Distributed Bio-Oil Reforming

2007 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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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:

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

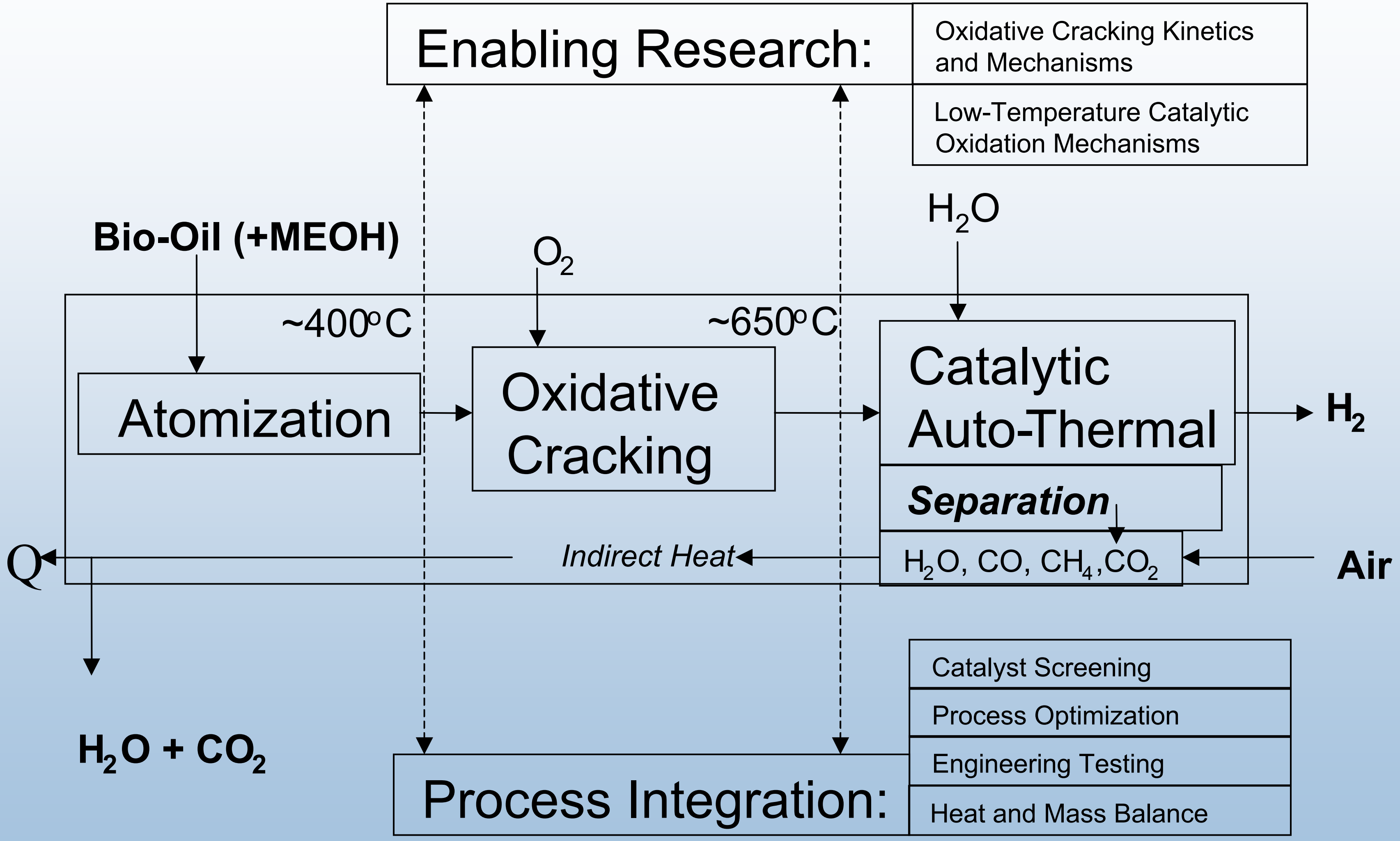
Practical Yield:

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

Separation

H_2O, CO, CH_4, CO_2

H_2

Air

Indirect Heat

Q

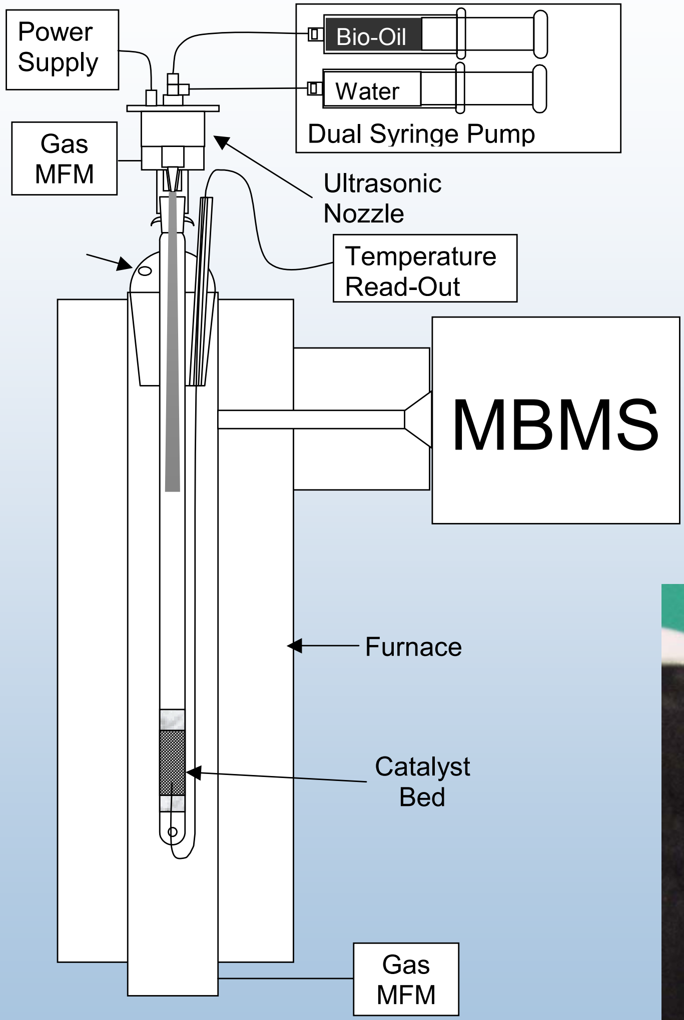
$H_2O + CO_2$

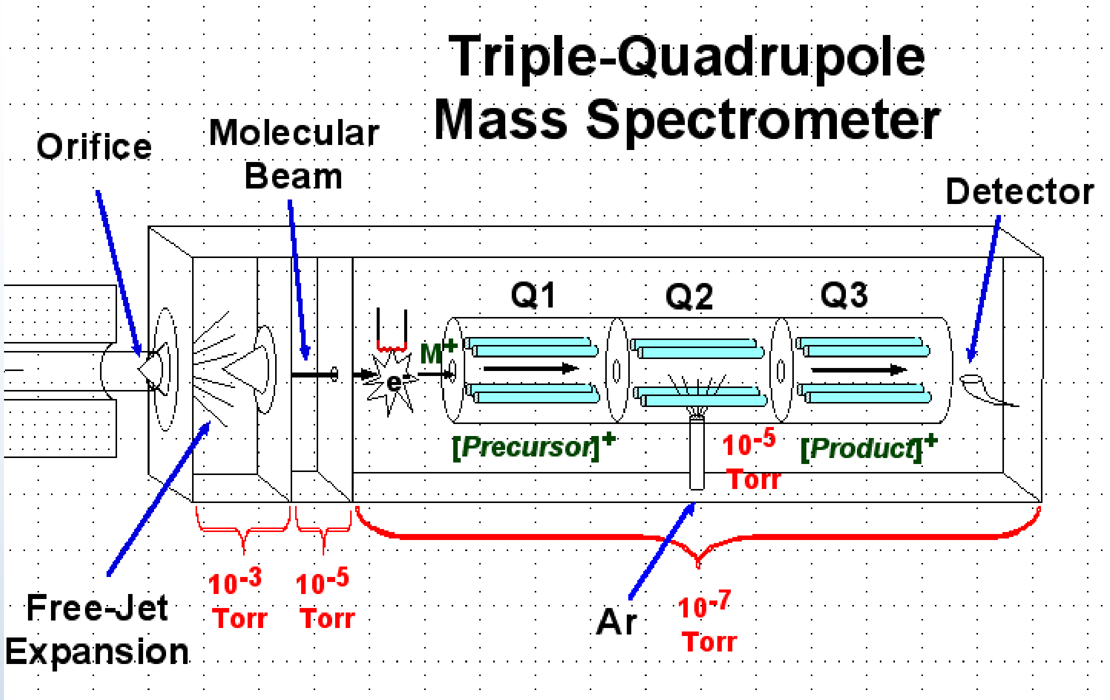
Process Integration:

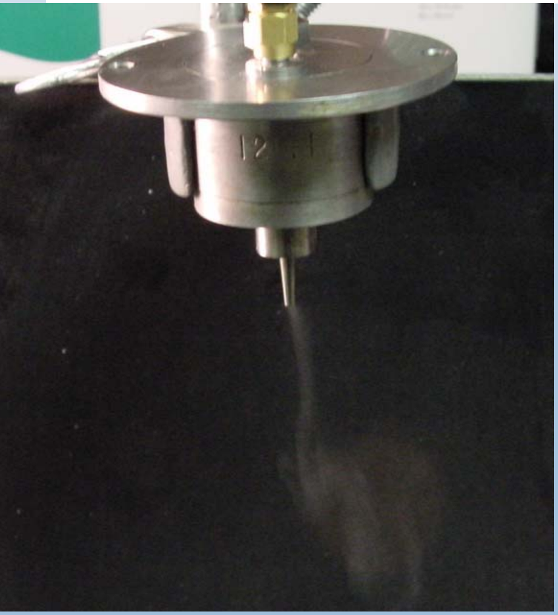
- Catalyst Screening
- Process Optimization
- Engineering Testing
- Heat and Mass Balance

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







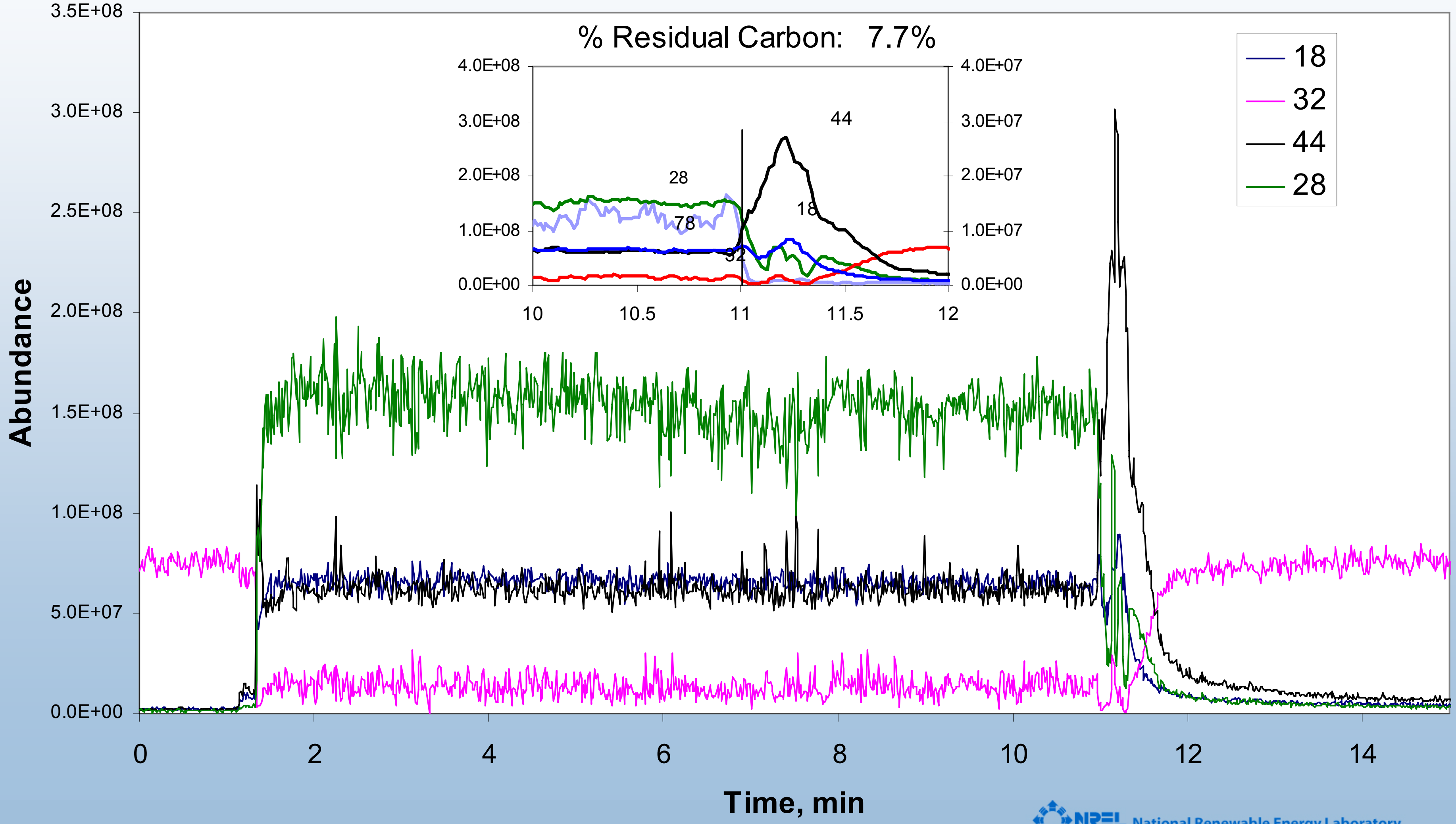
Ultrasonic Nozzle

- 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)



