Distributed Bio-Oil Reforming

2008 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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Overview

Timeline

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

Production Barriers

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

Budget

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

2012 Targets

- $3.80/gallon gasoline equivalent
- 72% energy efficiency (bio-oil to H_2)

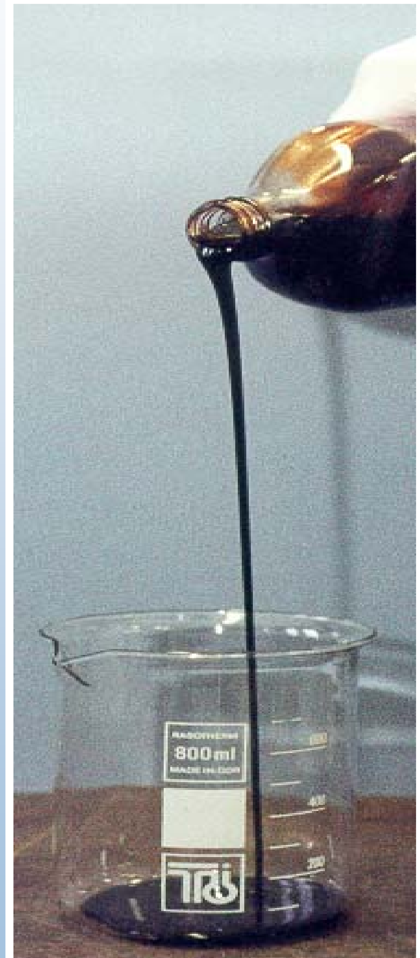
Partners

- 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)

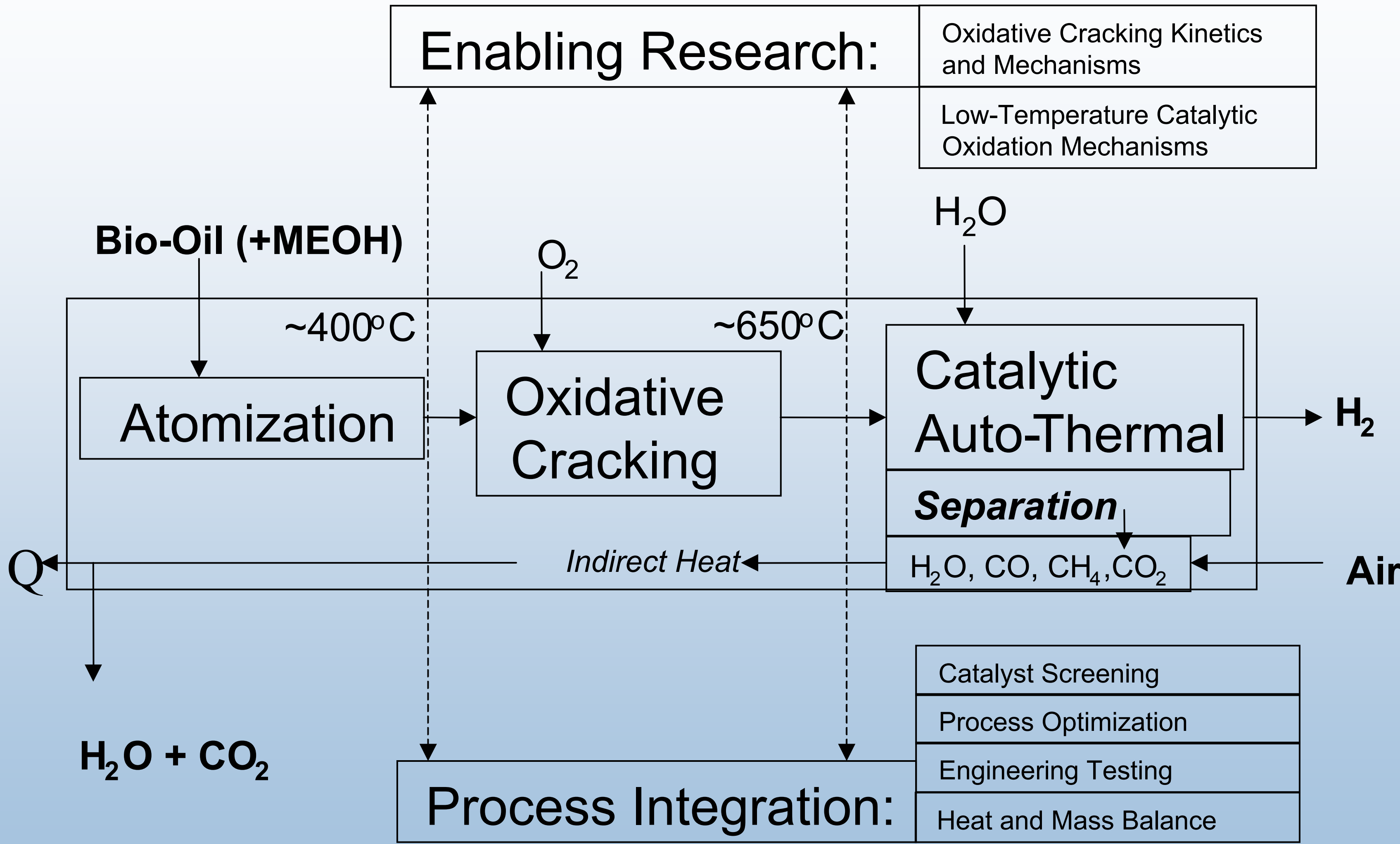
Overall Reaction:

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

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

Energy Efficiency Estimates are in Progress based on Aspen Modeling

Distributed Bio-Oil Reforming Approach



Objectives

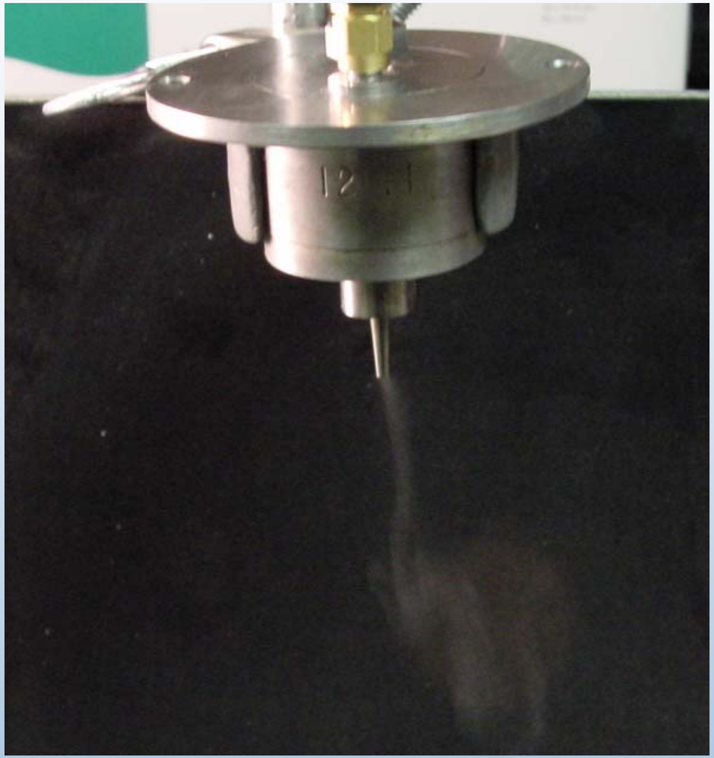
- Overall
  - Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry, deactivation, and regeneration strategy as a basis for process definition for automated distributed reforming; demonstrate the process
- FY 2008
  - Improve bio-oil atomization with 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)

