Distributed Bio-Oil Reforming

2006 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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Project ID#PD5

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Overview

Timeline

- Project start 2005
- Project end 2010
- 15% completed

Budget

- FY05 $100K
- FY06 $300K

Production Barriers

A. Fuel Processor Capital
B. Fuel Processor Manufacturing
C. Operation & Maintenance
D. Feedstock Issues
F. Control & Safety

Target $3.60/gge

Partners

- Colorado School of Mines (FY06) - Oxidative cracking
- Chevron (FY06) - Feedstock Project planned for FY06

Approach

Biomass → PYROLYSIS → Bio-oil

(Methanol) → Bio-oil

↓

VOLATILIZATION

↓

O_2 → Low Temperature Oxidative Cracking

↓

H_2O → REFORMING

↓

SHIFT

↓

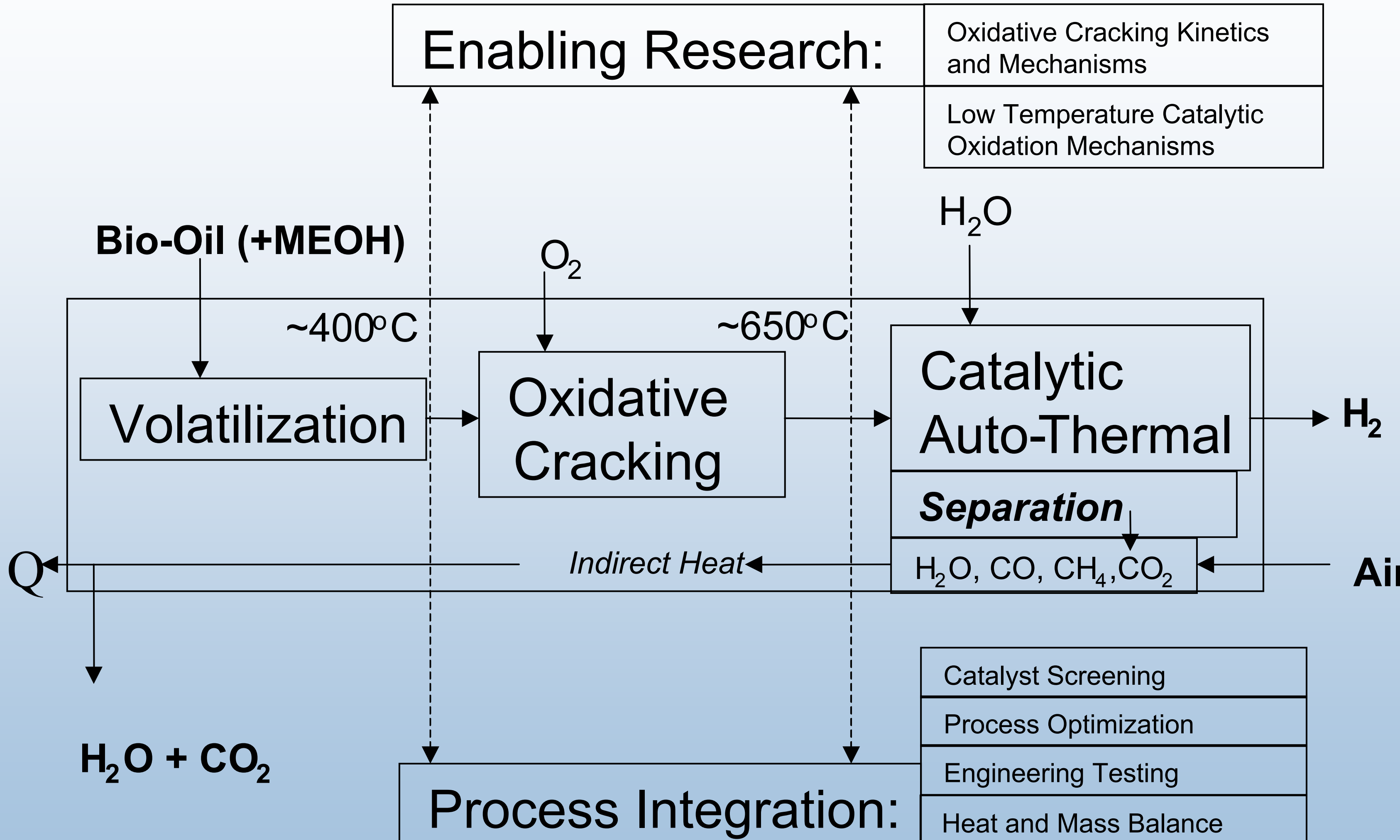
H_2 ← SEPARATION → CO_2

Show that bio-oil and blends with methanol can be fed without excessive coking and develop a process to meet HFC&IT cost and performance objectives.

Objectives

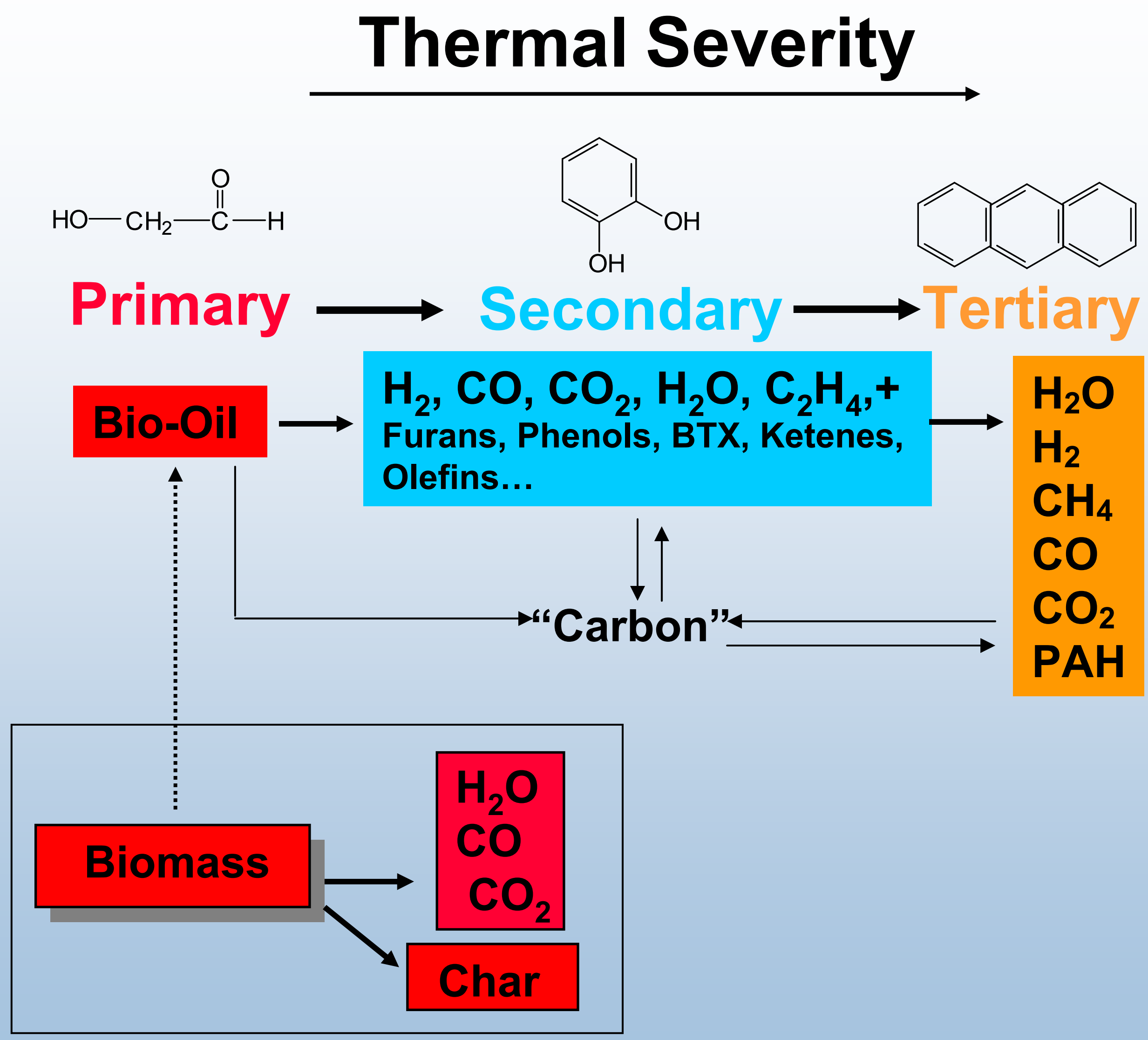
- Overall:
  - Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry, deactivation, and regeneration strategy as a basis for process definition for automated distributed reforming
- FY06
  - Demonstrate partial oxidation and show that it can reduce the required catalyst loading in the reforming step by 50%

