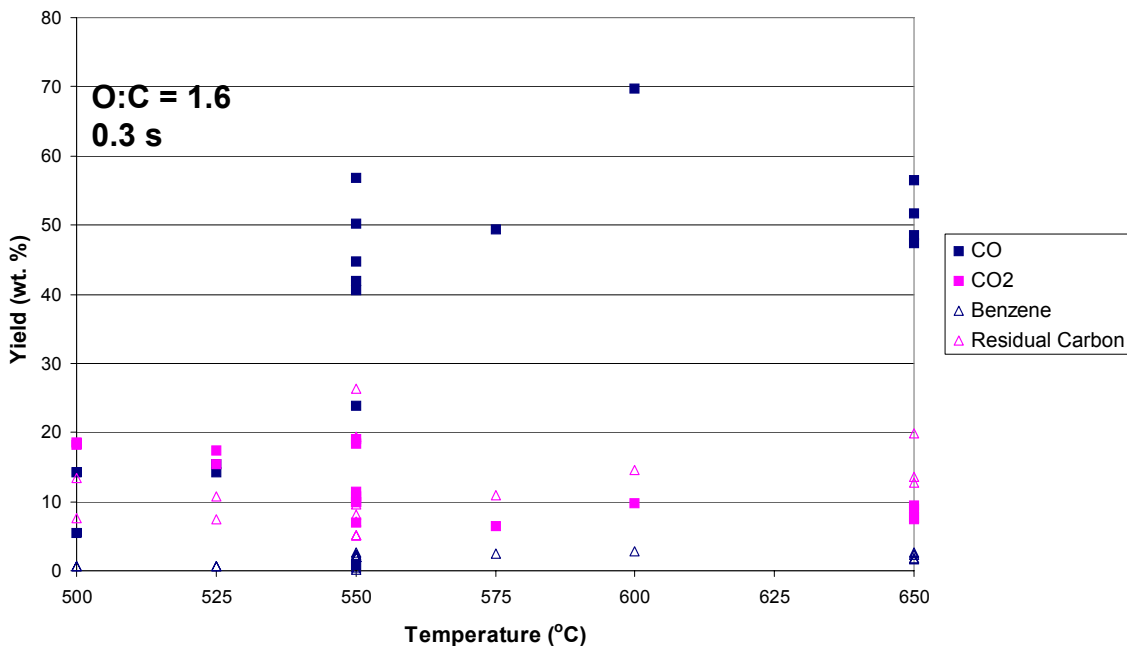

Under thermal cracking conditions, unconverted methanol and secondary products from the bio-oil predominate.

Under oxidative cracking conditions, H_2 (not shown), water, CO, and CO_2 predominate. Hence the role of the catalyst to be added is to finish the conversion and catalyze the water-gas shift.

**650C
0.3 s**

O:C of 0.81 is
Bio oil/Methanol with
no O₂ added

Yield (wt. %)

O:C (Molar Ratio)

- CO
- CO2
- Benzene
- Residual Carbon

Gas-phase
partial oxidation
leads to
high CO yields
with low CO_2.

**O:C = 1.6
0.3 s**

Yield (wt. %)

Temperature (°C)

