Distributed Bio-Oil Reforming

R. Evans, S. Czernik, R. French, M. Ratcliff
National Renewable Energy Laboratory

J. Marda, A. M. Dean
Colorado School of Mines

Bio-Derived Liquids Distributed Reforming
Working Group Meeting
HFC&IT Program

Baltimore, MD
October 24, 2006

Gasification

Partial oxidation

$$CH_{1.46}O_{.67} + 0.16\ O_2 \rightarrow CO + 0.73\ H_2$$

Biomass **Syngas**

Water-Gas Shift

$$CO + H_2O \longleftrightarrow CO_2 + H_2$$

$$CH_{1.46}O_{.67} + 0.16\ O_2 + H_2O \rightarrow CO_2 + 1.73\ H_2$$

Biomass **Hydrogen**

(14.3% yield)

Practical yields 10%

Pyrolysis

Thermal decomposition occurring in the absence of oxygen

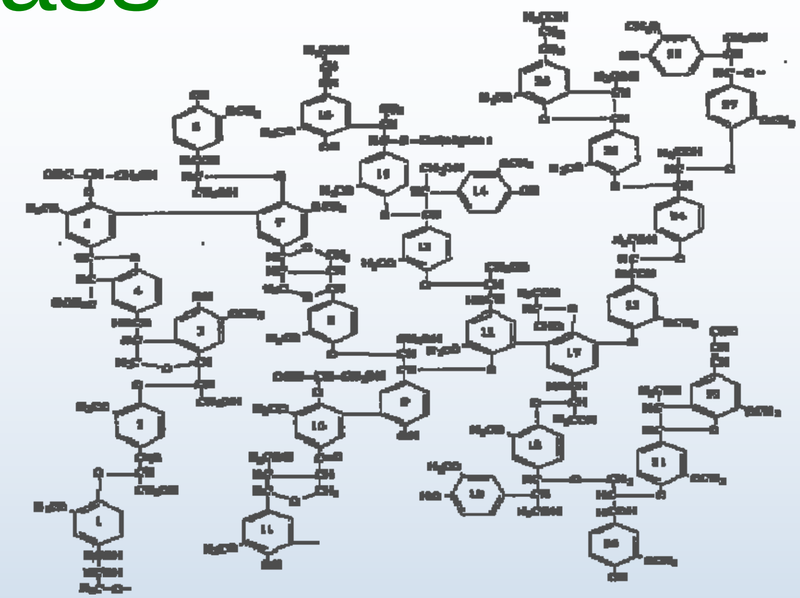
Is always the first step in combustion and gasification processes

Known as a technology for producing charcoal and chemicals for thousands years

Biomass

Lignin: 15%–25%

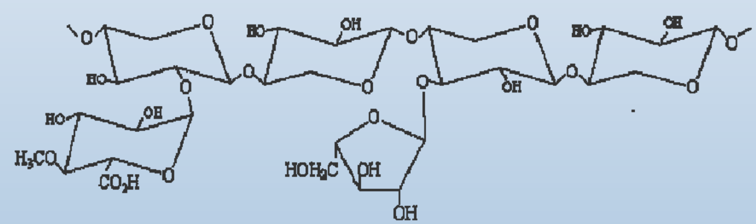
Complex aromatic structure



Hemicellulose: 23%–32%

Polymer of 5- and 6-carbon sugars

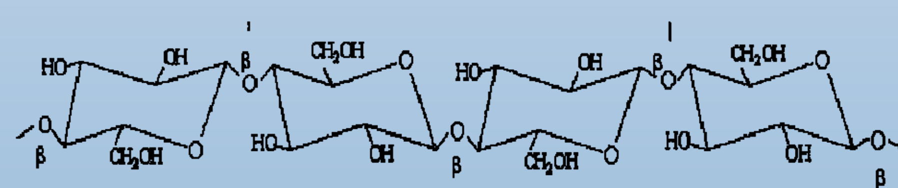
Xylose is the second most abundant sugar in the biosphere



