National Renewable Energy Laboratory
Innovation for Our Energy Future

Distributed Bio-Oil Reforming

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Project ID#
PDP_15_Czernik

Overview

TIMELINE

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

BUDGET

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

BARRIERS

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)

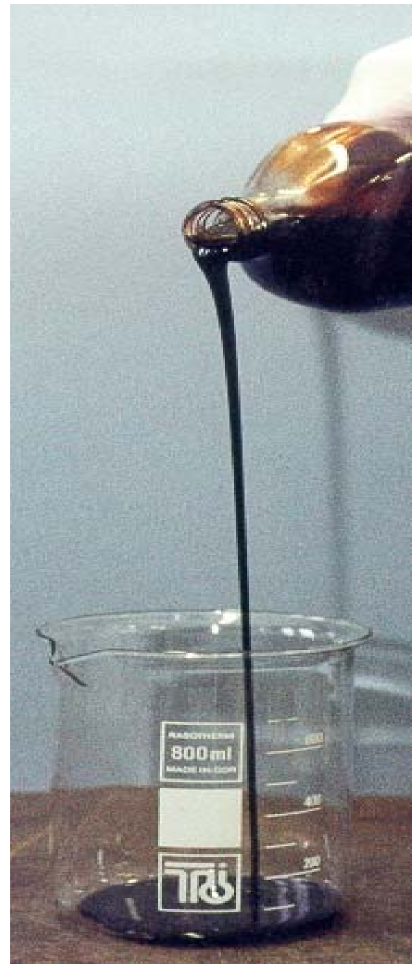
PARTNERS

- 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:

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

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

Catalytic Steam Reforming of Bio-oil:

Bio-oil (74 wt% $CH_{1.28}O_{0.41}$, 26 wt % H_2O) - 90 wt% of feed

CH_3OH - 10 wt% of feed

H_2O (2 mole ratio steam to carbon)

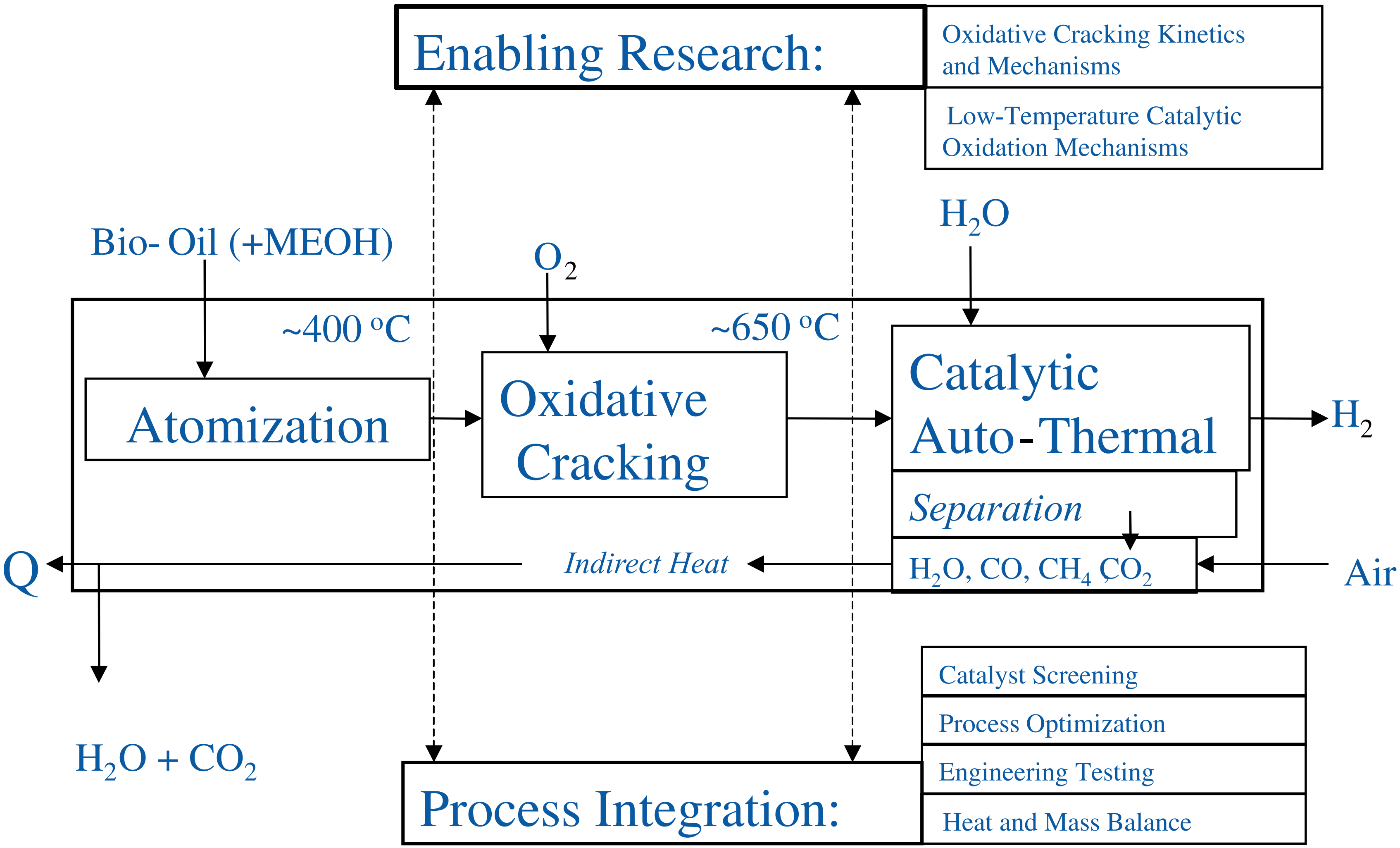
Overall Reaction:

$$CH_{2.18}O_{0.78} + 0.51O_2 + 0.19\, H_2O \rightarrow CO_2 + 1.28\, H_2$$

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

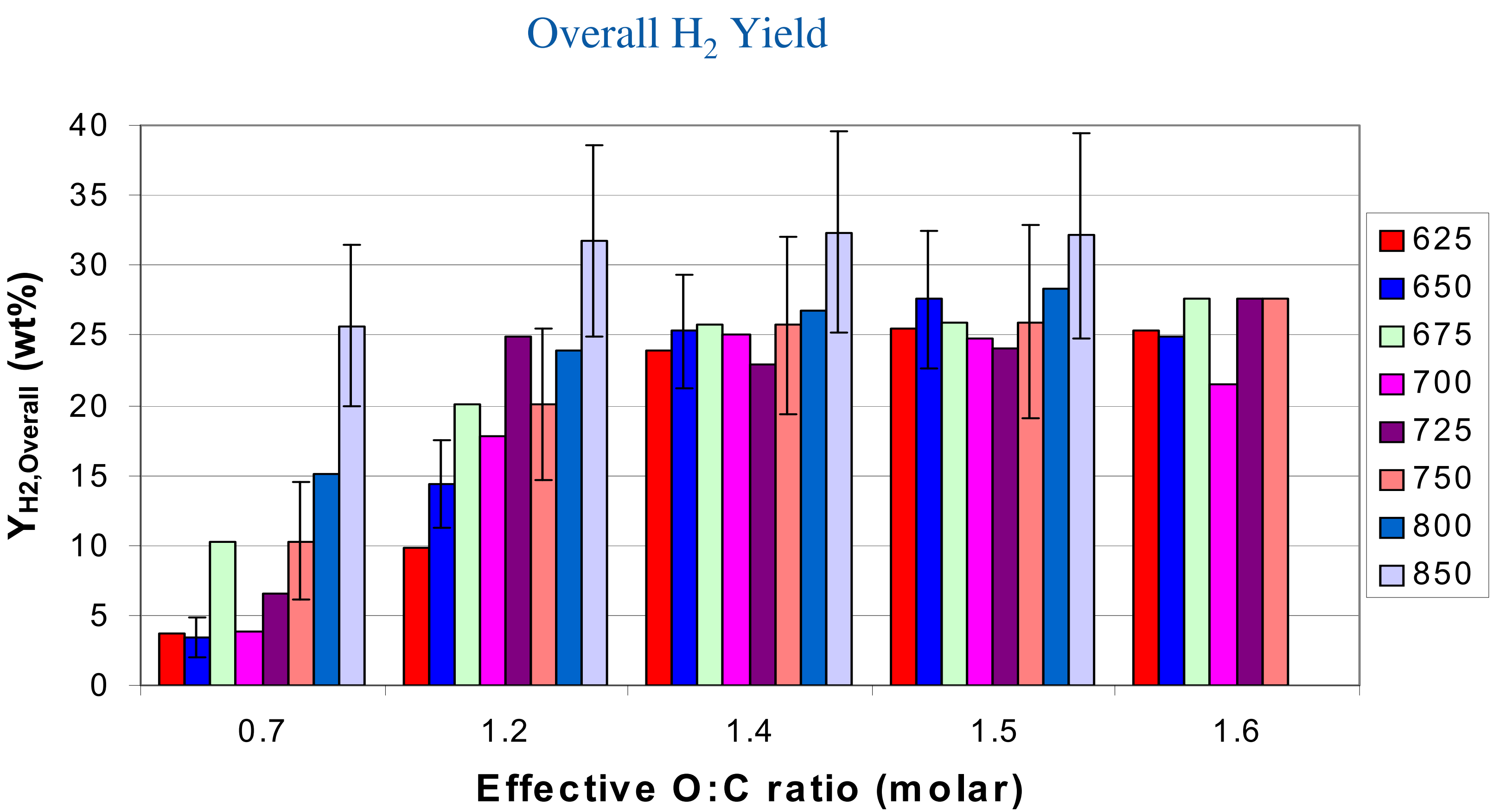
Technical Accomplishments

- FY 2006
  - Bio-oil volatilization method developed
  - Oxidative cracking to CO with minimal CO_2
- FY 2007
  - Demonstrated equilibrium catalytic conversion to syngas at low temperature and low H_2O/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

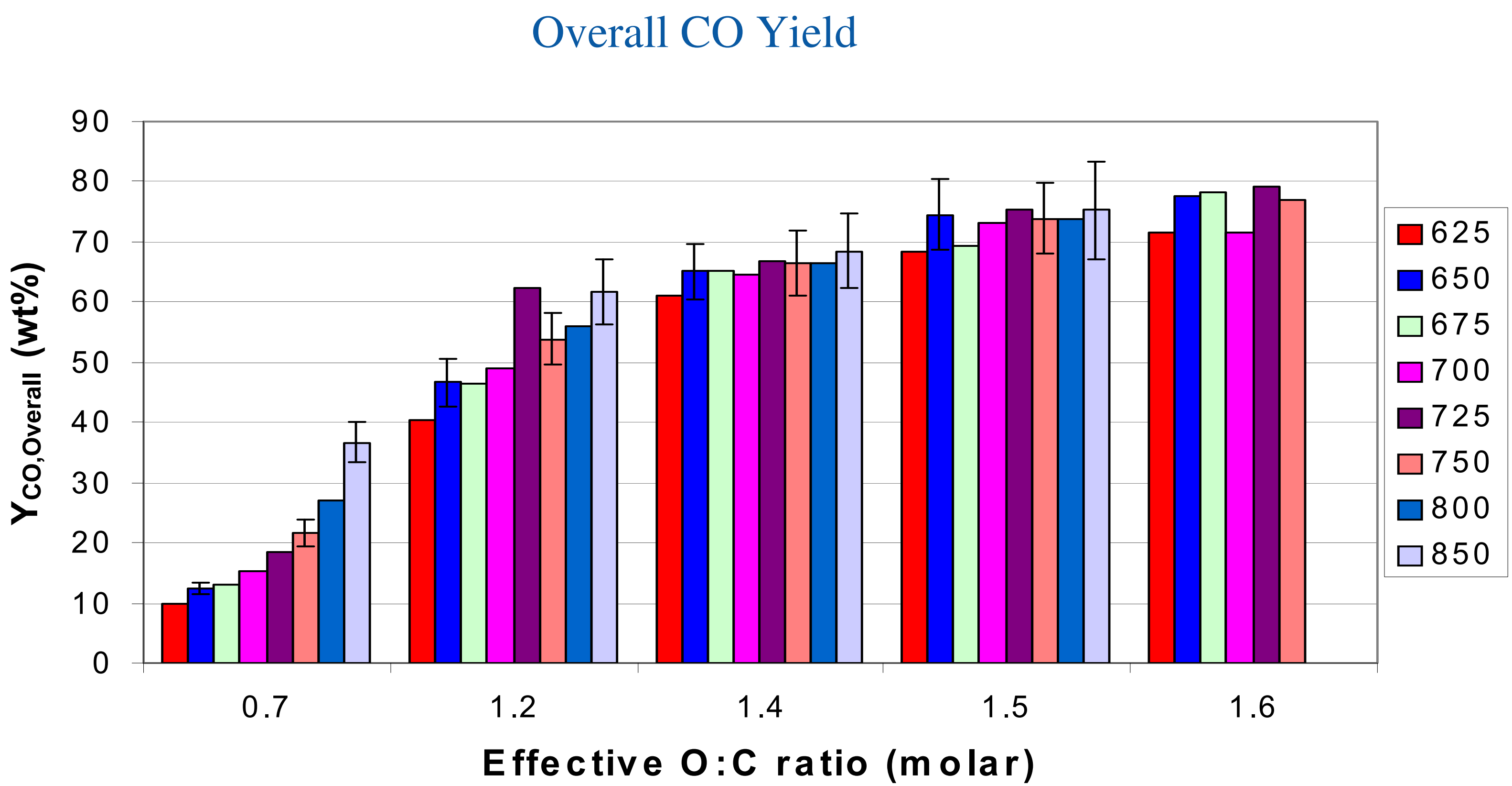
- The new ultrasonic nozzle can produce a fine mist even from high-viscosity liquids.
- Successful tests with 90 wt% bio-oil/10 wt% methanol mixture.
- Promising attempts of feeding neat bio-oil though 10 wt% methanol addition will likely be used to homogenize and stabilize bio-oil.
- Ultrasonic nozzle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