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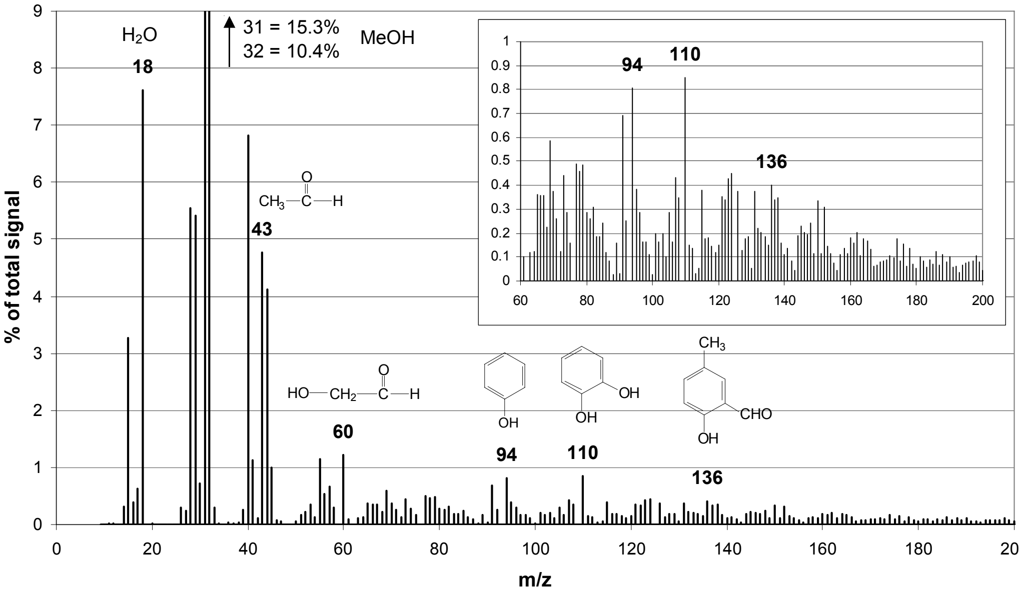
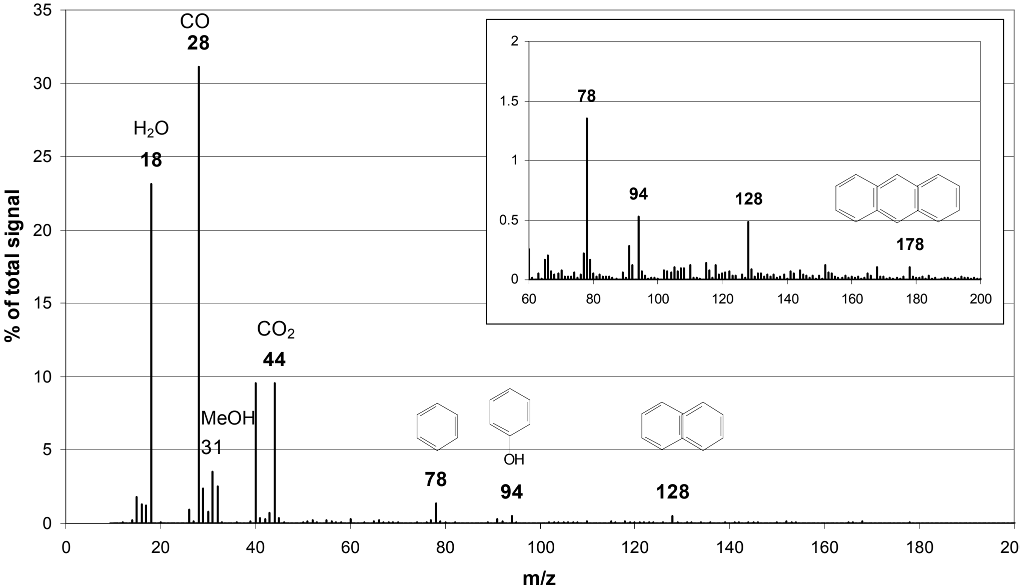
Thermal Cracking at 650 °C (0.3 s;O:C 0.81)

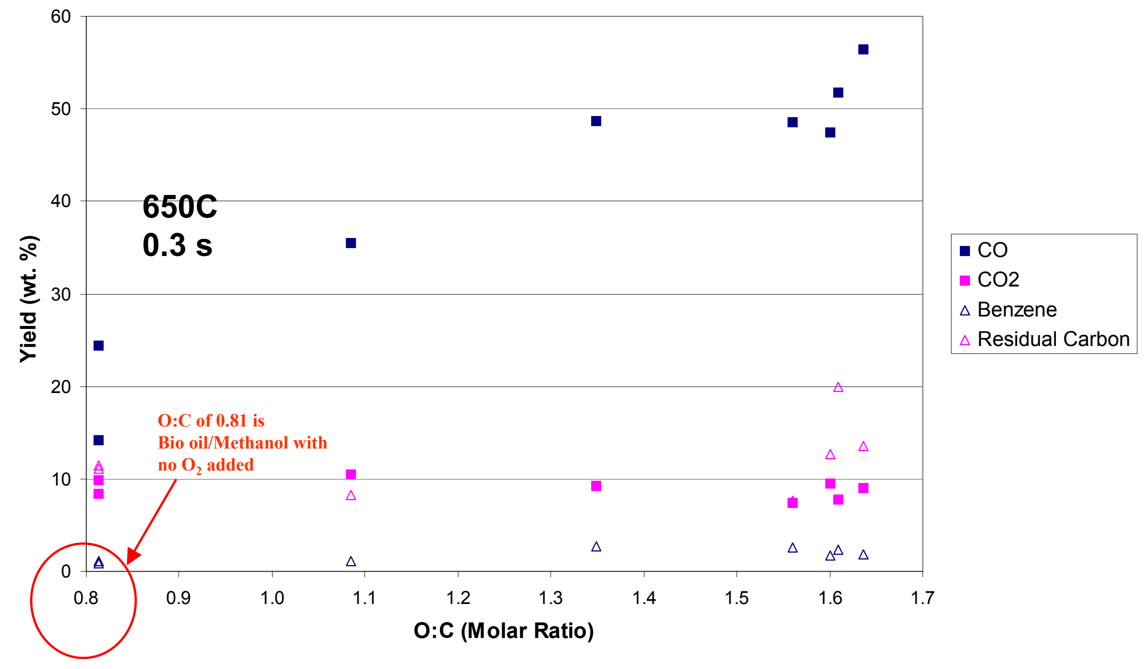


Oxidative Cracking at 650 °C (0.3 s;O:C 1.6)

