

Distributed Bio-Oil Reforming

2006 DOE Hydrogen, Fuel Cells & Infrastructure
Technologies Program Review

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National Renewable Energy Laboratory

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Overview

Timeline

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

Budget

- FY05 \$100K
- FY06 \$300K

Partners

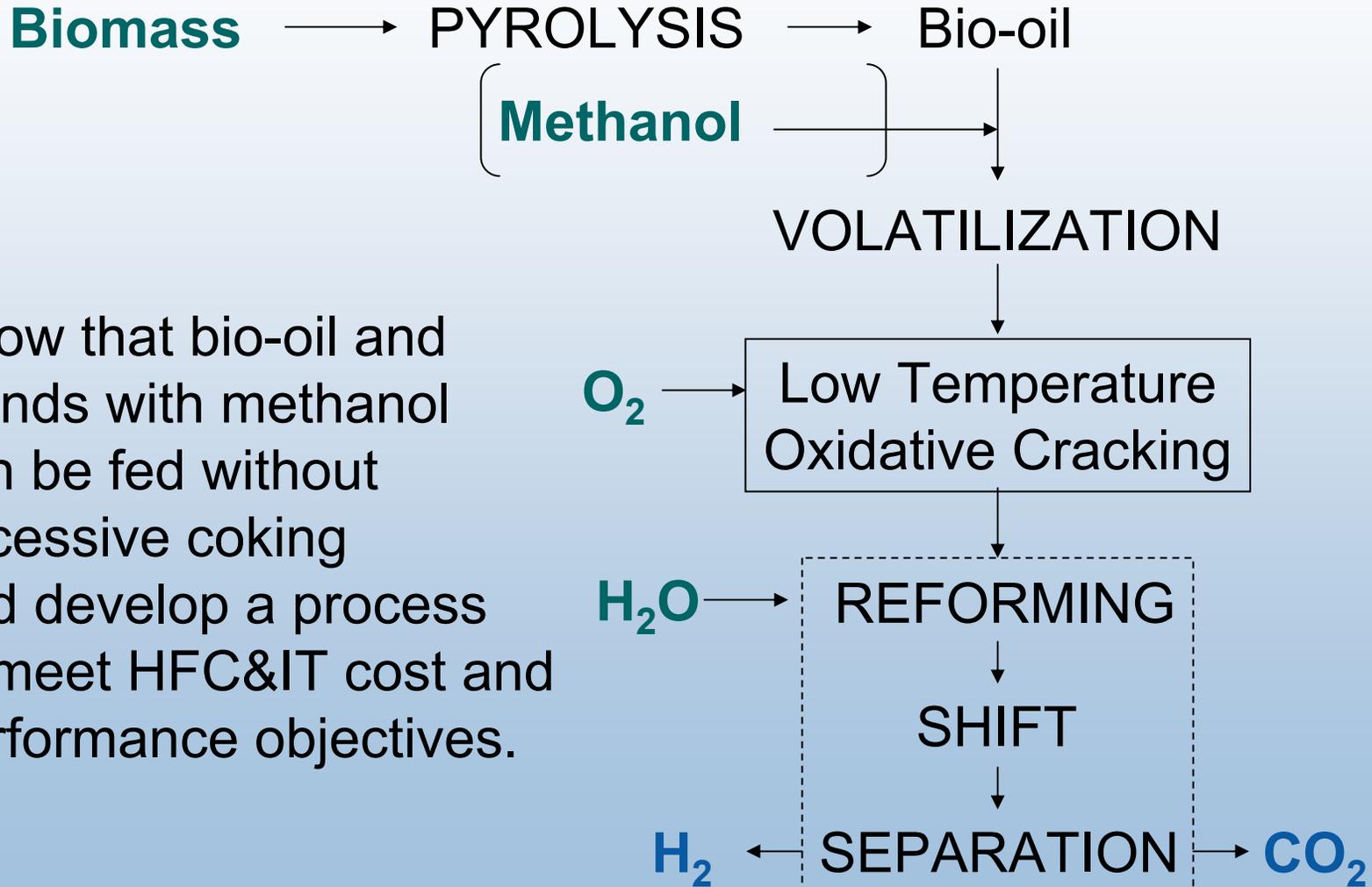
- Colorado School of Mines (FY06) - Oxidative cracking
- Chevron (FY06) - Feedstock Project planned for FY06

Production Barriers

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

Target \$3.60/gge

Approach

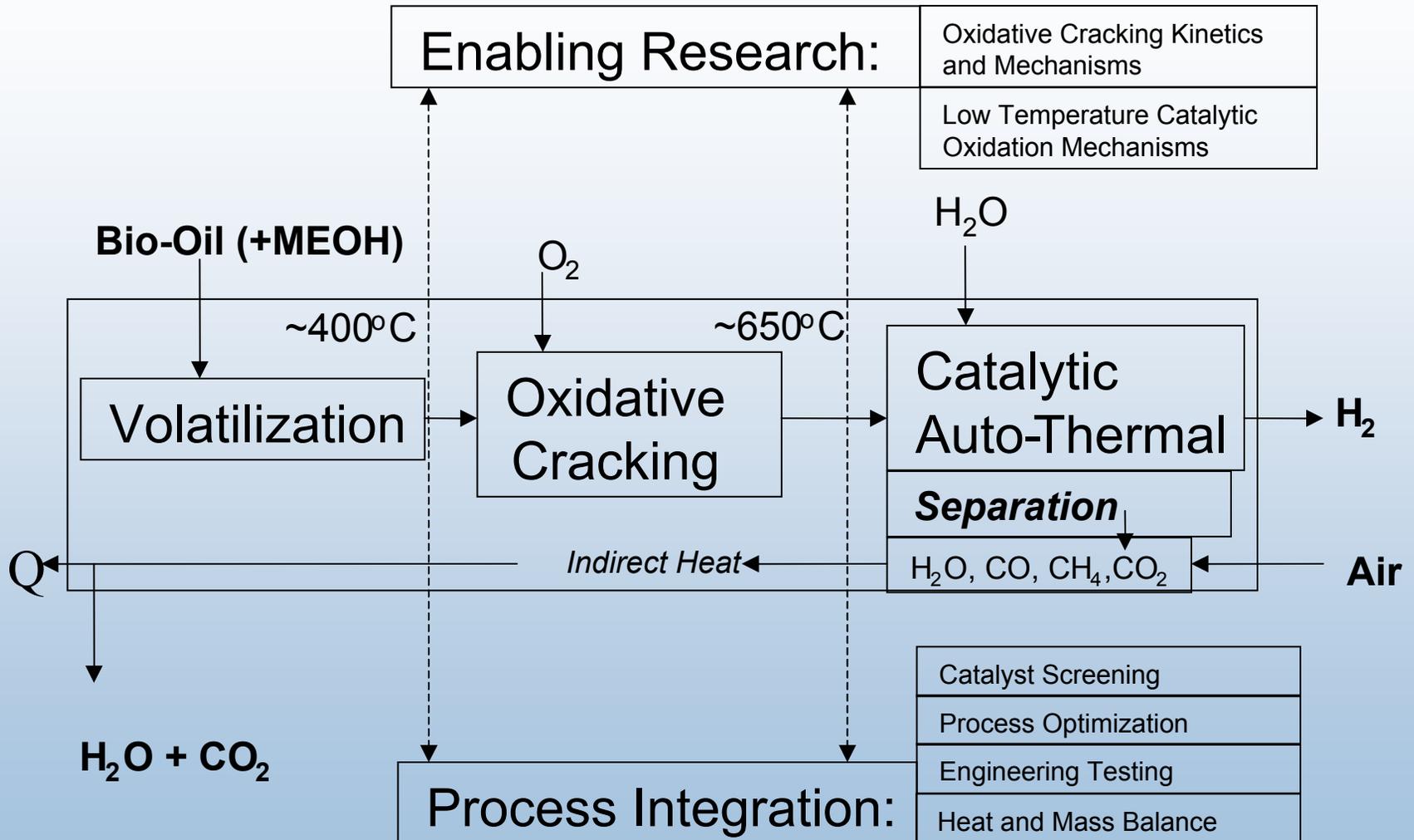


Show that bio-oil and blends with methanol can be fed without excessive coking and develop a process to meet HFC&IT cost and performance objectives.

