**Innovation for Our Energy Future** 

# 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

#### **Production Barriers**

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

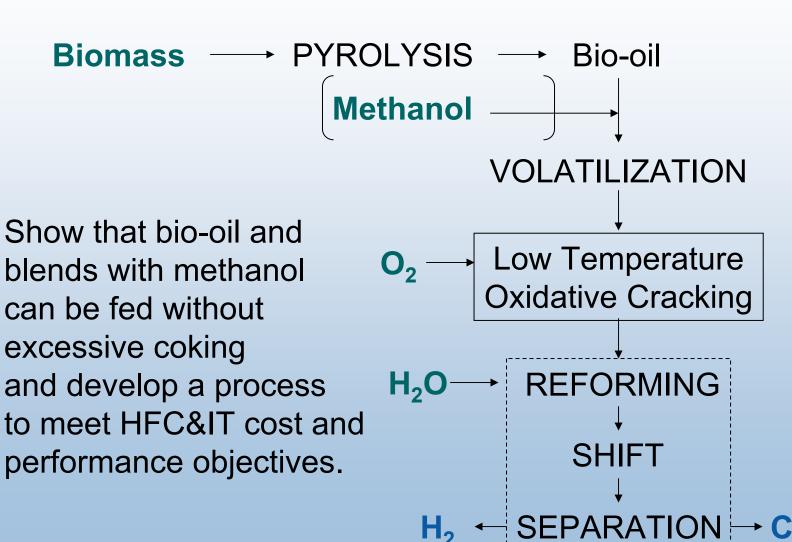
Target \$3.60/gge

#### **Partners**

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



# **Approach**



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# **Objectives**

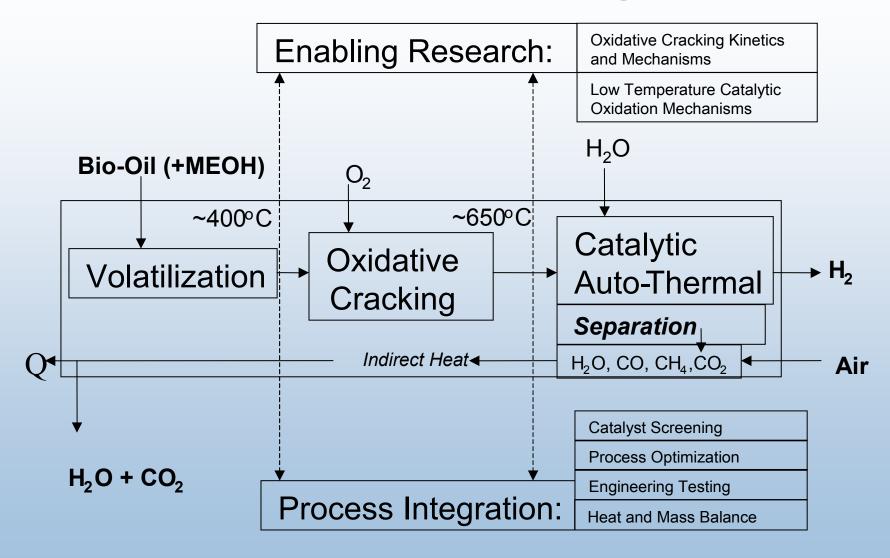
#### Overall:

 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

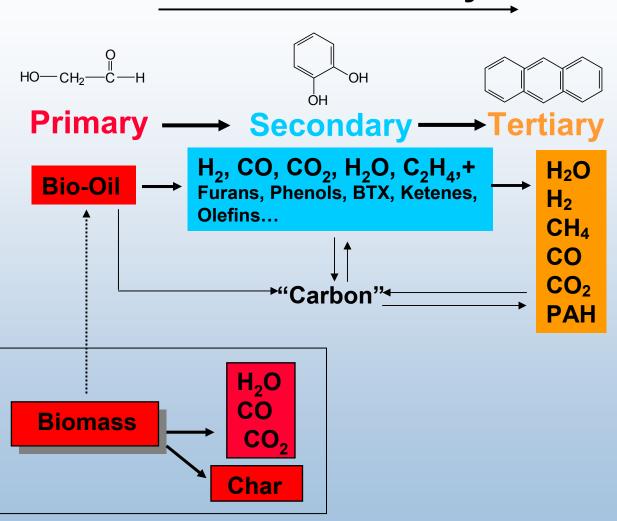


# **Technical Accomplishments**

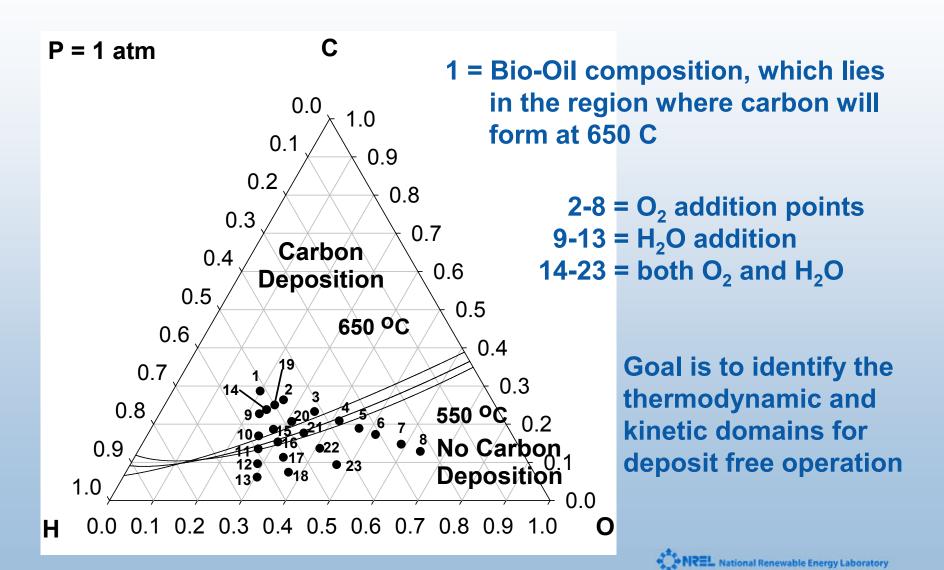
- FY05: Whole oil successfully run
  - With 10% MeOH addition, bio-oil processing was trouble free over short run durations (up to 16 hrs)
- FY06: Accomplishments to date
  - Bio-oil volatilization method developed
  - Oxidative cracking promising results
  - Progress toward July milestone on target