Progress in Process Development
2. Oxidative Cracking



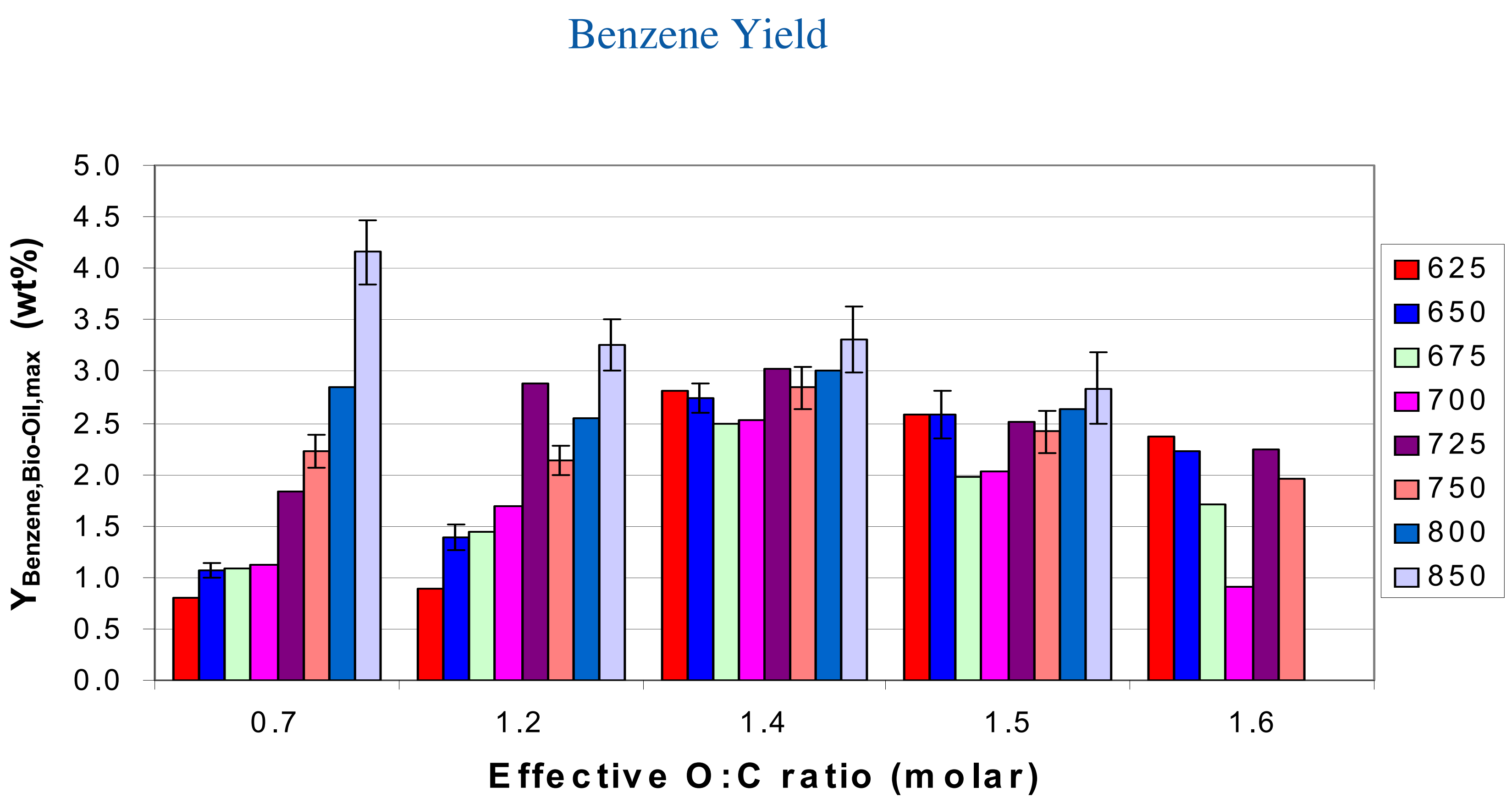
Hydrogen yields are 25-30% of the stoichiometric potential;
Those yields will significantly increase after completion of water-gas shift.

