National Renewable Energy Laboratory

Innovation for Our Energy Future

Distributed Bio-Oil Reforming

2008 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

R. J. Evans[1], S. Czernik[1],
R. French[1], M. M. Penev, M. Ratcliff[1],
J. Marda[2], A. M. Dean[2]

[1]National Renewable Energy Laboratory
[2]Colorado School of Mines

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Overview

Timeline

- Project start: 2005
- Project end: 2012
- 40% completed

Budget

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

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 (FY 2006) - Oxidative cracking
- University of Minnesota (FY2007) - Catalyst Development
- Chevron (FY 2006) – Feedstock Effects (3 year CRADA)

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:

Bio-oil (74 wt% $CH_{1.28}O_{0.41}$, 26 wt % H2O) - 90 wt% of feed

CH3OH - 10 wt% of feed

H2O (2.5 mole ratio steam to carbon)

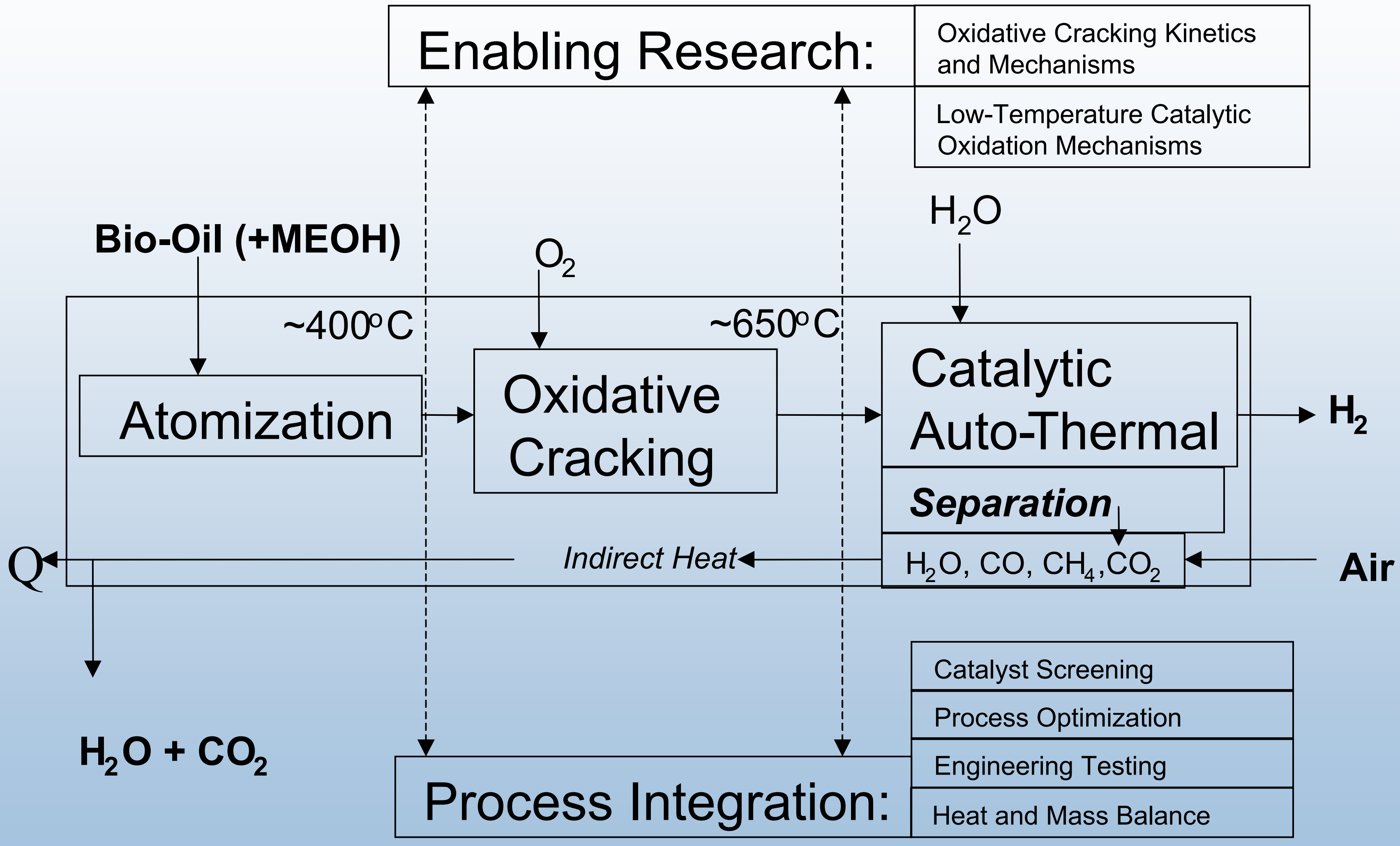
Overall Reaction:

$CH_{2.18}O_{0.78} + 0.51O_2 + 1.66\ H_2O \rightarrow CO_2 + 1.47\ H_2O + 1.28\ H_2$

***Estimated Practical Yield*: 9.3 wt %**

Energy Efficiency Estimates are in Progress based on Aspen Modeling

Distributed Bio-Oil Reforming Approach



Objectives

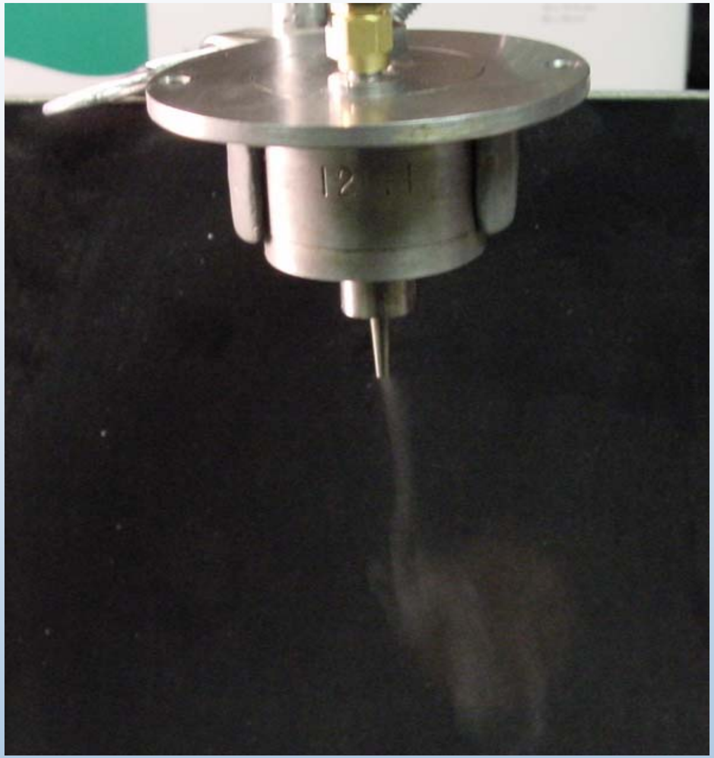
- Overall
  - Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry, deactivation, and regeneration strategy as a basis for process definition for automated distributed reforming; demonstrate the process
- FY 2008
  - Improve bio-oil atomization with less MeOH addition,
  - Study of partial oxidation at 650C
  - Demonstrated catalytic conversion consistent with $3.80/kg hydrogen
  - Design, build and operate a bench scale unit capable of long duration runs (8hrs/cycle) with better material balances