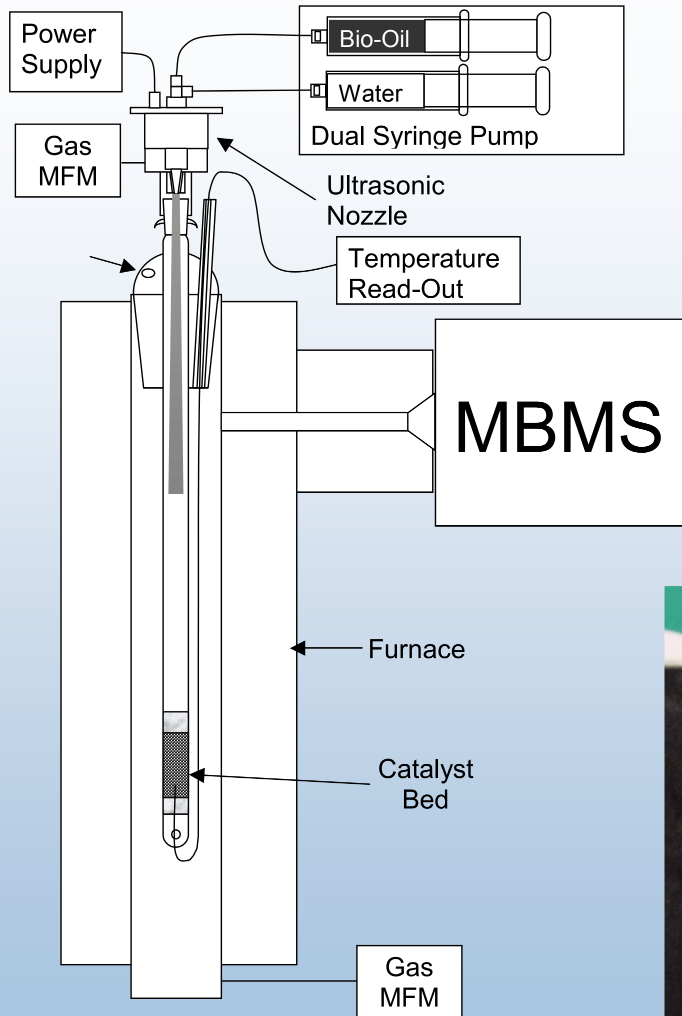
Bio-oil Injection Working Hypothesis

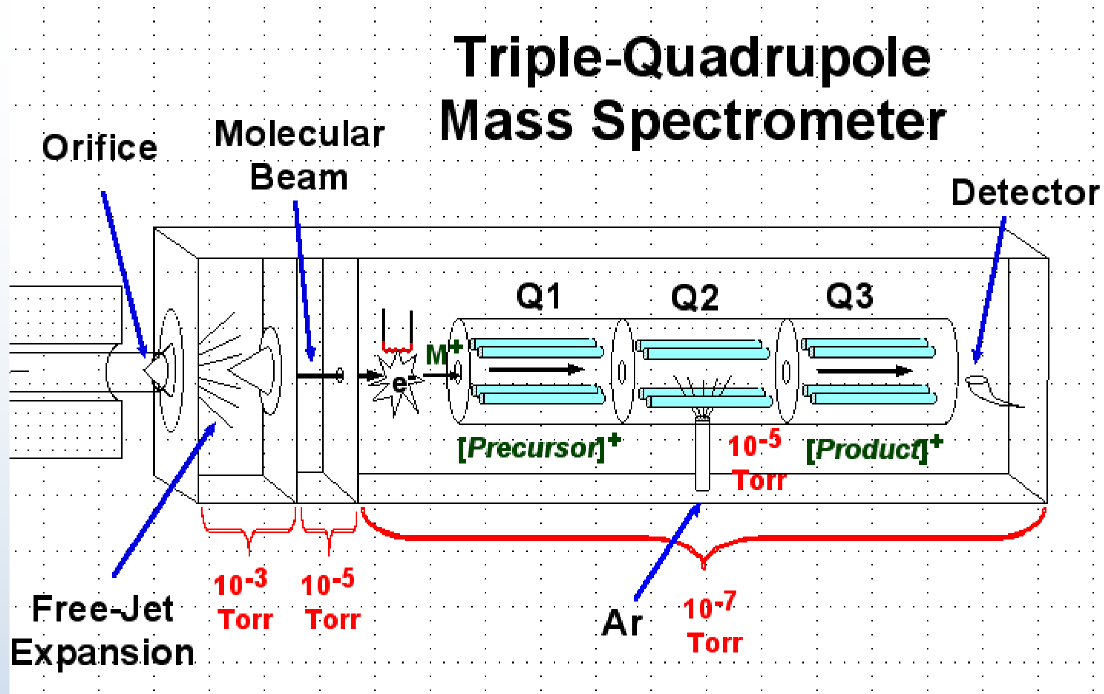
- Ultrasonic nozzle provides:
  - Rapid, uniform fuel-air mixing and temperature distribution
  - Reduces wall impingement
- Leading to:
  - Low carbon formation-
    - extreme analogy to diesel PM reduction via high injection pressure
  - High gas yields and selectivity control



