

Distributed Bio-Oil Reforming

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Overview

T I M E L I N E

- *Start date: 2005*
- *End date: 2012*
- *Percent complete: 60%*

B U D G E T

- FY 2005: \$100K
- FY 2006: \$300K
- FY 2007: \$350K
- FY 2008: \$700K
- FY 2009: \$0K

B A R R I E R S

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 (bio-oil to H₂)

P A R T N E R S

- Colorado School of Mines - Oxidative cracking
- University of Minnesota - Catalyst Development
- Chevron – Feedstock Effects (3 year CRADA)

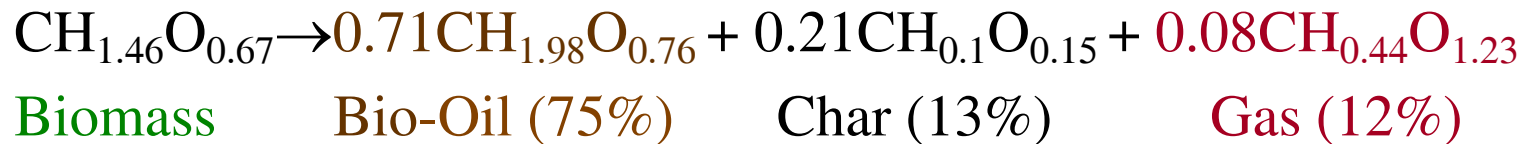
Distributed Production of Hydrogen via Biomass Pyrolysis

Biomass fast pyrolysis produces high yields of liquid product, bio-oil, which can be 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:

Bio-oil (74 wt% CH_{1.28}O_{0.41}, 26 wt % H₂O) - 90 wt% of feed
CH₃OH - 10 wt% of feed
H₂O (2 mole ratio steam to carbon)

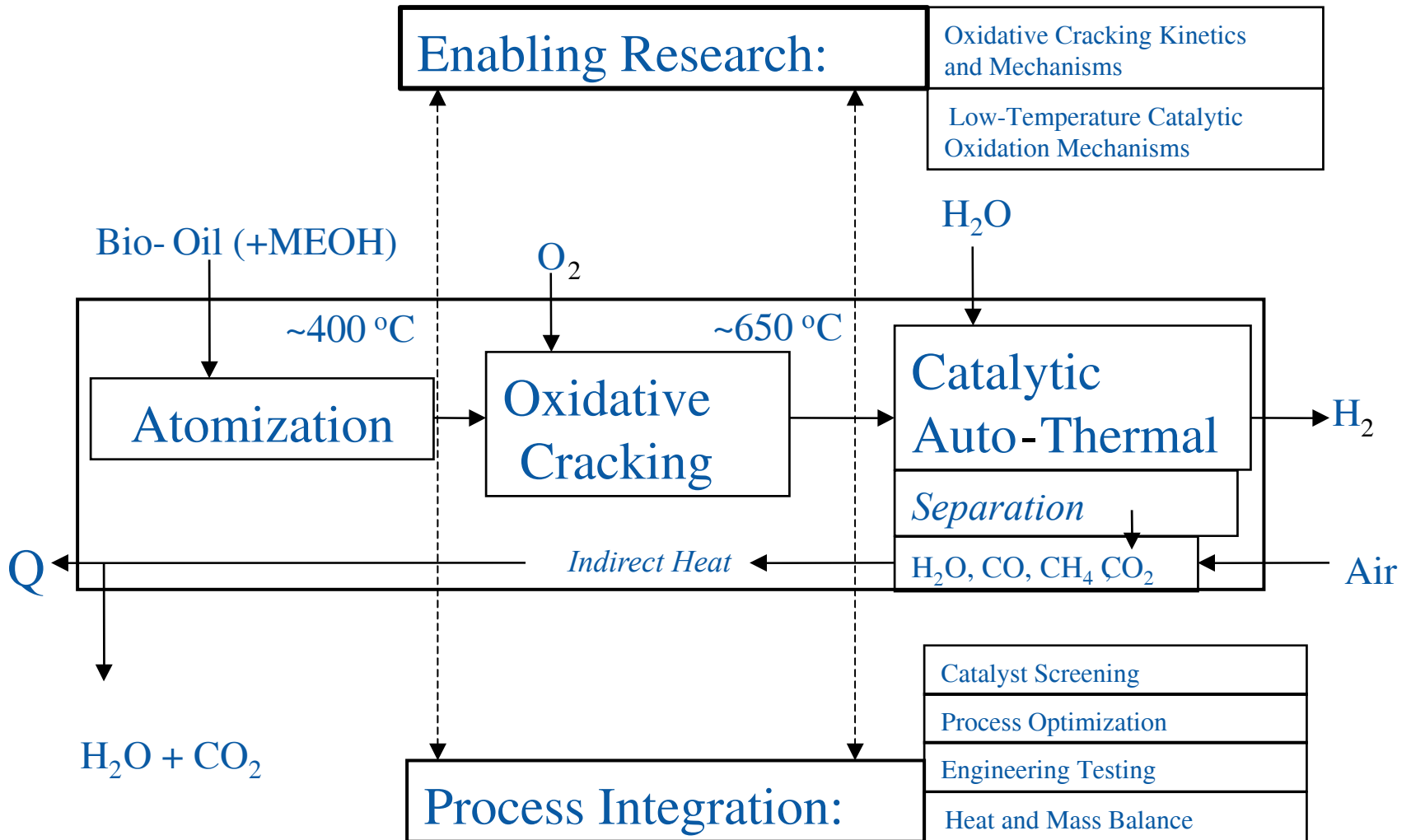
Overall Reaction:



Estimated Practical Yield: 9.3 wt %

Energy Efficiency Estimates are in Progress based on Aspen Modeling

Distributed Bio-Oil Reforming Approach



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 2009

Improve bio-oil atomization with less MeOH addition,

Demonstrate non-catalytic partial oxidation of bio-oil at bench scale

Demonstrate catalytic conversion of bio-oil to syngas at bench scale

Provide mass balance data for H₂A

Technical Accomplishments

- FY 2006
 - Bio-oil volatilization method developed
 - Oxidative cracking to CO with minimal CO₂
- FY 2007
 - Demonstrated equilibrium catalytic conversion to syngas at low temperature and low H₂O/C
- FY2008
 - Demonstrated catalyst performance
 - Designed and built a bench scale reactor system
- FY2009
 - Demonstrated operation of a bench-scale reactor system using 90 wt% bio-oil/10 wt% methanol mixture