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
  - Lower methanol content
  - Demonstrate catalyst performance (in progress)
  - Design, build, & operate bench scale system (in progress)

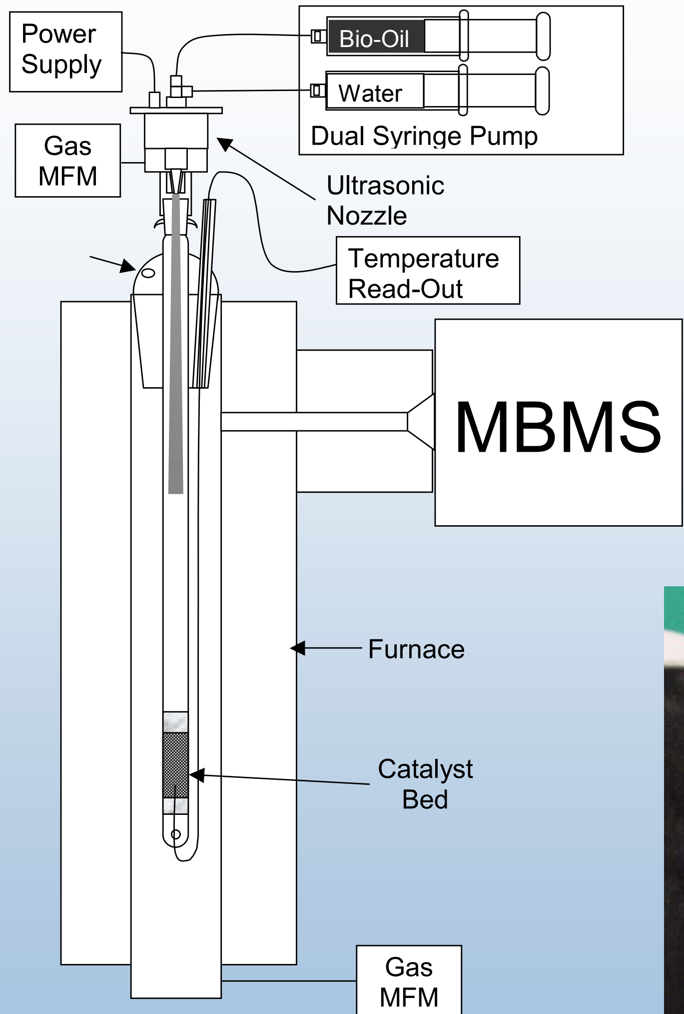
Bio-oil Injection Working Hypothesis

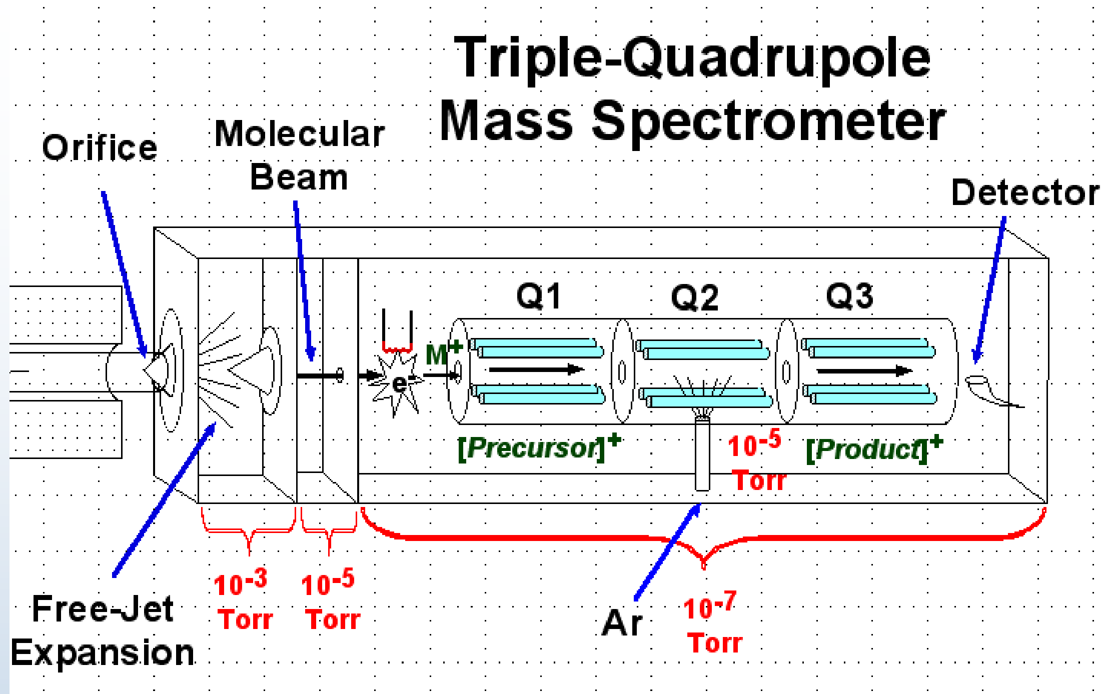
- Ultrasonic nozzle provides:
  - Rapid, uniform fuel-air mixing and temperature distribution
  - Reduces wall impingement
- Leading to:
  - Low carbon formation-
    - extreme analogy to diesel PM reduction via high injection pressure
  - High gas yields and selectivity control



Are Ultrasonics the Key?

- Understand reaction sensitivity to droplet size and spray angle.
- How do ultrasonic power requirements and costs respond to higher viscosity and scale-up?
- Can we leverage high pressure injection system technology for diesel fuels?
  - E.g., Technology being developed for residual fuels injection technology for clean locomotive and marine engines
- Other researchers reported positive results feeding bio-oil to diesel engines