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



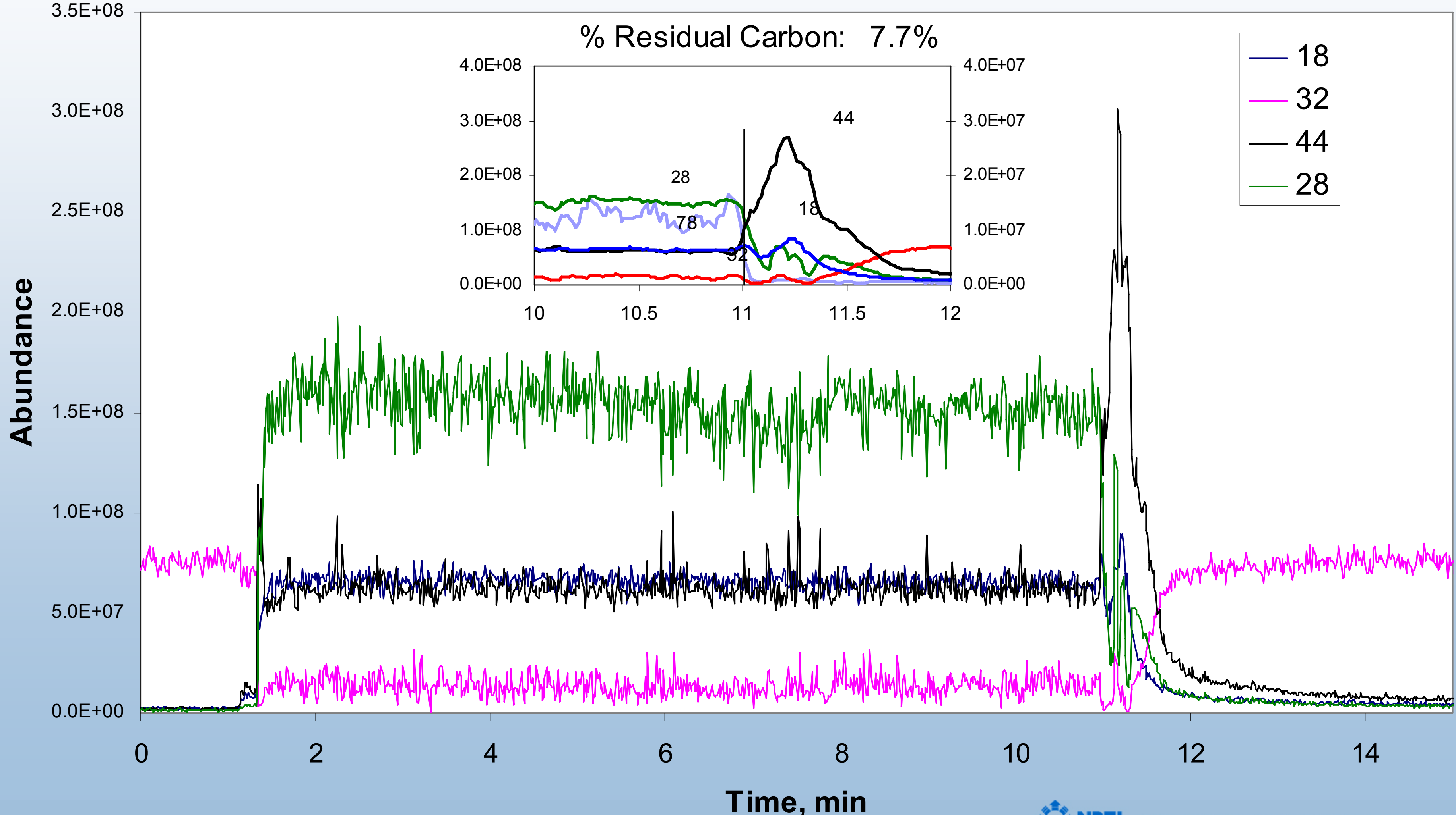


Ultrasonic Nozzle

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

Ultrasonic Nebulizer

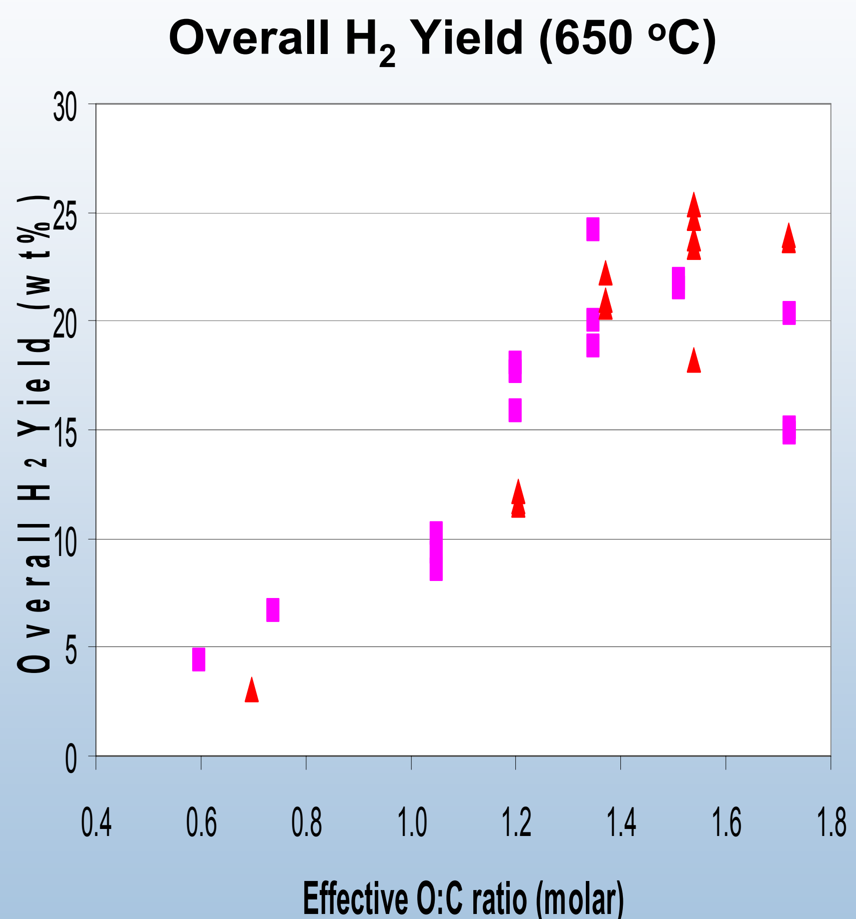
Oxidative Cracking 0.5 s @ 650 C

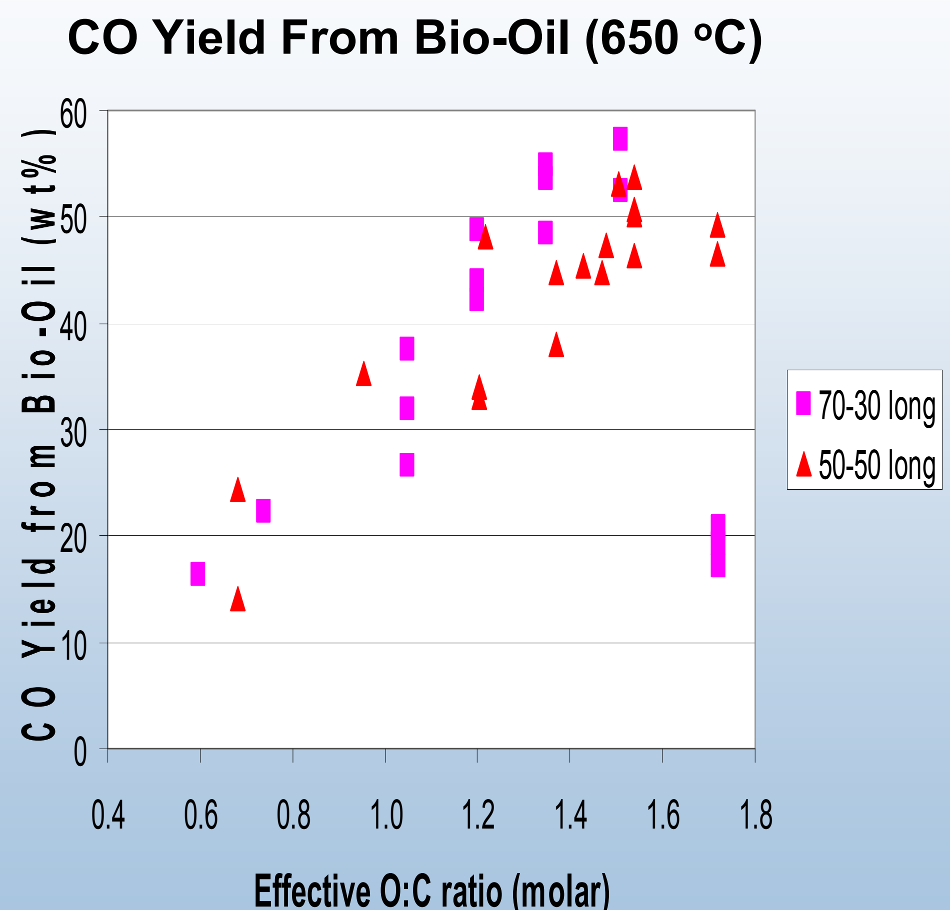


1. Bio-Oil Volatilization

- 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