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%

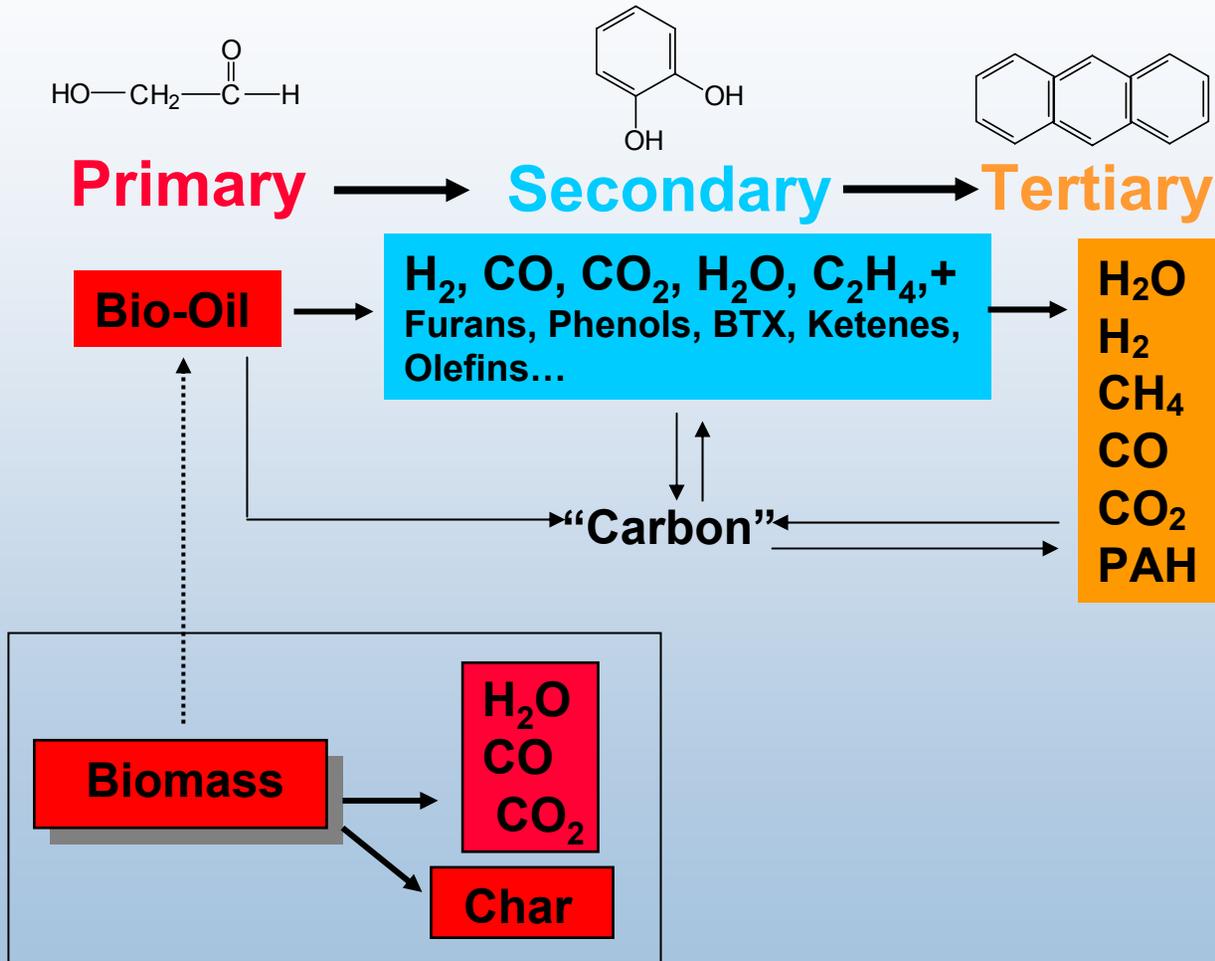
Distributed Bio-Oil Reforming Approach



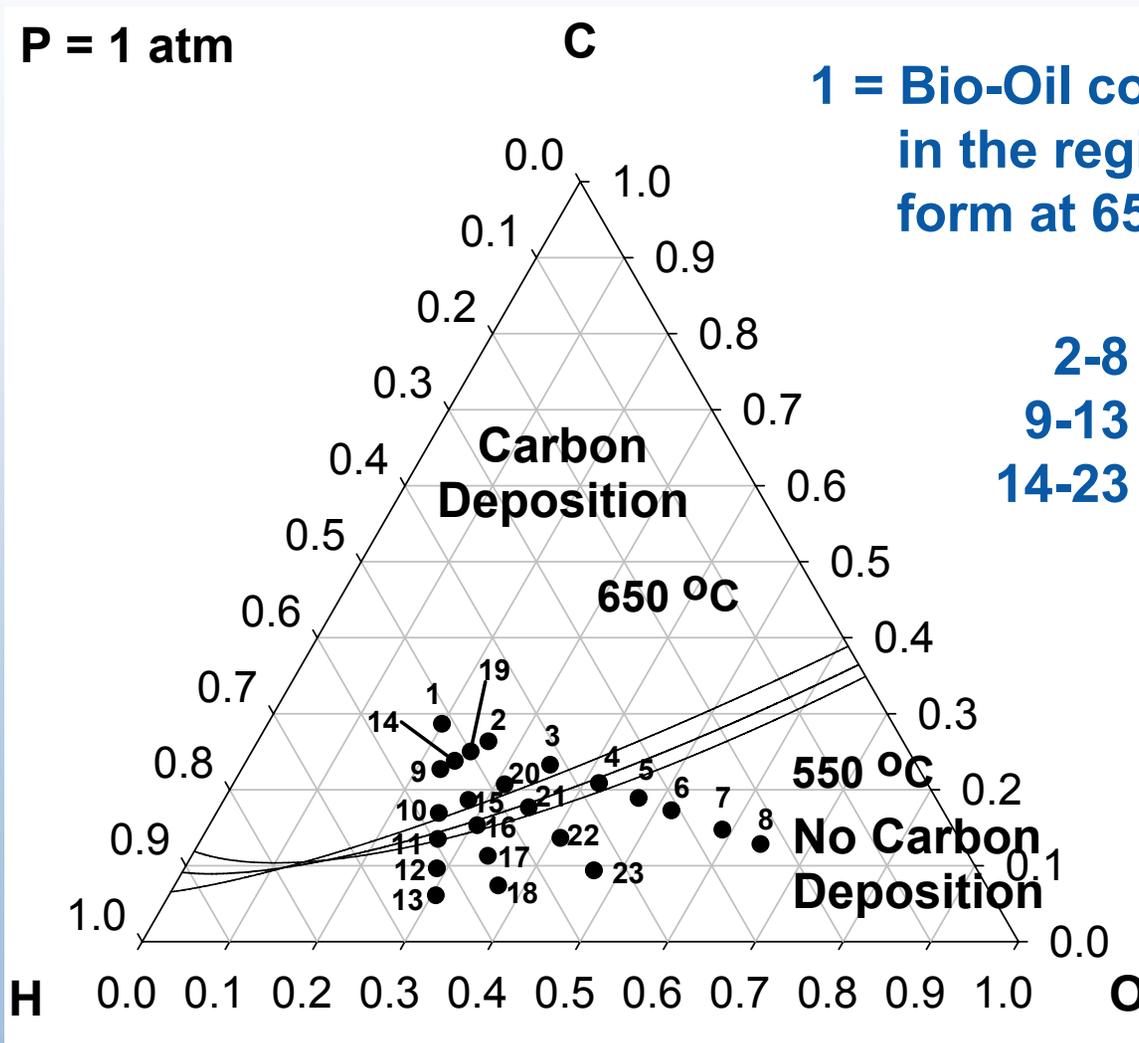
Technical Accomplishments

- 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



Equilibrium Modeling Results

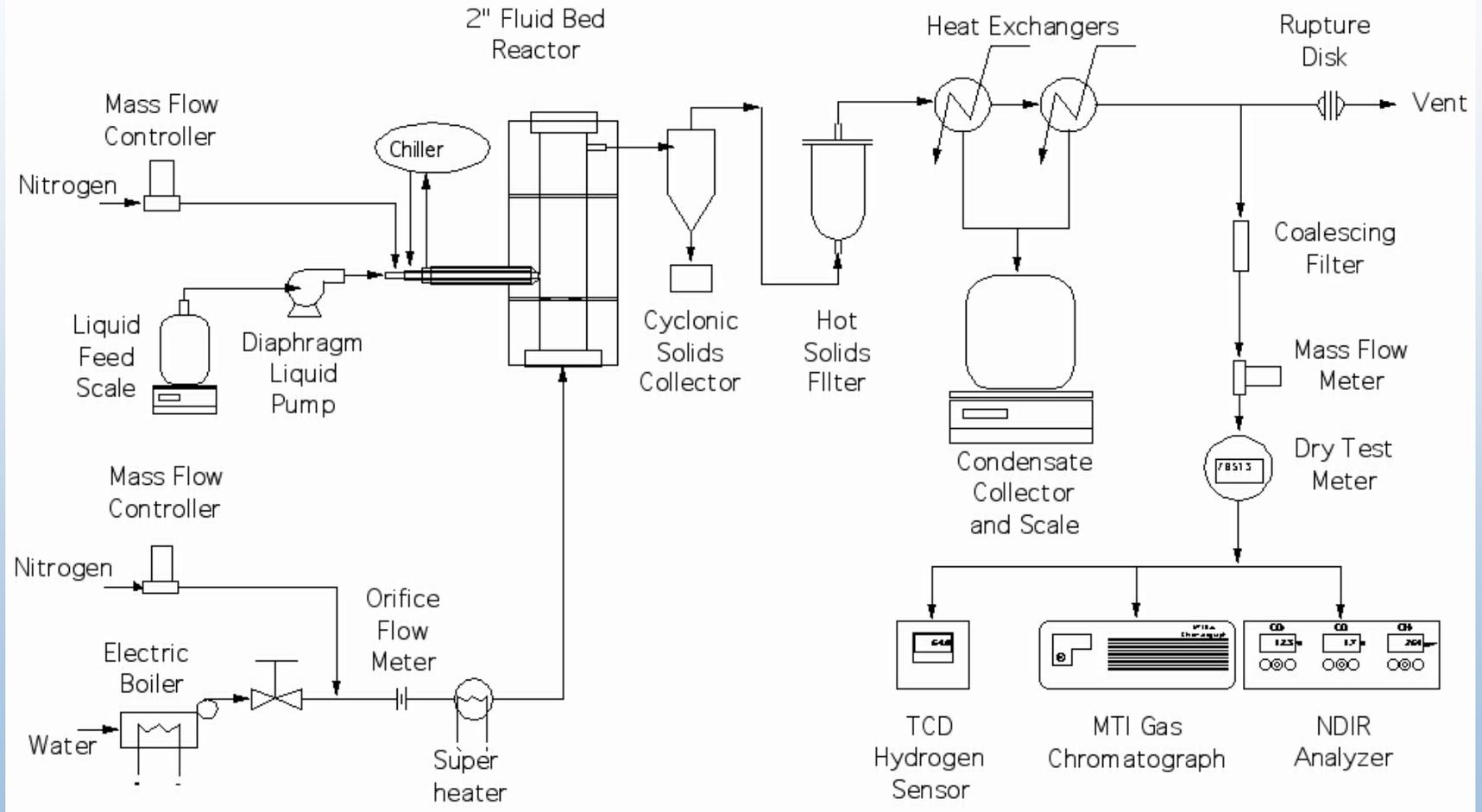


1 = Bio-Oil composition, which lies in the region where carbon will form at 650 °C