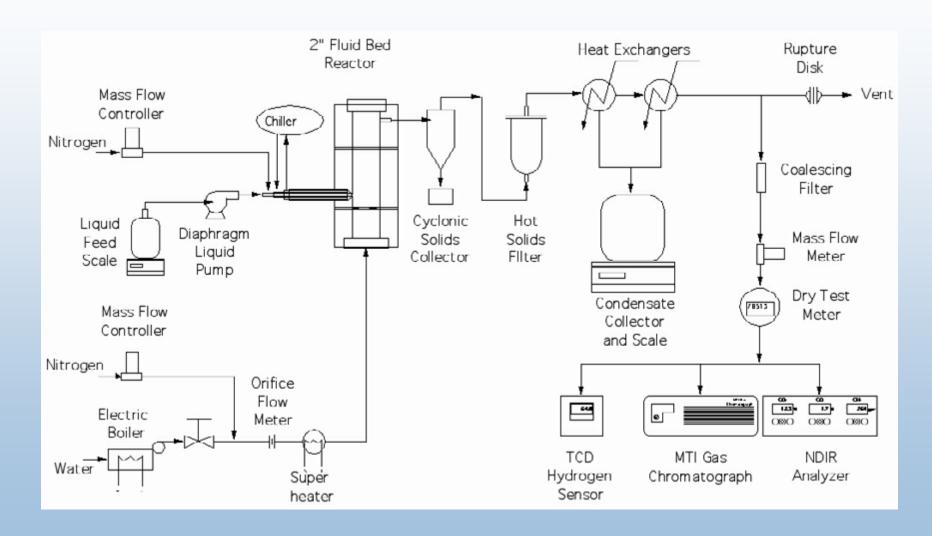
#### **Thermal Severity**



# **Equilibrium Modeling Results**



# **Spray Injector Reactor System**



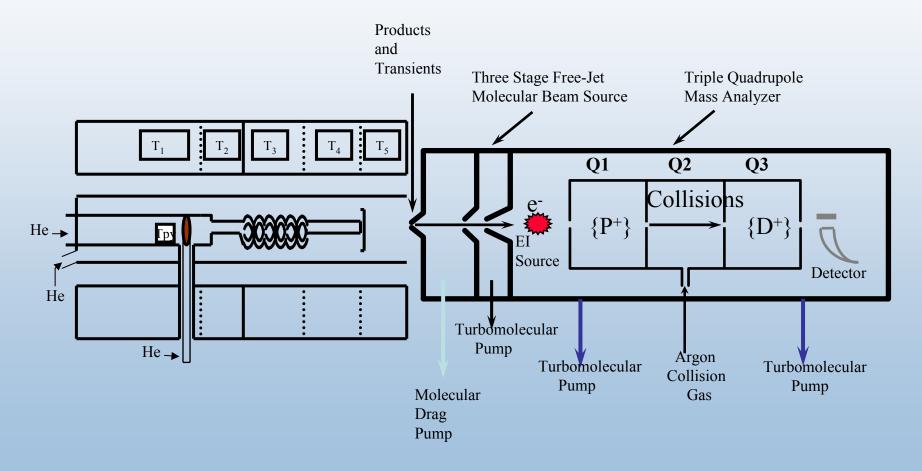
# **Spray Injector Results**

					Gas Composition, vol. %						
	Liq. Feed	Air coeff.									
Run	g/min	%	Temp, C	Time, s	$N_2$	$O_2$	$H_2$	CO	$CO_2$	CH <sub>4</sub>	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%

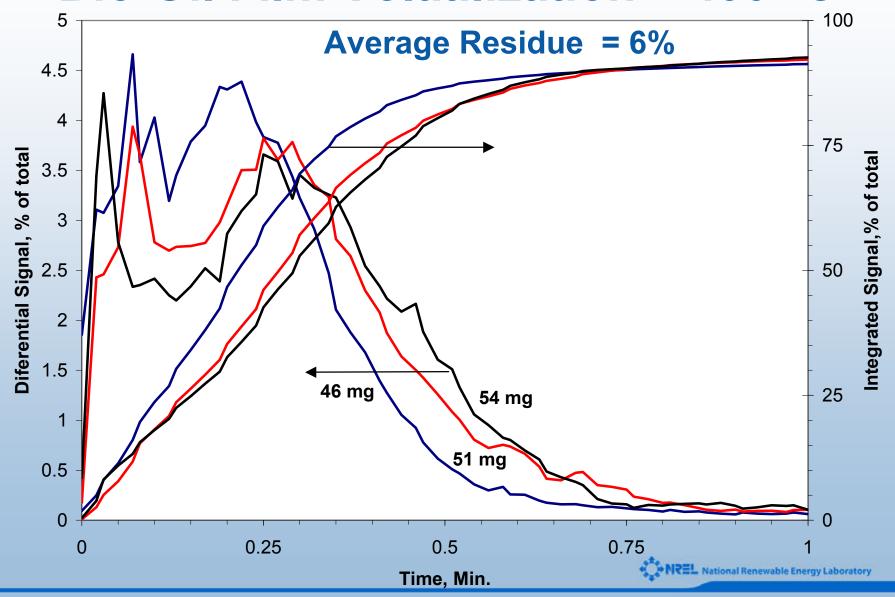
Spray injection resulted in low carbon conversion to CO and formation of aromatics and carbon