Distributed Bio-Oil Reforming Approach

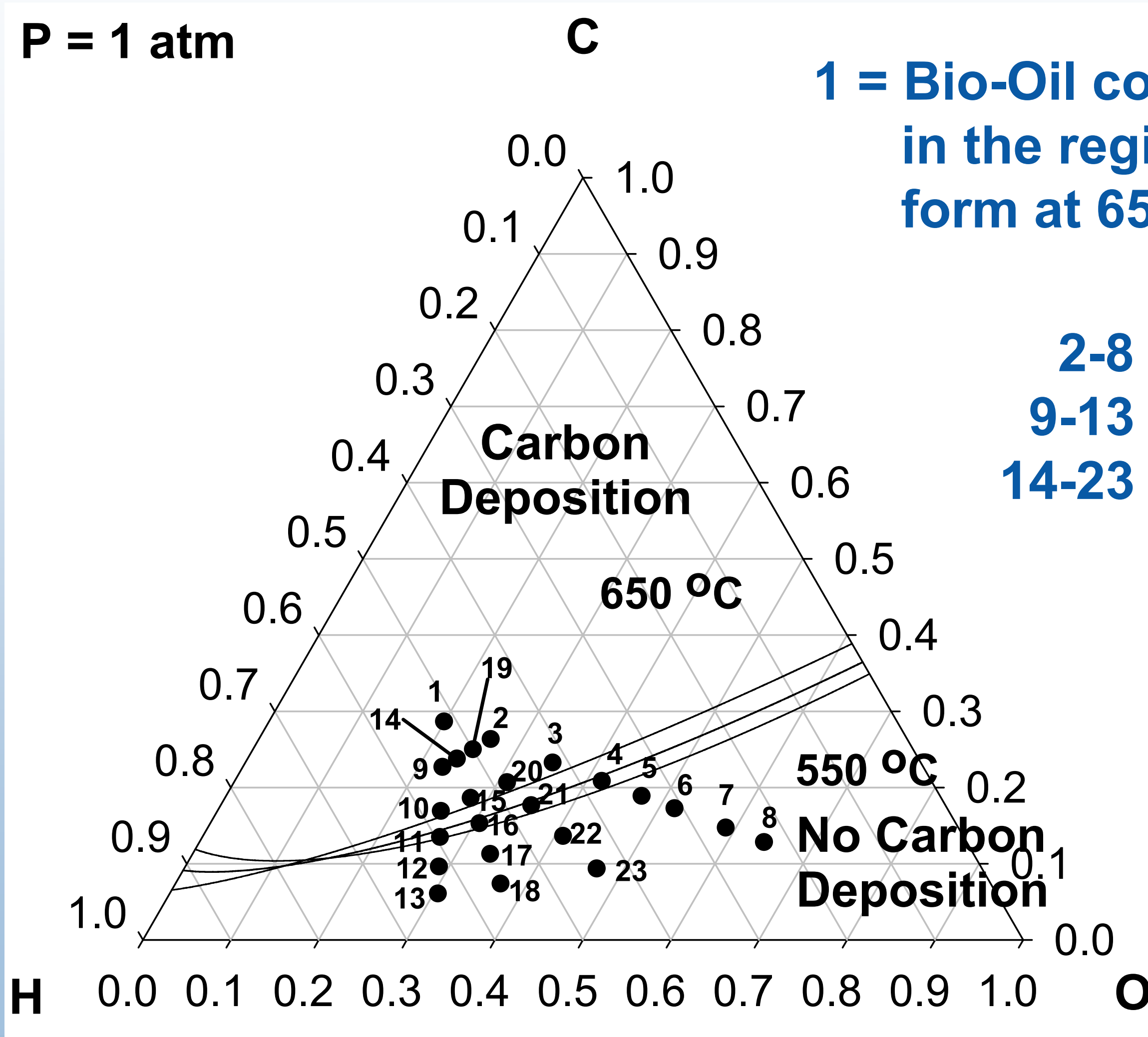


Technical Accomplishments

- FY05: Whole oil successfully run
  - With 10% MeOH addition, bio-oil processing was trouble free over short run durations (up to 16 hrs)
- FY06: Accomplishments to date
  - Bio-oil volatilization method developed
  - Oxidative cracking promising results
  - Progress toward July milestone on target


Thermal Severity
HO—CH2—C(=O)—H
OH
OH
Primary
Secondary
Tertiary
Bio-Oil
H2, CO, CO2, H2O, C2H4,+
Furans, Phenols, BTX, Ketenes,
Olefins…
H2O
H2
CH4
CO
CO2
PAH
"Carbon"
Biomass
H2O
CO
CO2
Char

Equilibrium Modeling Results

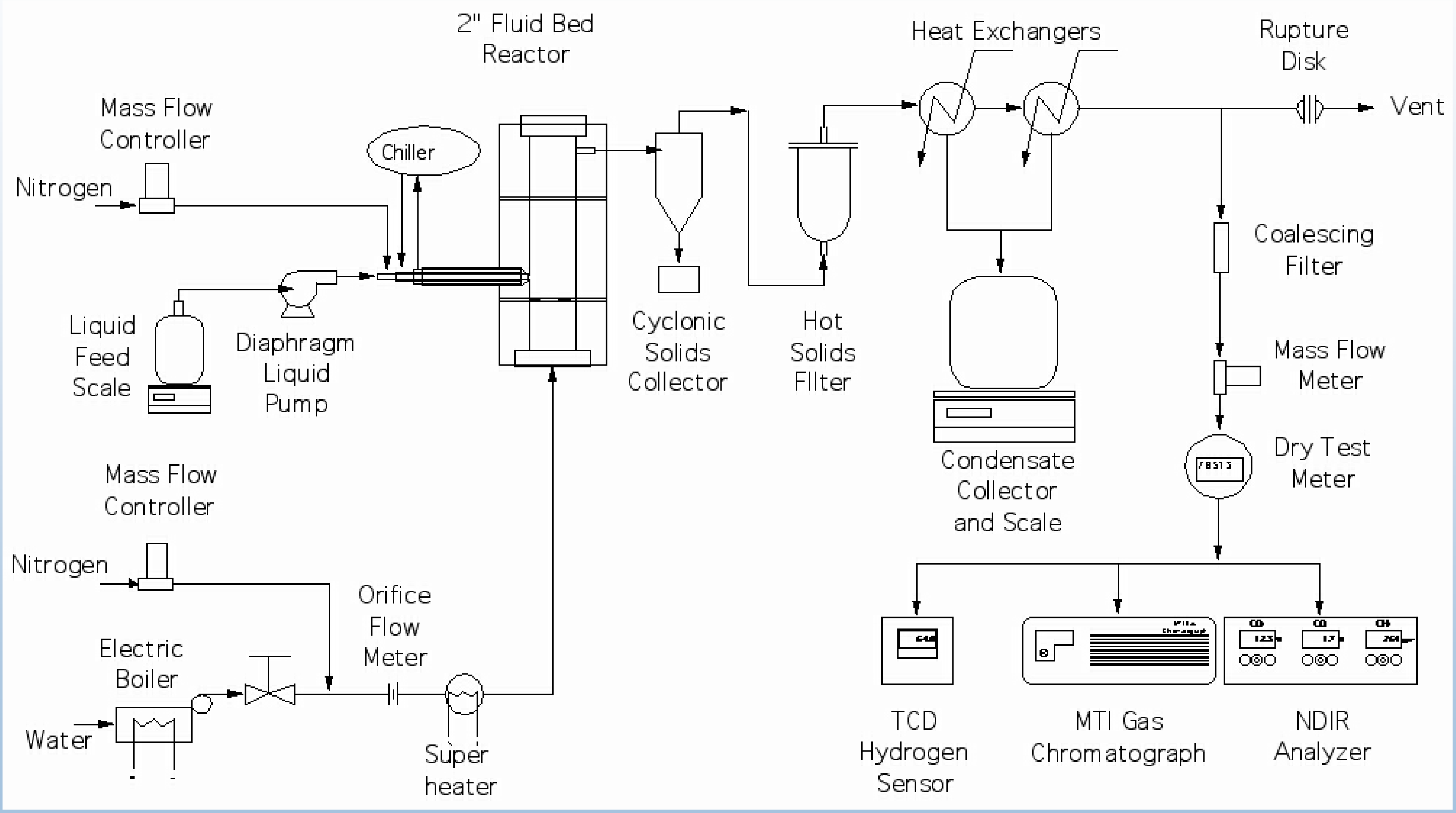


1 = Bio-Oil composition, which lies in the region where carbon will form at 650 C

2-8 = O_2 addition points
9-13 = H_2O addition
14-23 = both O_2 and H_2O

Goal is to identify the thermodynamic and kinetic domains for deposit free operation