2-8 = O₂ addition points
9-13 = H₂O addition
14-23 = both O₂ and H₂O

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

Spray Injector Reactor System

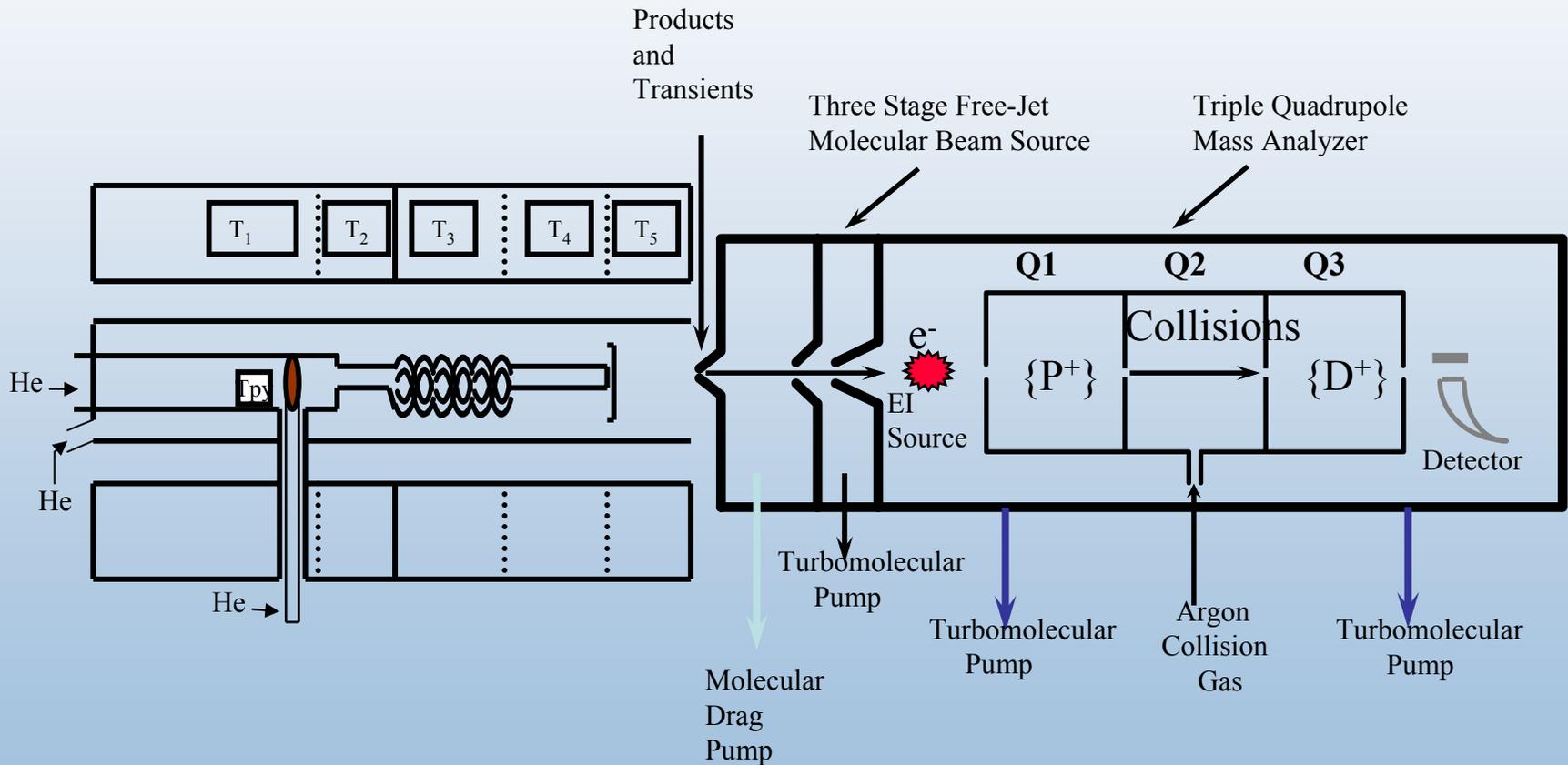


Spray Injector Results

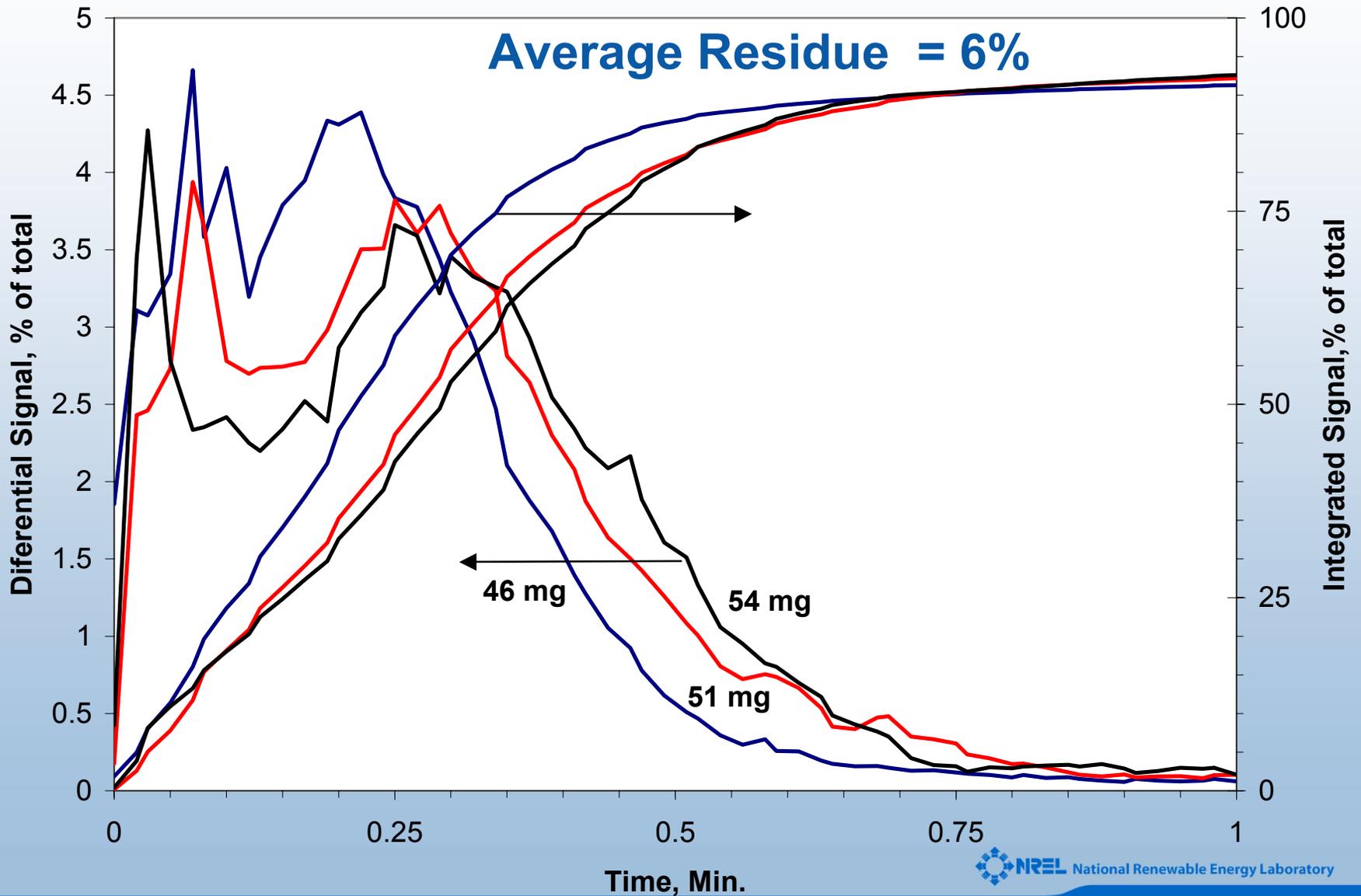
Run	Liq. Feed g/min	Air coeff. %	Temp, C	Time, s	Gas Composition, vol. %						C Bal, %
					N ₂	O ₂	H ₂	CO	CO ₂	CH ₄	
1	0.5	163	600	2.4	79	15.96	0.00	1.19	4.19	0.00	76%
2	0.5	162	599	1.1	78	17.18	0.00	0.59	4.16	0.00	68%
3	1.0	99	602	1.4	79	11.61	0.00	2.78	6.26	0.00	69%
4	1.0	65	601	1.5	79	5.27	0.00	4.06	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