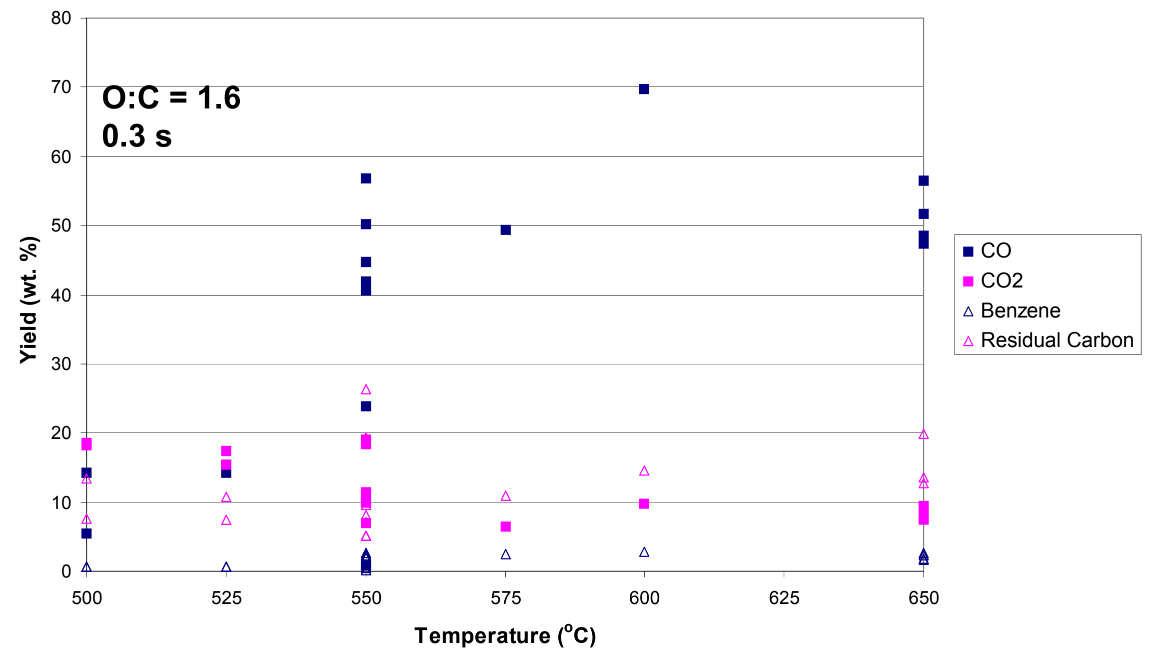


Under thermal cracking conditions, unconverted methanol and secondary products from the bio-oil predominate.

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.



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



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

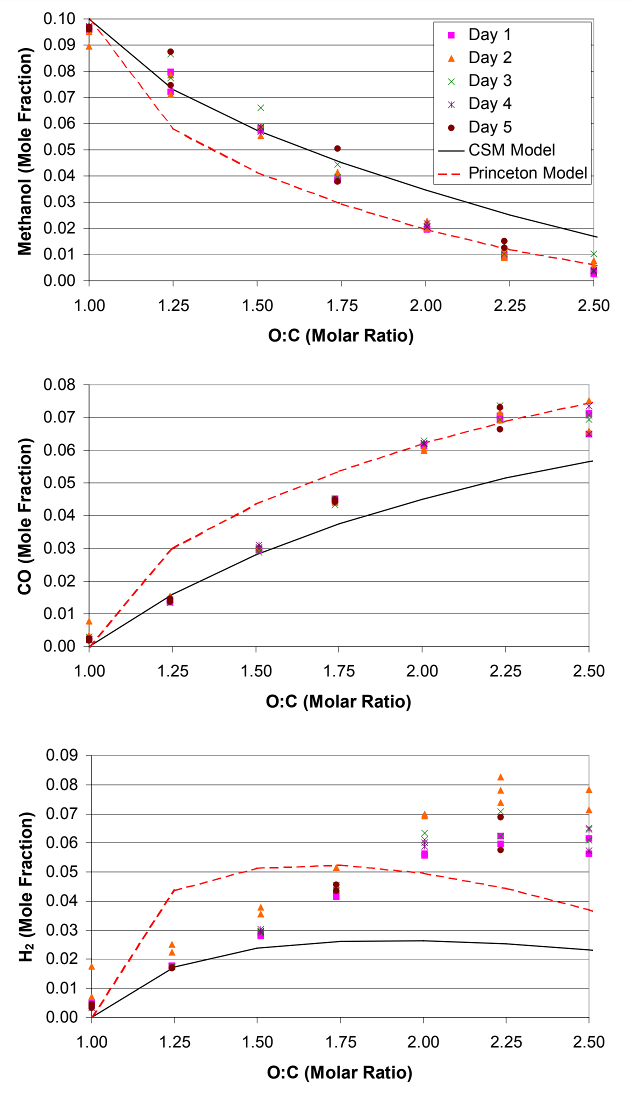
Modeling Methanol Pyrolysis and Partial Oxidation

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)