Cellulose: 38%–50%

Most abundant form of carbon in biosphere

Polymer of glucose



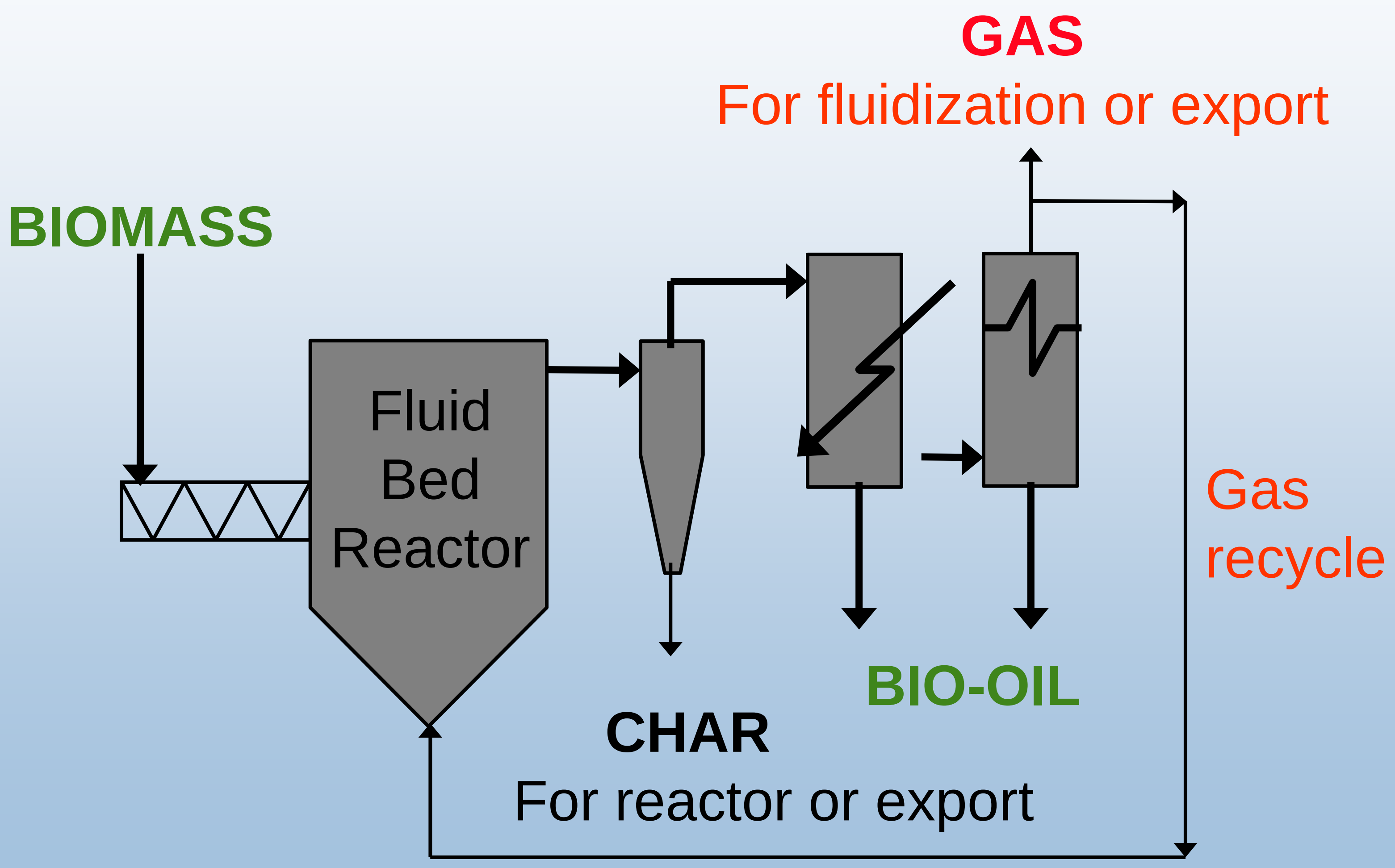
Biomass Pyrolysis Products

	Liquid	Char	Gas
FAST PYROLYSIS	**75%**	**12%**	**13%**
•moderate temperature			
•short residence time			
CARBONIZATION	**30%**	**35%**	**35%**
•low temperature			
•long residence time			
GASIFICATION	.1 - **5%**	**10%**	**85%**
•high temperature			
•Short to long residence time			