Progress in Process Development

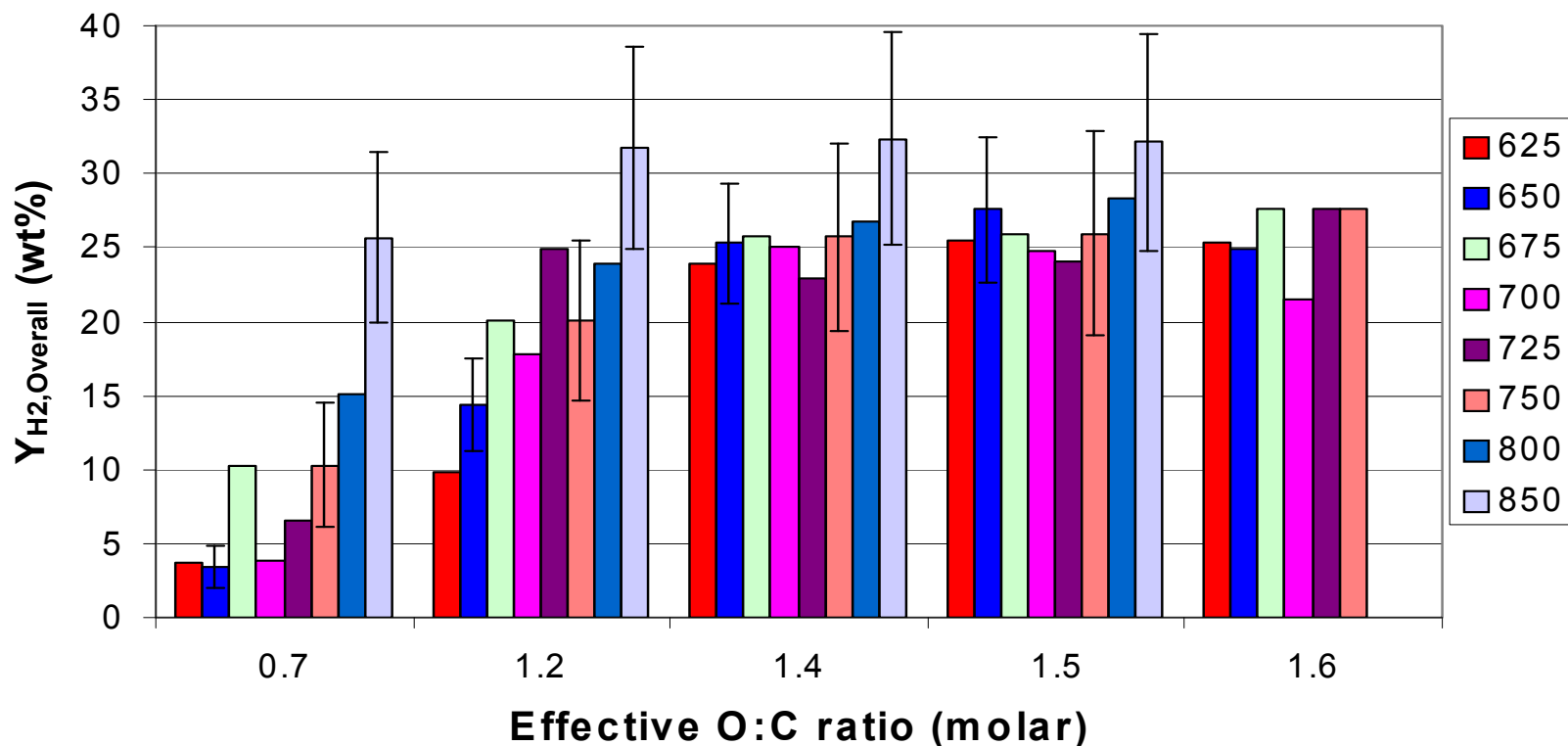
1. Bio-Oil Volatilization

- **The new ultrasonic nozzle can produce a fine mist even from high-viscosity liquids.**
- **Successful tests with 90 wt% bio-oil/10 wt% methanol mixture.**
- **Promising attempts of feeding neat bio-oil though 10 wt% methanol addition will likely be used to homogenize and stabilize bio-oil.**
- **Ultrasonic nozzle will likely be replaced by a high-pressure injector in larger-scale units.**