Progress in Process Development
2. Oxidative Cracking



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

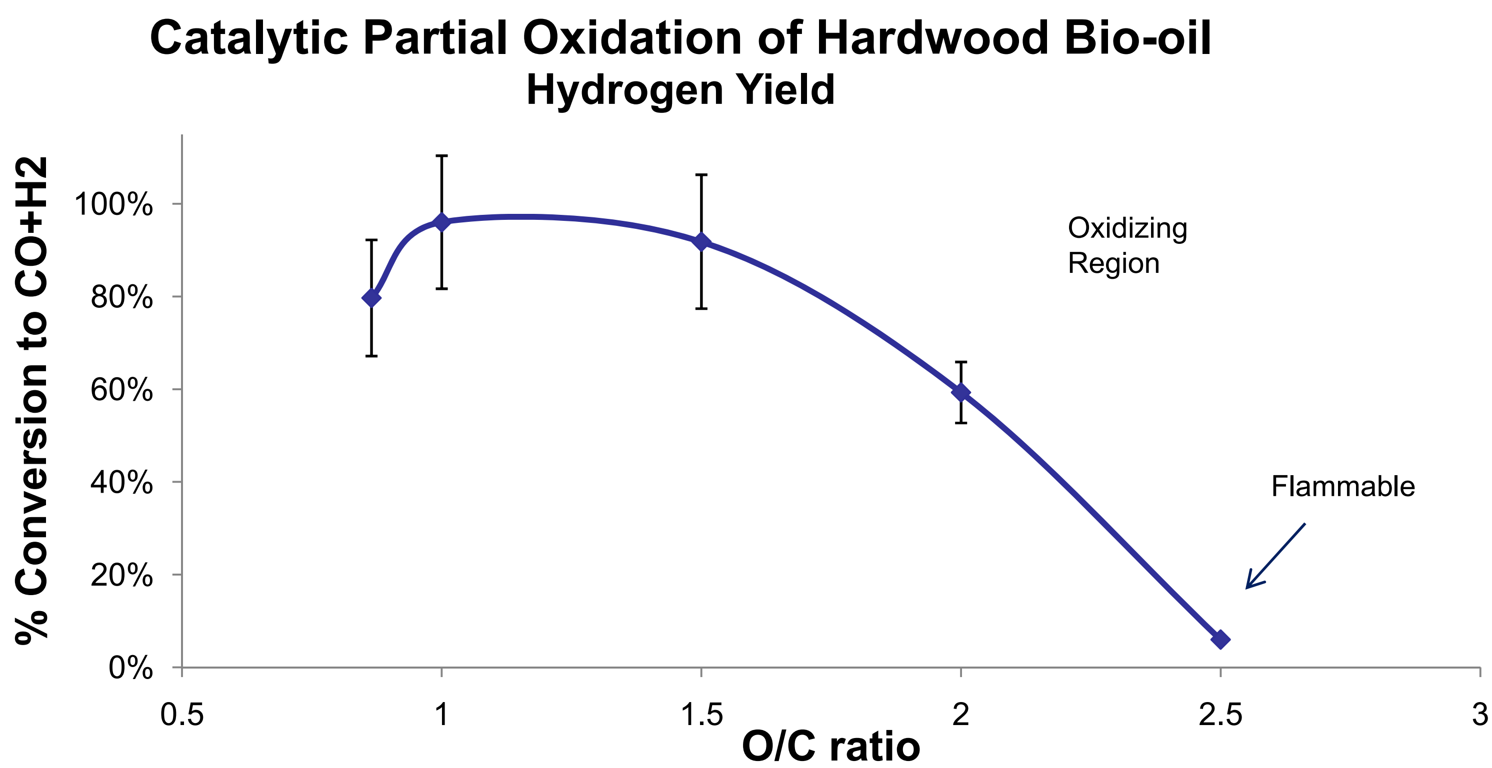
Progress in Process Development
2. Oxidative Cracking



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

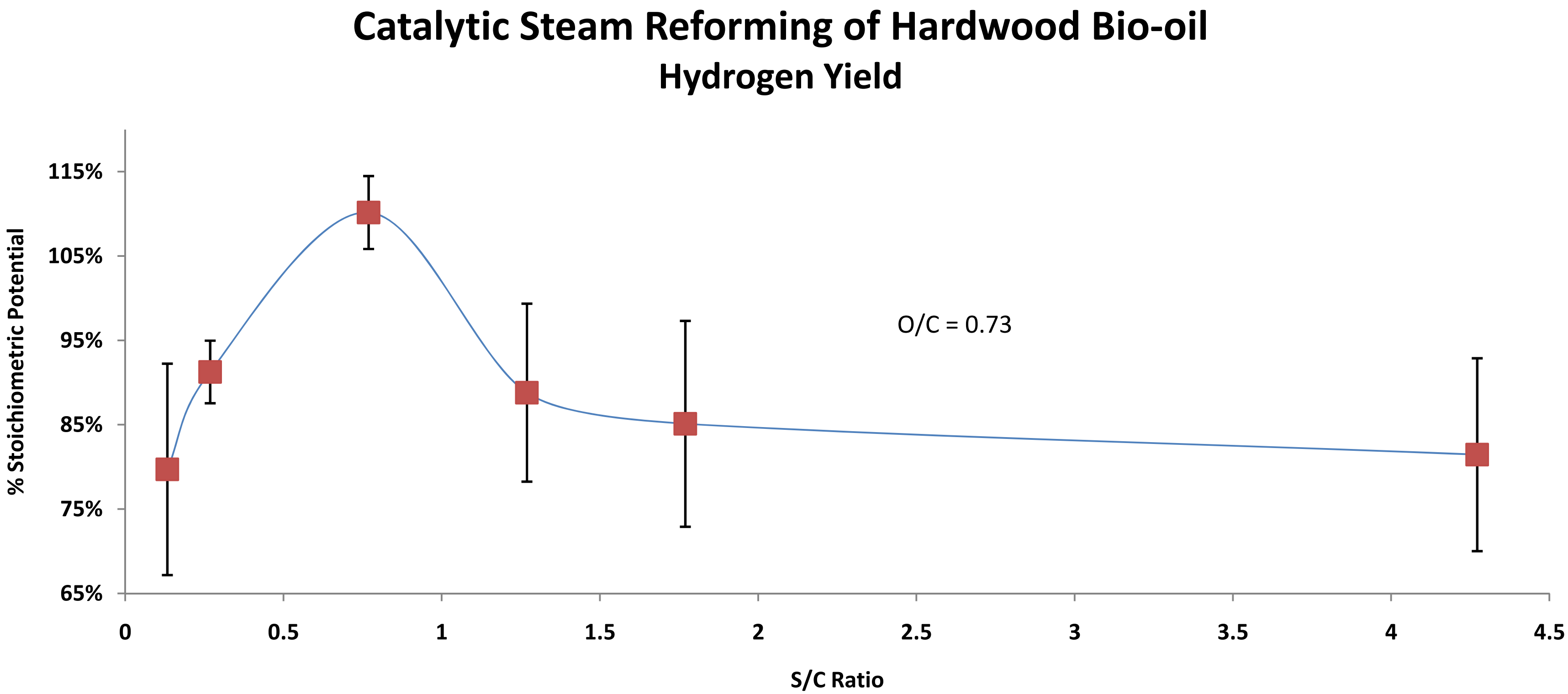
Progress in Process Development
3. Catalytic Conversion