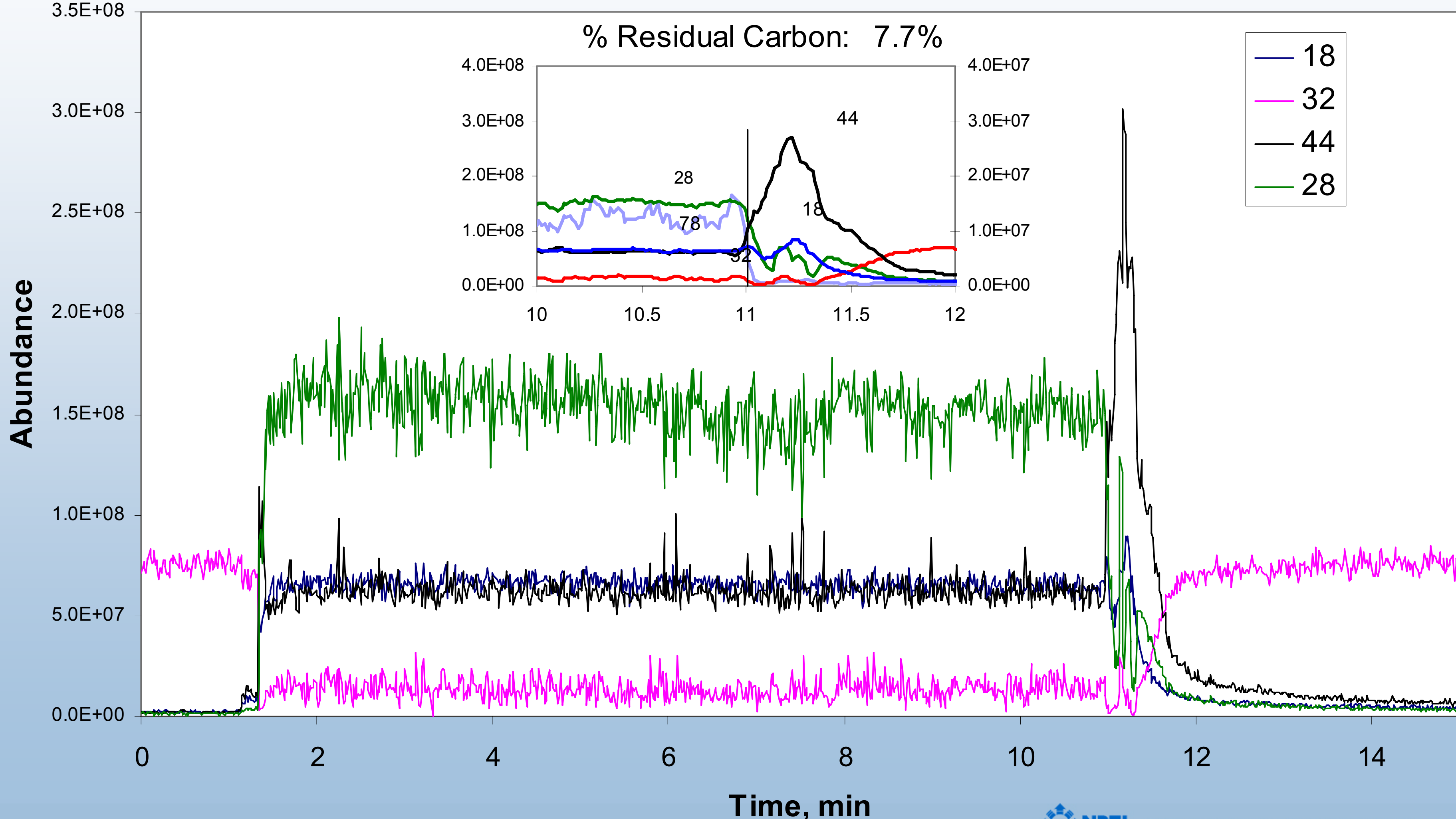


Ultrasonic Nozzle

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

Ultrasonic Nebulizer

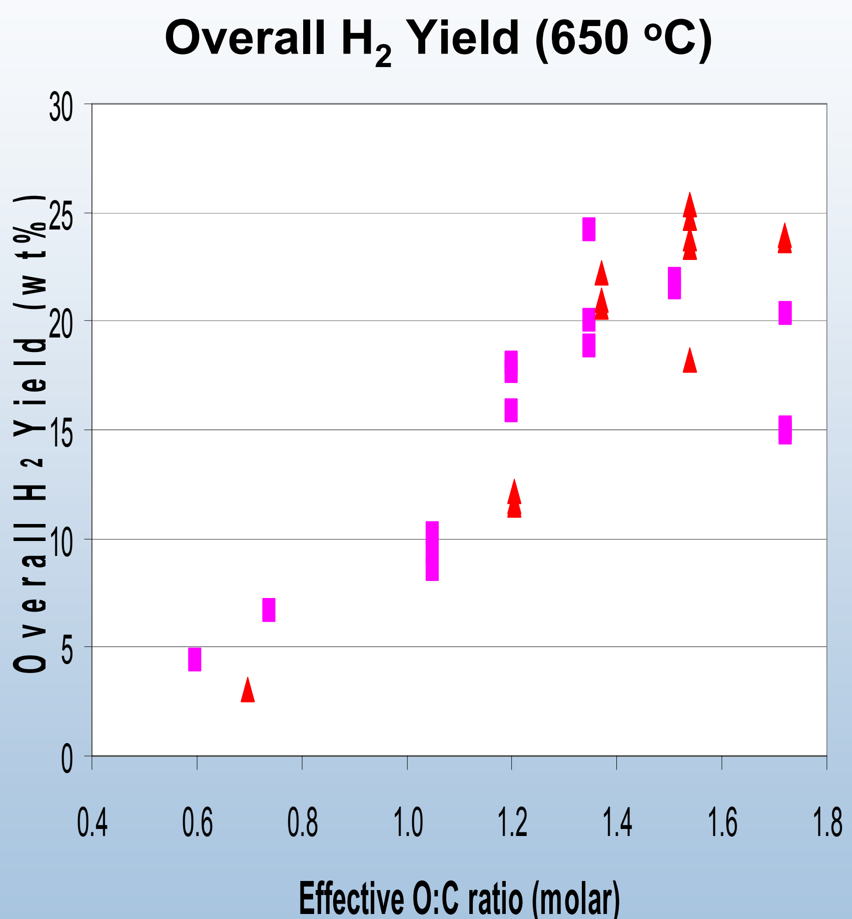
Oxidative Cracking 0.5 s @ 650 C

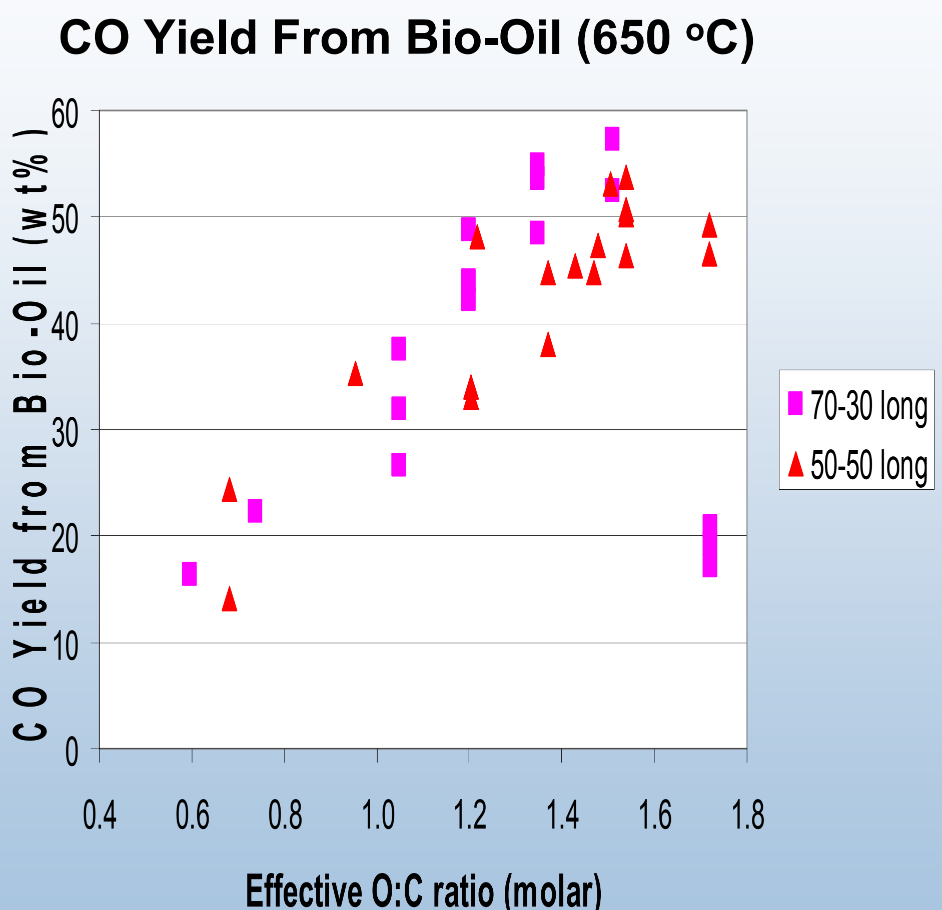


1. Bio-Oil Volatilization

- The new nozzle is capable of higher power inputs and can handle higher viscosity feeds but produces a larger particle size
  - Key experiments to be performed on MeOH level and mass transfer with the new system
- Not successfully run to date due to reactor modifications and component failure
  - Due back in service next week
- Other key activities are dependent on new experimental series with the nozzle
  - The new nozzle is capable of higher power inputs and can handle higher viscosity feeds but produces a larger particle size