Progress in Process Development

2. Oxidative Cracking

Overall H₂ Yield

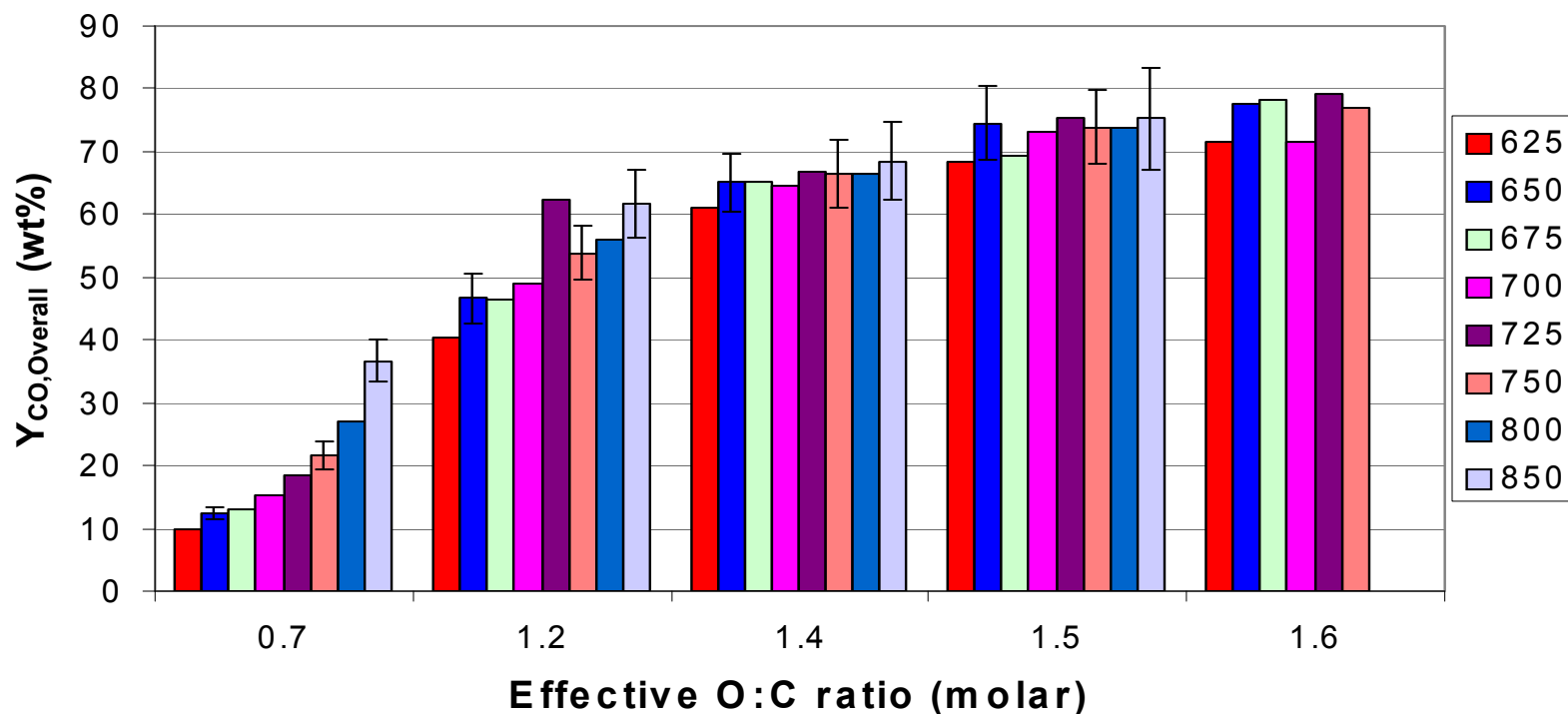


Hydrogen yields are 25-30% of the stoichiometric potential;
Those yields will significantly increase after completion of water-gas shift.

Progress in Process Development

2. Oxidative Cracking

Overall CO Yield

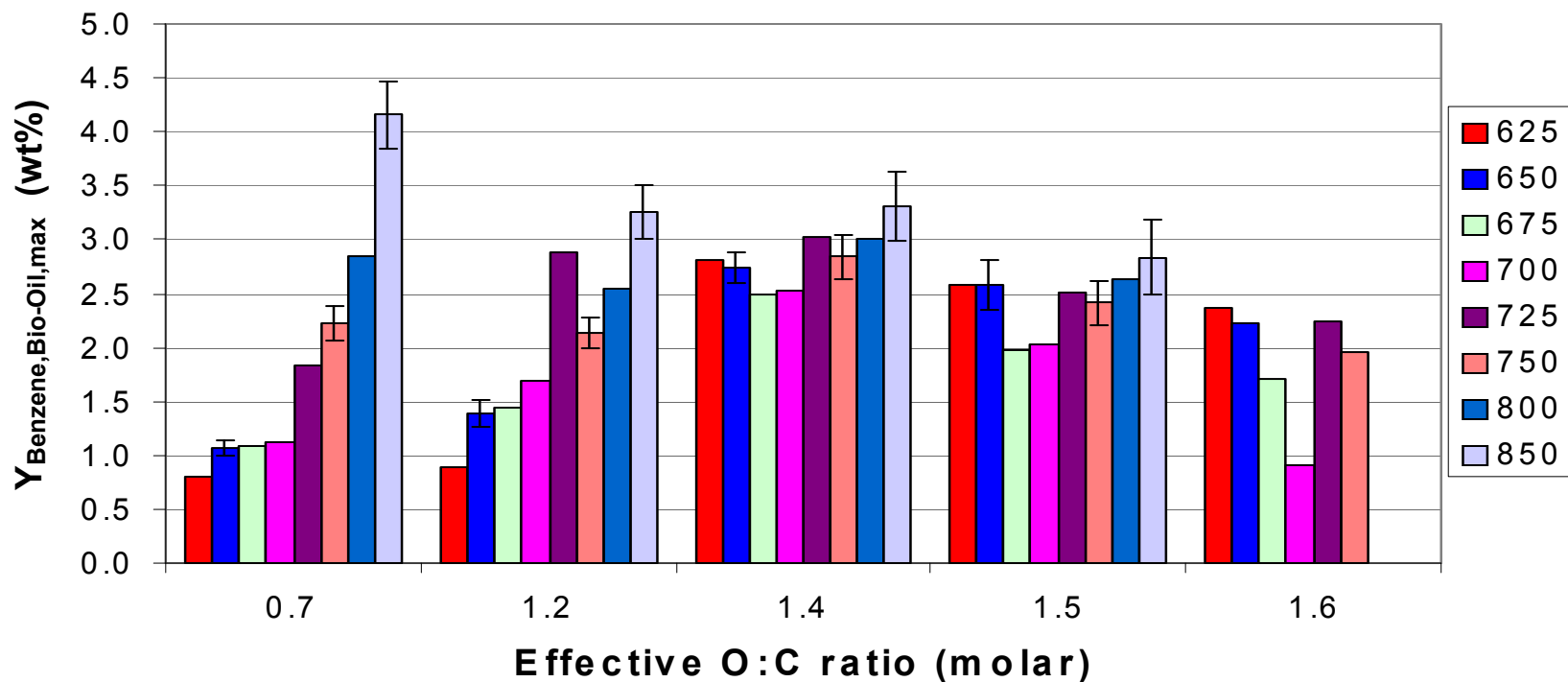


>70% carbon can be converted to CO by non-catalytic POX;
O:C ratio has much stronger effect than temperature on CO yields