- CO
- CO2
- Benzene
- Residual Carbon

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

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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)
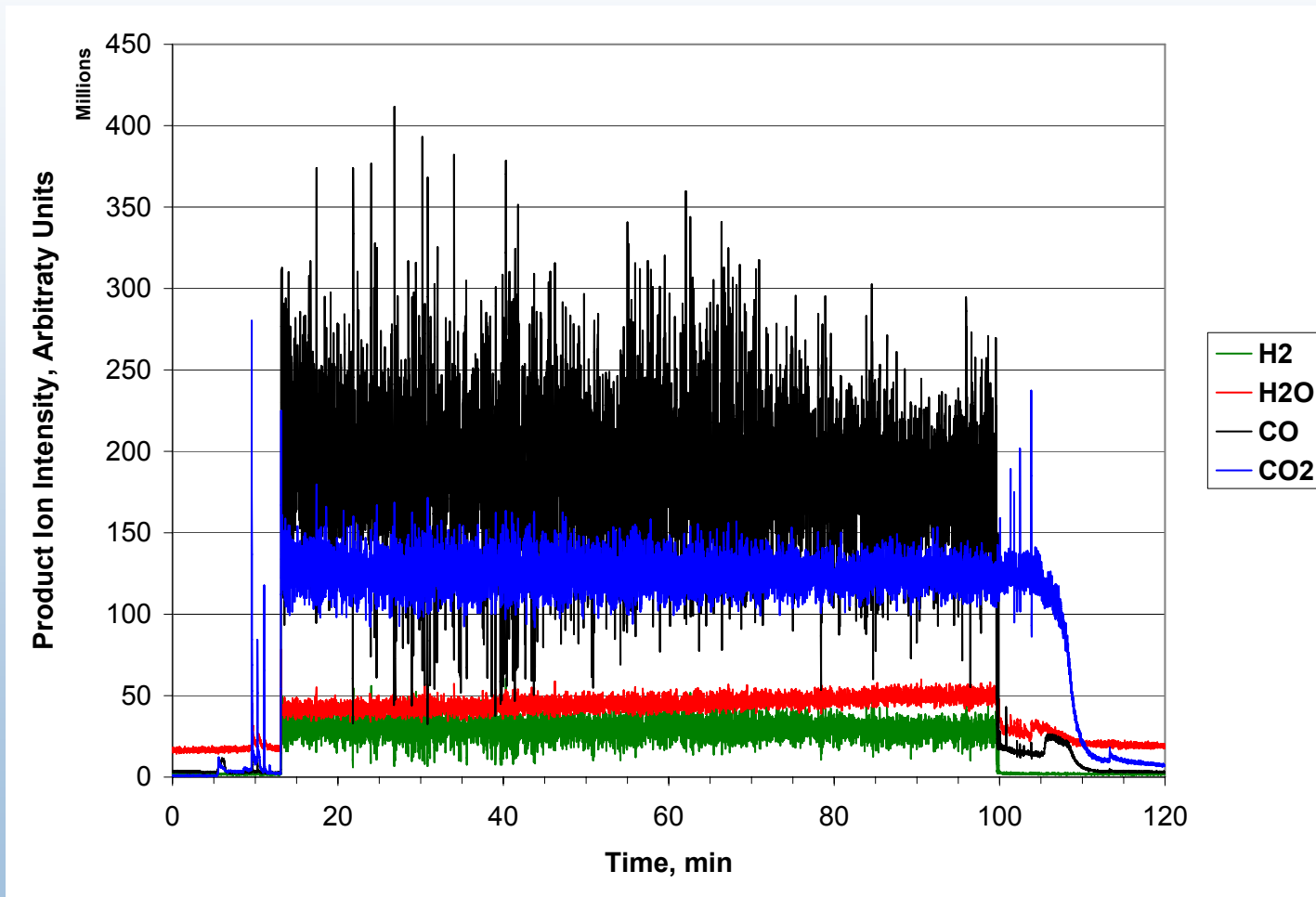
Issue: Need to account for potential temperature change.
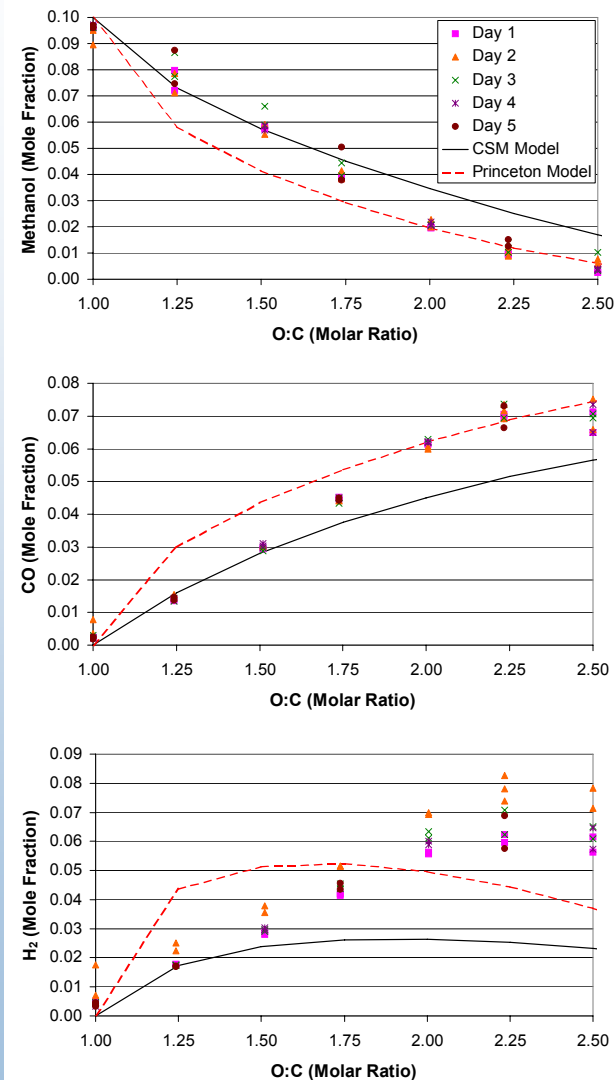
Catalytic Conversion
Oxidative Cracking .3 s @ 650ºC + .25% Rh on Al_2O_3