2. Oxidative Cracking Experiments Using 30 % Methanol

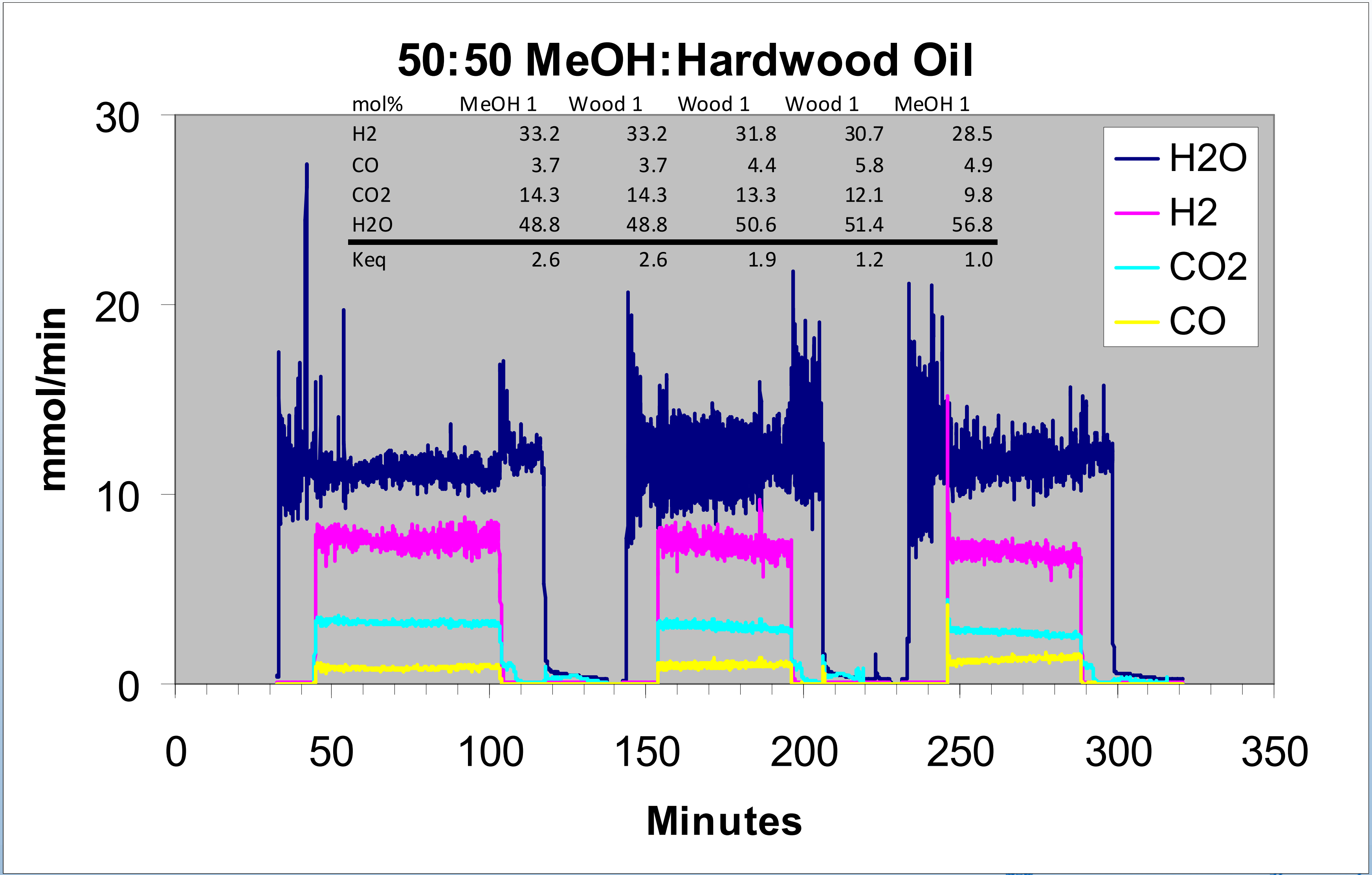




Effect of effective O:C ratio for two methanol addition levels (50% and 30%) and two gas phase residence times (200 and 300 ms) on H2 and CO yields.

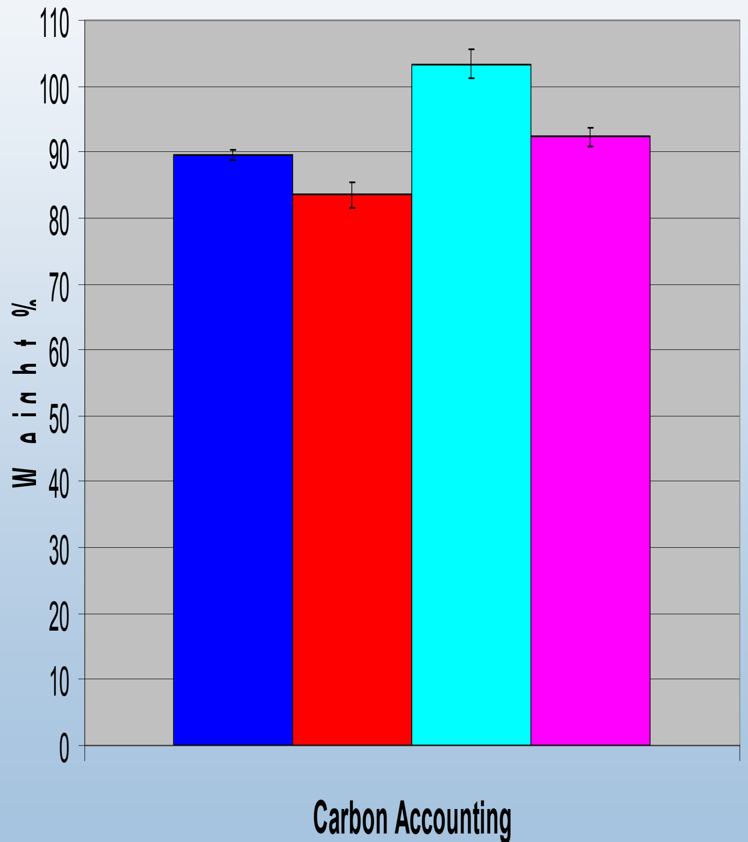
Integrated System under “std” Conditions