Progress in Process Development

2. Oxidative Cracking

Benzene Yield

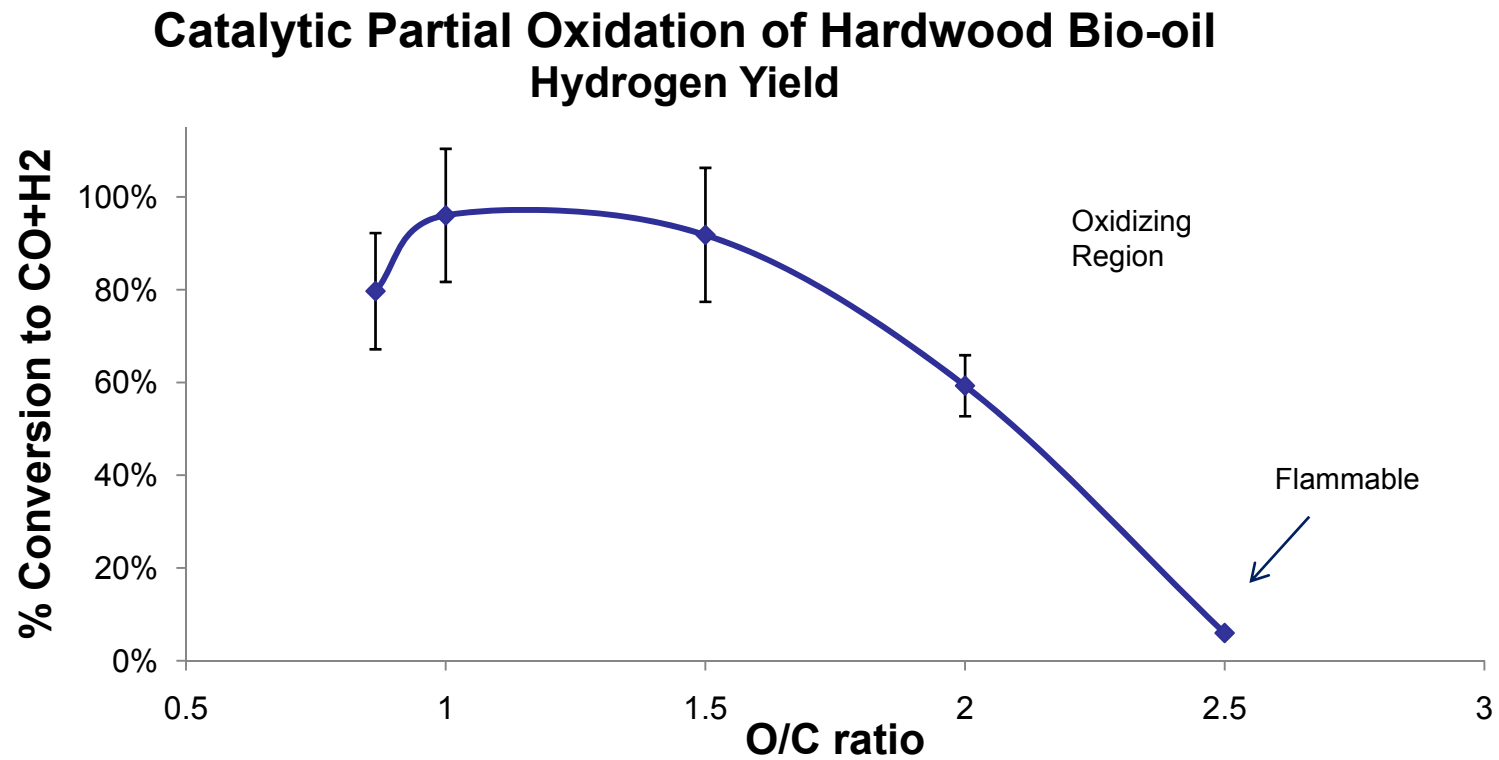


At O:C>1.4 temperature has little effect on benzene (aromatics) formation

Progress in Process Development

3. Catalytic Conversion

University of Minnesota catalyst (Lanny Schmidt's group): 1 wt % Rh and 1 wt % ceria on alumina



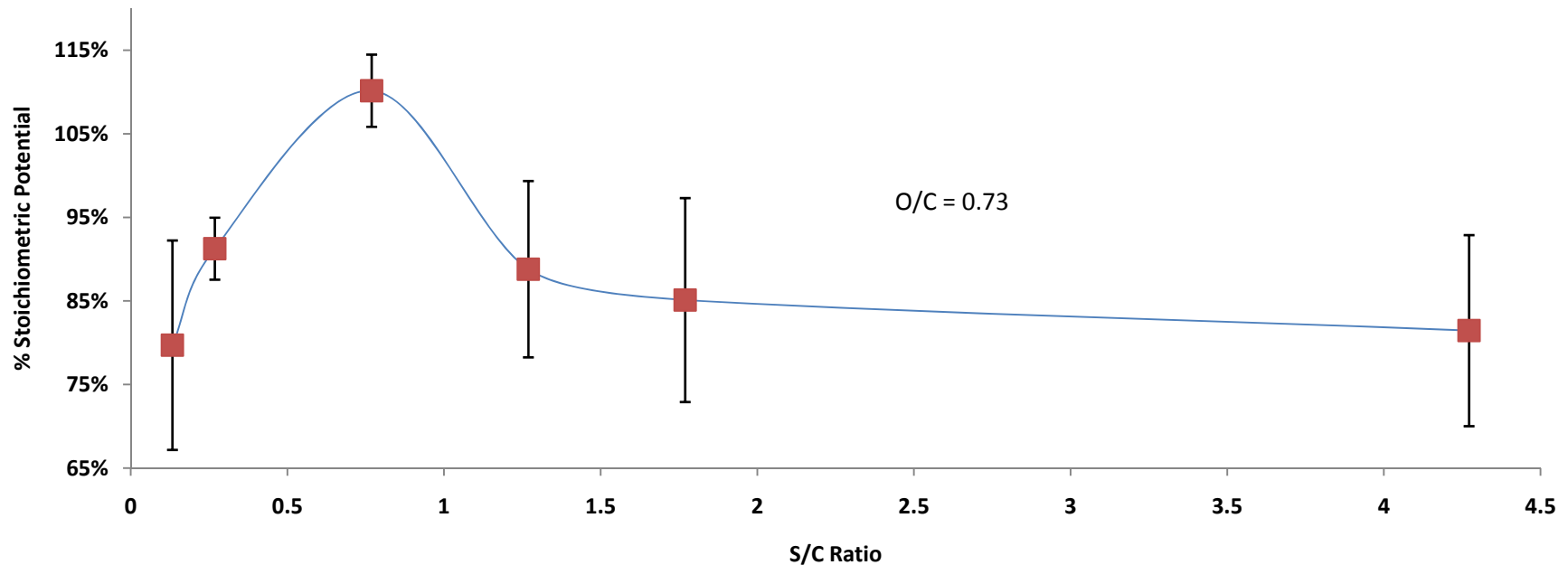
1 – 1.5 is the optimal range of O/C for catalytic POX of bio-oil