Bio-Oil:Methanol (50:50)

Methanol Conversion

Hydrogen Yield

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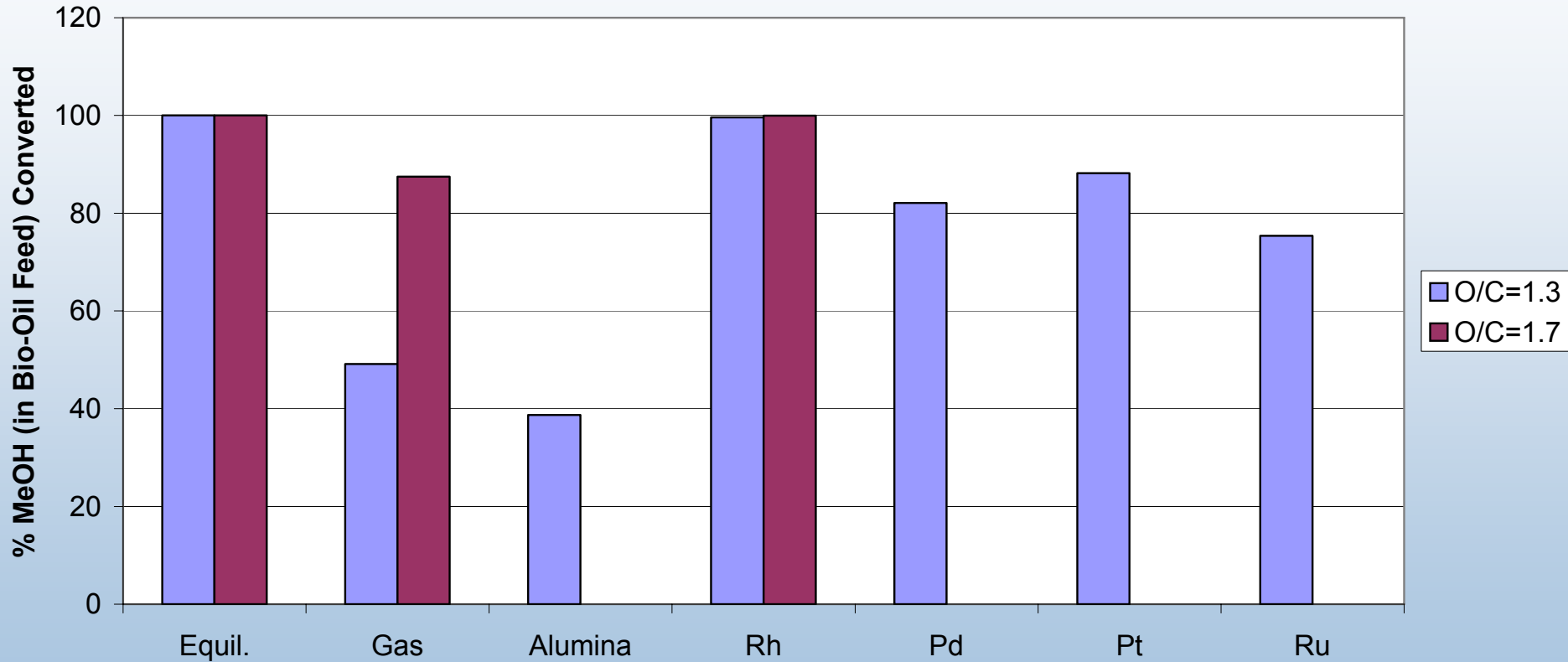