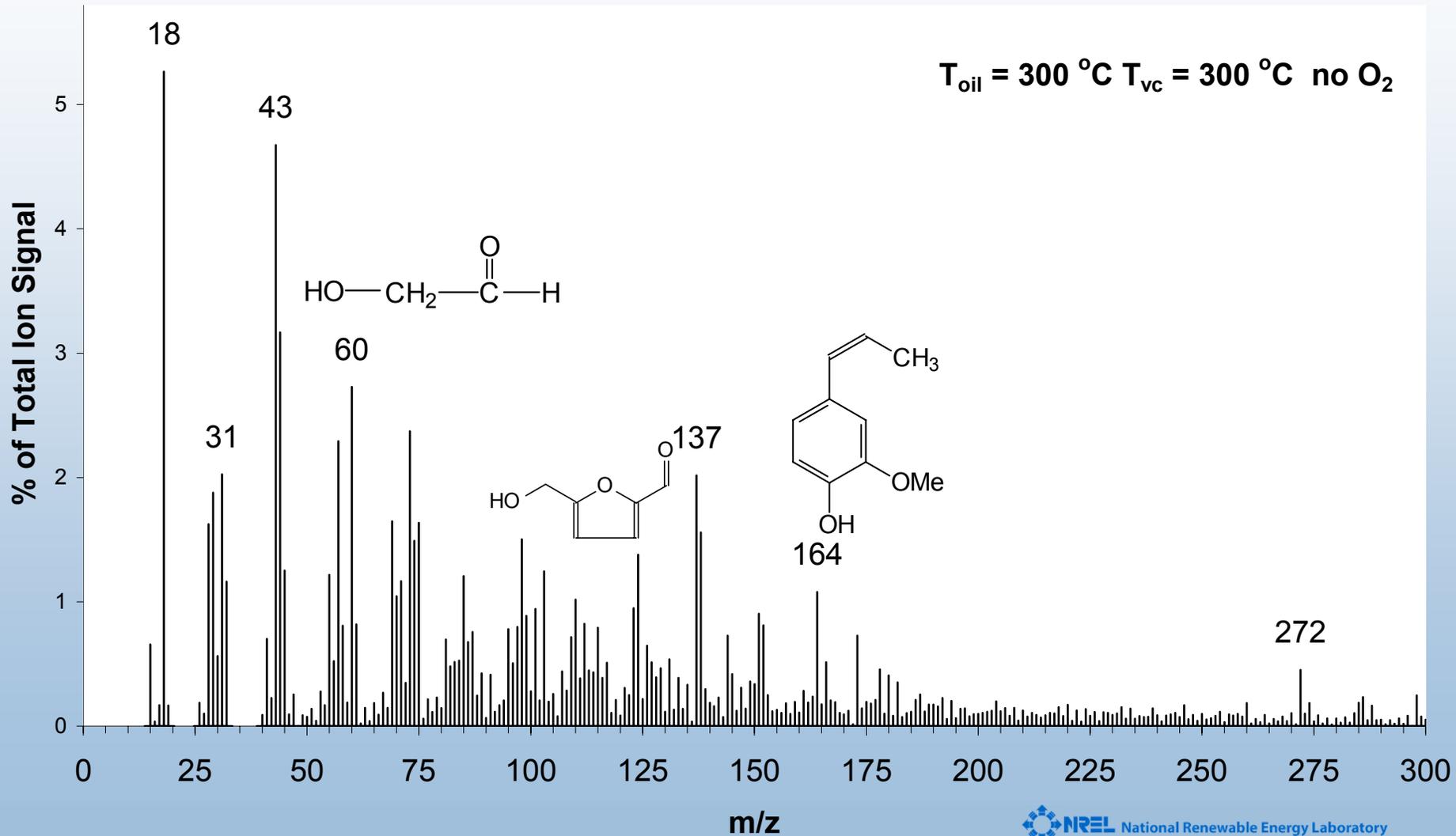


Bio-Oil Film Volatilization – 400 °C



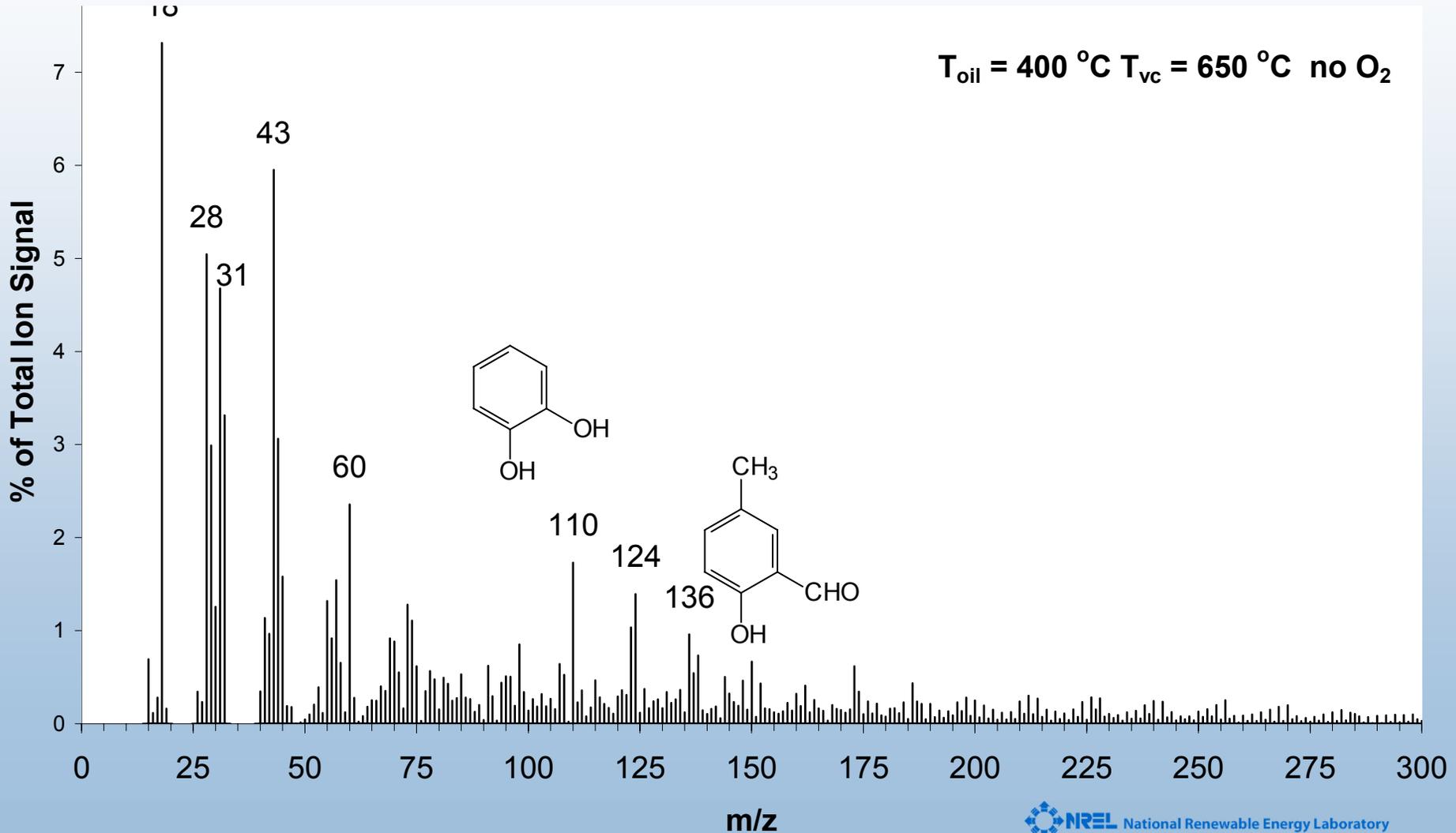
Bio-Oil Film Volatilization

MBMS Bio-Oil Spectrum



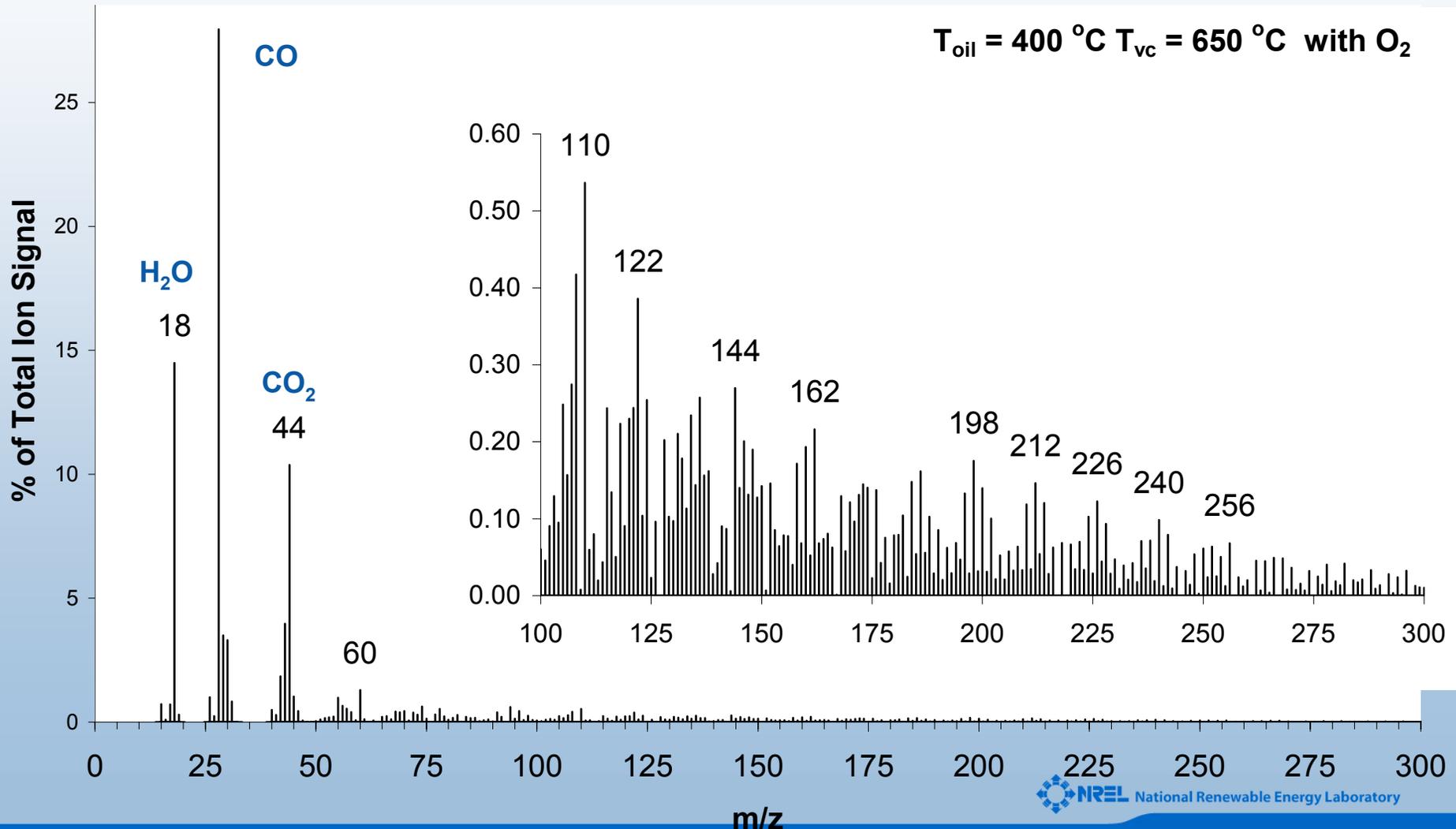
Bio-Oil Film Volatilization

Cracking 0.5 s @ 650 C

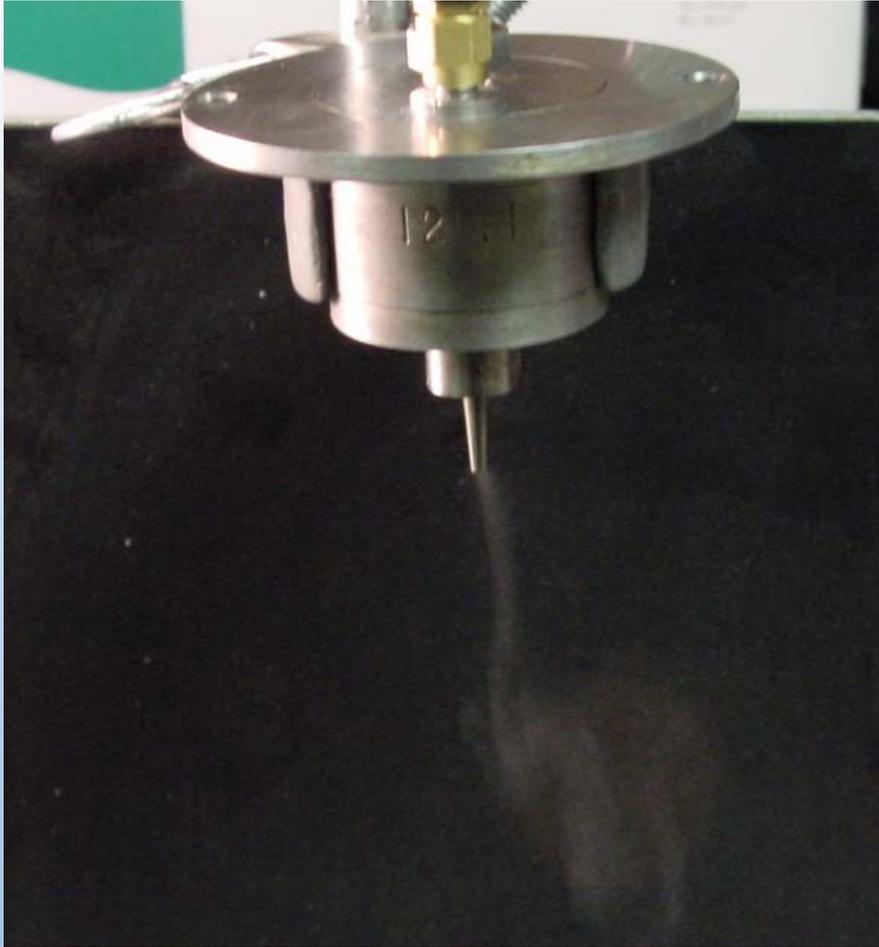