Progress in Process Development

3. Catalytic Conversion

University of Minnesota catalyst (Lanny Schmidt's group): 1 wt % Rh and 1 wt % ceria on alumina

Catalytic Steam Reforming of Hardwood Bio-oil Hydrogen Yield



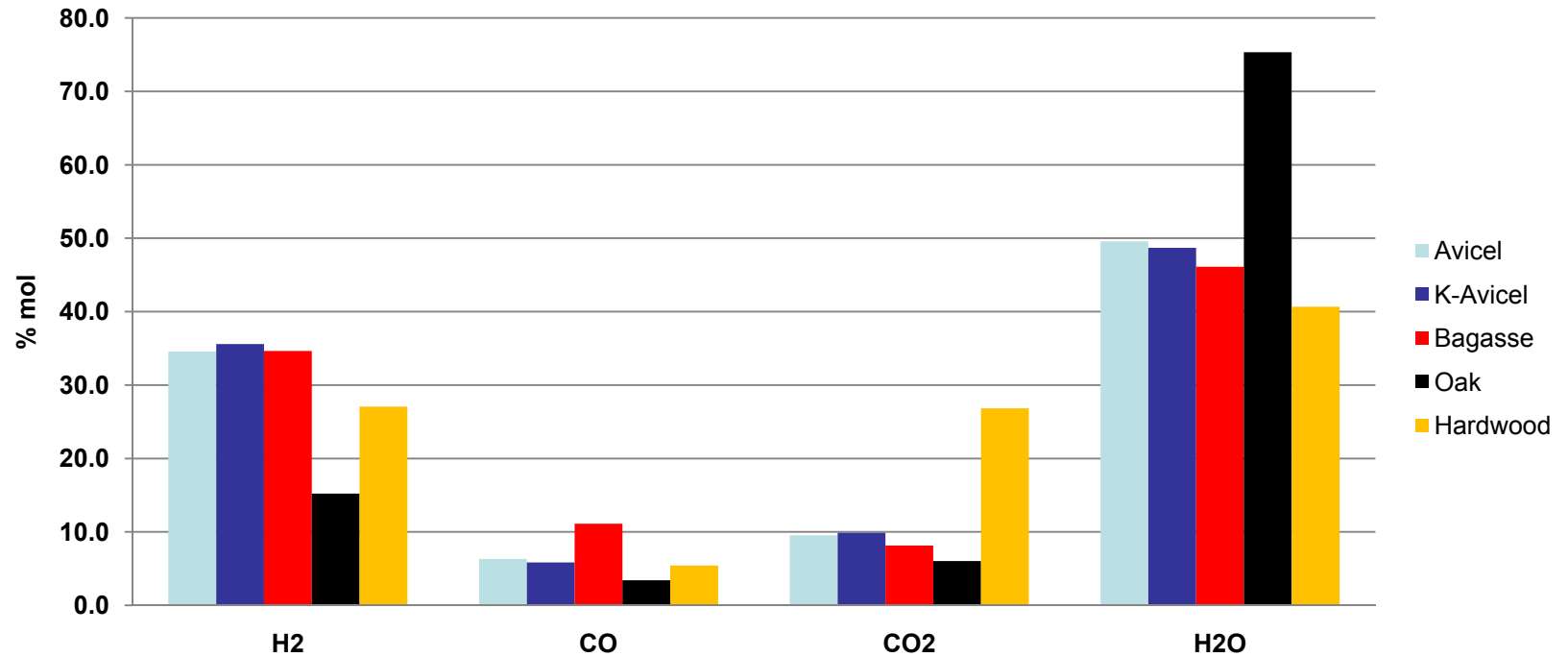
80-90% of stoichiometric yield of hydrogen was produced by catalytic steam reforming of bio-oil for the whole S/C range