Spray Injector Reactor System

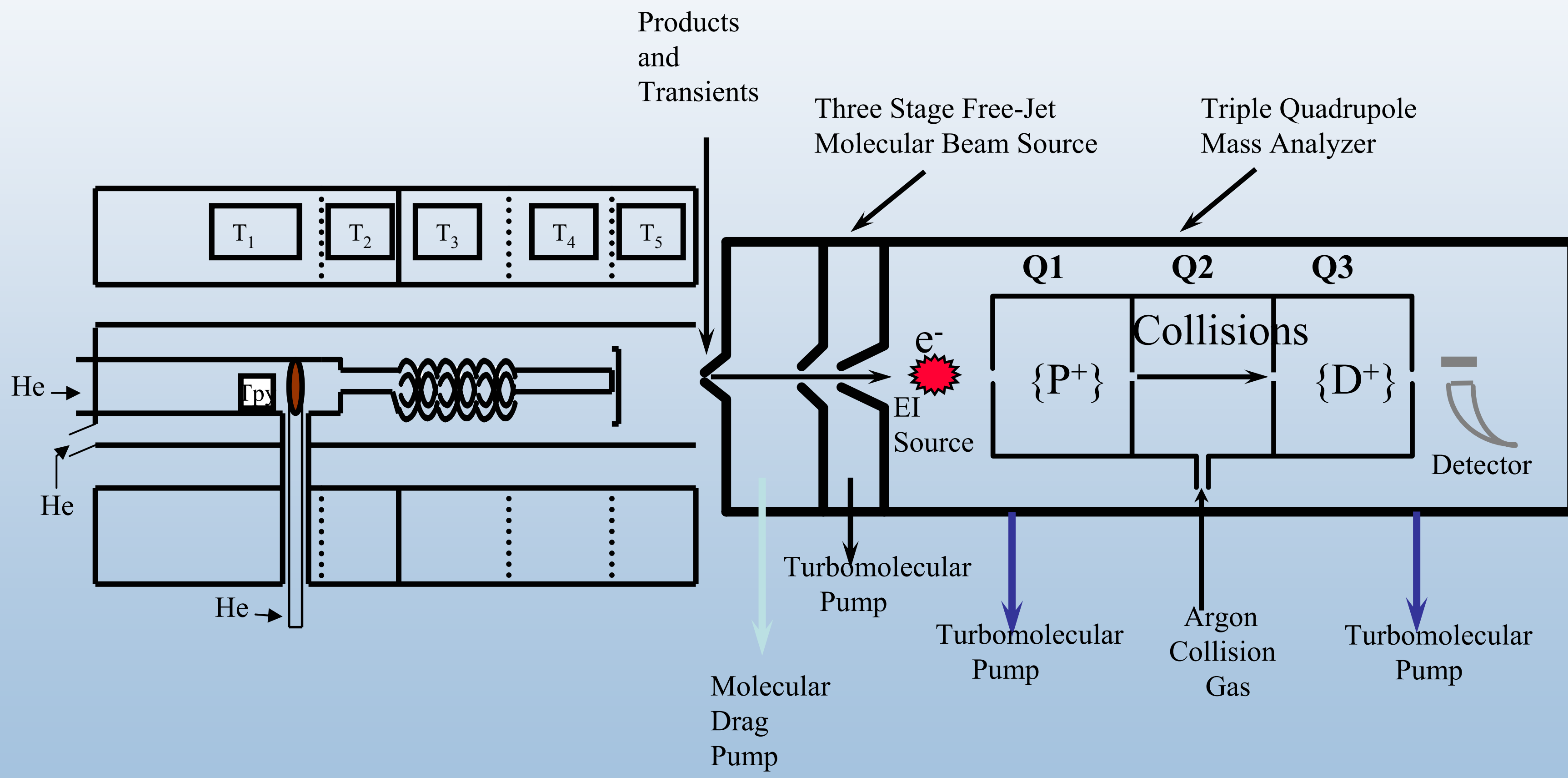


Spray Injector Results

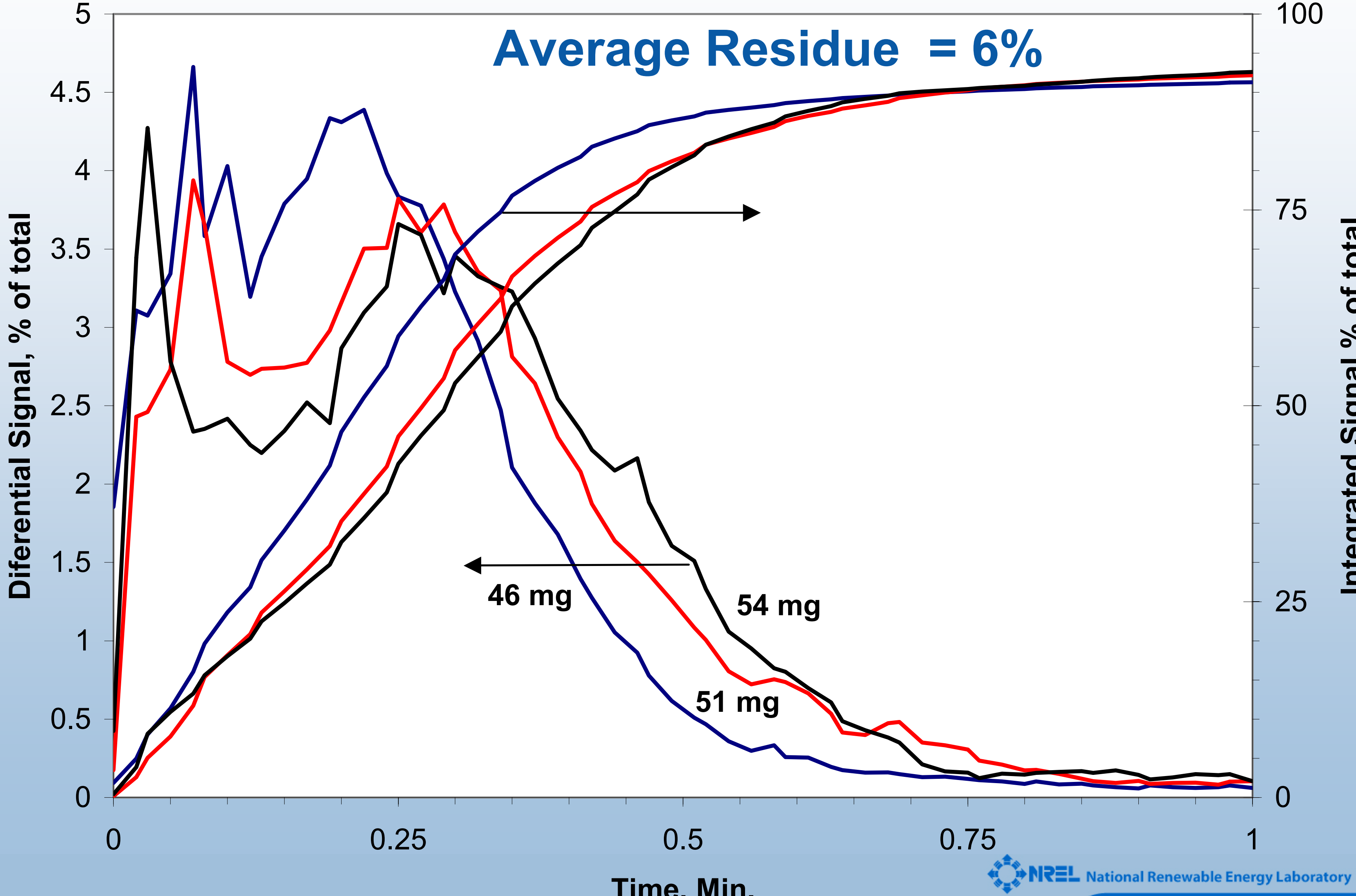
					Gas Composition, vol. %						
Run	Liq. Feed g/min	Air coeff. %	Temp, C	Time, s	N_2	O_2	H_2	CO	CO_2	CH_4	C Bal, %
1	0.5	163	600	2.4	79	15.96	0.00	1.19	4.19	0.00	76%
2	0.5	162	599	1.1	78	17.18	0.00	0.59	4.16	0.00	68%
3	1.0	99	602	1.4	79	11.61	0.00	2.78	6.26	0.00	69%
4	1.0	65	601	1.5	79	5.27	0.00	4.06	11.64	0.00	65%
5	1.0	66	636	1.4	80	2.28	0.00	5.96	11.74	0.08	74%
6	**1.0**	**59**	**650**	**1.4**	**78**	**0.95**	**0.82**	**6.92**	**13.36**	**0.23**	**71%**
7	1.0	53	649	1.4	75	0.48	1.45	11.05	11.27	0.40	65%
8	**1.0**	**47**	**650**	**1.4**	**72**	**0.24**	**3.24**	**14.75**	**9.33**	**0.72**	**56%**
9	1.0	34	647	1.4	29	0.19	22.11	32.11	15.38	1.63	32%
10	0.9	54	698	1.3	73	0.13	2.56	12.52	10.94	0.63	70%
11	1.0	52	748	2.9	68	0.00	6.55	13.20	11.21	1.26	76%
12	1.0	54	750	2.7	75	0.03	3.92	9.05	11.23	0.74	72%