Bio-Oil Film Volatilization

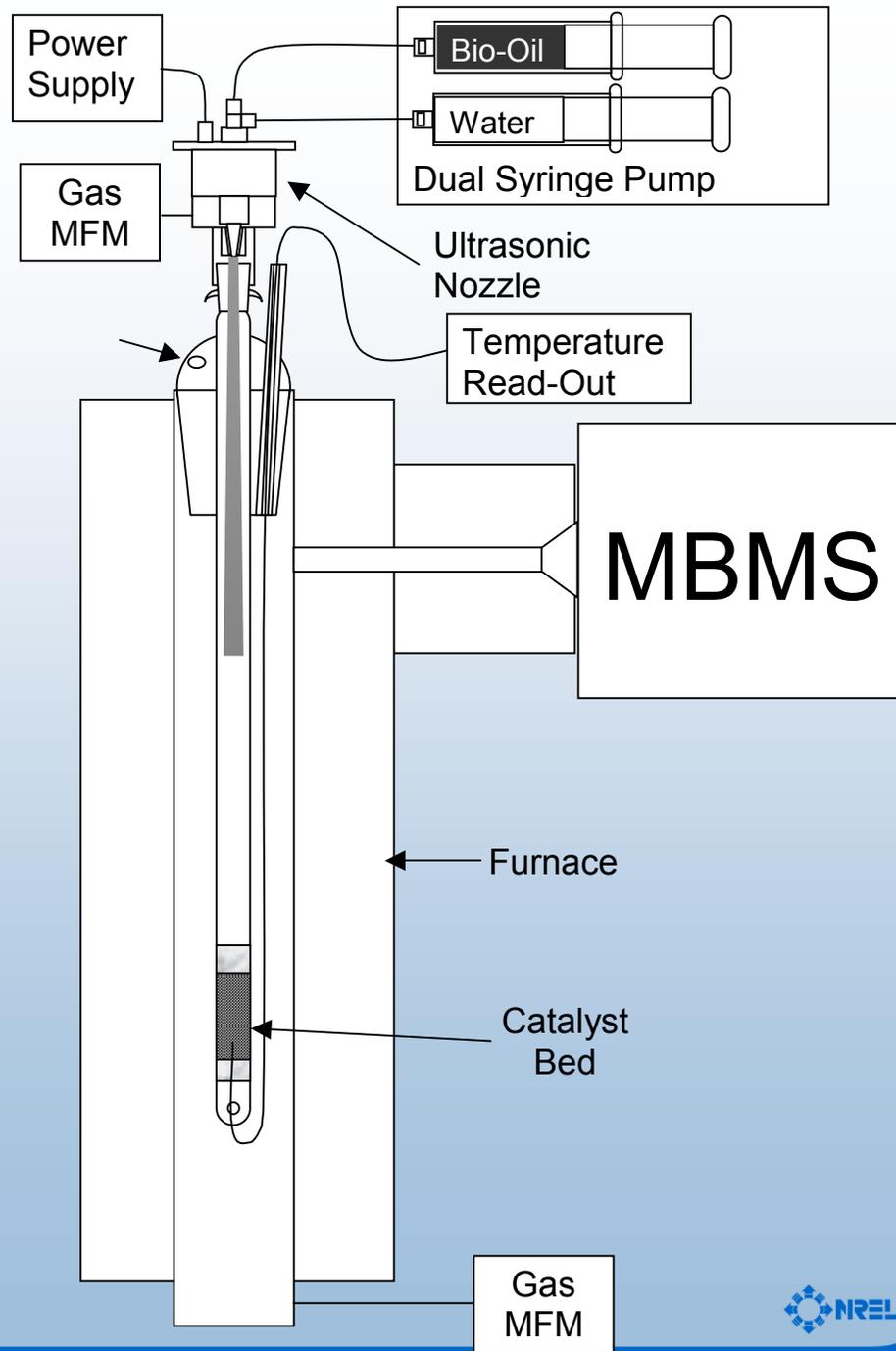
Oxidative Cracking 0.5 s @ 650 C



Ultrasonic Nozzle

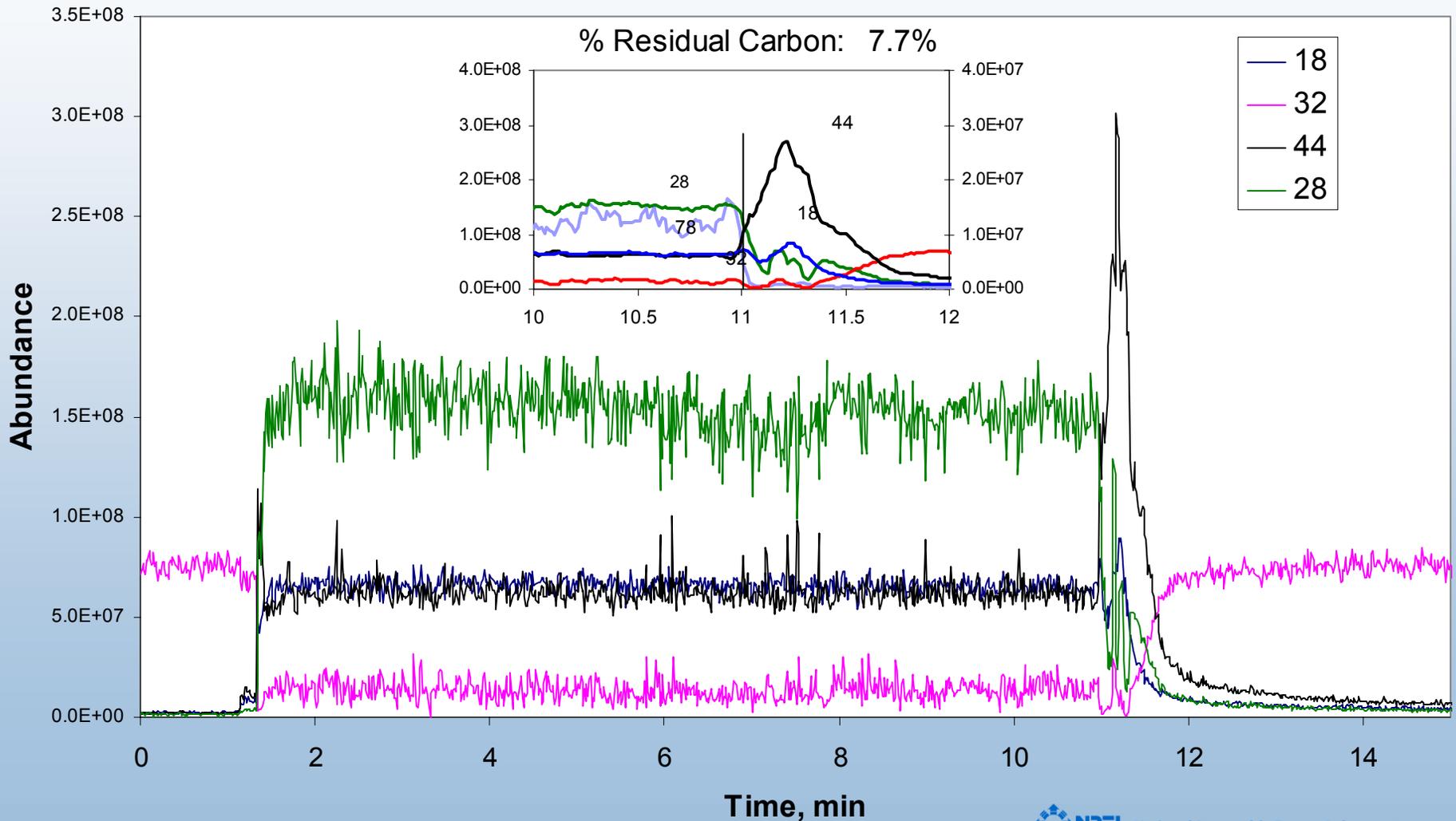


- Generating a fine mist at 0.3g/min
- Enables steady liquid feed at low rates



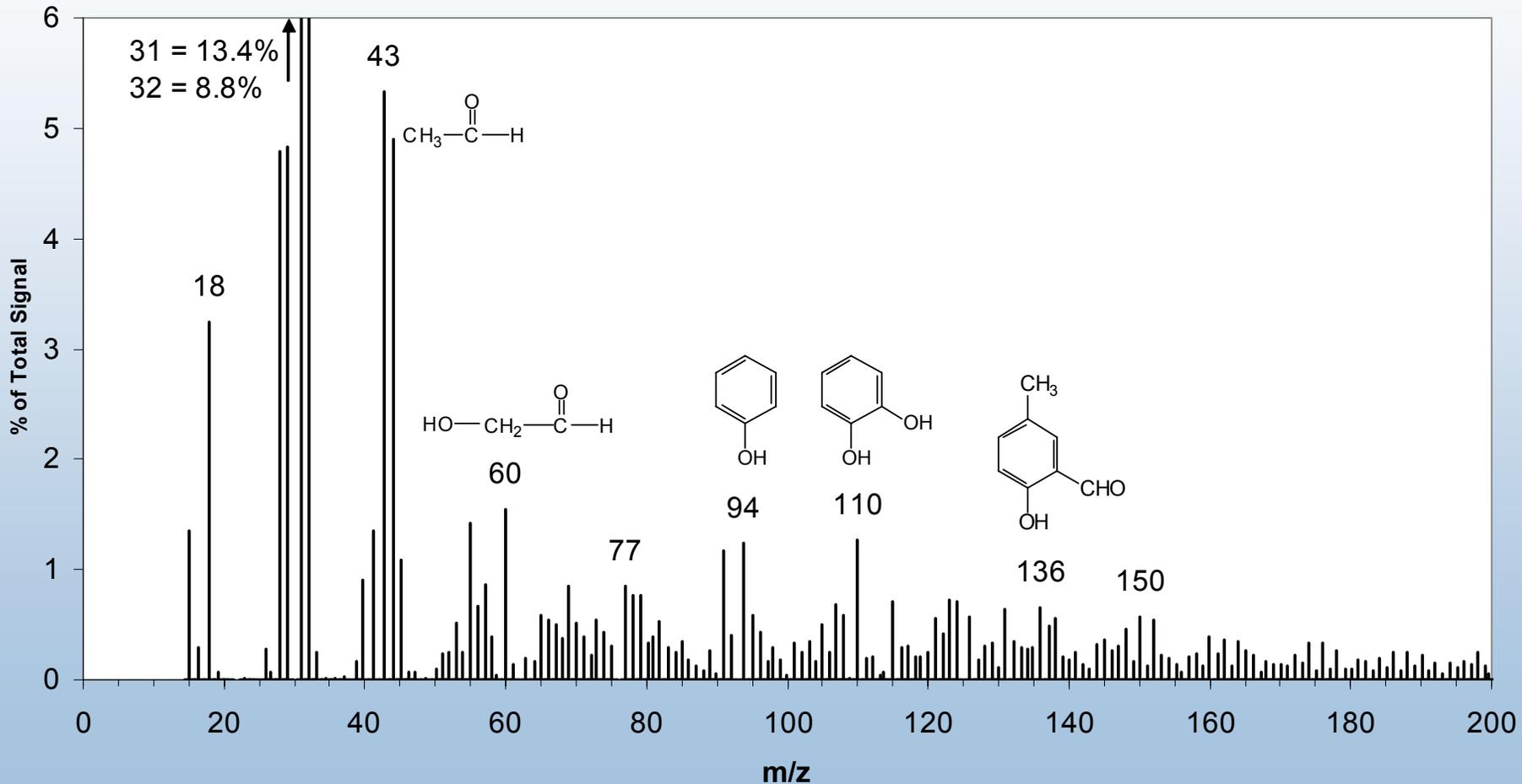
Ultrasonic Nebulizer