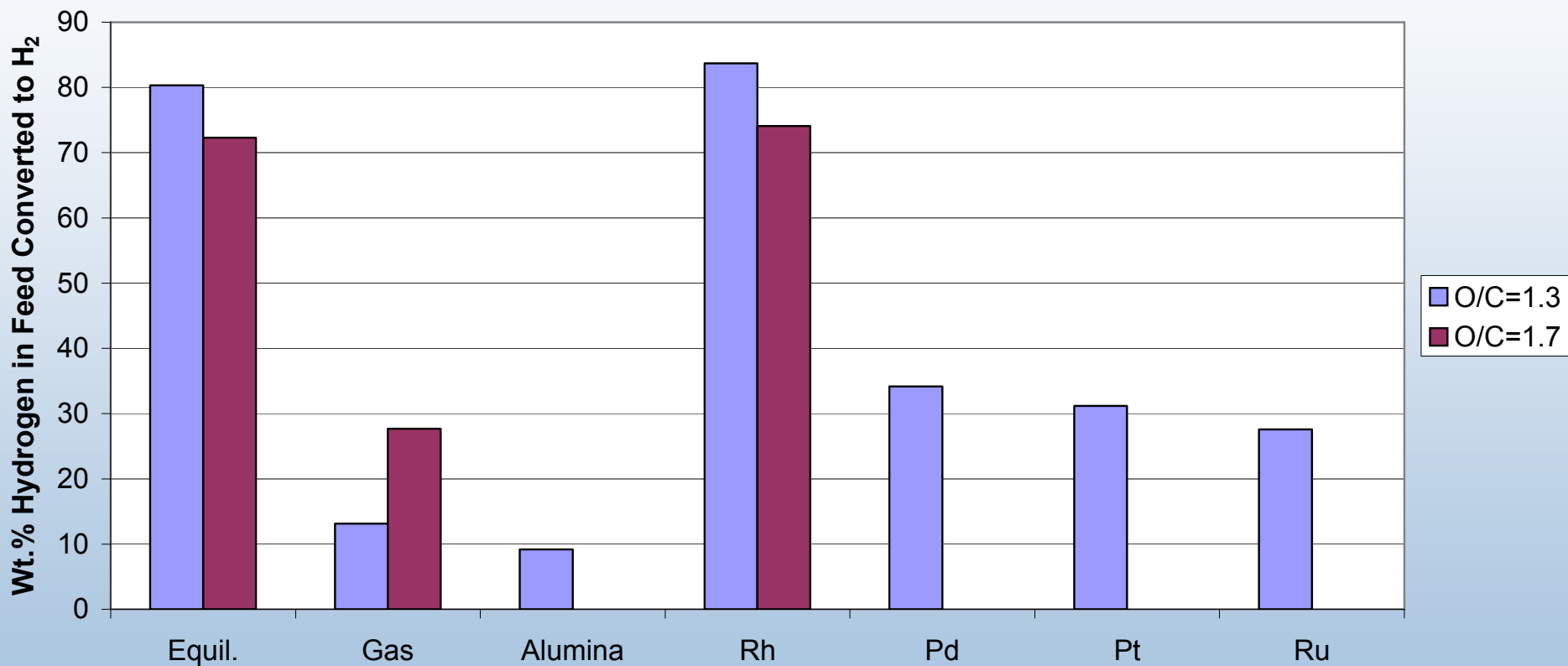
CO$_2$ Yield
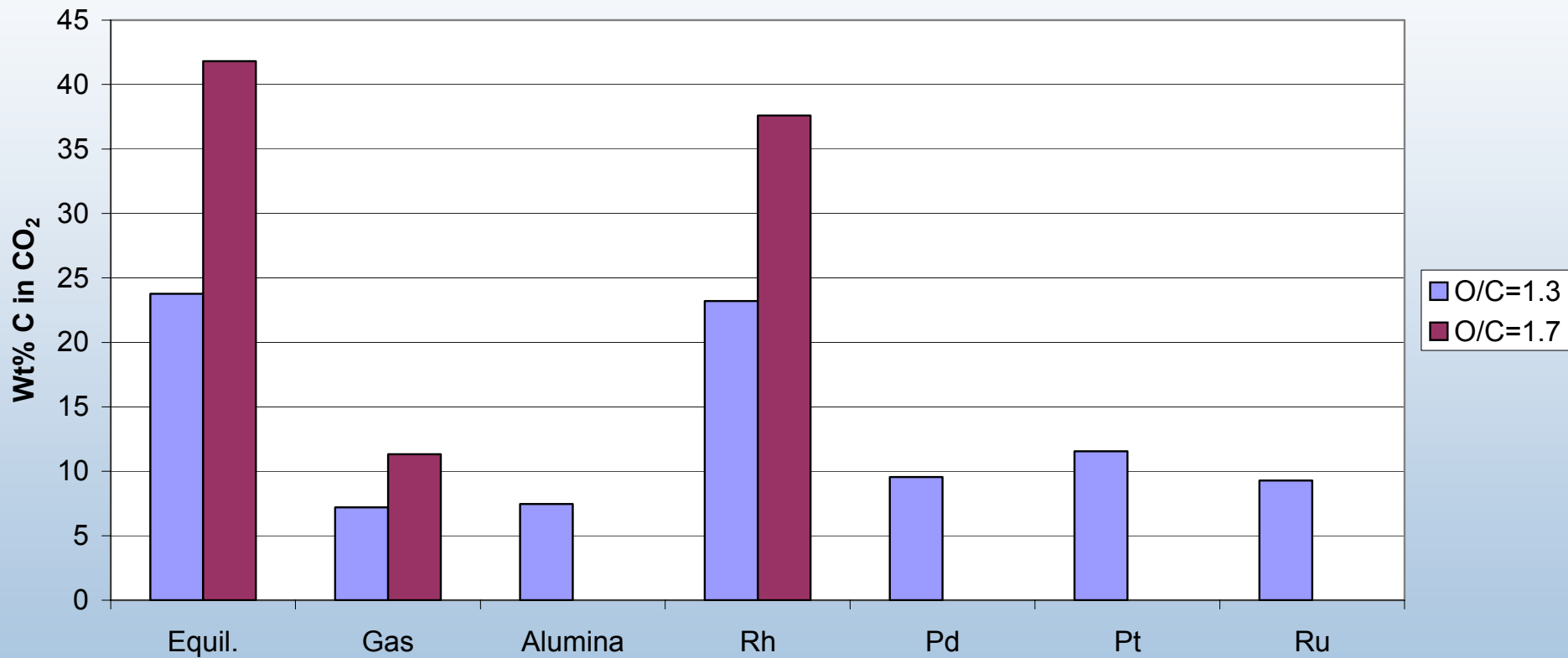
CO Yield
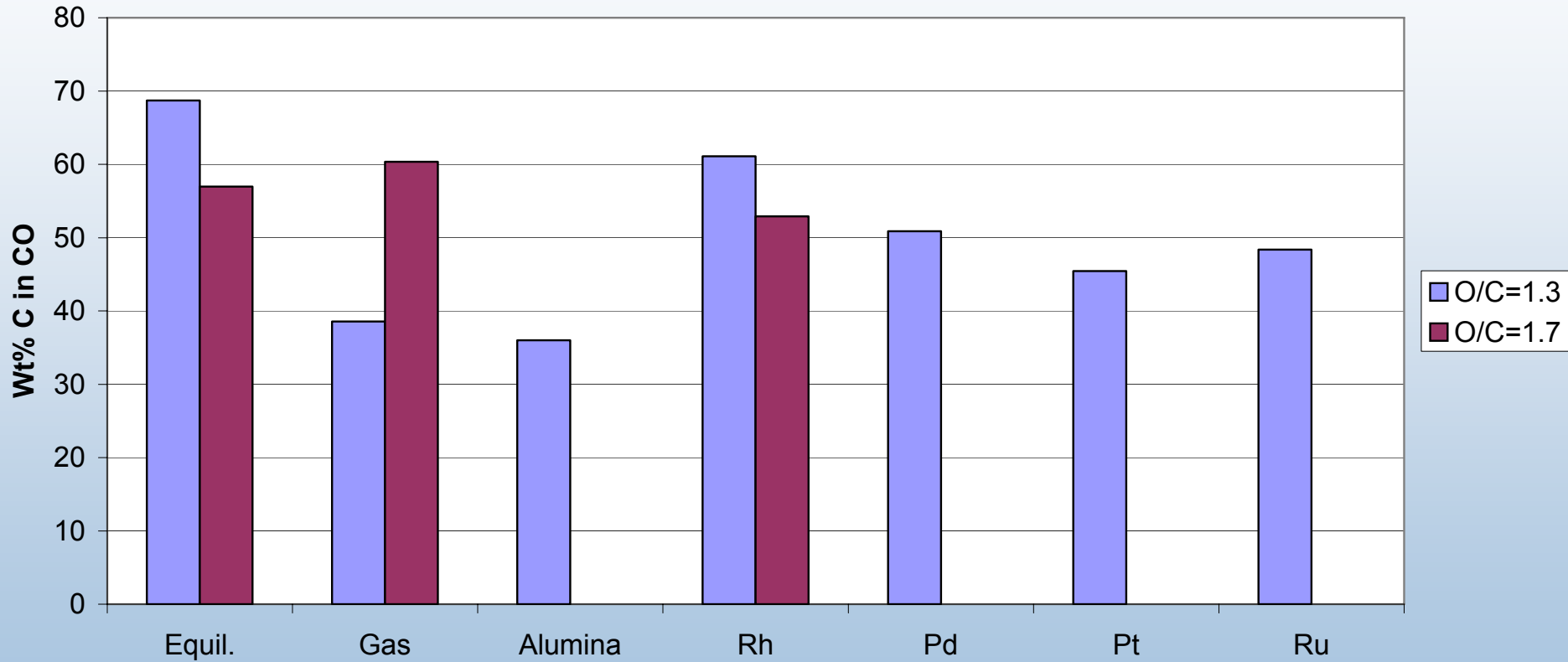
By-products are typically above equilibrium levels and thought to be generated from non-volatile species in aerosols and processes in the gas phase.