Spray injection resulted in low carbon conversion to CO and formation of aromatics and carbon

Schematic of Pyrolysis Reactor & NREL's MBMS Sampling System

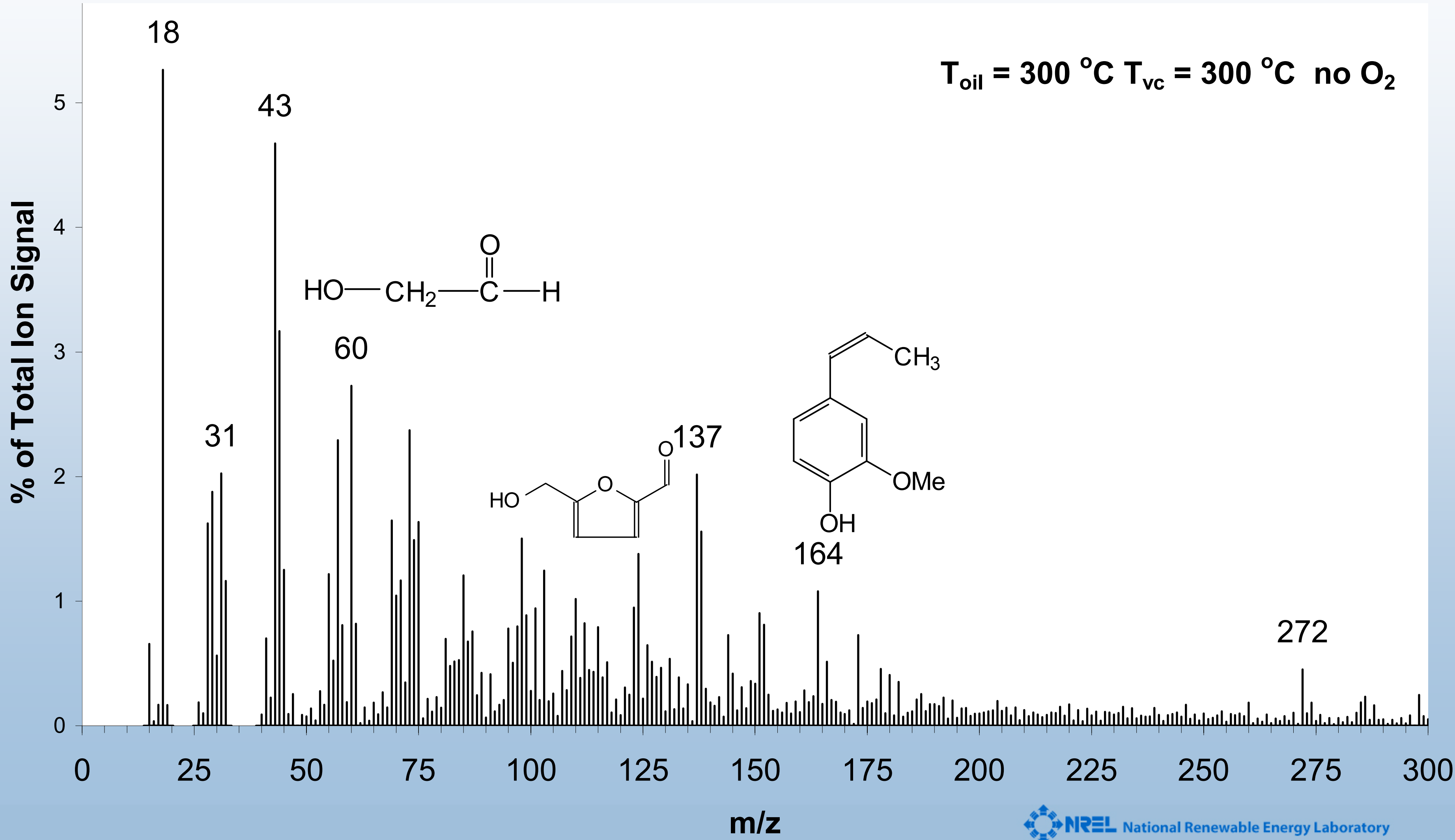


Bio-Oil Film Volatilization – 400 °C



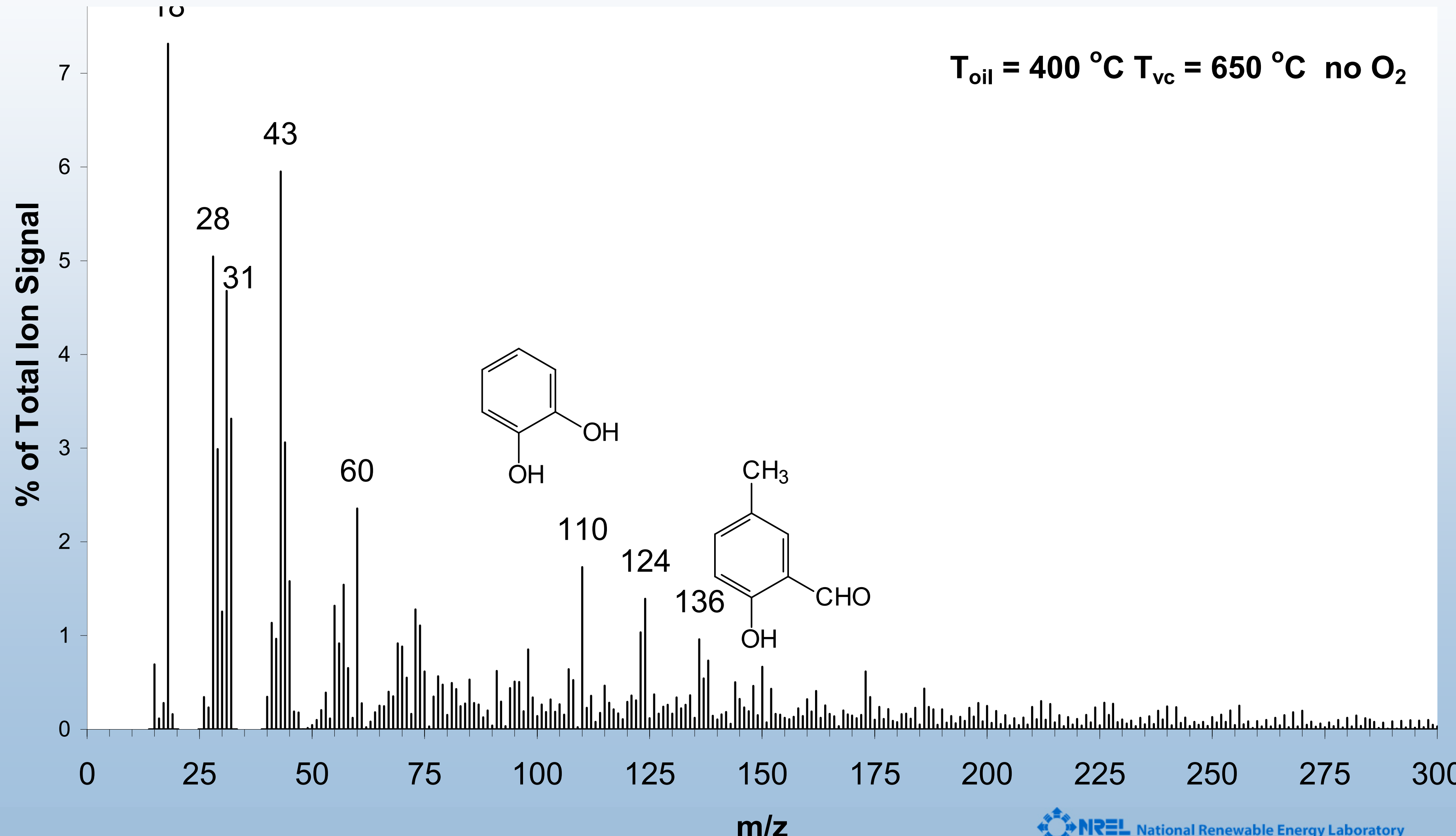