# Schematic of Pyrolysis Reactor & NREL's MBMS Sampling System

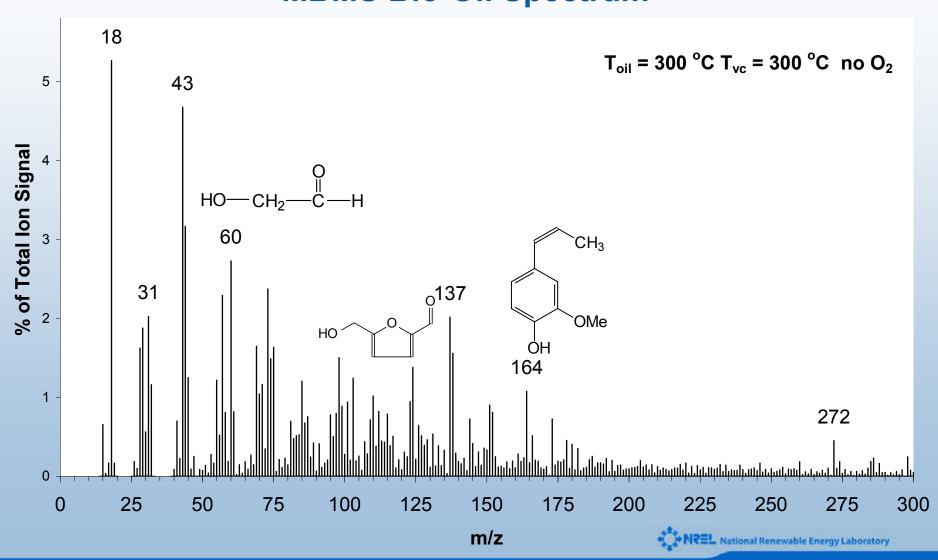


#### Bio-Oil Film Volatilization – 400 °C



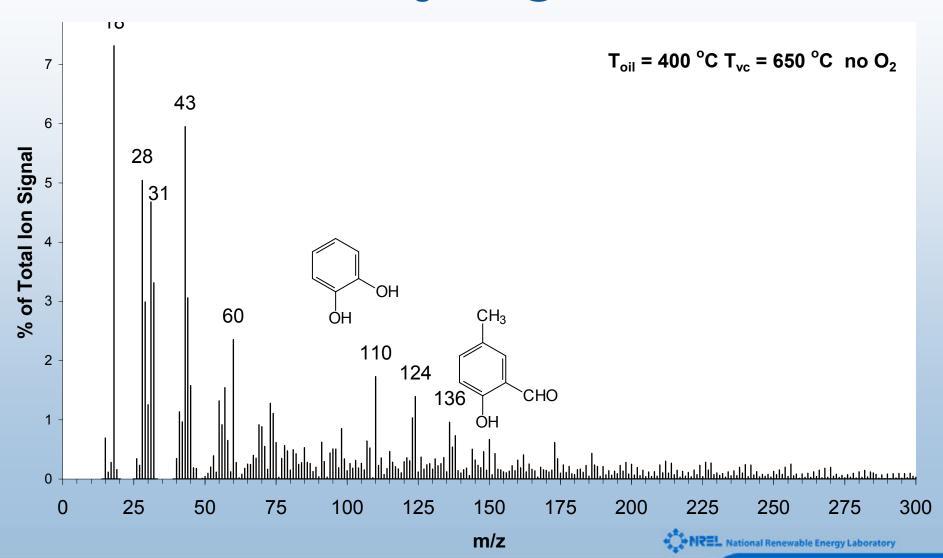
#### **Bio-Oil Film Volatilization**

#### **MBMS Bio-Oil Spectrum**



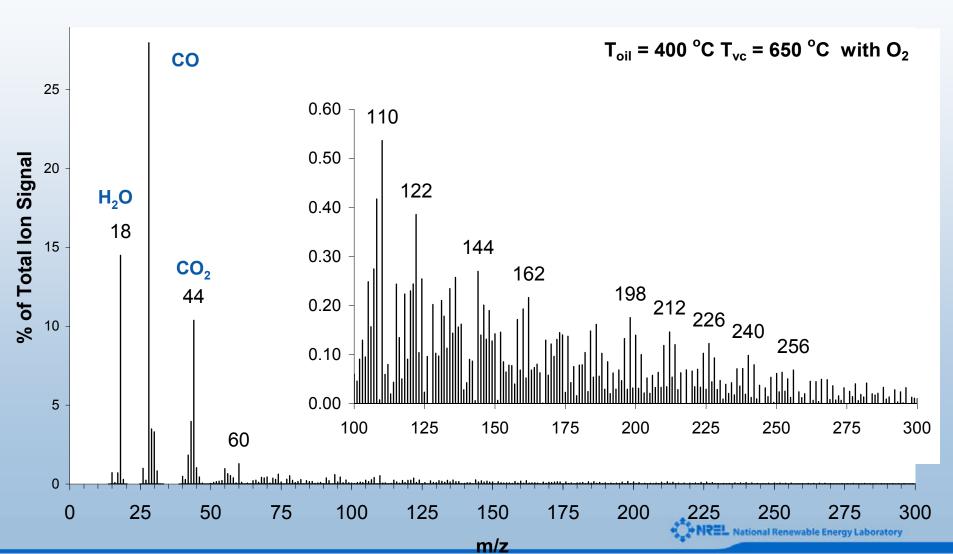
#### **Bio-Oil Film Volatilization**

Cracking 0.5 s @ 650 C

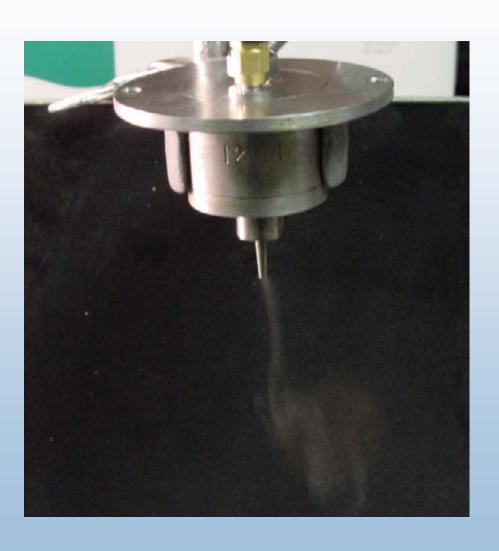


#### **Bio-Oil Film Volatilization**

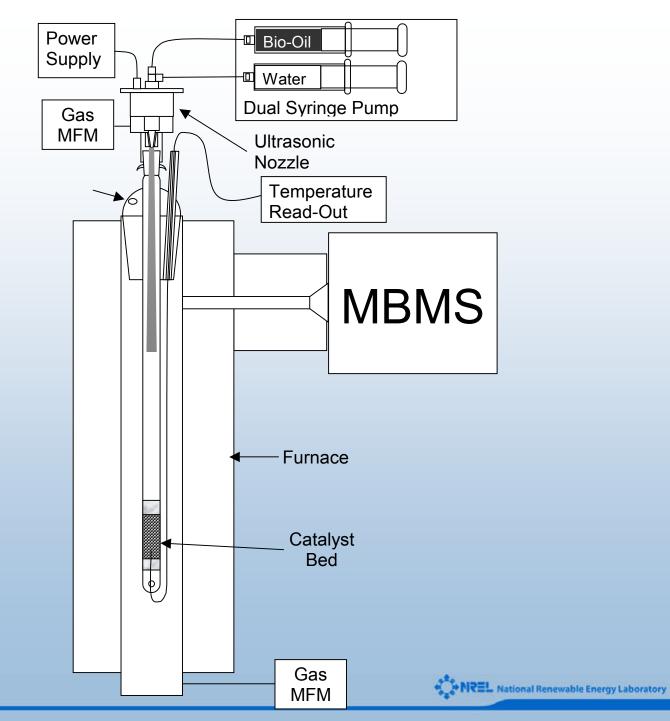
Oxidative Cracking 0.5 s @ 650 C



## **Ultrasonic Nozzle**

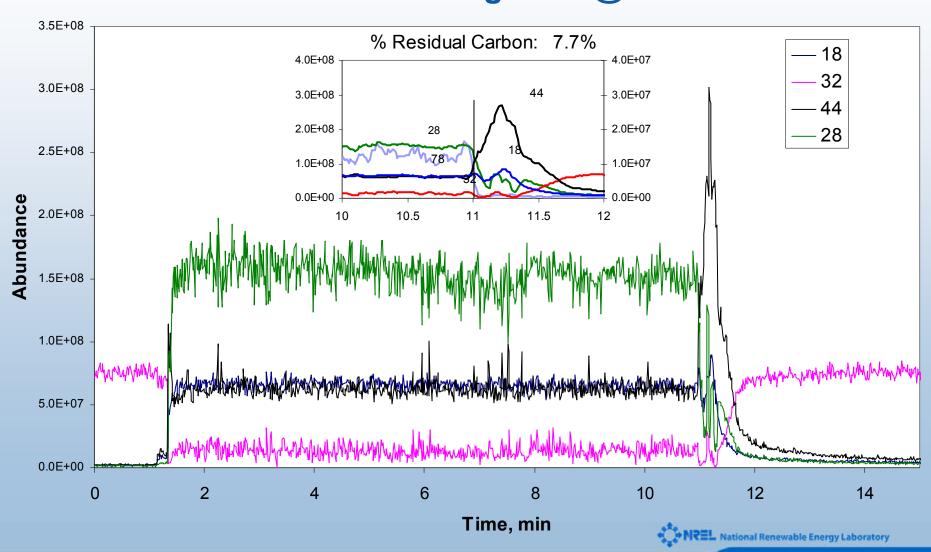


- Generating a fine mist at 0.3g/min
- Enables steady liquid feed at low rates



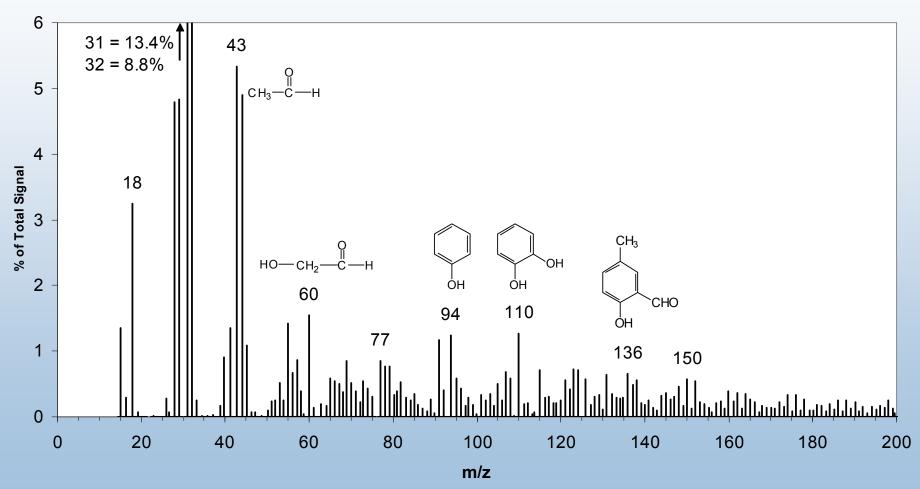