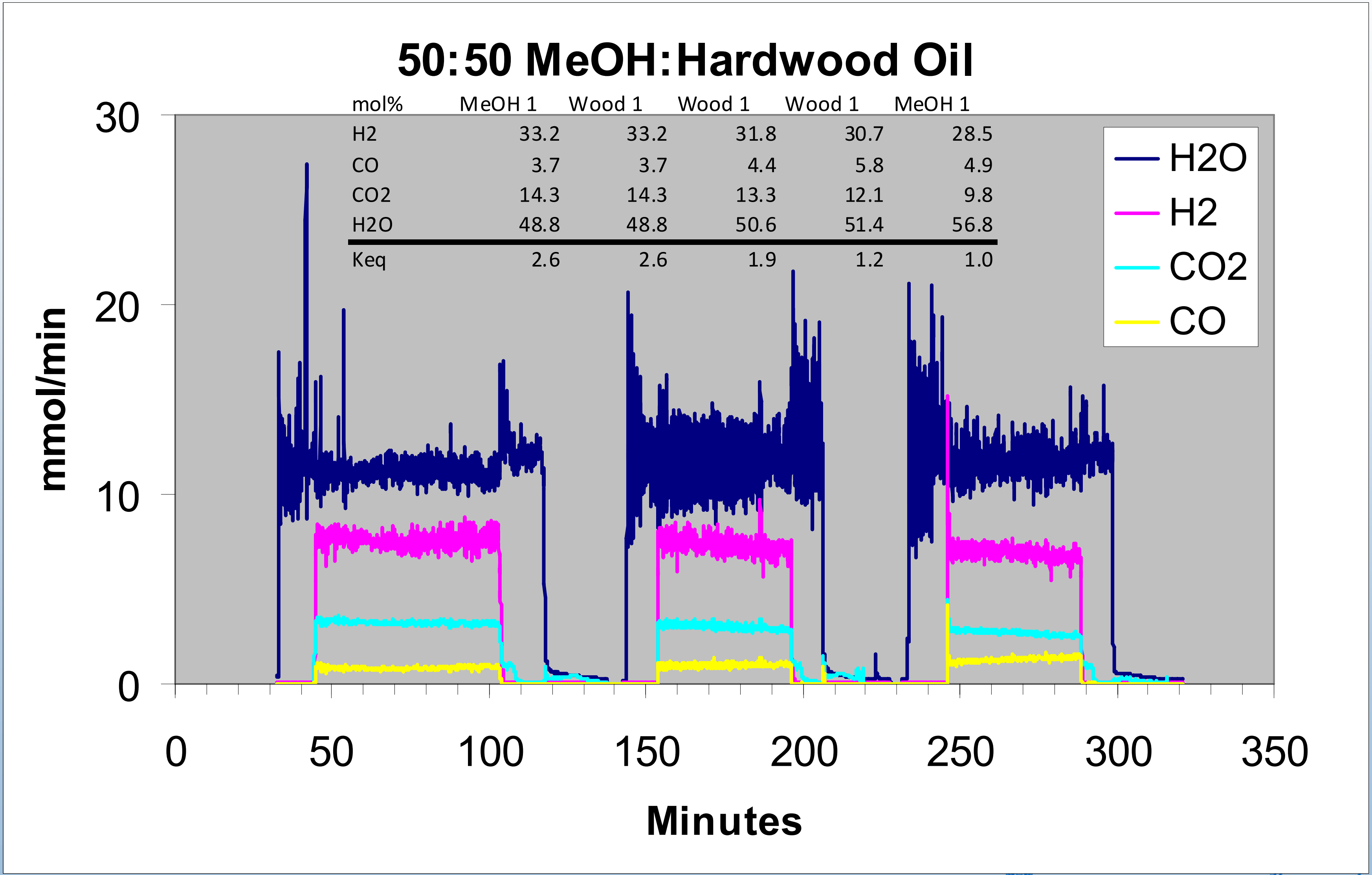




Effect of effective O:C ratio for two methanol addition levels (50% and 30%) and two gas phase residence times (200 and 300 ms) on H2 and CO yields.

Integrated System under “std” Conditions

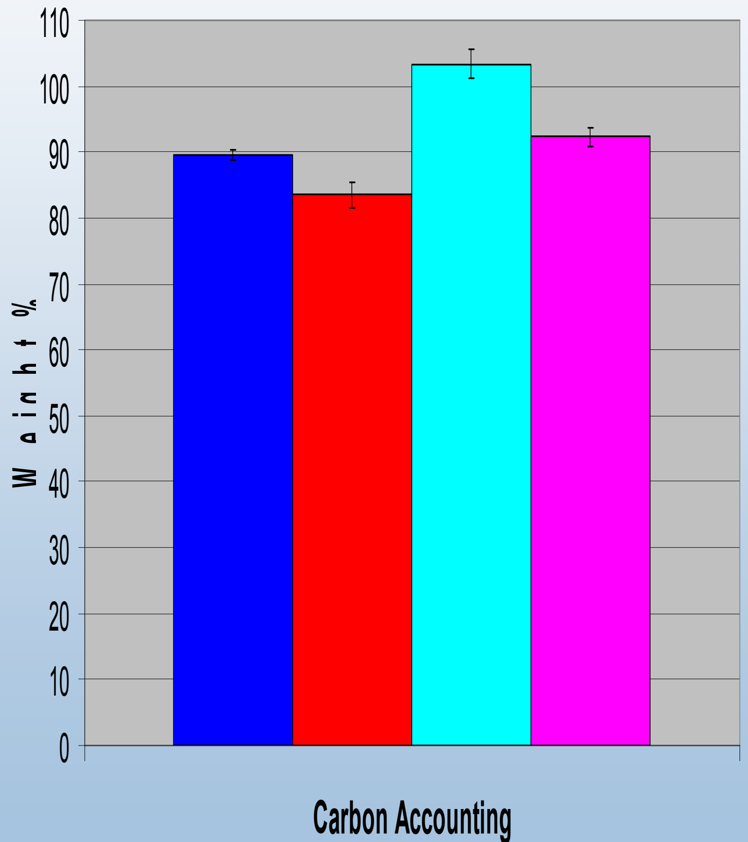
Vapor RT=0.3 s; WHSV[0.5%Rh/Al_2O_3]=3.5; S/C=2.5; O/C_{eff}=1.3