Bio-Oil Film Volatilization

MBMS Bio-Oil Spectrum



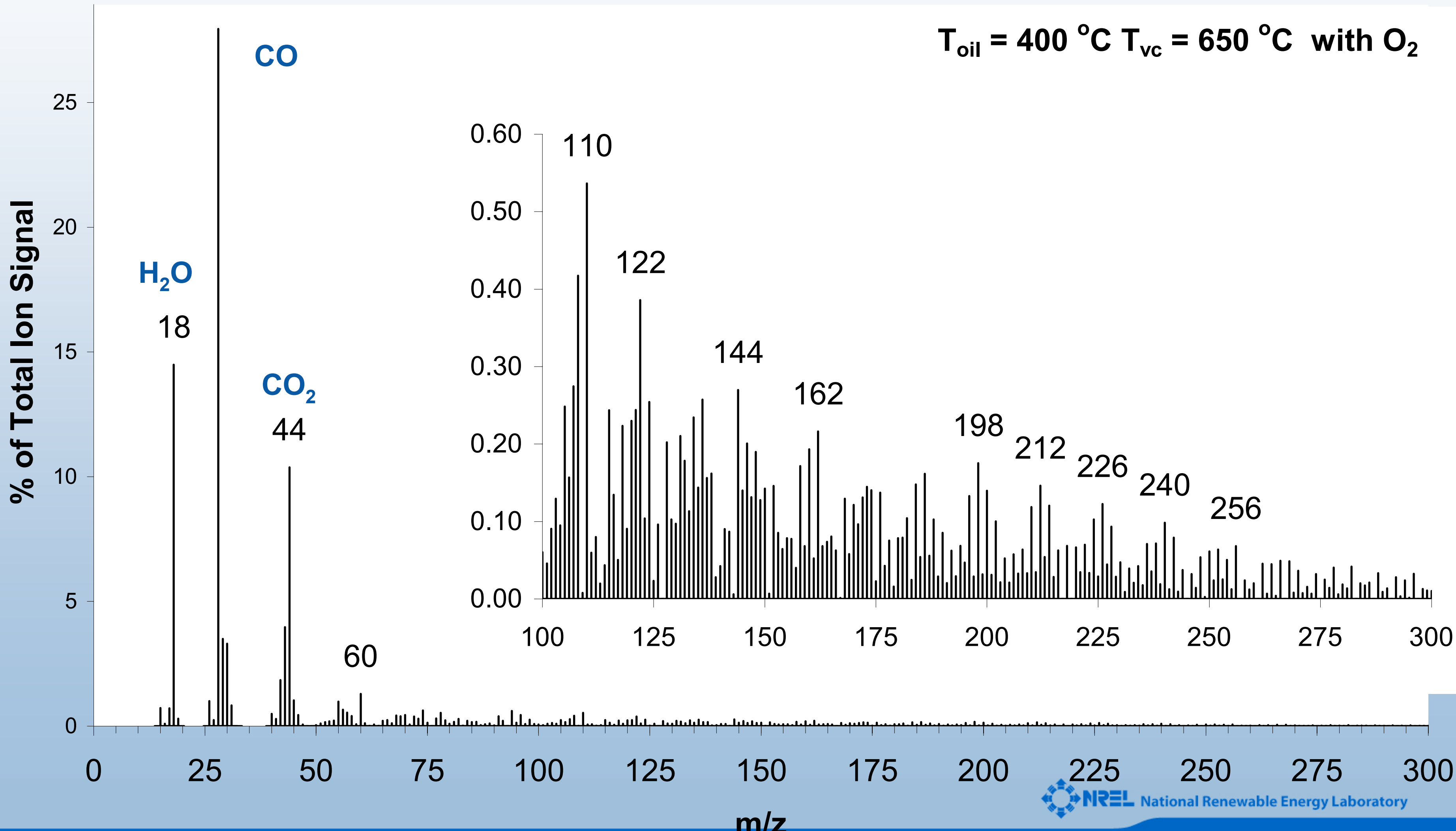
Bio-Oil Film Volatilization

Cracking 0.5 s @ 650 C

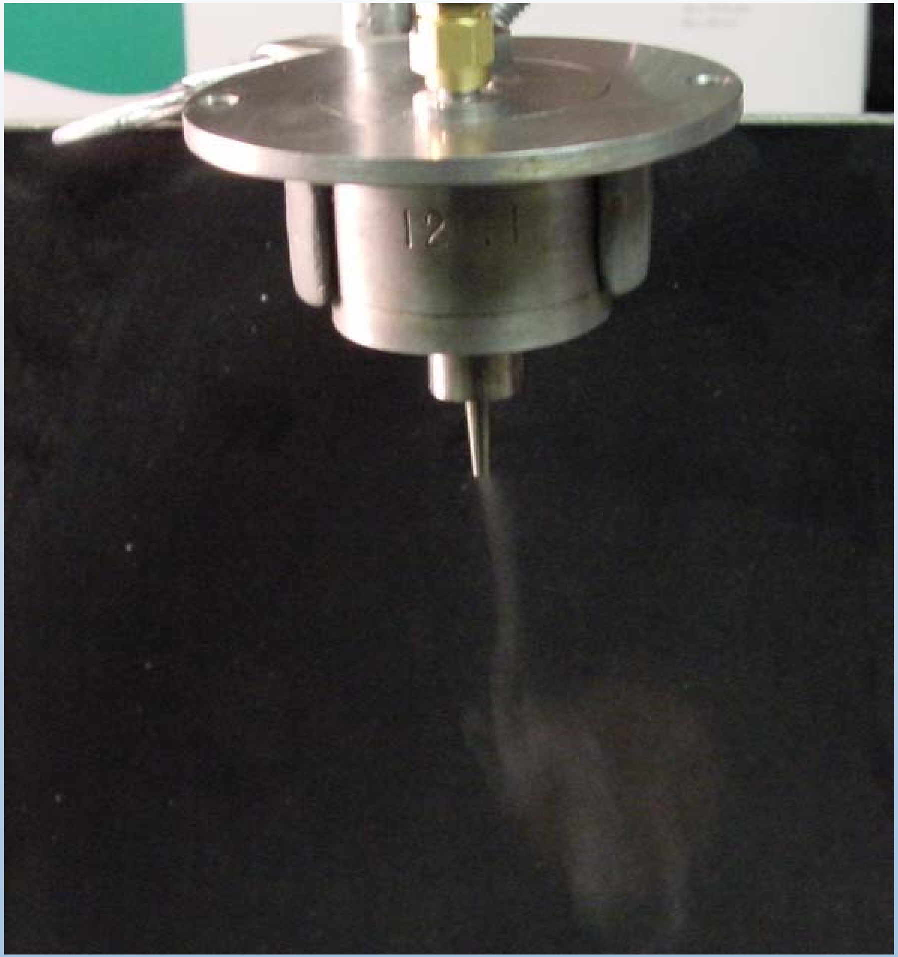


Bio-Oil Film Volatilization

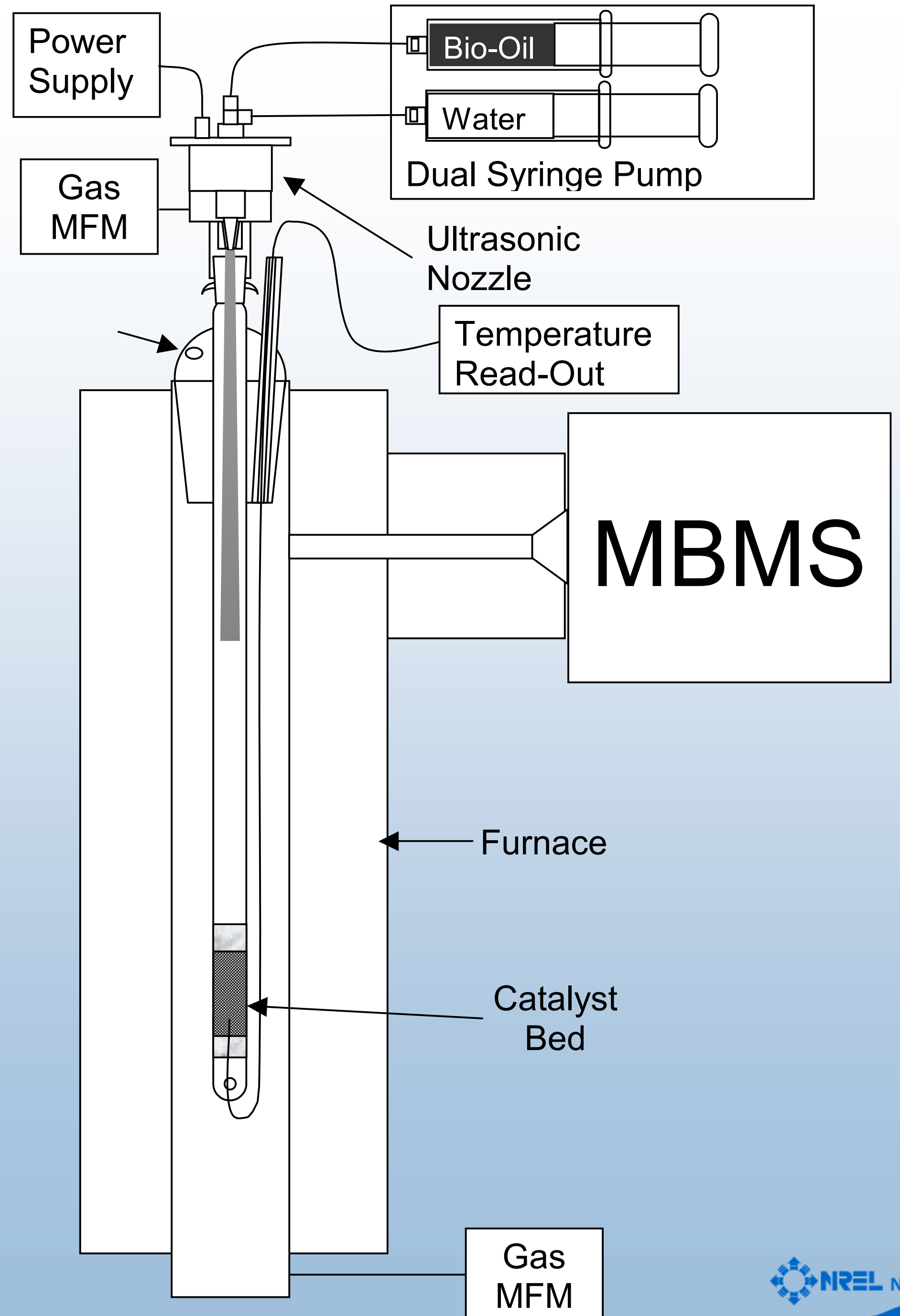
Oxidative Cracking 0.5 s @ 650 C