Oxidative Cracking 0.5 s @ 650 C



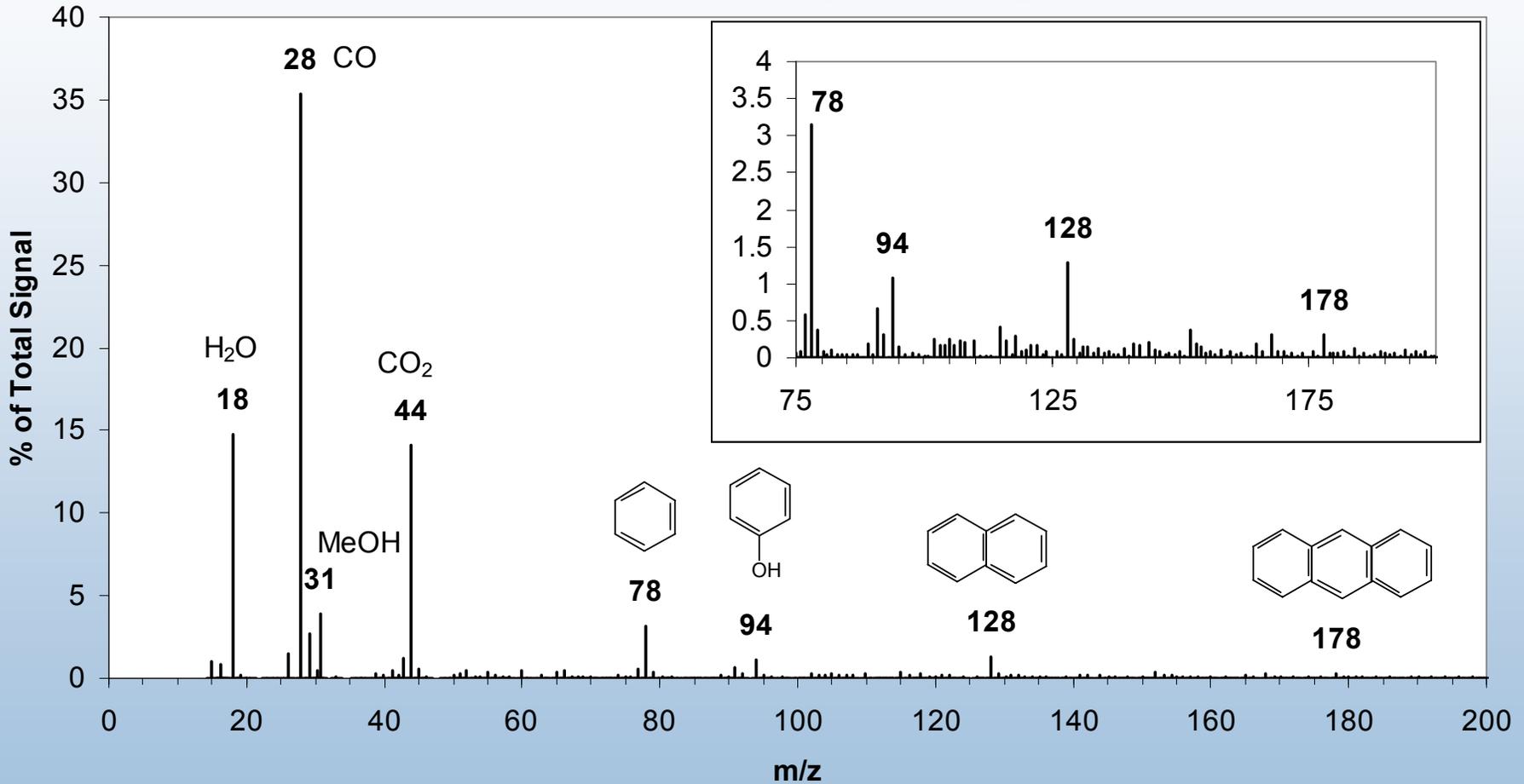
Ultrasonic Nebulizer

Thermal Cracking 0.5 s @ 650 C



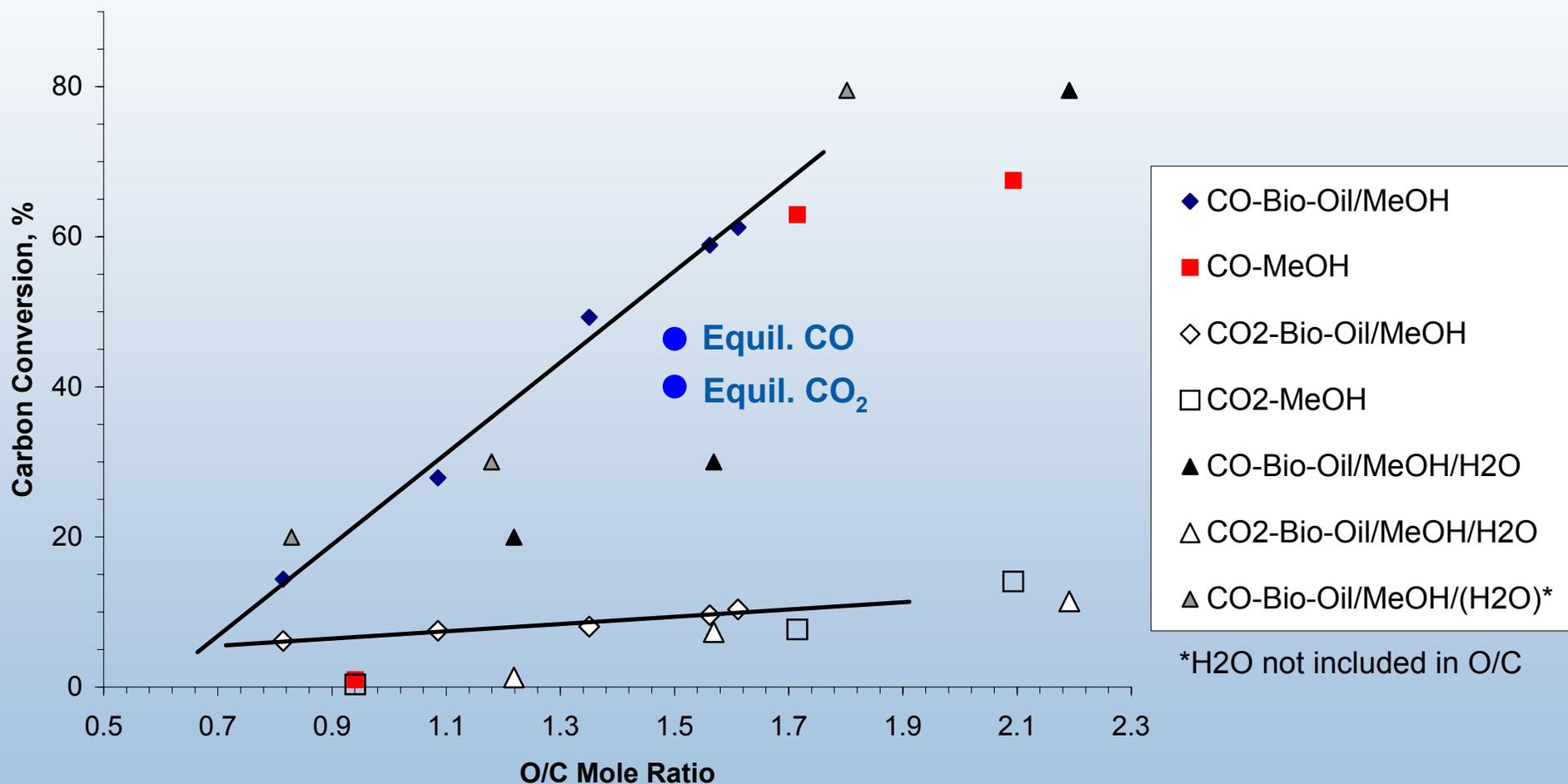
Ultrasonic Nebulizer

Oxidative Cracking 0.5 s @ 650 C

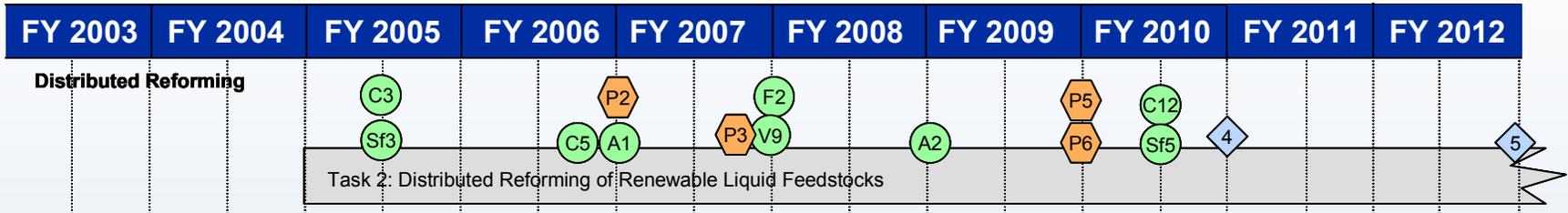


Carbon Conversion

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.