## **Ultrasonic Nebulizer**

#### Oxidative Cracking 0.5 s @ 650 C



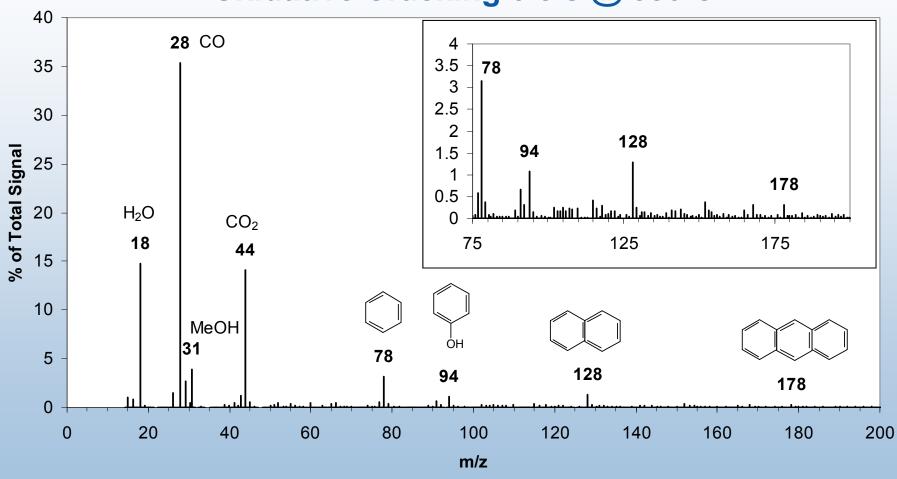
#### **Ultrasonic Nebulizer**

Thermal Cracking 0.5 s @ 650 C



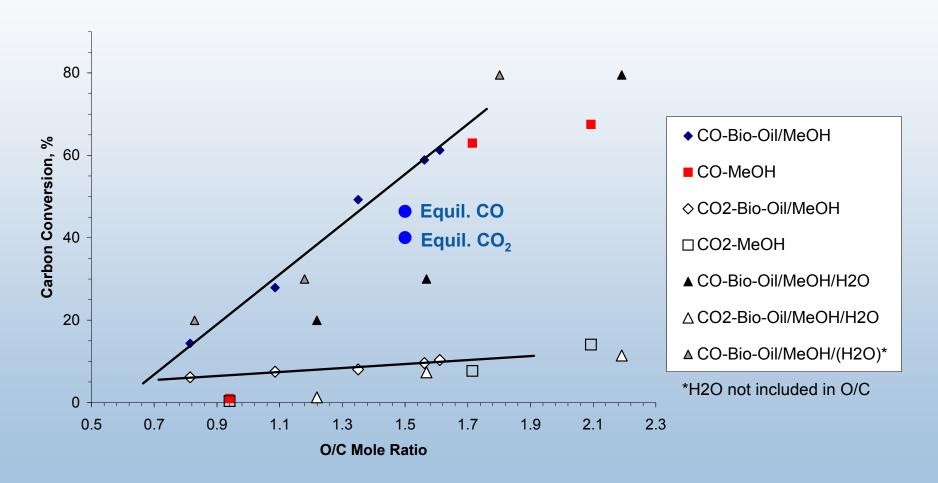
#### **Ultrasonic Nebulizer**

Oxidative Cracking 0.5 s @ 650 C



#### **Carbon Conversion**

Oxidative Cracking 0.5 s @ 650 C



# **Project Timeline**

FY 2003 FY 2004	FY 2005	FY 2006	FY 2007	FY 20	08 FY 2	2009	FY 2010	FY 2011	FY 2012
Distributed Reforming	<b>C</b> 3	(F	P2	F2)		(P	5 C12		
	Sf3	C5 (A	A1) P3	<u>(v9</u>	A2	P	6 Sf5	1	5
	Task 2: Distrib	ited Reforming of	Renewable Li	quid Feedstoc	ks				<

#### 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.

#### <u>Outputs</u>



- 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**