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



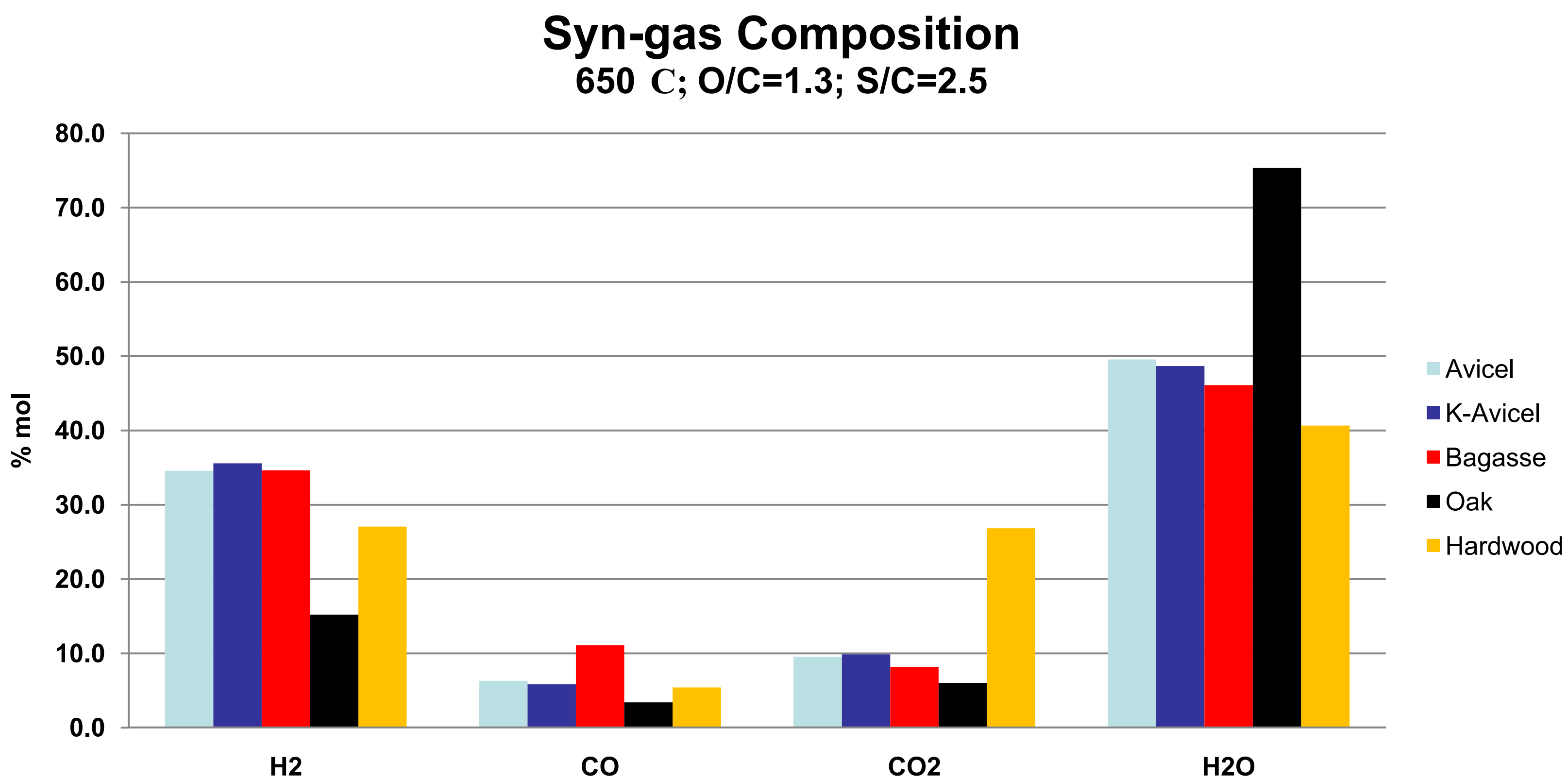
1 – 1.5 is the optimal range of O/C for catalytic POX of bio-oil