Ultrasonic Nozzle

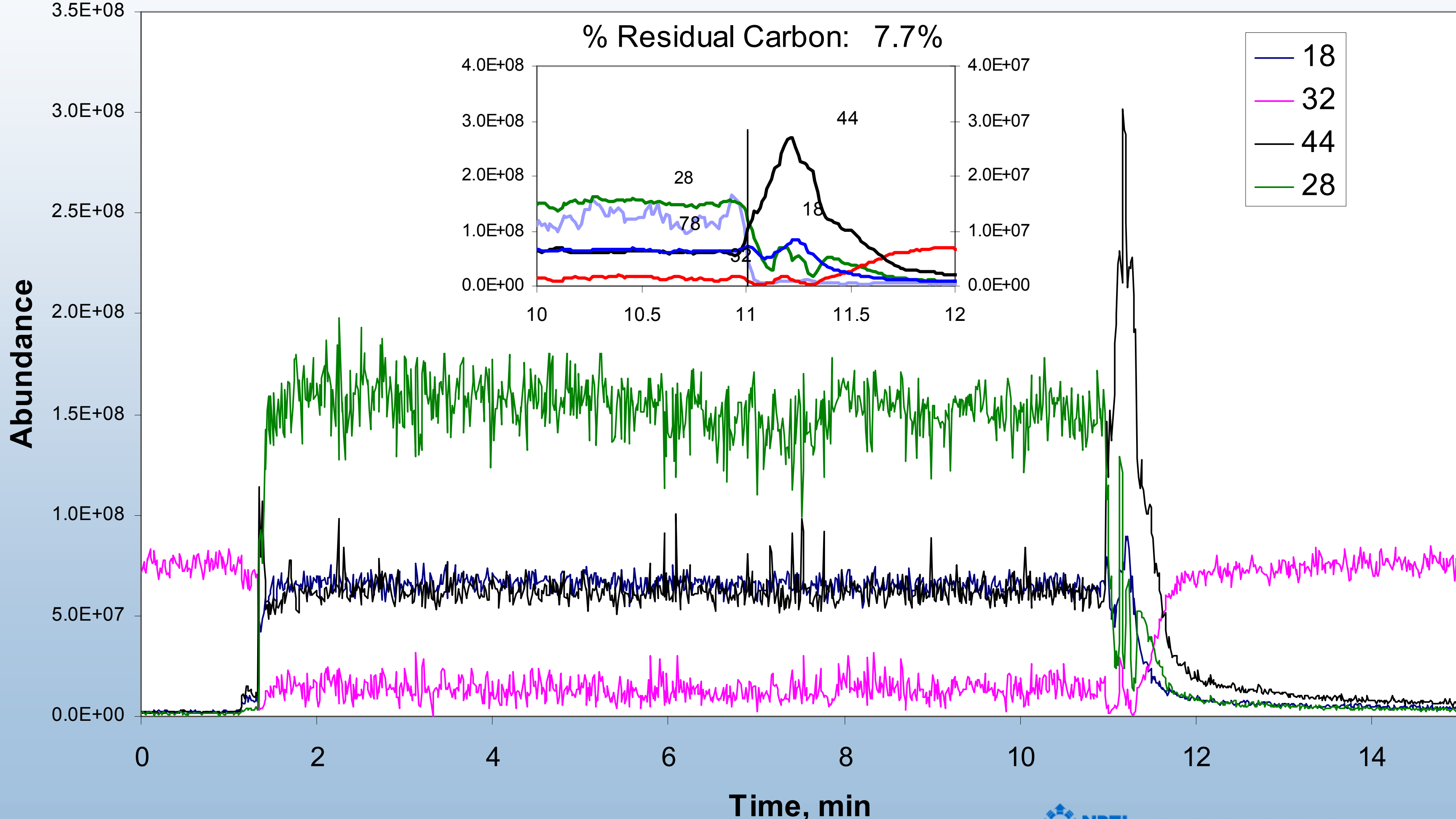


- Generating a fine mist at 0.3g/min
- Enables steady liquid feed at low rates


Power Supply
Bio-Oil
Water
Dual Syringe Pump
Gas MFM
Ultrasonic Nozzle
Temperature Read-Out
MBMS
Furnace
Catalyst Bed
Gas MFM