Task Name	2005	2006	2007	2008	2009	2010	2011
Bio-Oil Volatilization							
Processing Options							
Modification and Characterization				<u> </u>			
Injector Development							
Coking Studies							
Go / No Go on Bio-Oil performance			5/3	1			
Oxidative Cracking							
Proof of Concept		<u> </u>					8 8 8 8 8 8
Reduce Catalyst Loading by 50%		6/3	0				
Partial Oxidation Database							
Modeling and Optimization				<u> </u>			
Jon Marda Thesis				5/30			
Catalytic Auto-Thermal Reforming				- 2			
Catalyst Development							
Integrated Separation							
Concept Evaluation							
Membrane Support				<u>.</u>			
Integrated Laboratory System Experiment							
Go / No Go on Conceptual Design				6/1			
Systems Engineering							
Oxygen, Steam and Heat Integration							**************************************
Engineering Design and Construction					<del>-</del>		
Prototype System Developed					6/3	30	
Heat and Mass Balances						<b>_</b>	
Process Upsets							
Long Duration Runs				1		Ž	
Demonstrate Distributed Hydrogen Production from							12/3
Bio-Oil for \$3.6/gge				1 1 1 1 1 1 1 1			
Safety Analysis				1 1 1 1			
Review and Analysis of Pressure, O2, H2				<b>—</b>			
Systems Integration							

#### **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	<ul><li>Colorado School of Mines</li><li>Chevron</li></ul>
Future Work	<ul><li>Low Temperature Oxidative</li><li>Cracking Proof of Concept in FY06</li><li>Catalysis in FY07</li></ul>

## 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