% C in Feed Converted to Carbon Deposits

	Equil.	Gas	Rh
O/C=1.3	3.6	1.0	4.4
O/C=1.7	0.0	0.9	1.4

% C in Feed Converted to Methane

% C in Feed Converted to Benzene

	Equil.	Gas	Rh
O/C=1.3	0.0	1.3	1.4
O/C=1.7	0.0	2.7	0.5
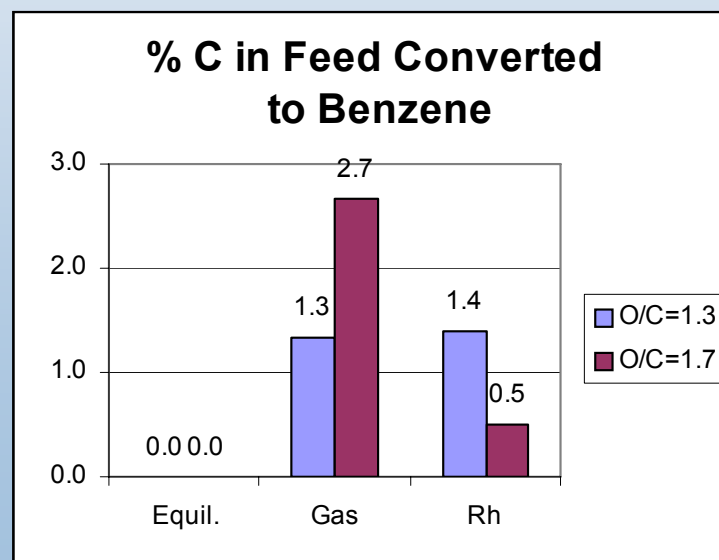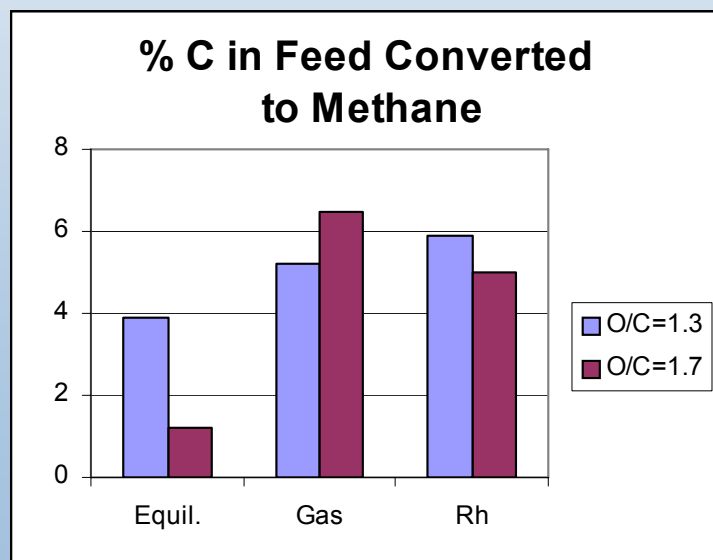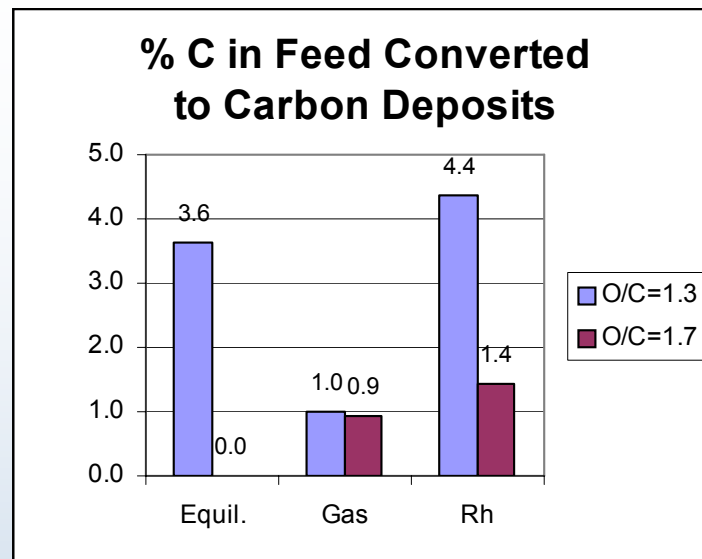
Process Comparison