Fast Pyrolysis

- Fast pyrolysis is a thermal process that rapidly heats biomass to a carefully controlled temperature (~500°C), then very quickly cools the volatile products (<2 sec) formed in the reactor
- Offers the unique advantage of producing a liquid that can be stored and transported
- Has been developed in many reactor configurations; at present is at early stage of development (100 t/day commercial plant)

Bubbling Fluid Bed Pyrolysis



Fast 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	Char	Gas
	75%	13%	12%

Catalytic Steam Reforming of Bio-oil

$CH_{1.98}O_{0.76} + 1.24\ H_2O \longrightarrow CO_2 + 2.23\ H_2$

Bio-oil **Steam** **Hydrogen**

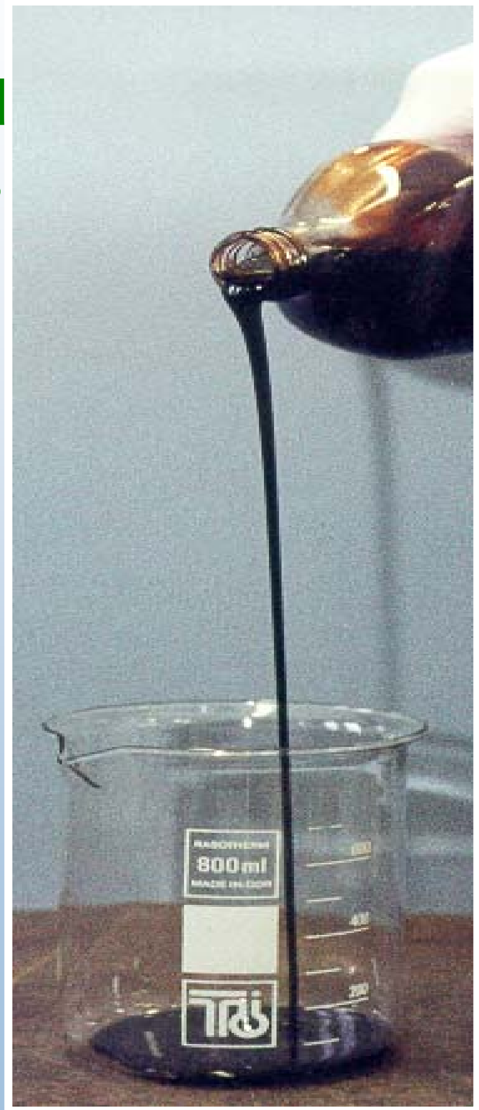
Biomass ⟶ **13.0% yield H_2**

Practical yield 10%

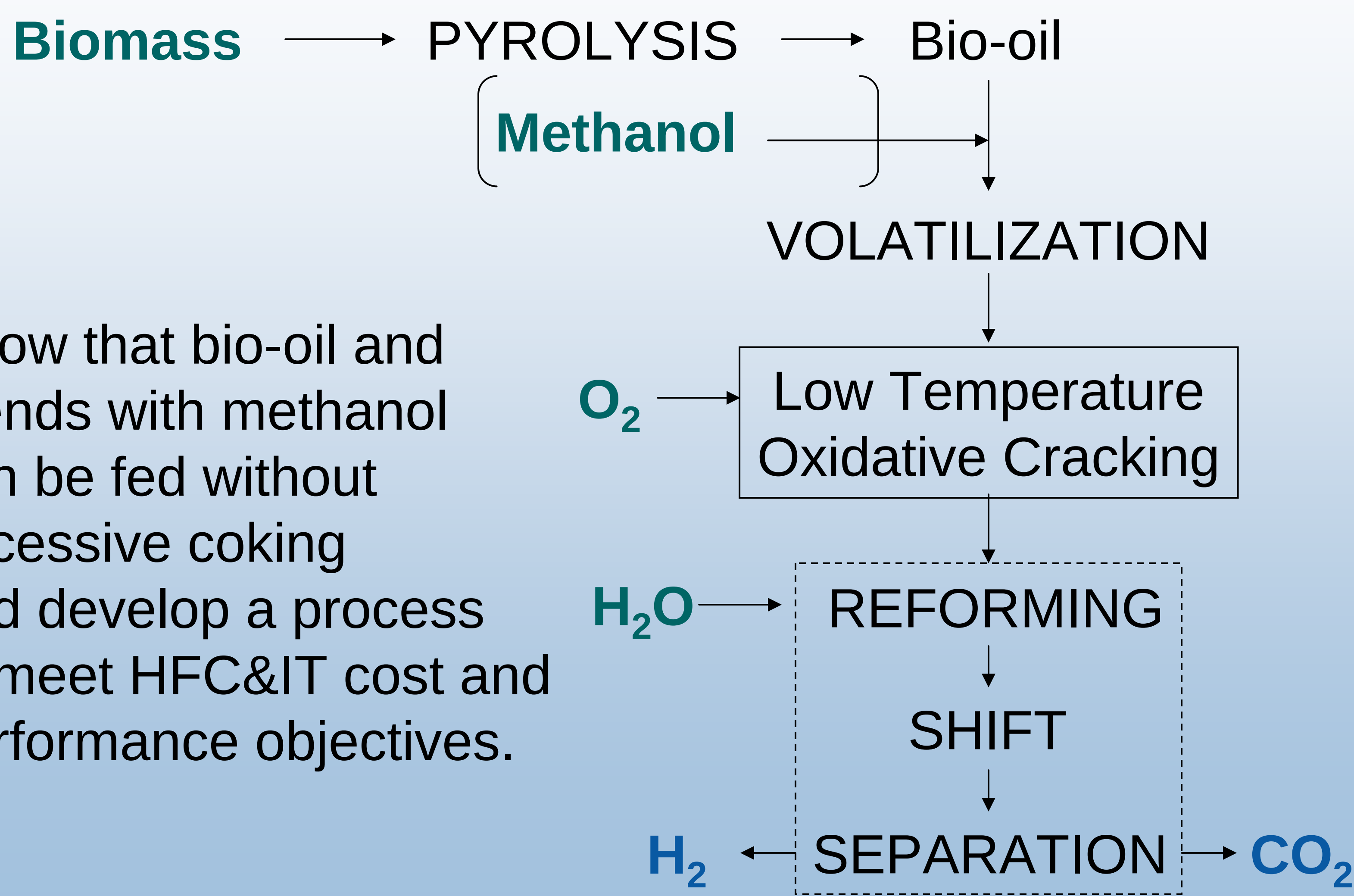
Fast Pyrolysis Bio-oil

Bio-oil is water miscible and is comprised of many oxygenated organic chemicals

- **Dark brown mobile liquid,**
- **Combustible,**
- **Not miscible with hydrocarbons,**
- **Heating value ~ 17 MJ/kg,**
- **Density ~ 1.2 kg/l,**
- **Acid, pH ~ 2.5,**
- **Pungent odour,**
- **"Ages" - viscosity increases with time**