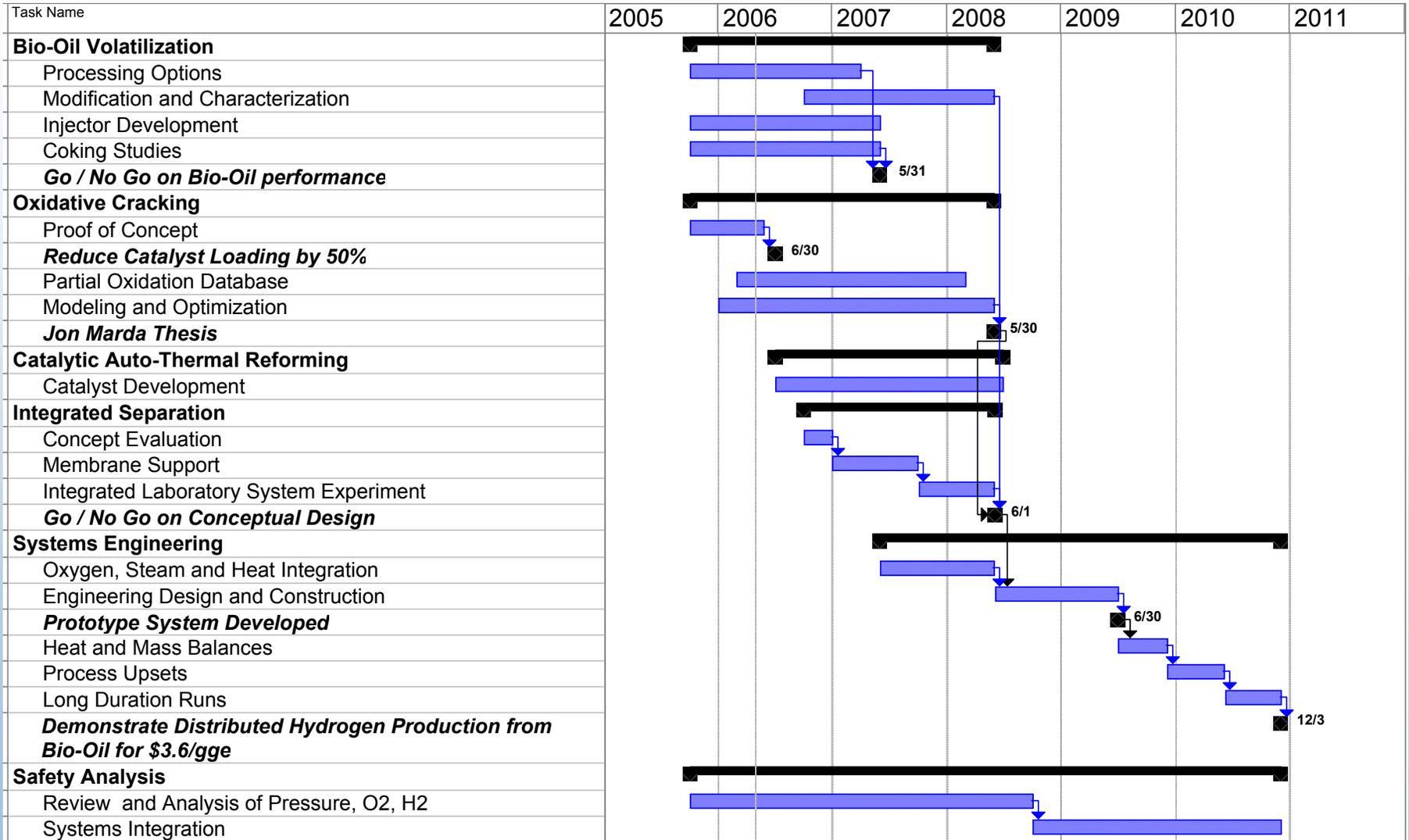
Outputs

- 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 techno-economic 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

<i>Relevance</i>	Near Term Renewable Feedstock for Distributed Reforming
<i>Approach</i>	Bio-Oil Processed at Low Temp Homogeneous and Catalytic Auto-Thermal Reforming
<i>Accomplishments</i>	Progress in Volatilization and Oxidative Cracking
<i>Collaborations</i>	<ul style="list-style-type: none">•Colorado School of Mines•Chevron
<i>Future Work</i>	<ul style="list-style-type: none">•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