	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
Water addition, Kg/hr	**1668**	**407**
Catalyst load, kg	**1734**	**430**
Temperature, C	**800**	**600**
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
Total reactor volume, L	**5029**	**632**

Program Timeline
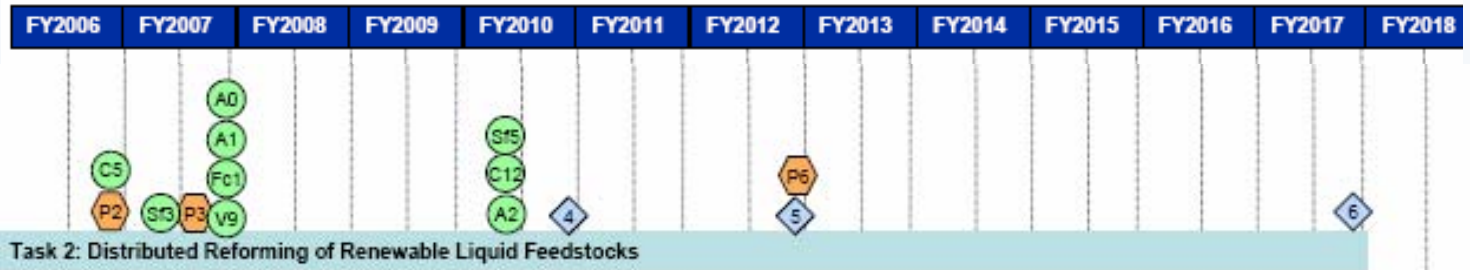
Task 2: Distributed Reforming of Renewable Liquid Feedstocks