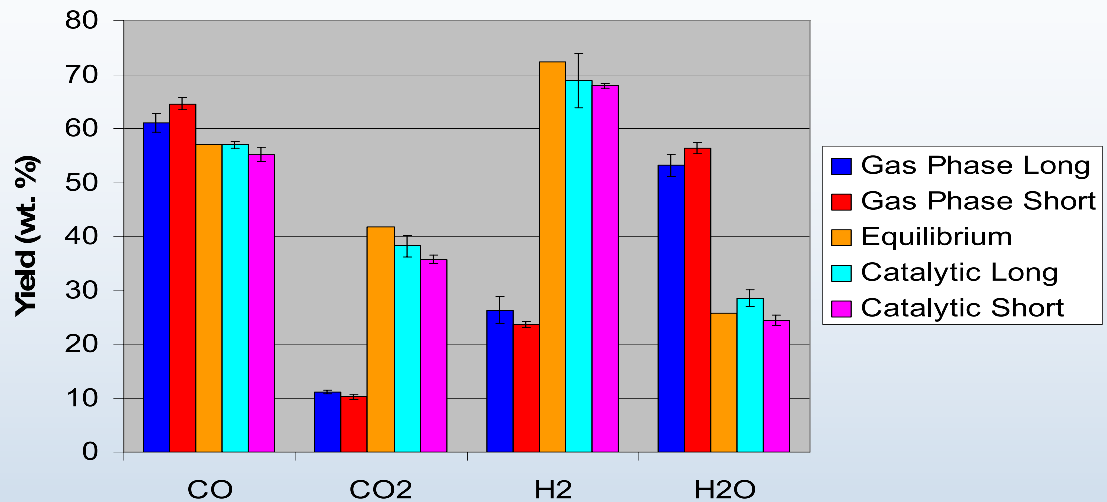


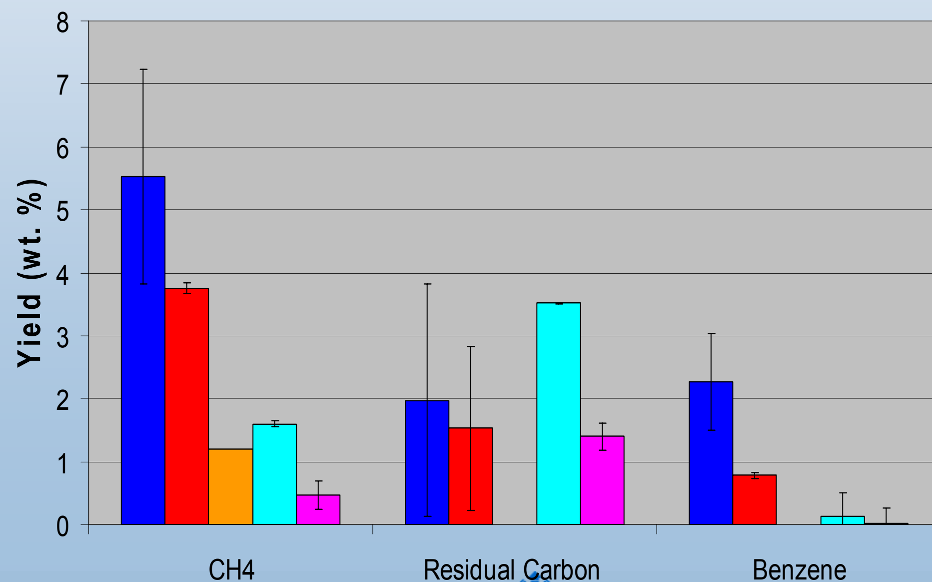
mol%	MeOH 1	Wood 1	Wood 1	Wood 1	MeOH 1
H2	33.2	33.2	31.8	30.7	28.5
CO	3.7	3.7	4.4	5.8	4.9
CO2	14.3	14.3	13.3	12.1	9.8
H2O	48.8	48.8	50.6	51.4	56.8
Keq	2.6	2.6	1.9	1.2	1.0

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)