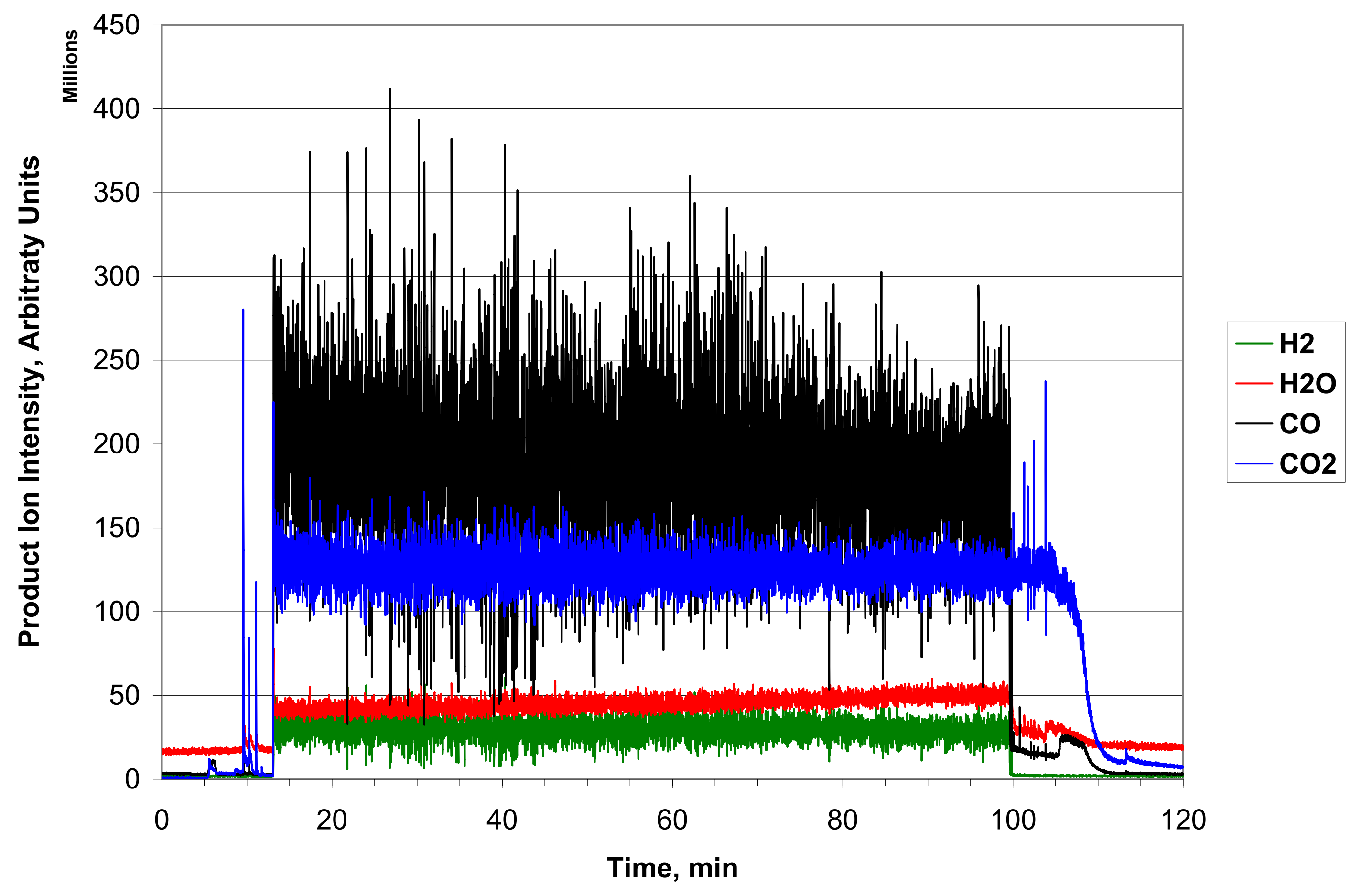
Issue: Need to account for potential temperature change.