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

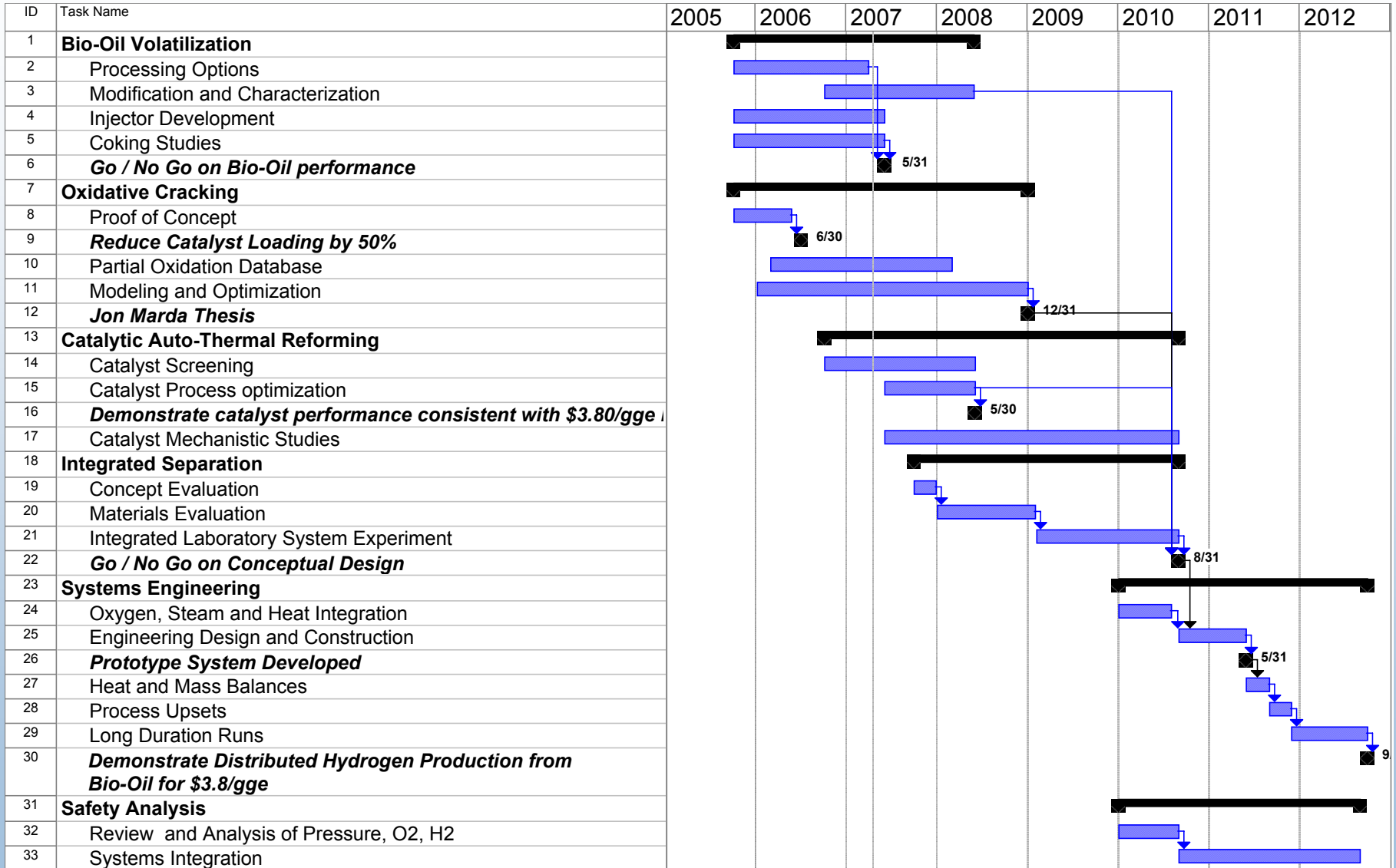**P2**   Output to Delivery, Storage, Fuel Cells, Tech Validation : Assessment of H2 quality cost and issues from production 4Q, 2006

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, 2006

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

ID	Task Name	2005	2006	2007	2008	2009	2010	2011	2012
1	**Bio-Oil Volatilization**								
2	Processing Options								
3	Modification and Characterization								
4	Injector Development								
5	Coking Studies								
6	*Go / No Go on Bio-Oil performance*			5/31					
7	**Oxidative Cracking**								
8	Proof of Concept								
9	*Reduce Catalyst Loading by 50%*		6/30						
10	Partial Oxidation Database								
11	Modeling and Optimization								
12	*Jon Marda Thesis*					12/31			
13	**Catalytic Auto-Thermal Reforming**								
14	Catalyst Screening								
15	Catalyst Process optimization								
16	*Demonstrate catalyst performance consistent with $3.80/gge*			5/30					
17	Catalyst Mechanistic Studies								
18	**Integrated Separation**								
19	Concept Evaluation								
20	Materials Evaluation								
21	Integrated Laboratory System Experiment								
22	*Go / No Go on Conceptual Design*						8/31		
23	**Systems Engineering**								
24	Oxygen, Steam and Heat Integration								
25	Engineering Design and Construction								
26	*Prototype System Developed*							5/31	
27	Heat and Mass Balances								
28	Process Upsets								
29	Long Duration Runs								
30	*Demonstrate Distributed Hydrogen Production from Bio-Oil for $3.8/gge*								9
31	**Safety Analysis**								
32	Review and Analysis of Pressure, O2, H2								
33	Systems Integration								

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

Relevance	Near-Term Renewable Feedstock for Distributed Reforming
Approach	•Bio-Oil Processed at Low Temp • Homogeneous and Catalytic Auto-Thermal Reforming
Accomplishments	System for Bio-Oil Volatilization, Oxidative Cracking, and Catalysis
Collaborations	•Colorado School of Mines •Chevron
Future Work	•Oxidative Cracking Mechanism and Catalysis in FY 2007 •System Development in FY 2008