Progress in Process Development

3. Catalytic Conversion

Product Gas Composition from Different Feedstocks

Syn-gas Composition 650 C; O/C=1.3; S/C=2.5



Progress in Process Development

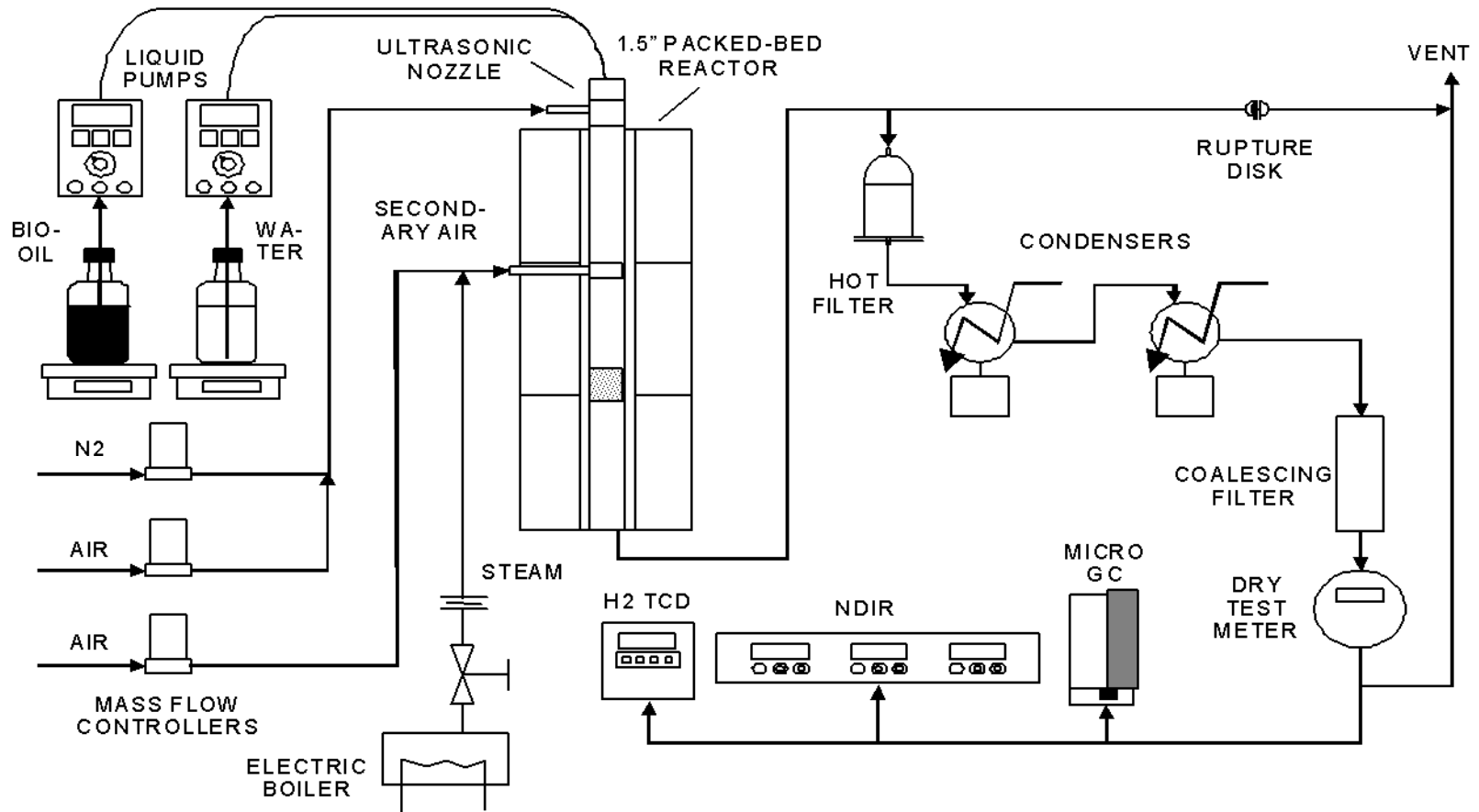
4. Bench-scale Reactor



- Built out of quartz:
 $d = 30 \text{ mm}$; $h = 450 \text{ mm}$
- Connected to the feeding and condensation systems
- Feed rate 1-2 g/min 90 wt% bio-oil/10 wt% methanol solution
- On-line product gas composition monitoring
- 1-4 hour runs
- Detailed product analysis
- Improved mass balance