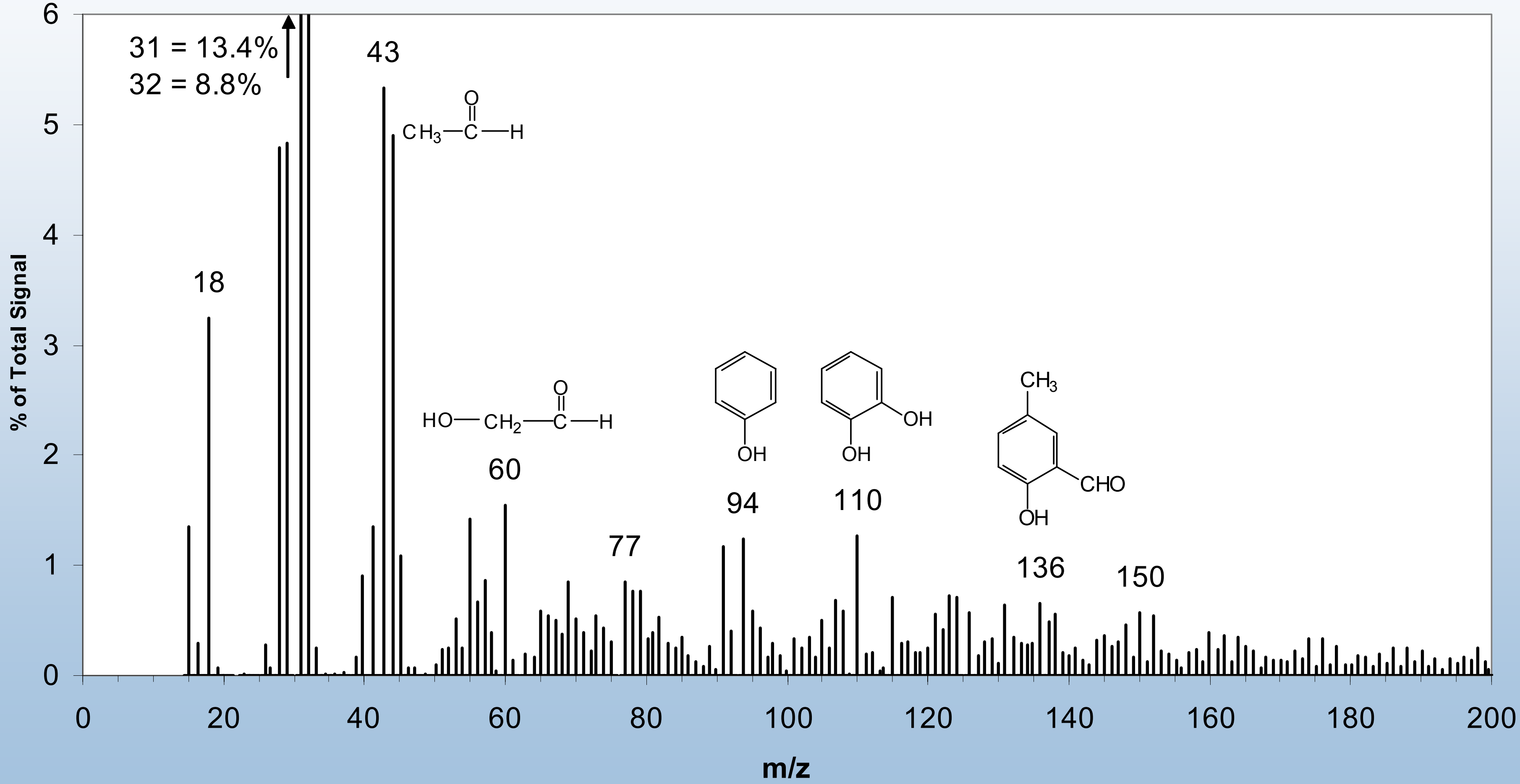
Ultrasonic Nebulizer

Oxidative Cracking 0.5 s @ 650 C



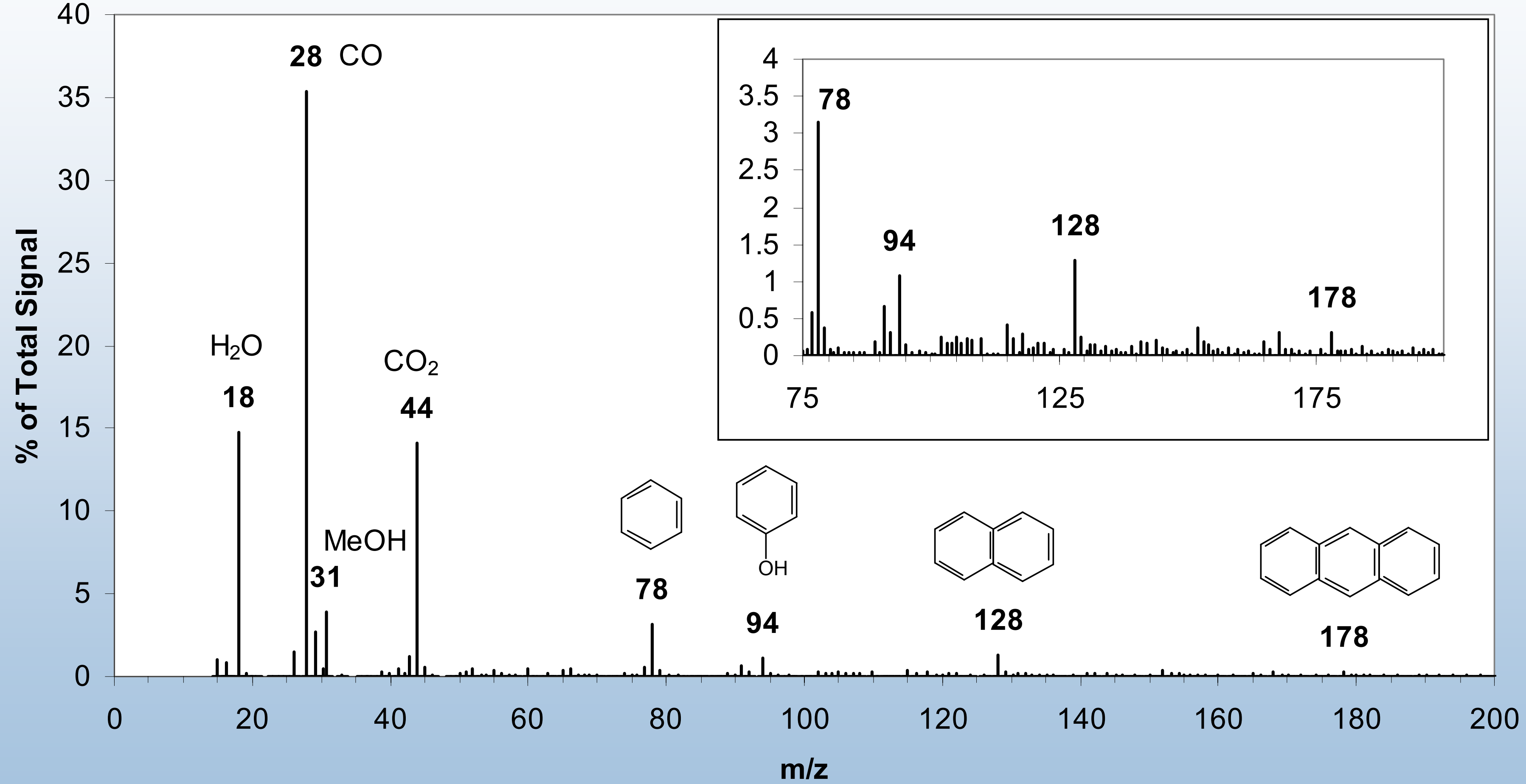
Ultrasonic Nebulizer

Thermal Cracking 0.5 s @ 650 C



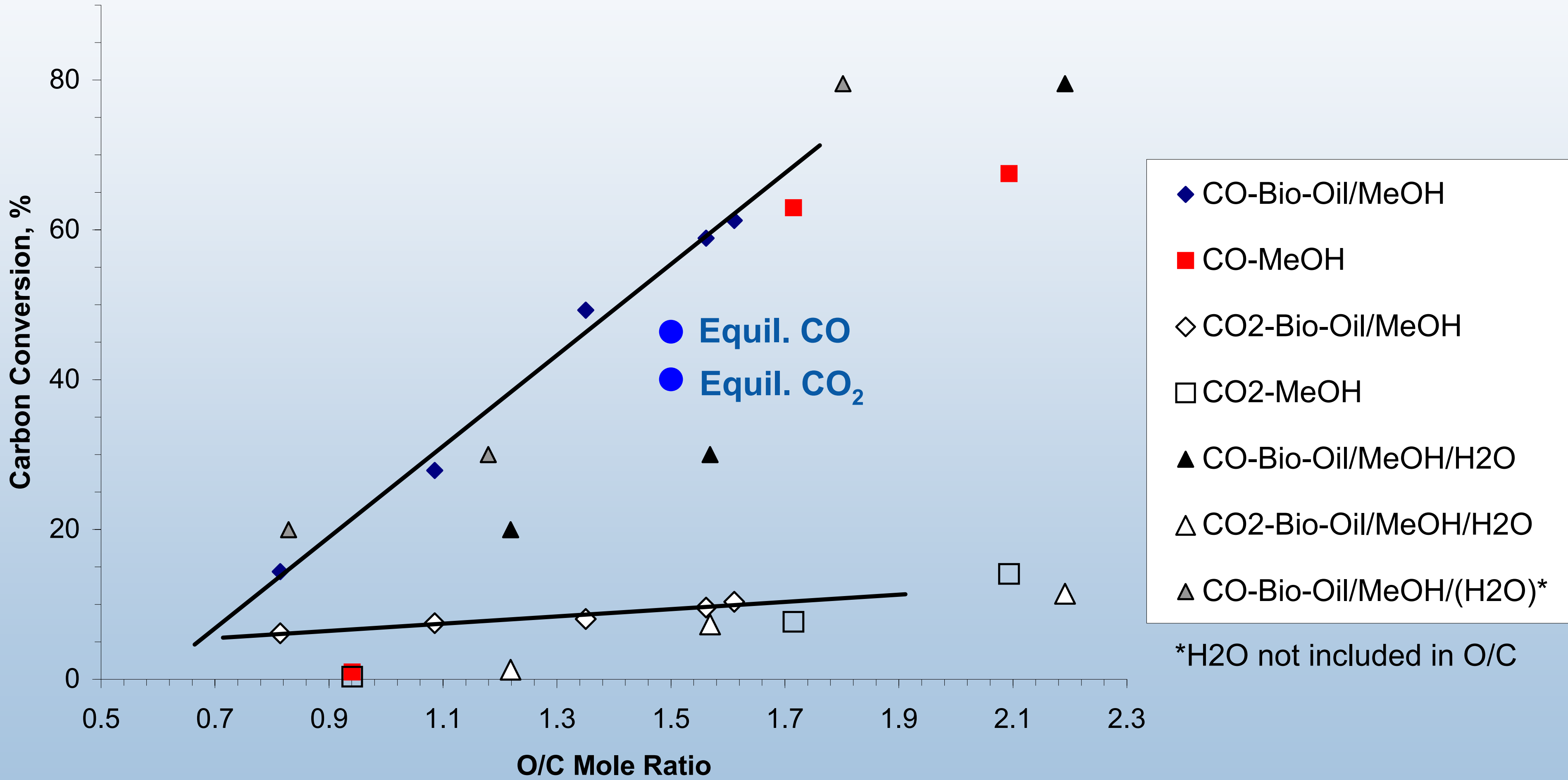
Ultrasonic Nebulizer

Oxidative Cracking 0.5 s @ 650 C

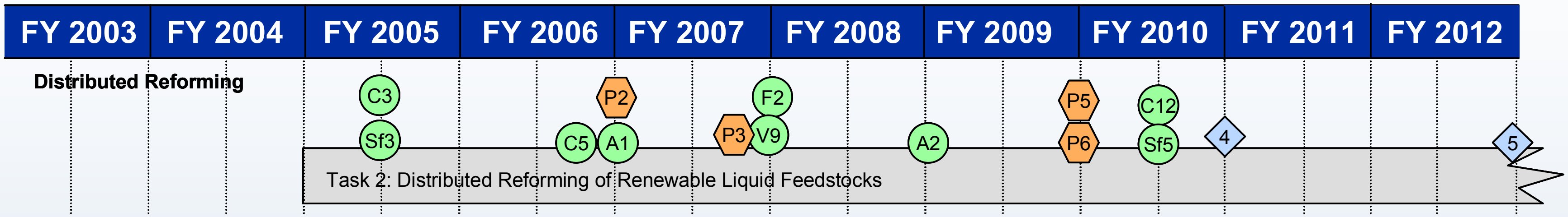


Carbon Conversion

Oxidative Cracking 0.5 s @ 650 C



Project Timeline



Milestones

4 Verify feasibility of achieving $3.60/gge for renewable liquids distributed reforming.
5 Down-select research for distributed production from bio-derived renewable liquids.

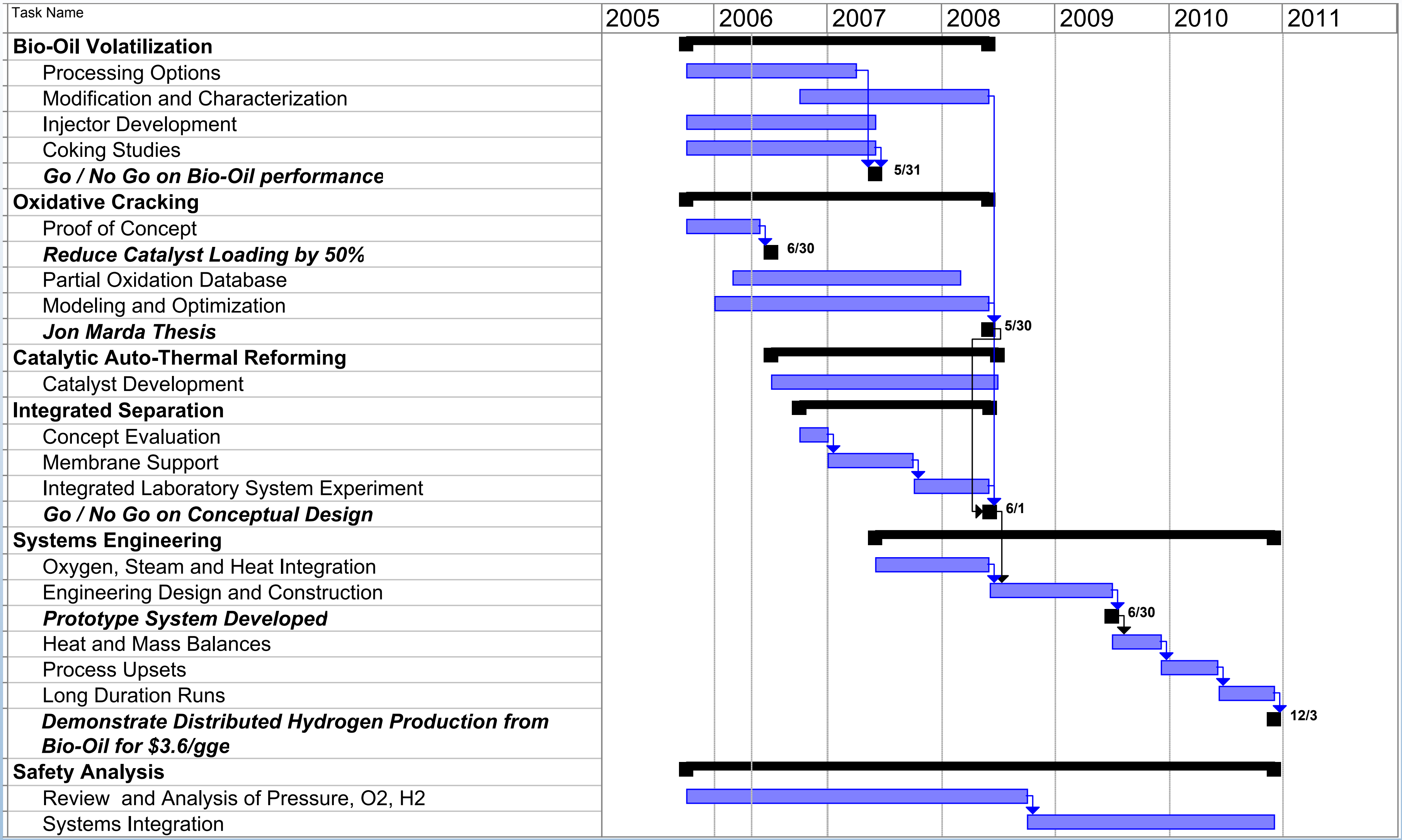
Outputs

P2 Output to Delivery, Storage and Fuel Cells: Assessment of fuel contaminant composition.
P3 Output to Systems Analysis and Systems Integration: Impact of hydrogen purity on cost and performance.
P5 Output to Systems Analysis and Systems Integration: Impact of hydrogen purity on cost and performance.
P6 Output to Delivery, Storage and Fuel Cells: Assessment of fuel contaminant composition.

Inputs

C3 Input from Codes and Standards: Preliminary Assessment of Safety, Codes and Standards requirements for the hydrogen delivery infrastructure.
Sf3 Input from Safety: Safety requirements and protocols for refueling.
C5 Input from Codes and Standards: Completed hydrogen fuel quality standard as ISO Technical Specification.
A1 Input from Systems Analysis: Complete technoeconomic analysis on production and delivery technologies currently being researched to meet overall Program hydrogen fuel objective.
F2 Input from Fuel Cells: Research results of advanced reformer development.
V9 Input from Technology Validation: Final report on safety and O&M of three refueling stations.
A2 Input from Systems Analysis: Initial recommended hydrogen quality at each point in the system.
C12 Input from Codes and Standards: Final hydrogen fuel quality standard as ISO Standard.
Sf5 Input from Safety: Safety requirements and protocols for refueling.

Project Timeline