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



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

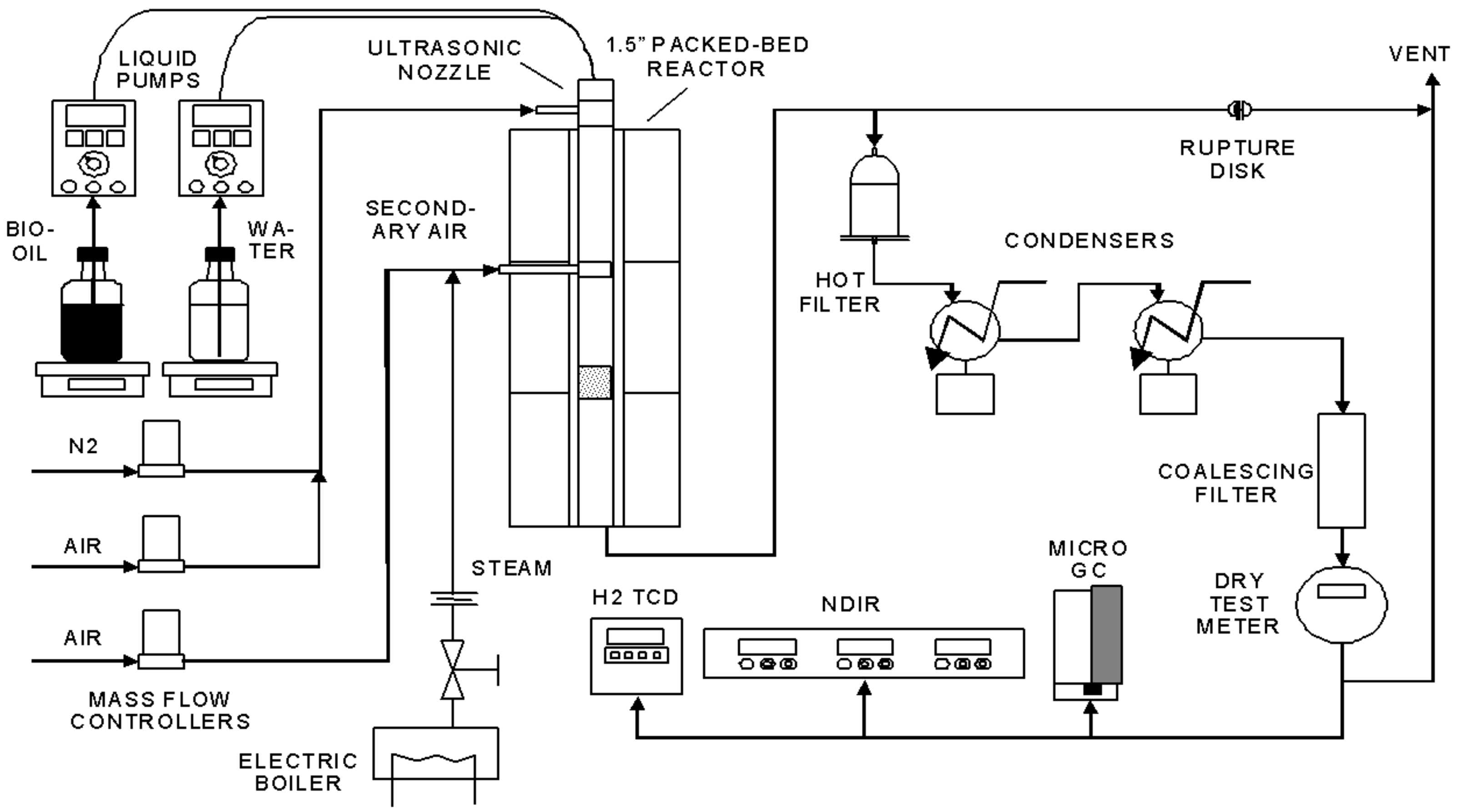
Product Gas Composition from Different Feedstocks



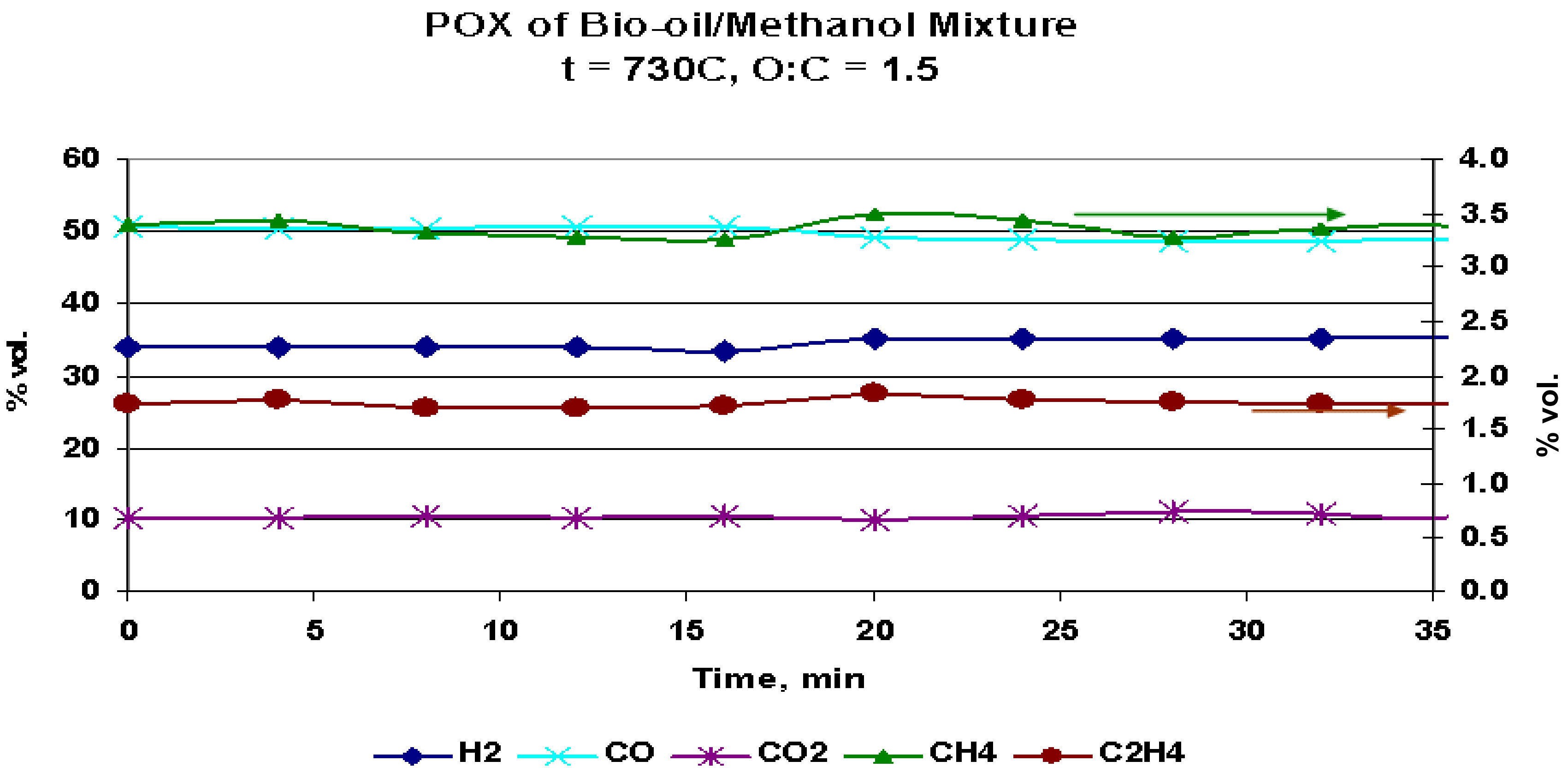
4. Bench-scale Reactor

- Built out of quartz:
  d = 30 mm; h = 450 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