Vapor RT=0.3 s; WHSV[0.5%Rh/Al_2O_3]=3.5; S/C=2.5; O/C_{eff}=1.3

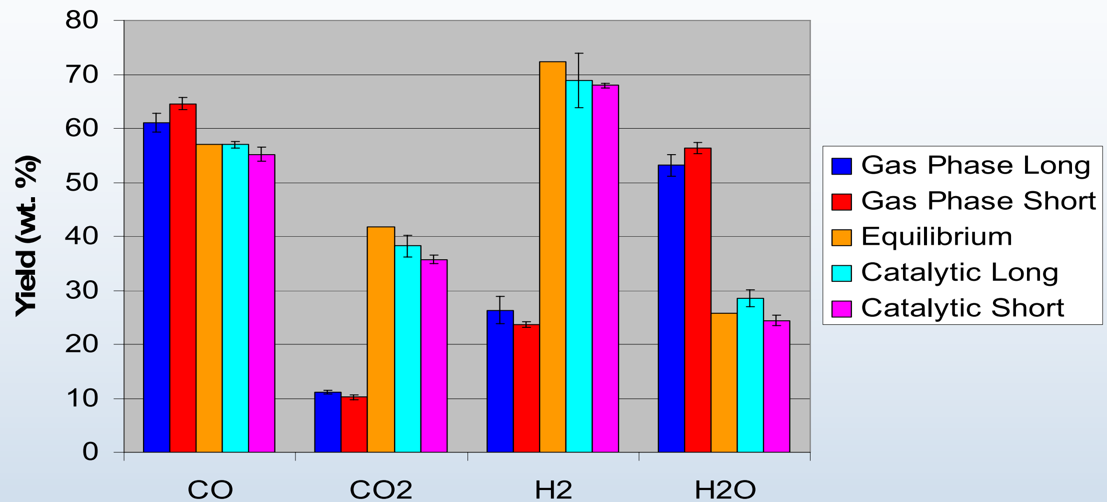


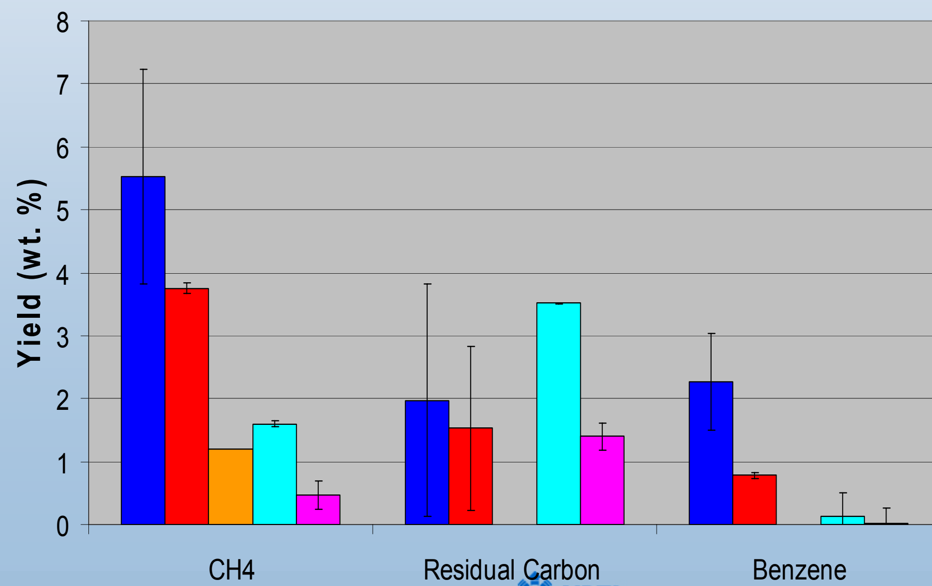
3. Catalysis
Impact of oxidative Cracking Step

Catalyst from University of Minnesota (Lanny Schmidt's group) and is 1 wt % Rh and 1 wt % ceria on alumina (O:C = 1.7)