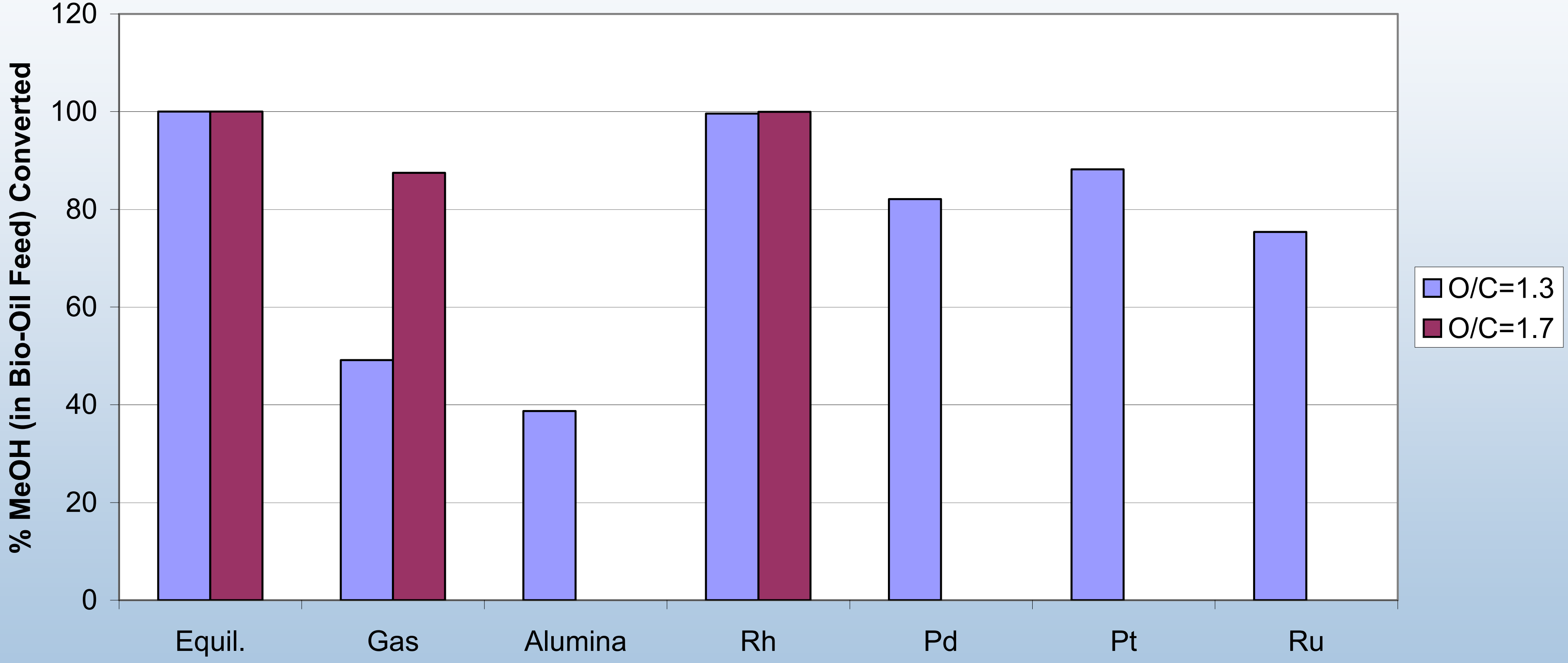
Catalytic Conversion

Oxidative Cracking .3 s @ 650°C + .25% Rh on Al_2O_3

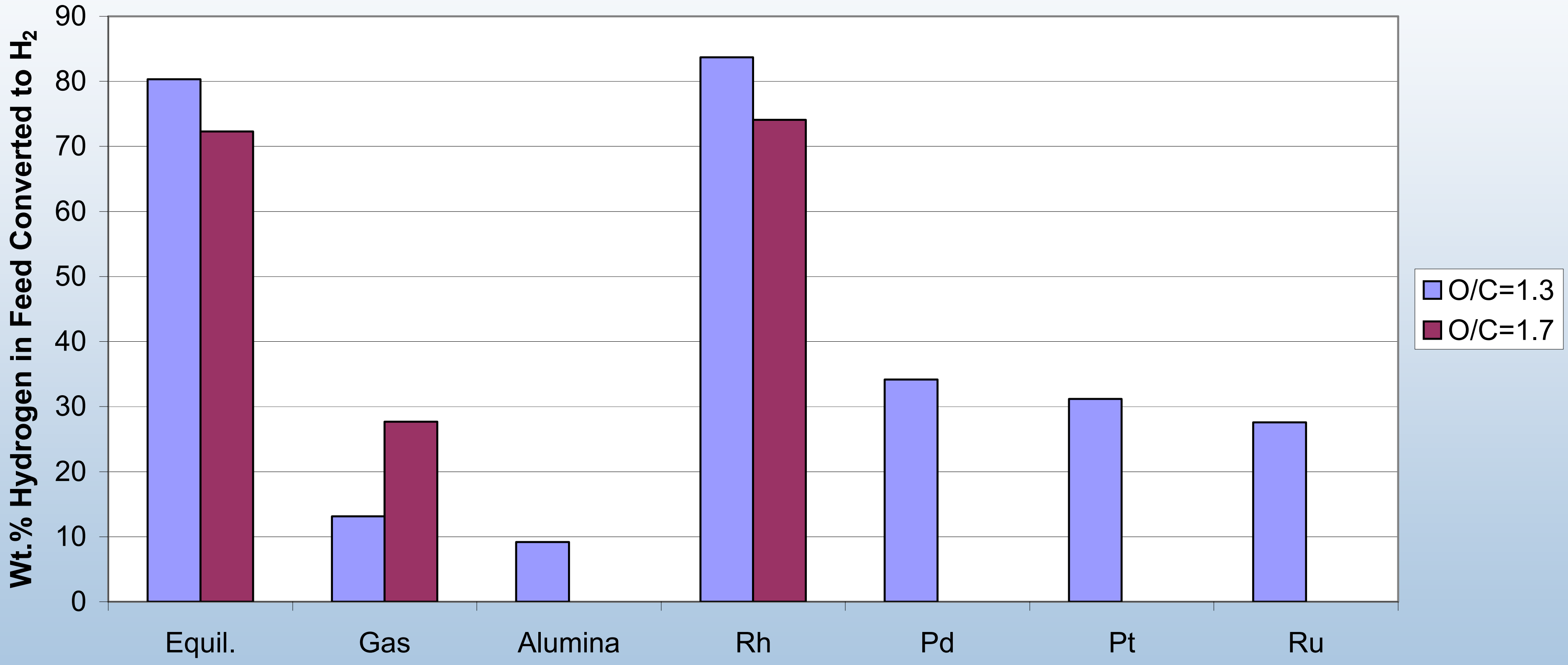
Bio-Oil:Methanol (50:50)