Progress in Process Development

4. Bench Scale Reactor System

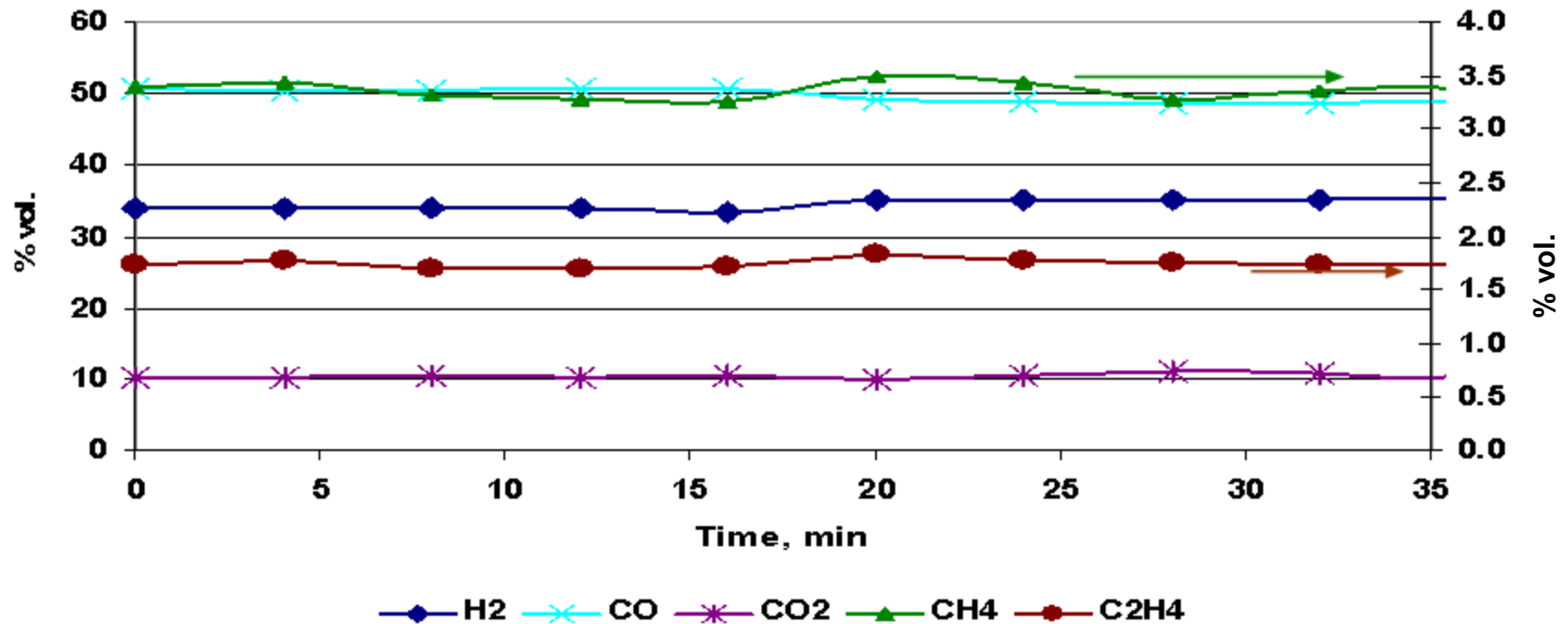


Progress in Process Development

4. Bench Scale Reactor System

Gas Composition from POX of Bio-oil/Methanol

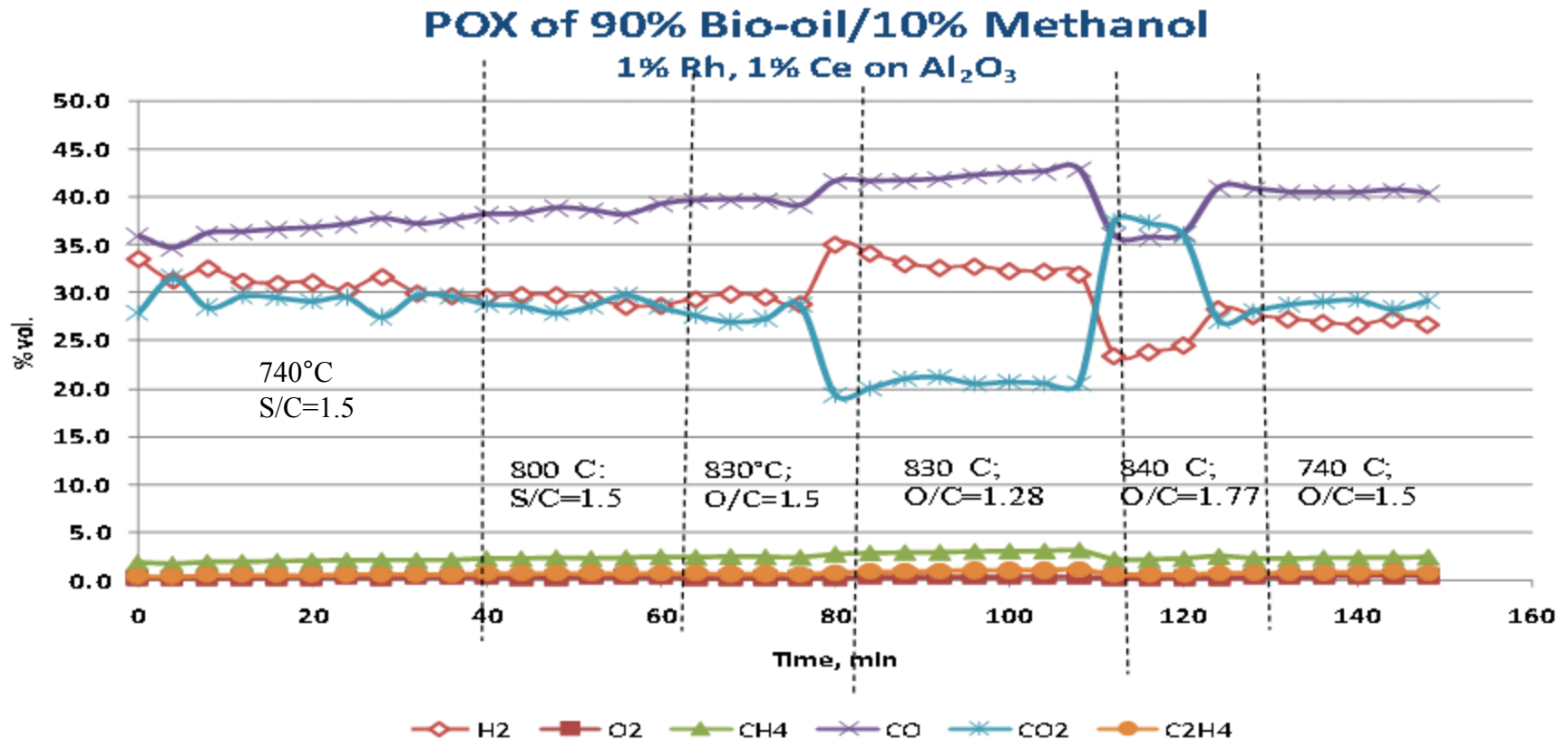
POX of Bio-oil/Methanol Mixture
 $t = 730\text{C}$, $\text{O:C} = 1.5$



Progress in Process Development

4. Bench Scale Reactor System

Gas Composition from Catalytic POX of Bio-oil/Methanol at different process conditions



Hydrogen Cost

1500 kg/day station used for H2A analysis.

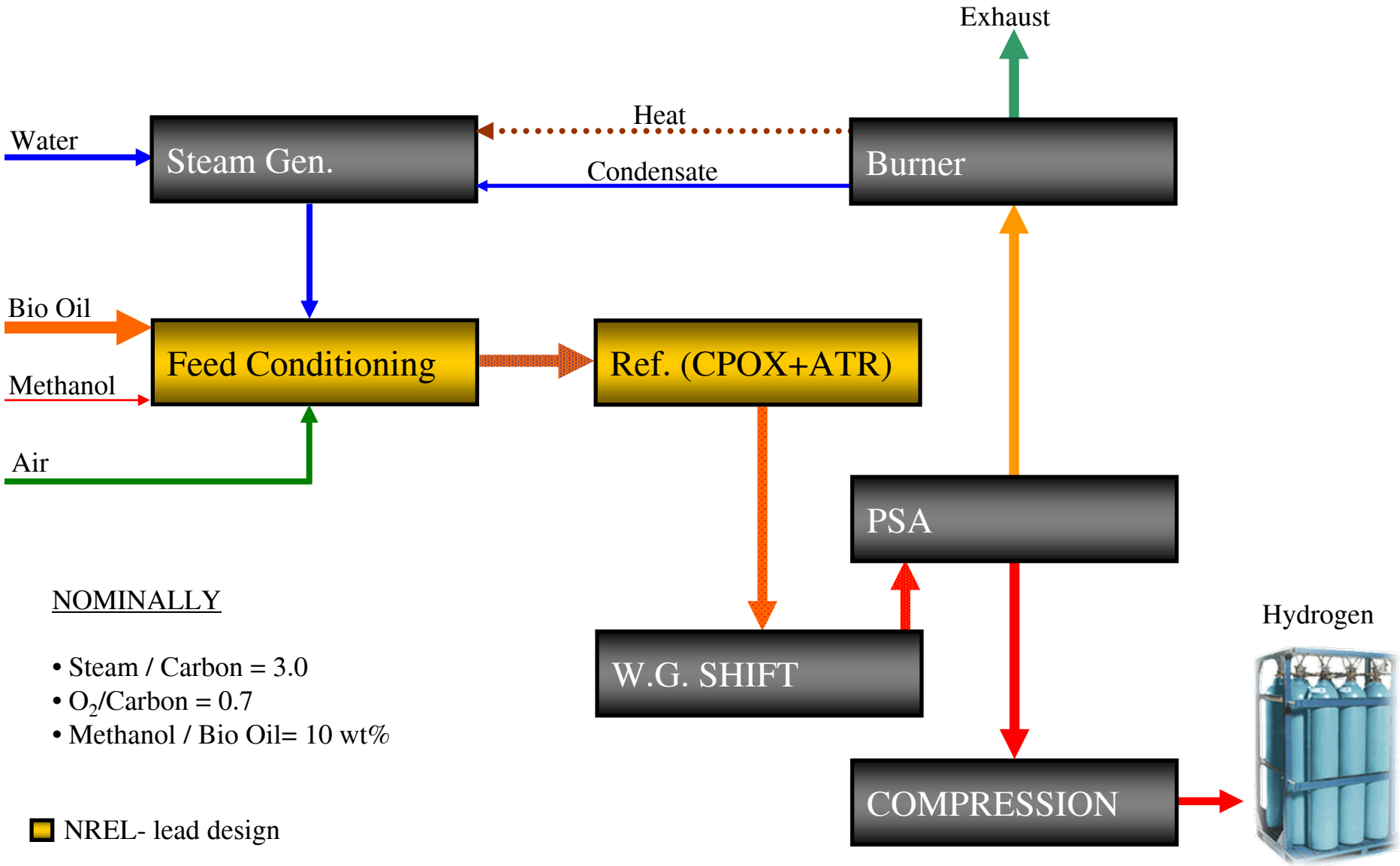
Capital Costs \$1,660,000 (\$2.03/gge).