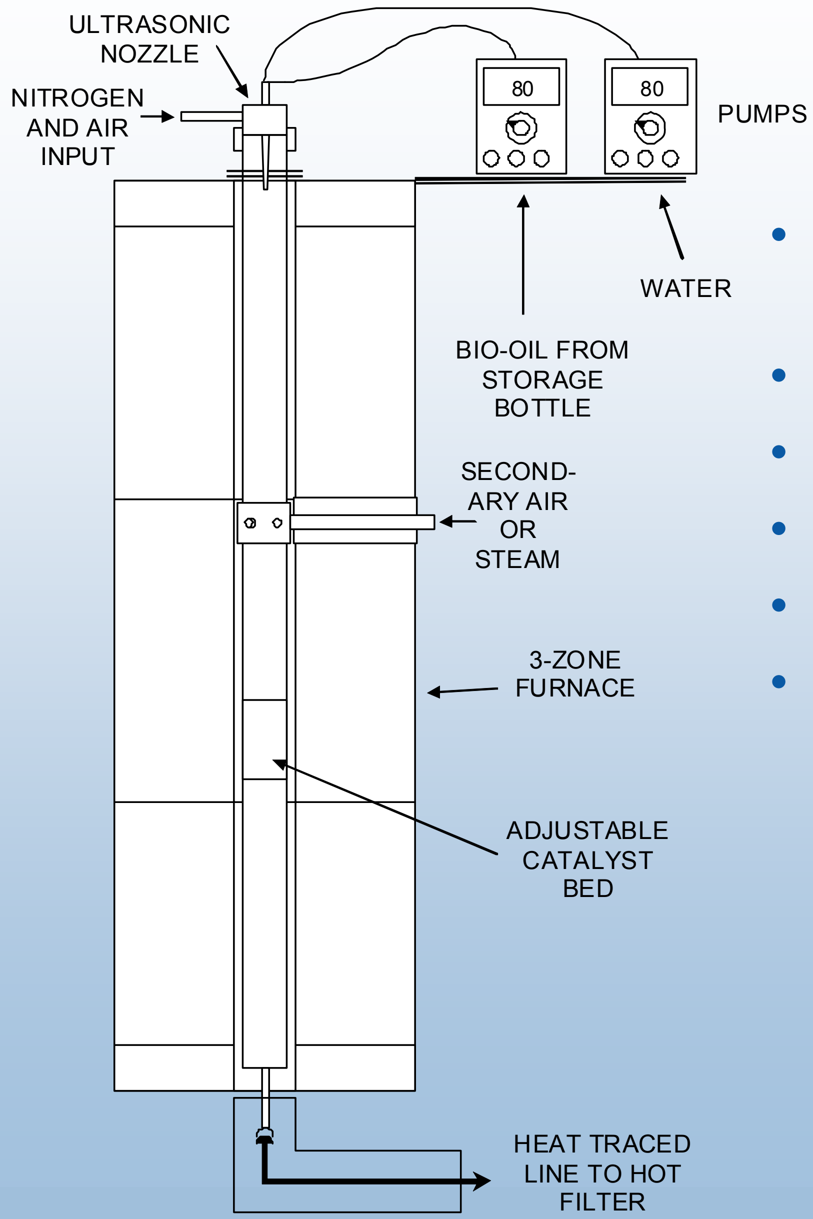


Carbon Accounting includes CO, CO_2, CH_4, CH_3OH, Benzene, and Residual Carbon



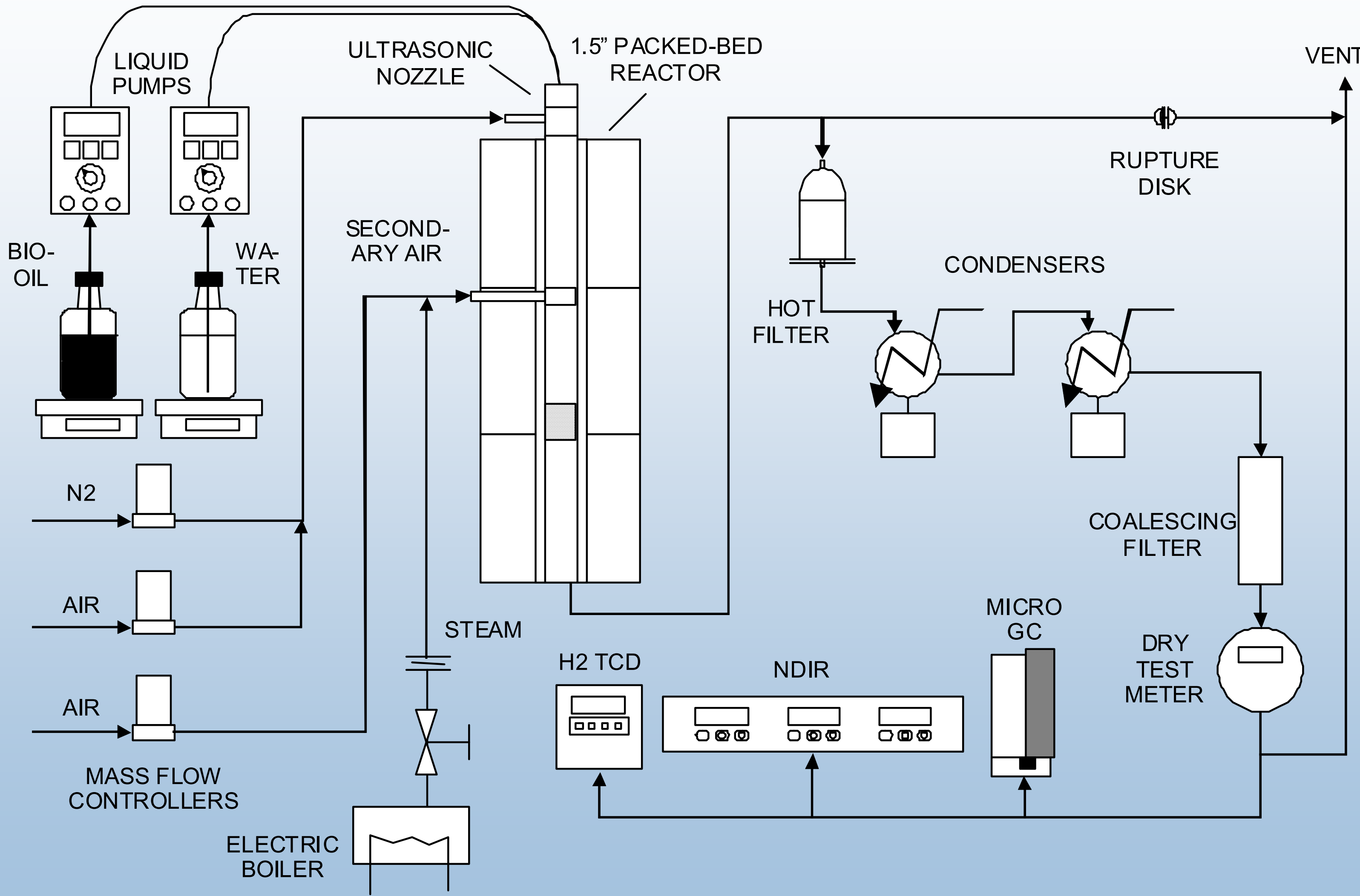


Bench Scale Reactor Design

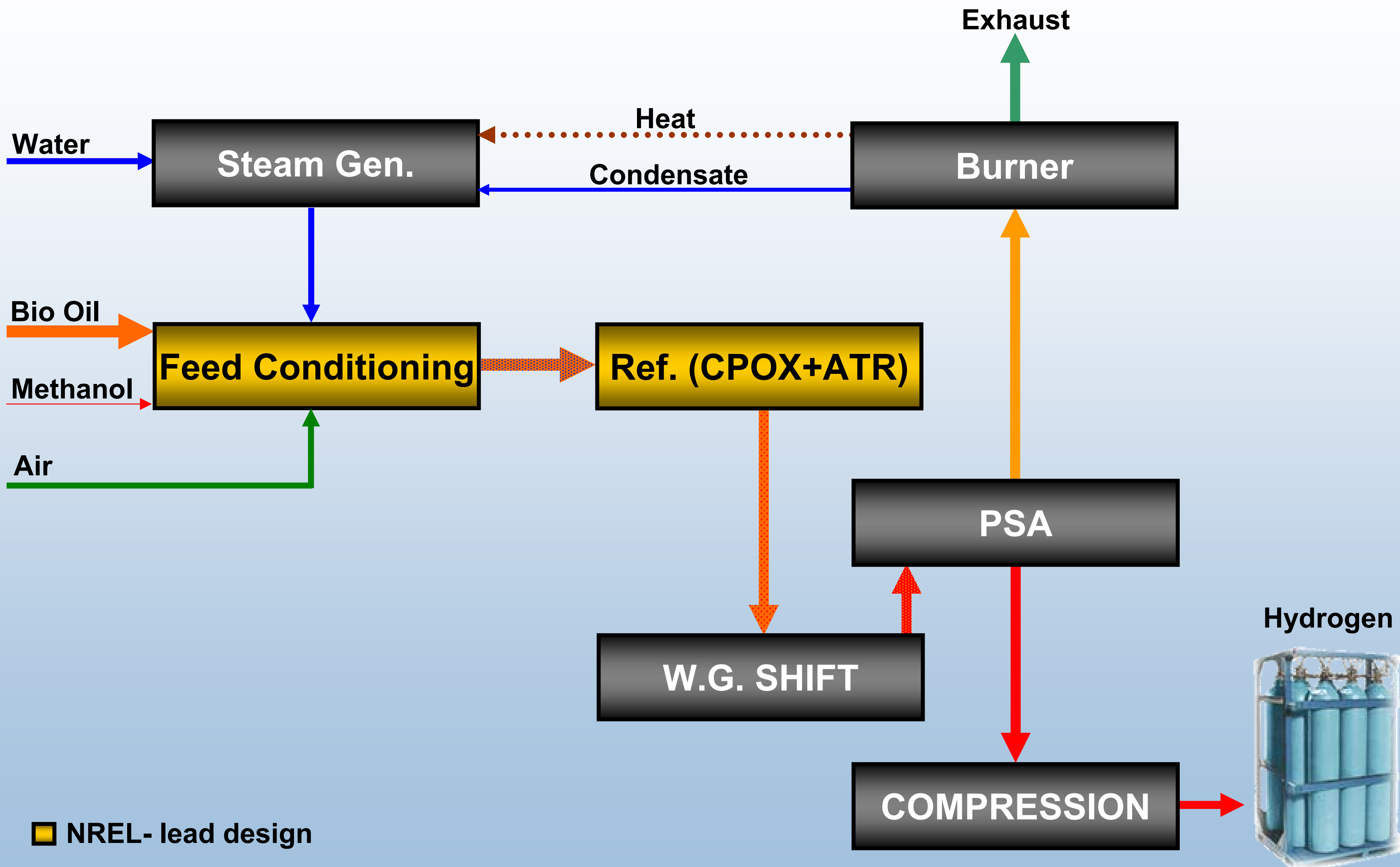


- Take advantage of existing equipment
- Build out of quartz
- Long duration runs
- Detailed product analysis
- Improved material balance
- Design and lab arrange-ments are in progress