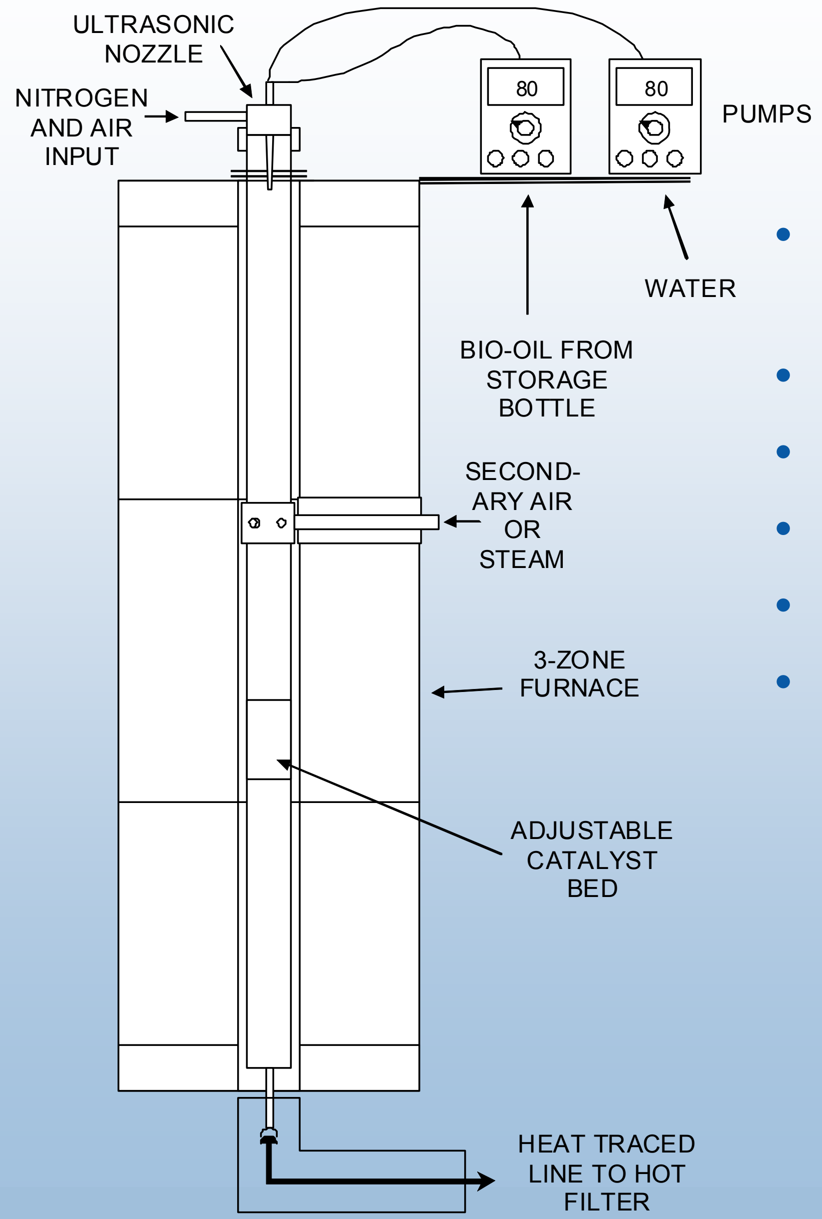






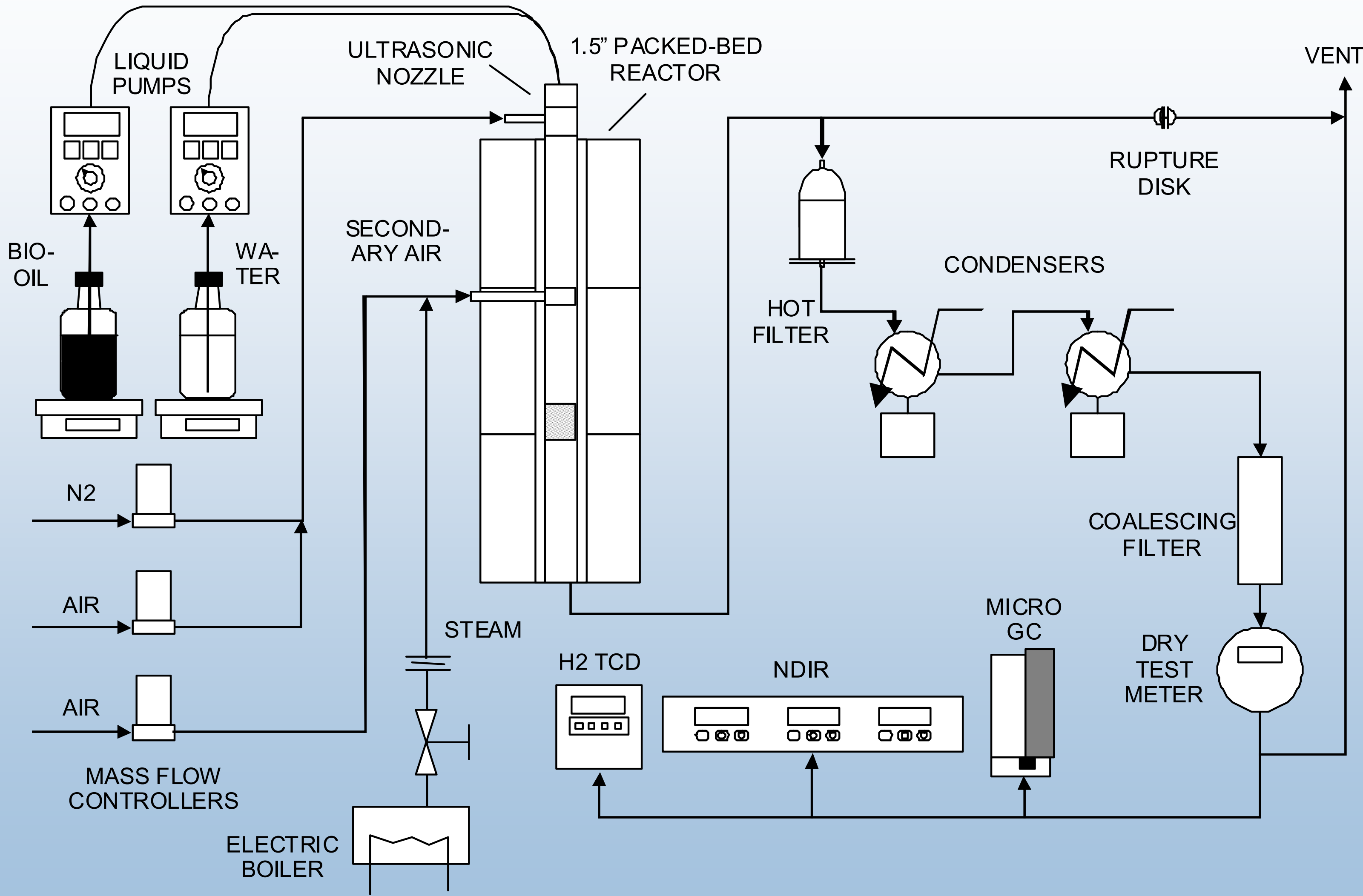
Carbon Accounting includes CO, CO_2, CH_4, CH_3OH, Benzene, and Residual Carbon