Total cost of delivered hydrogen **\$4.48/gge**

\$2.59/gge for the production

\$1.88/gge for compression, distribution, and dispensing.

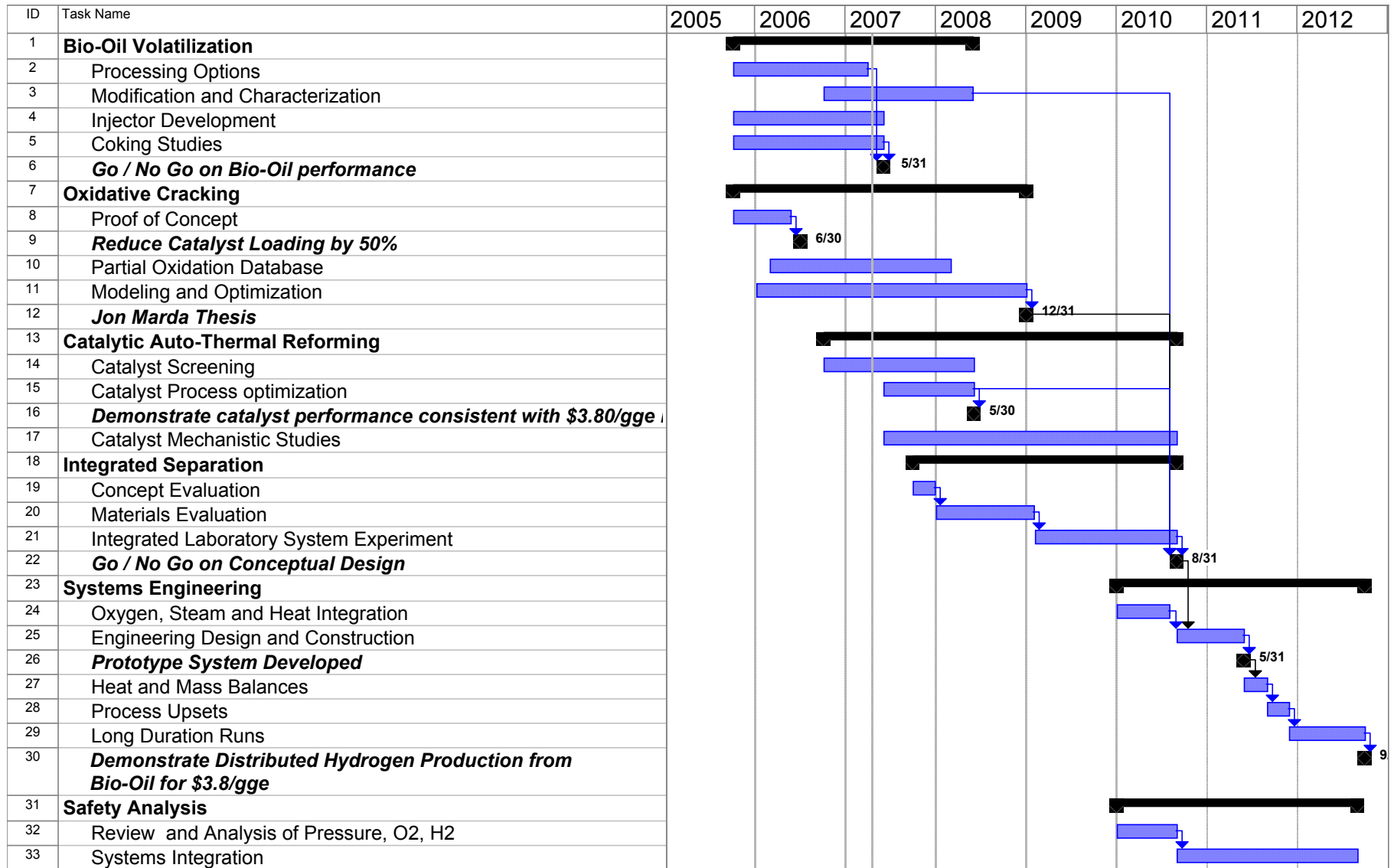
Process Subsystems Outline



Summary

- Bench-scale reactor system tests of non-catalytic and catalytic partial oxidation of bio-oil were performed using 90 wt% bio-oil/10 wt% methanol mixtures
- Carbon-to-gas conversion at bench-scale was slightly less than that achieved in micro scale system
- Rhodium catalyst enhanced bio-oil to syngas conversion by POX with and without added steam
- Bio-oils from herbaceous feedstock were more difficult to process and left more deposits than wood bio-oils
- Experimental results from bench-scale system will be used as to validate ASPEN simulations based on micro-scale data.

Project Timeline



Future Work

- **FY 2009: Produce process performance data as a function of process conditions (temperature, catalyst, O/C, S/C) using the bench-scale system**
 - Integrated laboratory experiment
 - Optimization work
 - Long-term catalyst performance test
 - Assess the impact of the bench-scale results on the process design and on hydrogen production cost
- **FY 2010: “Go/no-go” on conceptual design**
- **FY 2011: Prototype system**
- **FY 2012: Long duration runs to validate the process**