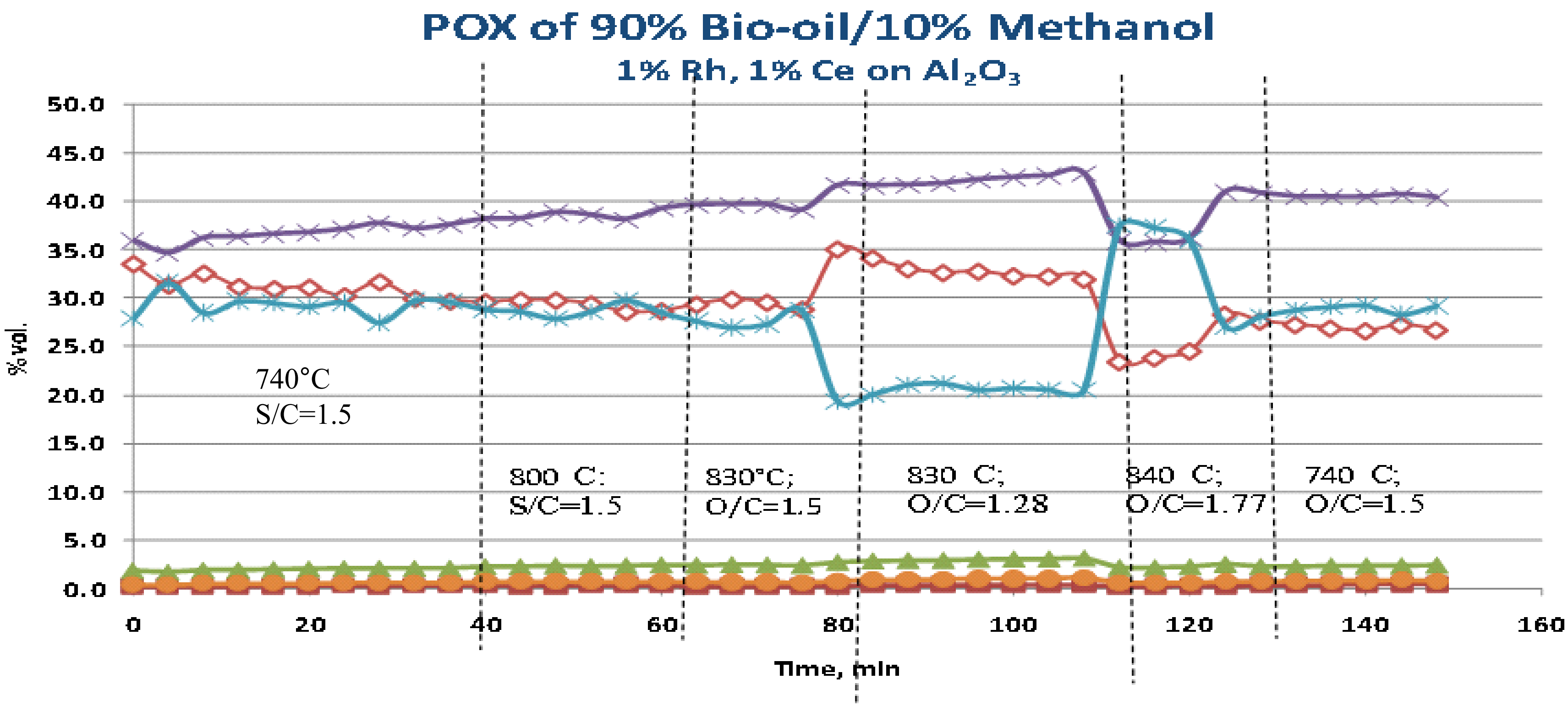
Progress in Process Development
4. Bench Scale Reactor System



Gas Composition from POX of Bio-oil/Methanol



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



Hydrogen Cost

1500 kg/day station used for H2A analysis.