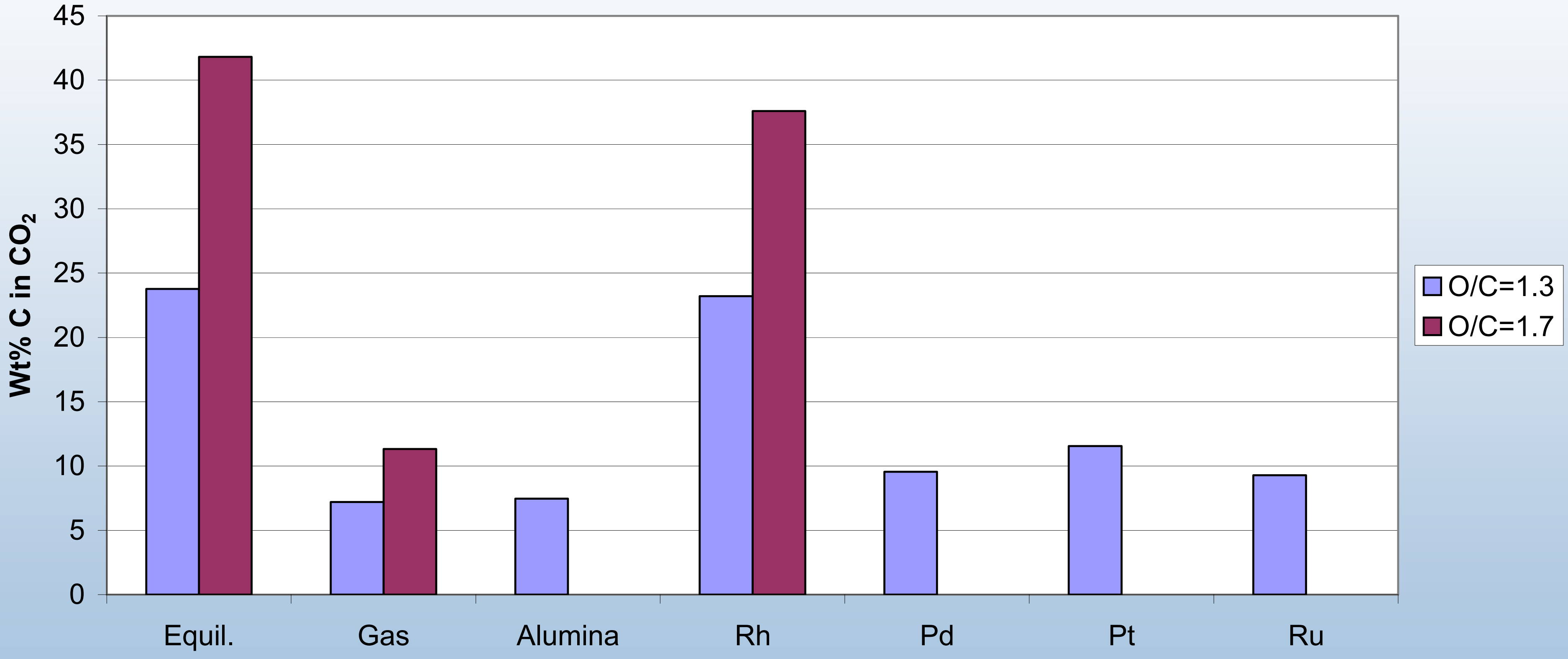
Methanol Conversion



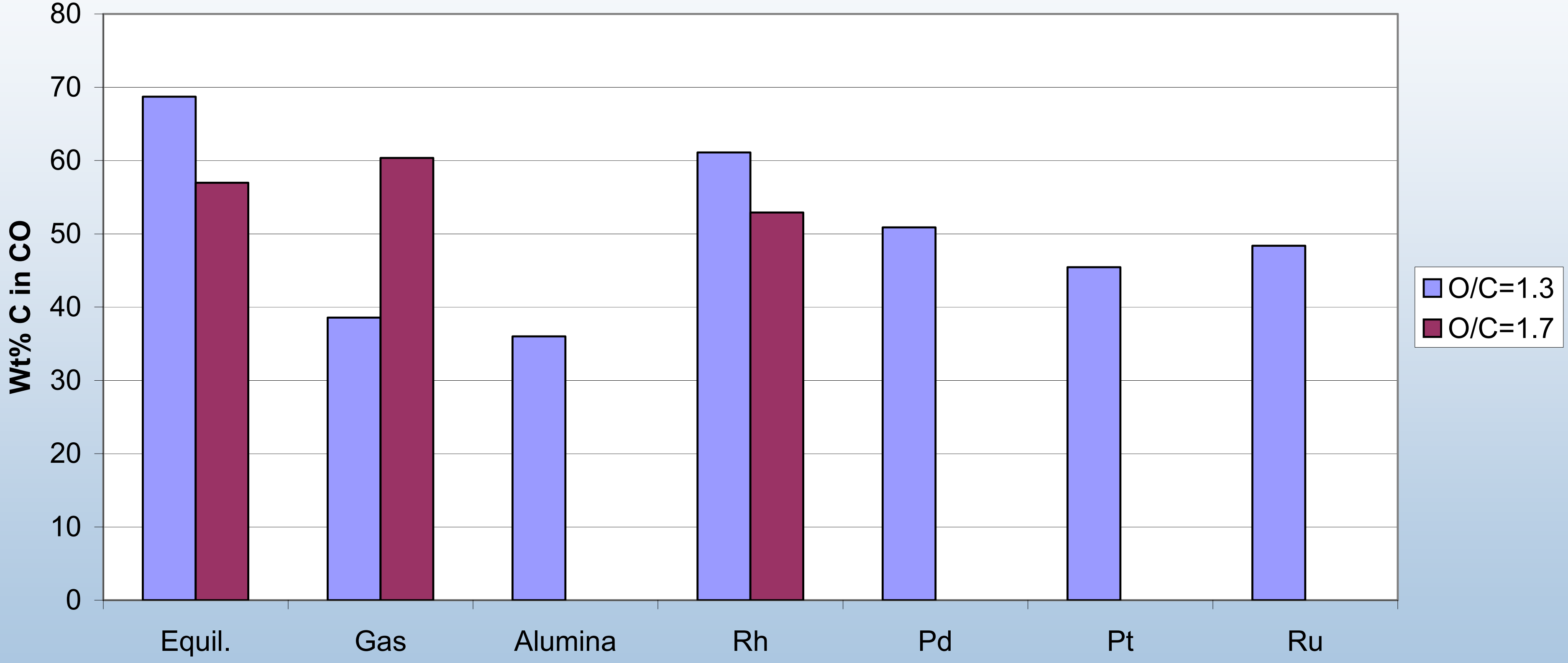
Hydrogen Yield



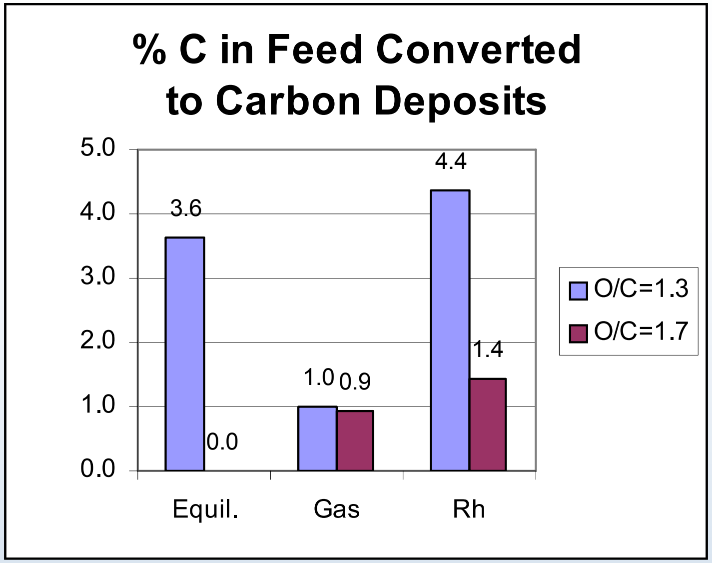
CO_2 Yield

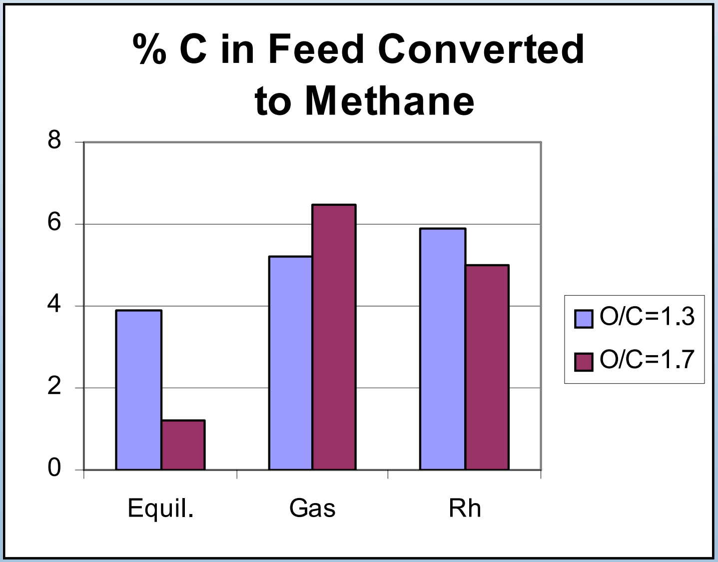

45
40
35
30
25
20
15
10
5
0
Wt% C in CO_2
Equil.
Gas
Alumina
Rh
Pd
Pt
Ru
O/C=1.3
O/C=1.7

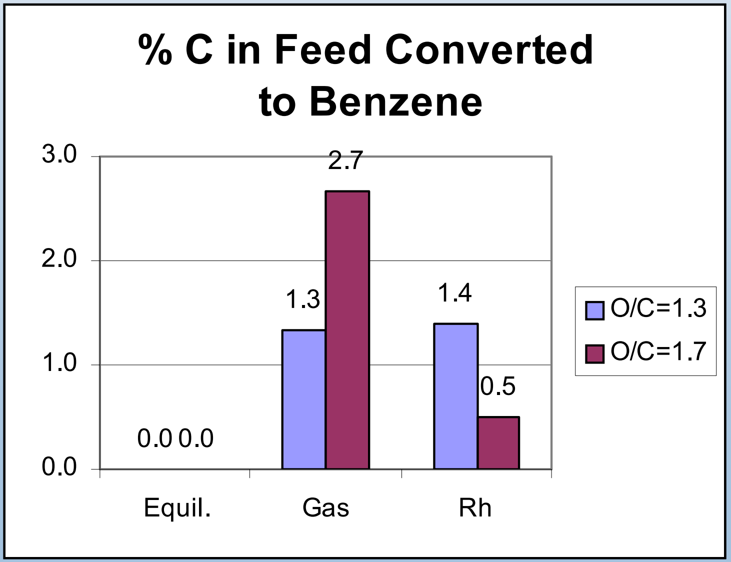
CO Yield


80
70
60
50
40
30
20
10
0
Wt% C in CO
Equil.
Gas
Alumina
Rh
Pd
Pt
Ru
O/C=1.3
O/C=1.7