Bench Scale Reactor Design

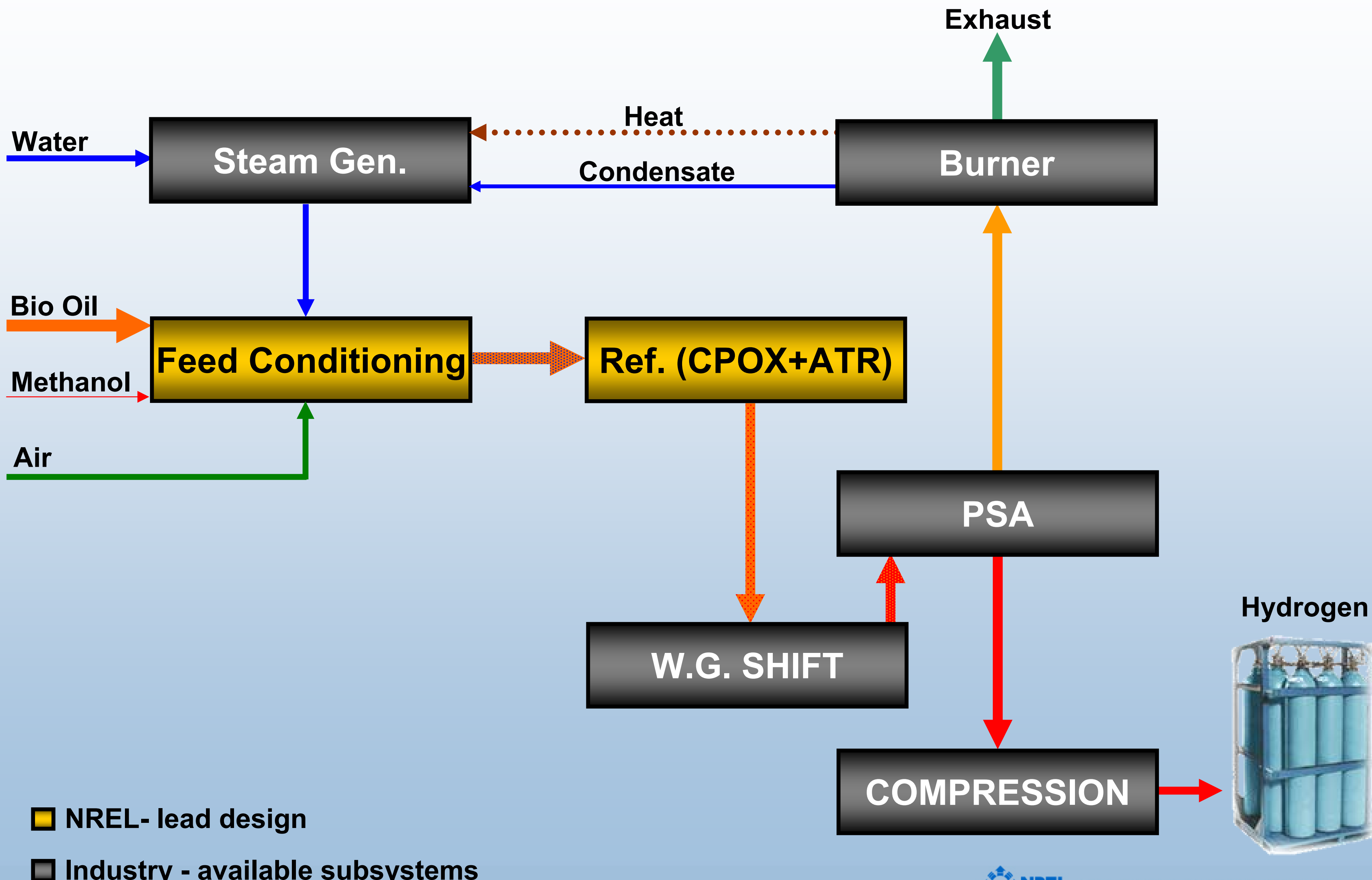


- Take advantage of existing equipment
- Build out of quartz
- Long duration runs
- Detailed product analysis
- Improved material balance
- Design and lab arrange-ments are in progress