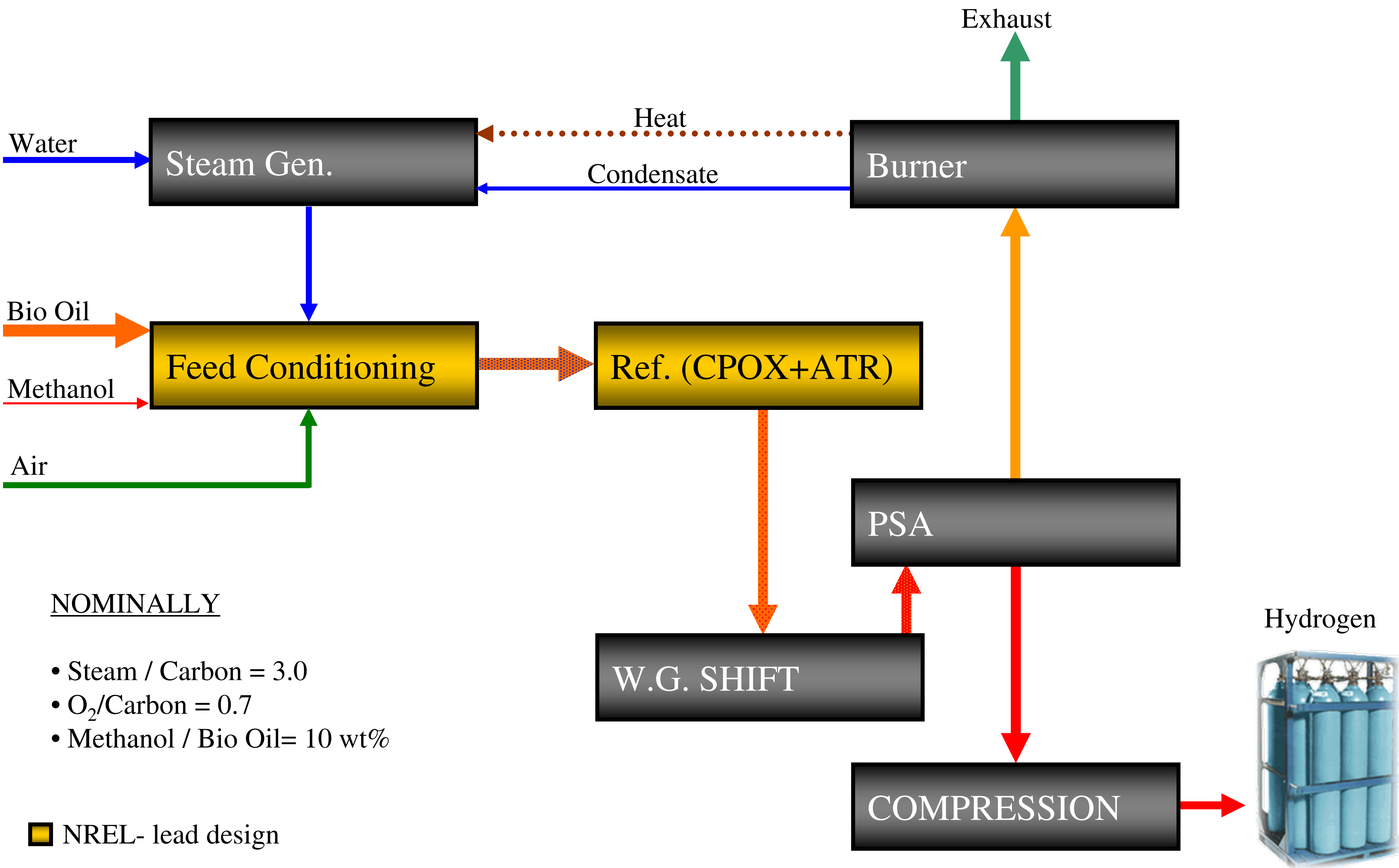
Capital Costs $1,660,000 ($2.03/gge).

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



NOMINALLY

- Steam / Carbon = 3.0
- O_2/Carbon = 0.7
- Methanol / Bio Oil= 10 wt%

NREL- lead design

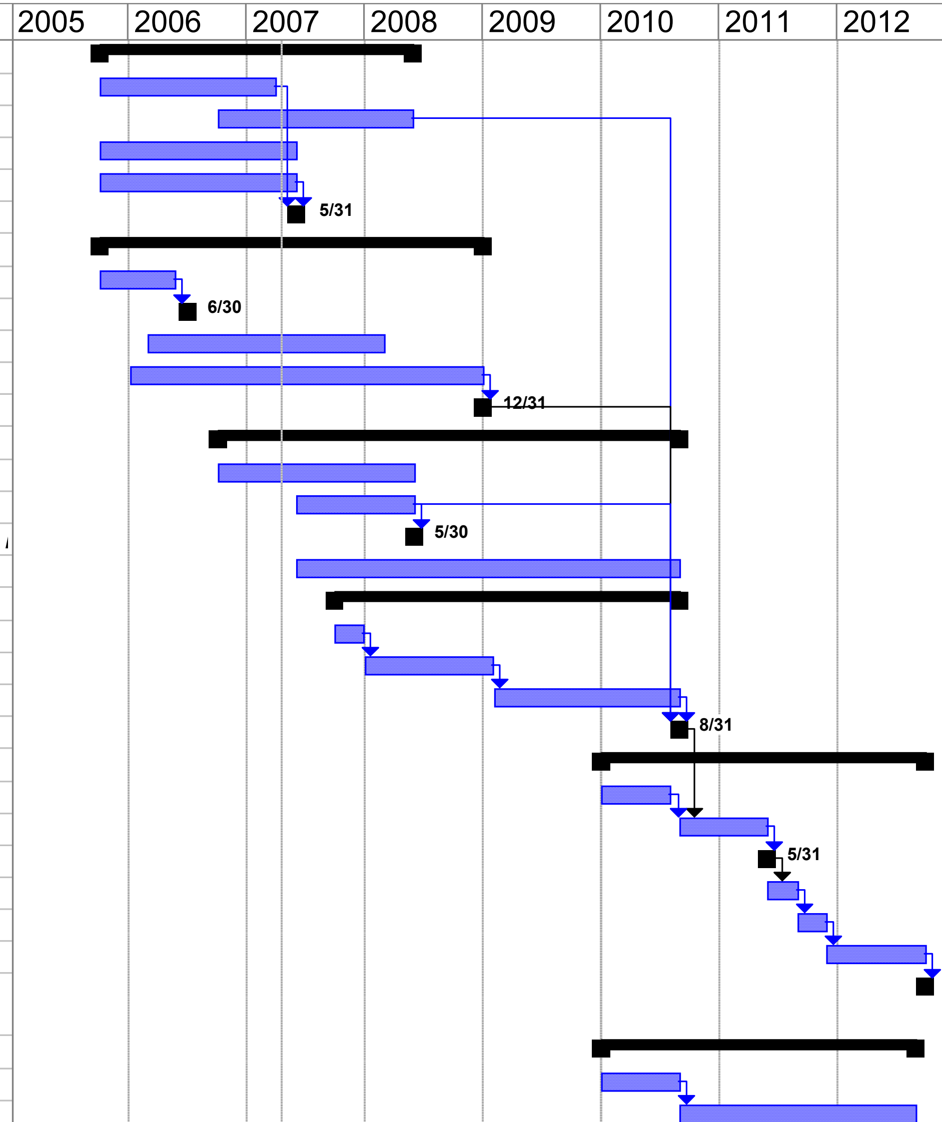
Industry - available subsystems

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

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 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**