Bench Scale Reactor System

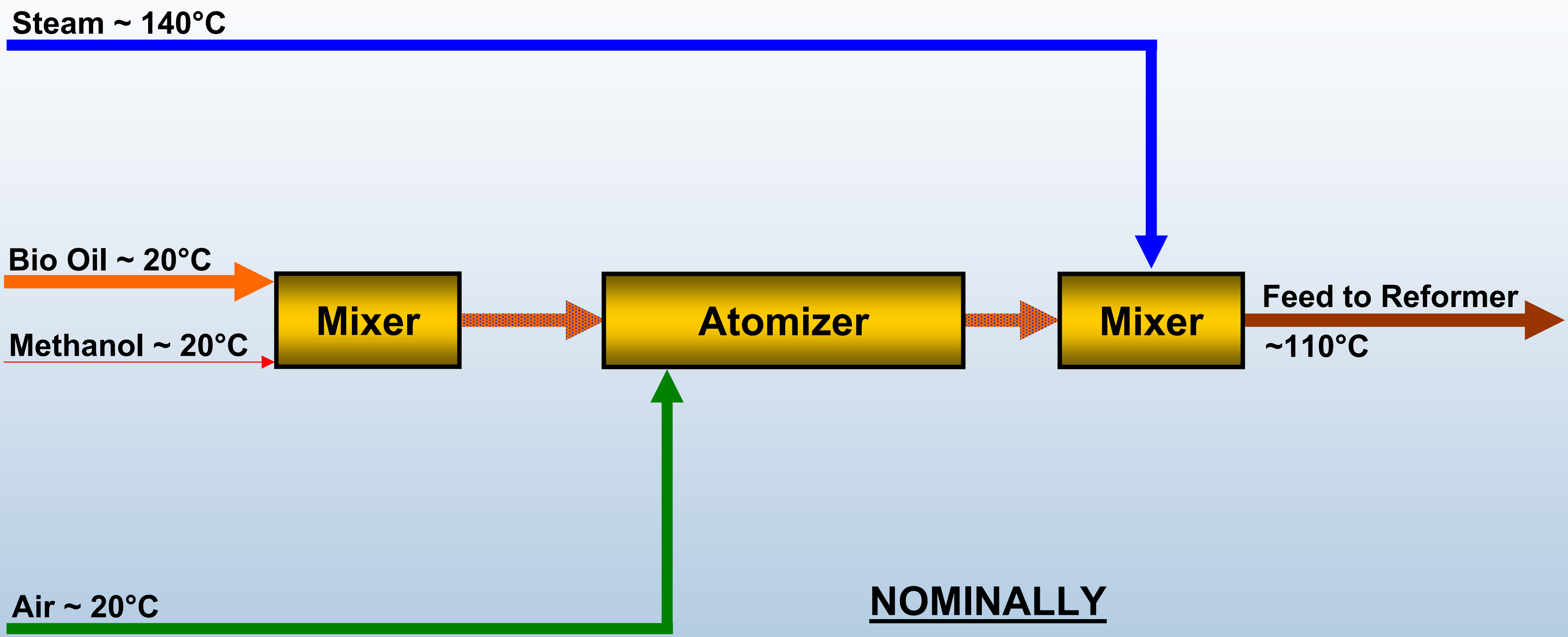


Process Subsystems Outline



- NREL- lead design
- Industry - available subsystems

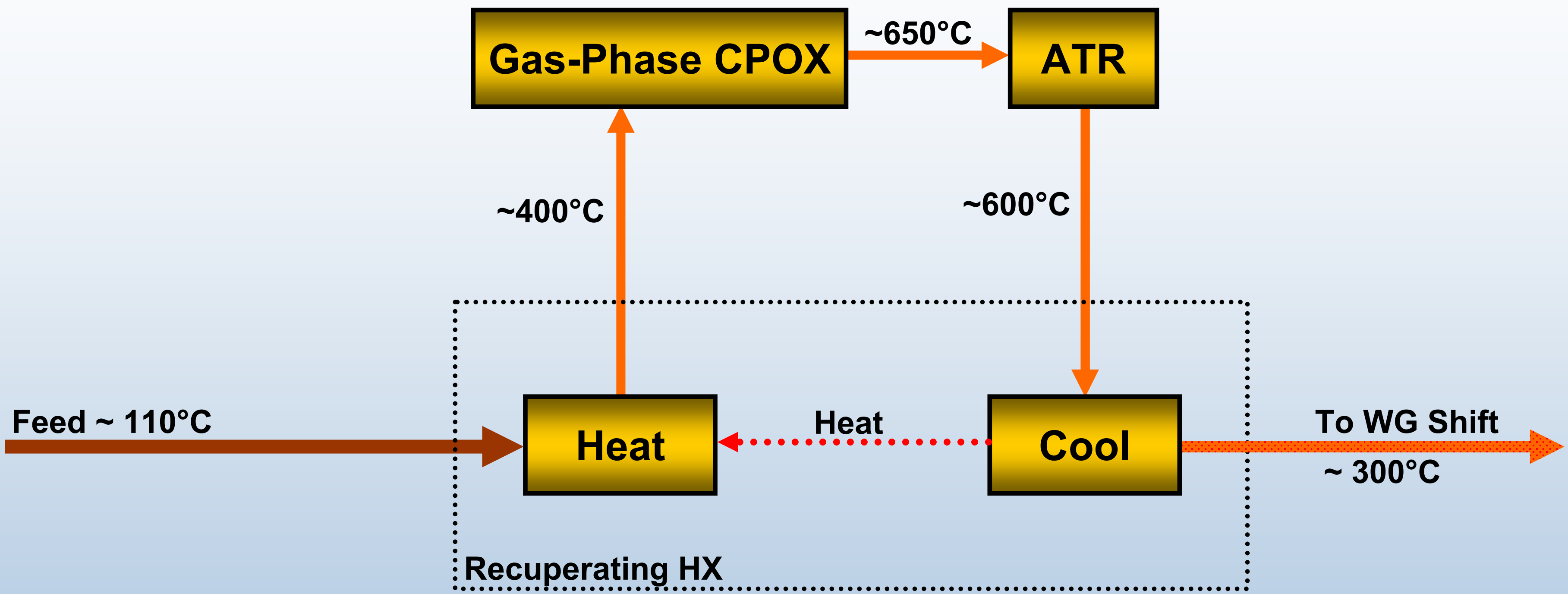
Feed Conditioning



NOMINALLY

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

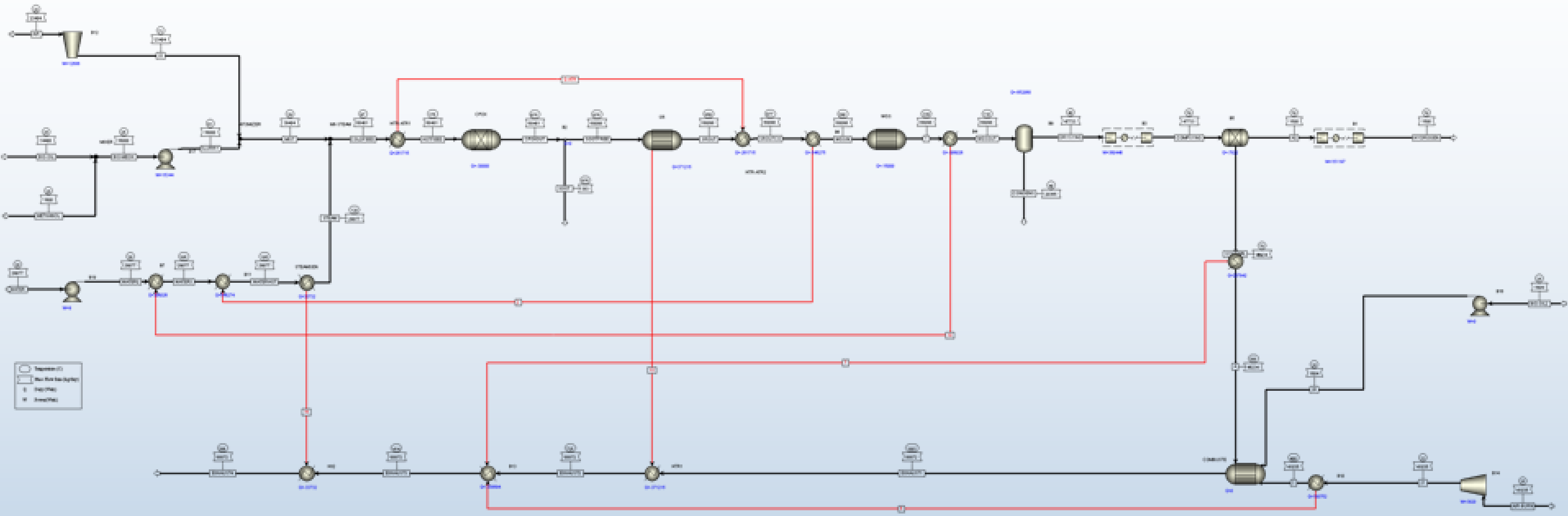
Reforming Conditioning



NOTE

- Carbon deposition from CPOX may need cyclic burn-out (parallel reactors)
- Optimization and agreement of kinetics still under consideration (ATR-in T°C)

Initial ASPEN Models Generated



ASPEN Mass & Energy Balance Models

Study overall efficiency potential

- auxiliaries considerations
- heat loss considerations
- supplemental fuel combusted for steam generation
- initial operating conditions

Trade-off system designs

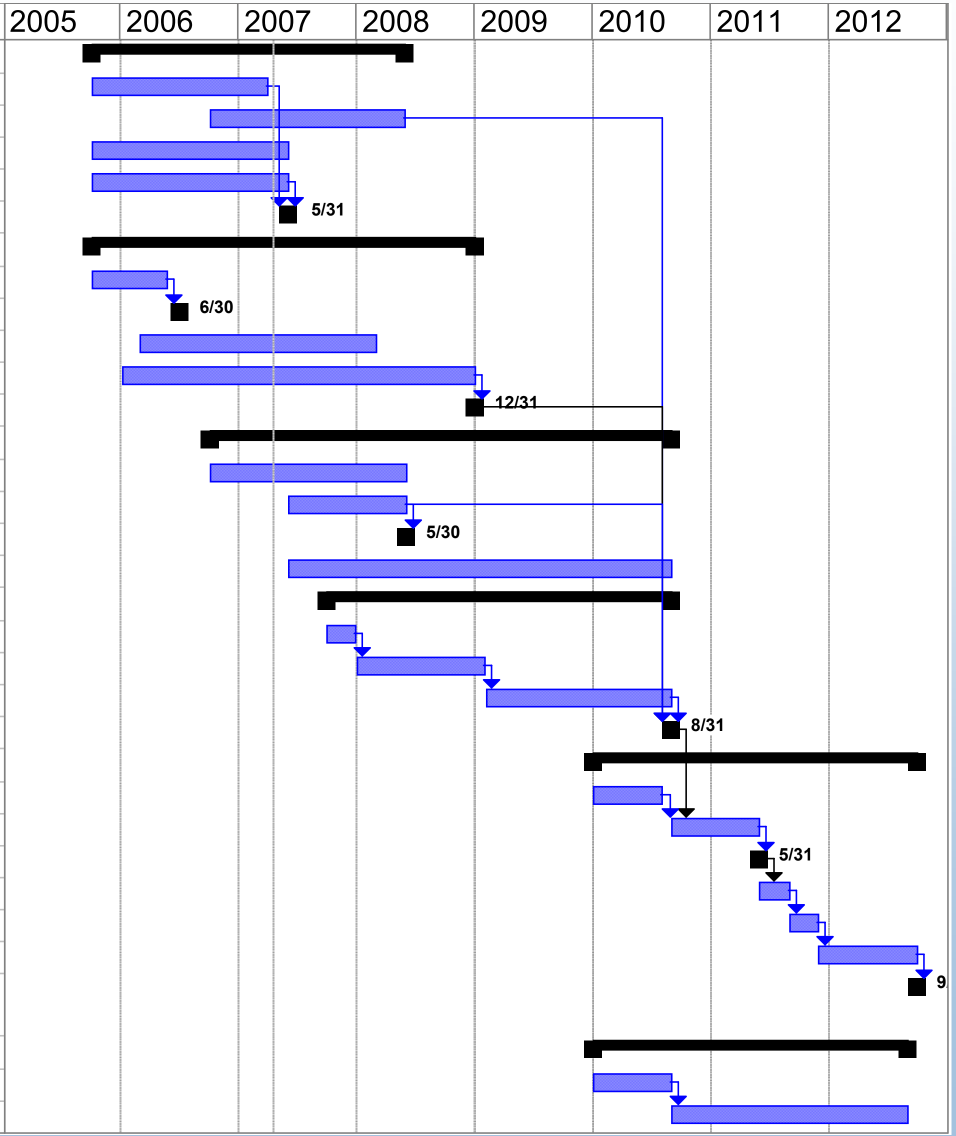
- enriched oxygen feed
- hydrogen purification (PSA vs. electrochemical separation)

Summary

- High conversion of bio-oil in non-catalytic step leads to significant yield of CO at 650 C
- Lower methanol levels (<30%) have yet to be demonstrated due to technical problems with the new system
- Rhodium catalyst used to attain equilibrium levels of H_2 with and without added steam
- Catalyst deactivation and regeneration under current base line conditions are important issues in results to date
- Feedstock effects are under study
- Experimental results used as a guideline for ASPEN simulations

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, O_2, H_2
33	Systems Integration



Future Work

- FY2008
  - Reduction of methanol addition
  - Continued catalyst testing (deactivation & poisoning)
    - Feed, Temperature, composition, Steam, O2, WHSV
  - Bench-scale system development
  - Gas Phase Temperature effects 600^{o}C to 700^{o}C
    - Model compound experiments and kinetic modeling
  - Continued Aspen simulations
- FY 2009:
  - Integrated laboratory experiment
  - Optimization work continues
  - Tests for long-term catalyst testing
- FY 2010: "Go/no-go" on conceptual design
- FY 2011: Prototype system
- FY 2012: Long duration runs