Future Work

- FY06
  - July milestone: Oxidative cracking proof of concept
- FY07
  - Catalyst testing and collaborative development for this new approach with emphasis on deactivation and poisoning
  - "Go/no go" on bio-oil performance
  - Kinetic modeling and process optimization
  - Reaction engineering
- FY08
  - Bench scale bio-oil reforming tests for long-term testing
  - Prototype design
  - "Go/no go" on conceptual design
- FY09
  - Scale up system development
- FY10
  - 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	Progress in Volatilization and Oxidative Cracking
Collaborations	•Colorado School of Mines •Chevron
Future Work	•Low Temperature Oxidative Cracking Proof of Concept in FY06 •Catalysis in FY07

Response to Reviewers Comments

- ***Project would benefit from commercial and university collaborations***
  - Work to date has been proof of concept
  - Collaboration began in FY06 with School of Mines on modeling and Chevron on feedstock effects
  - Discussions with UMN on catalysis and GE on prototype development in progress
- ***More detailed collaborative research plan needed***
  - Elements are in the plan, pending budget
    - Bio-feed variation effects
    - Oxidative cracking kinetics
    - Catalytic oxidation mechanisms
    - Factor interactions
    - Catalyst development

Publications and Presentations

Czernik, S. and French, R., Production of Hydrogen from Plastics by Pyrolysis and Catalytic Steam Reforming, *Energy & Fuels*, 2006, 20, 754-758

Czernik, S., Evans, R., and French, R., Hydrogen from Biomass; Distributed Production by Steam Reforming of Biomass Pyrolysis Oil, 1st International Symposium on Hydrogen from Renewable Resources, 231 ACS National Meeting, Atlanta, GA, March 26-30, 2006

Critical Assumptions and Issues

- Bio-Oil Volatilization
- Oxidative Homogeneous Cracking Performance & Benefits
- Catalyst Design and Performance
- Carbon Deposit Removal and Catalyst Regeneration Management
- Process Energy
- Hydrogen Separation