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

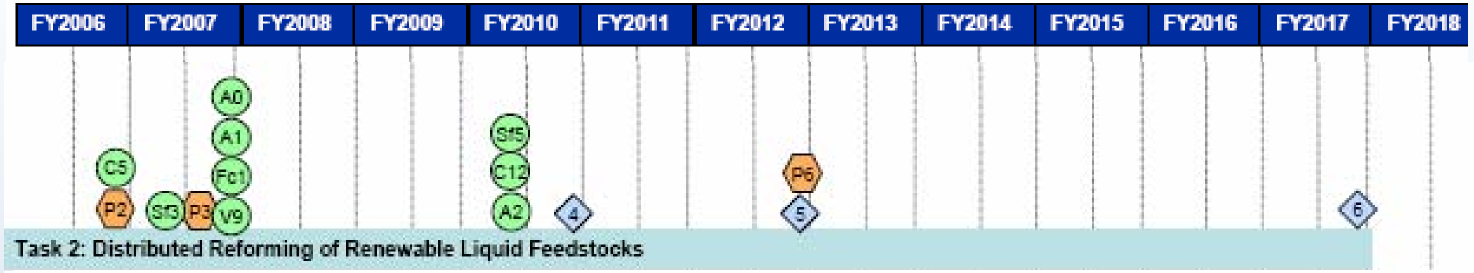

% C in Feed Converted to Methane


% C in Feed Converted to Benzene

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



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

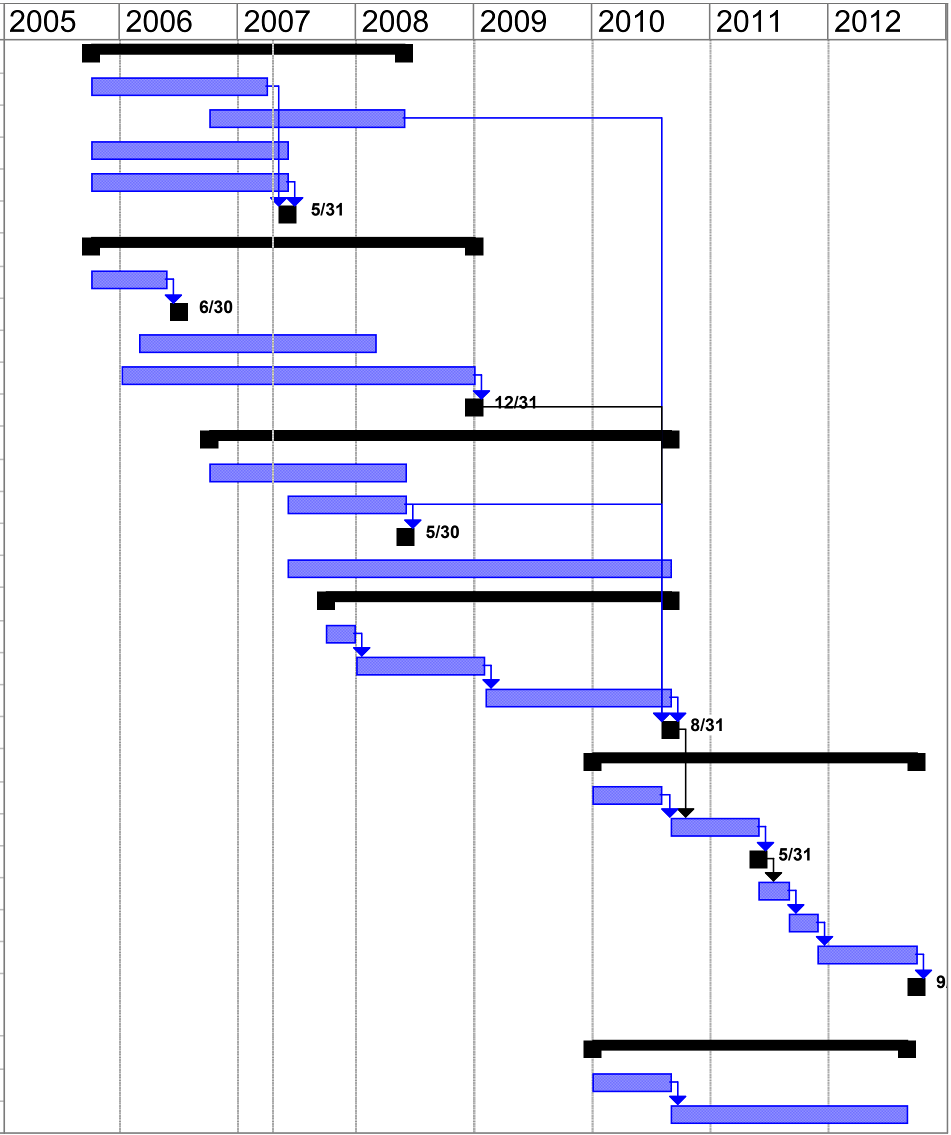
P1	Output to Technology Validation: Hydrogen production technology for distributed systems using natural gas with projected cost of \$3.00/gge hydrogen at the pump, untaxed, assuming 500 units of production per year. 4Q, 2005
P2	Output to Delivery, Storage, Fuel Cells , Tech Validation : Assessment of 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
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***
7	**Oxidative Cracking**
8	Proof of Concept
9	***Reduce Catalyst Loading by 50%***
10	Partial Oxidation Database
11	Modeling and Optimization
12	***Jon Marda Thesis***
13	**Catalytic Auto-Thermal Reforming**
14	Catalyst Screening
15	Catalyst Process optimization
16	***Demonstrate catalyst performance consistent with $3.80/gge***
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***
23	**Systems Engineering**
24	Oxygen, Steam and Heat Integration
25	Engineering Design and Construction
26	***Prototype System Developed***
27	Heat and Mass Balances
28	Process Upsets
29	Long Duration Runs
30	***Demonstrate Distributed Hydrogen Production from Bio-Oil for $3.8/gge***
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