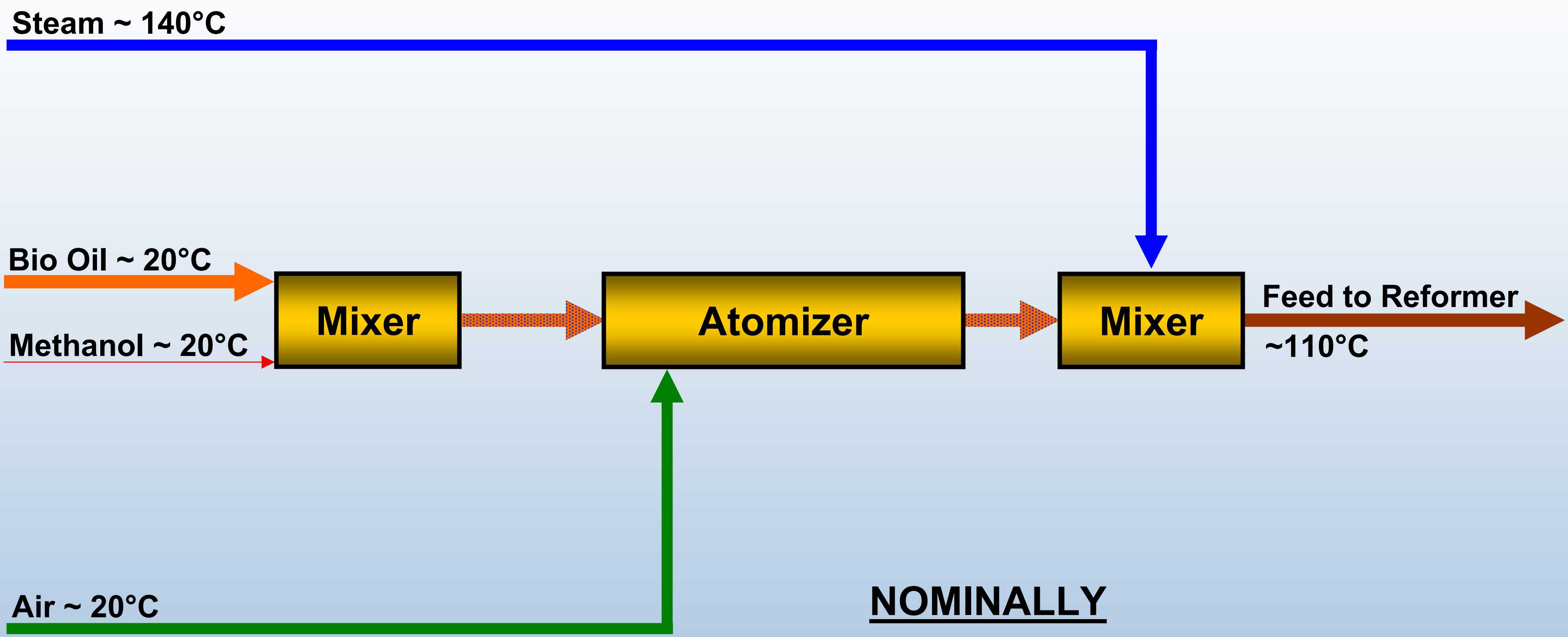
Bench Scale Reactor System



Process Subsystems Outline



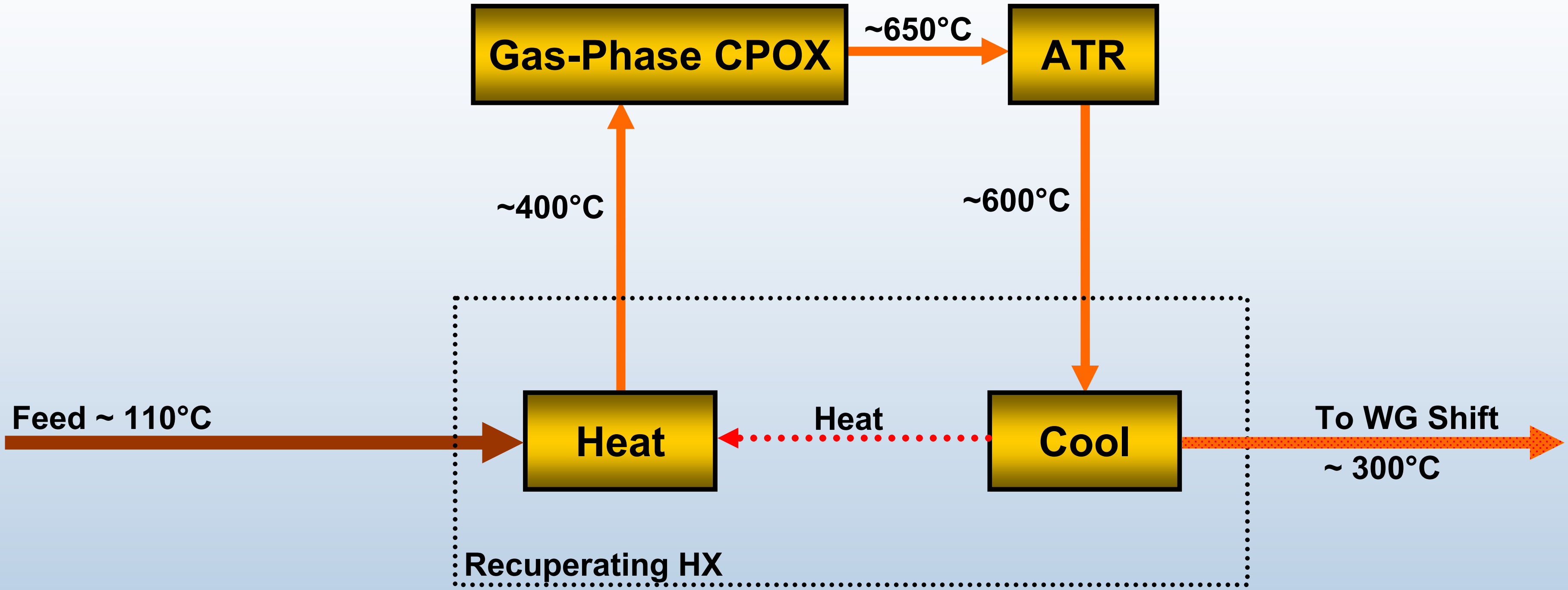
Feed Conditioning



NOMINALLY

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

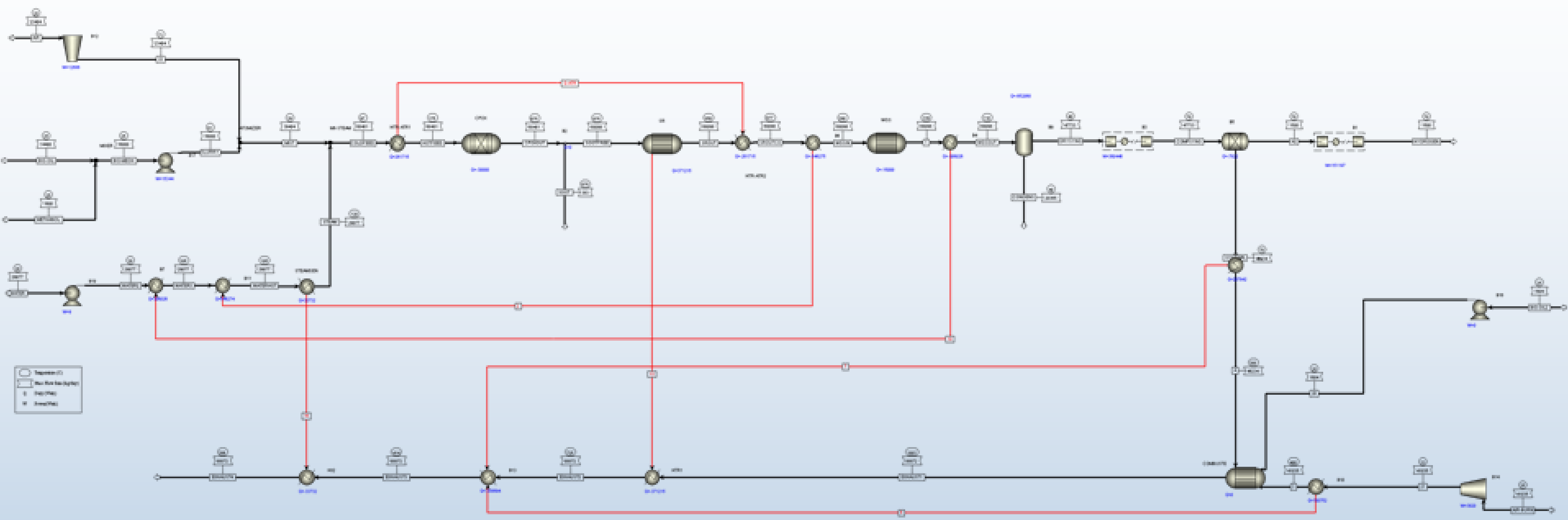
Reforming Conditioning



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

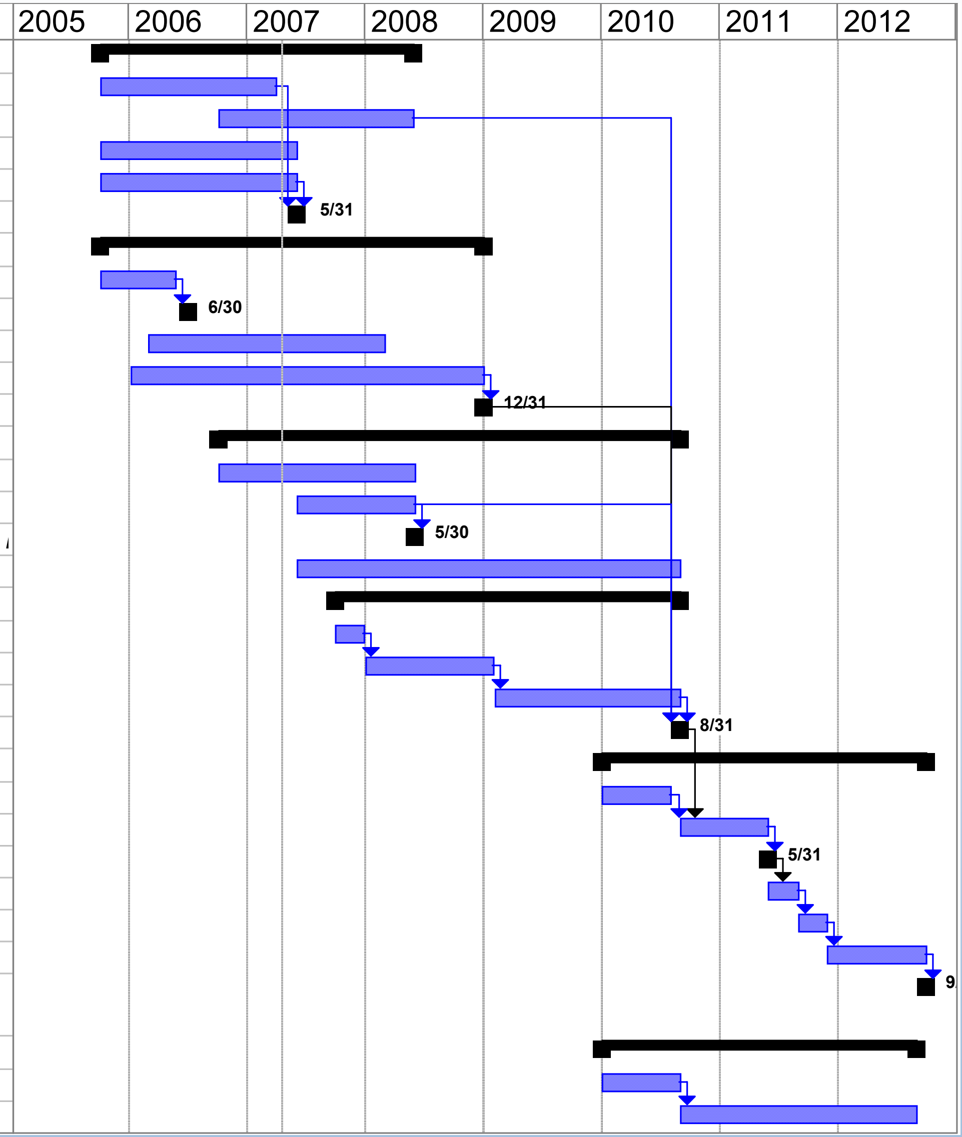
- enriched oxygen feed
- hydrogen purification (PSA vs. electrochemical separation)

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, O2, H2
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