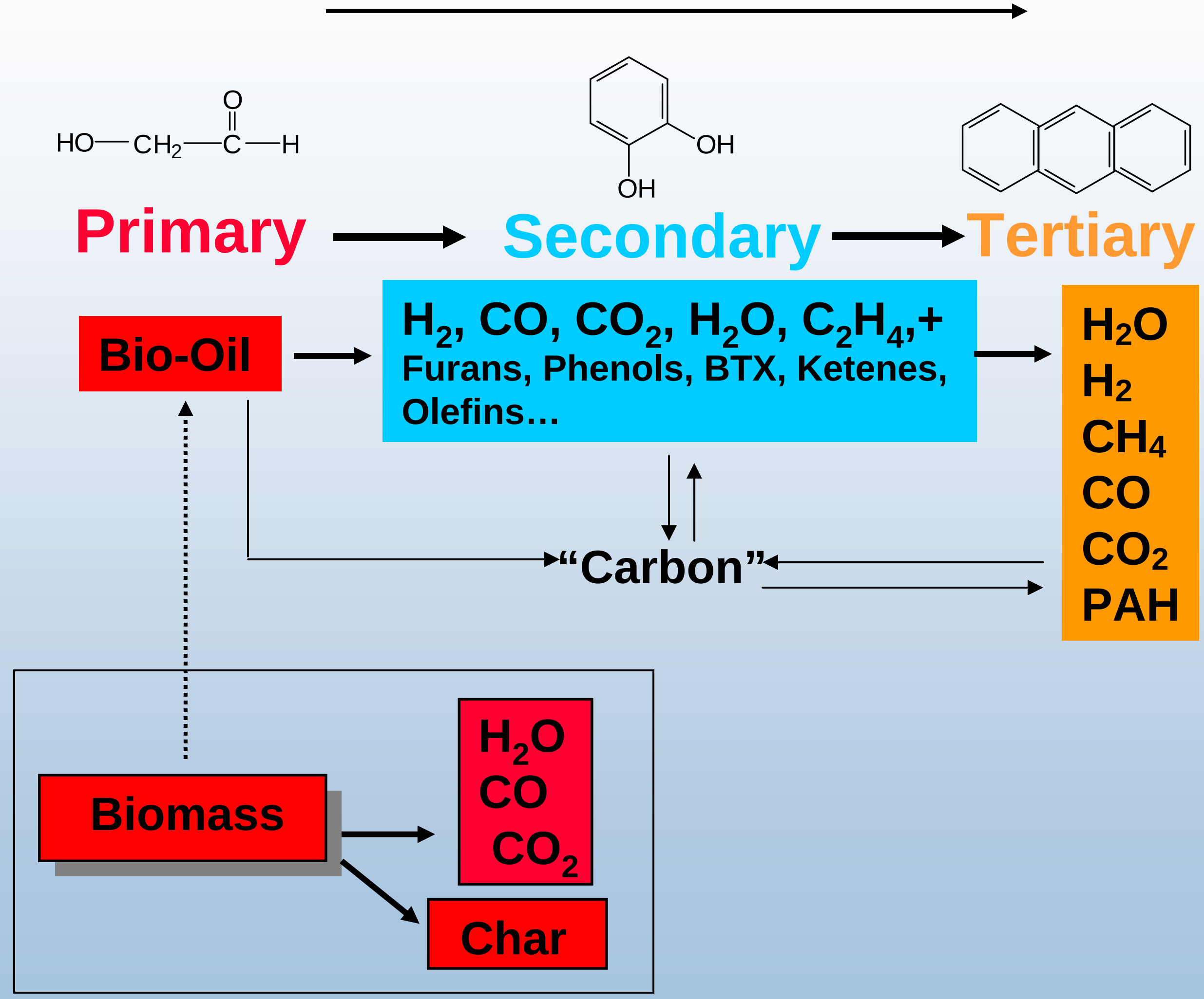


Approach

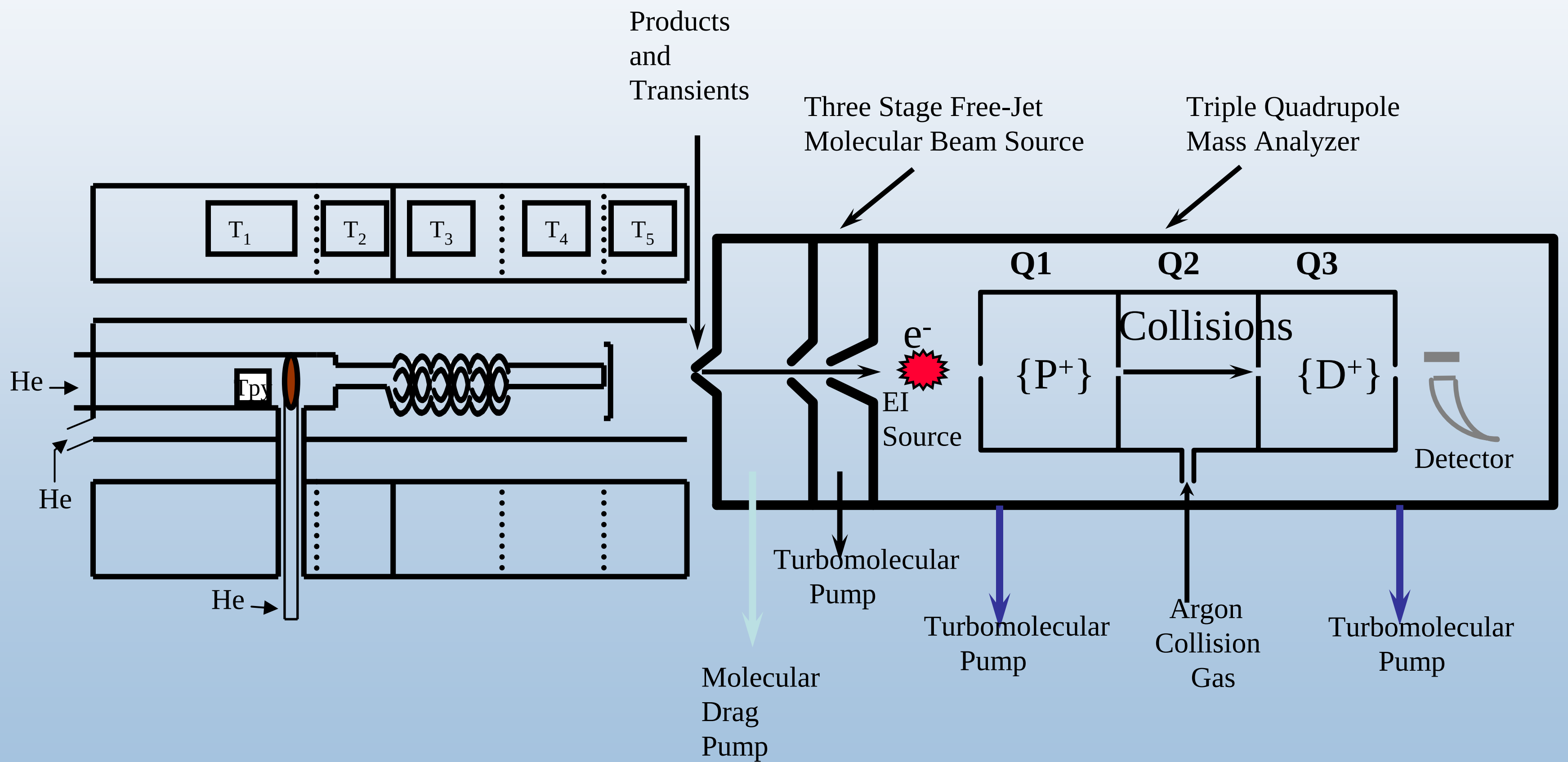


Show that bio-oil and blends with methanol can be fed without excessive coking and develop a process to meet HFC&IT cost and performance objectives.

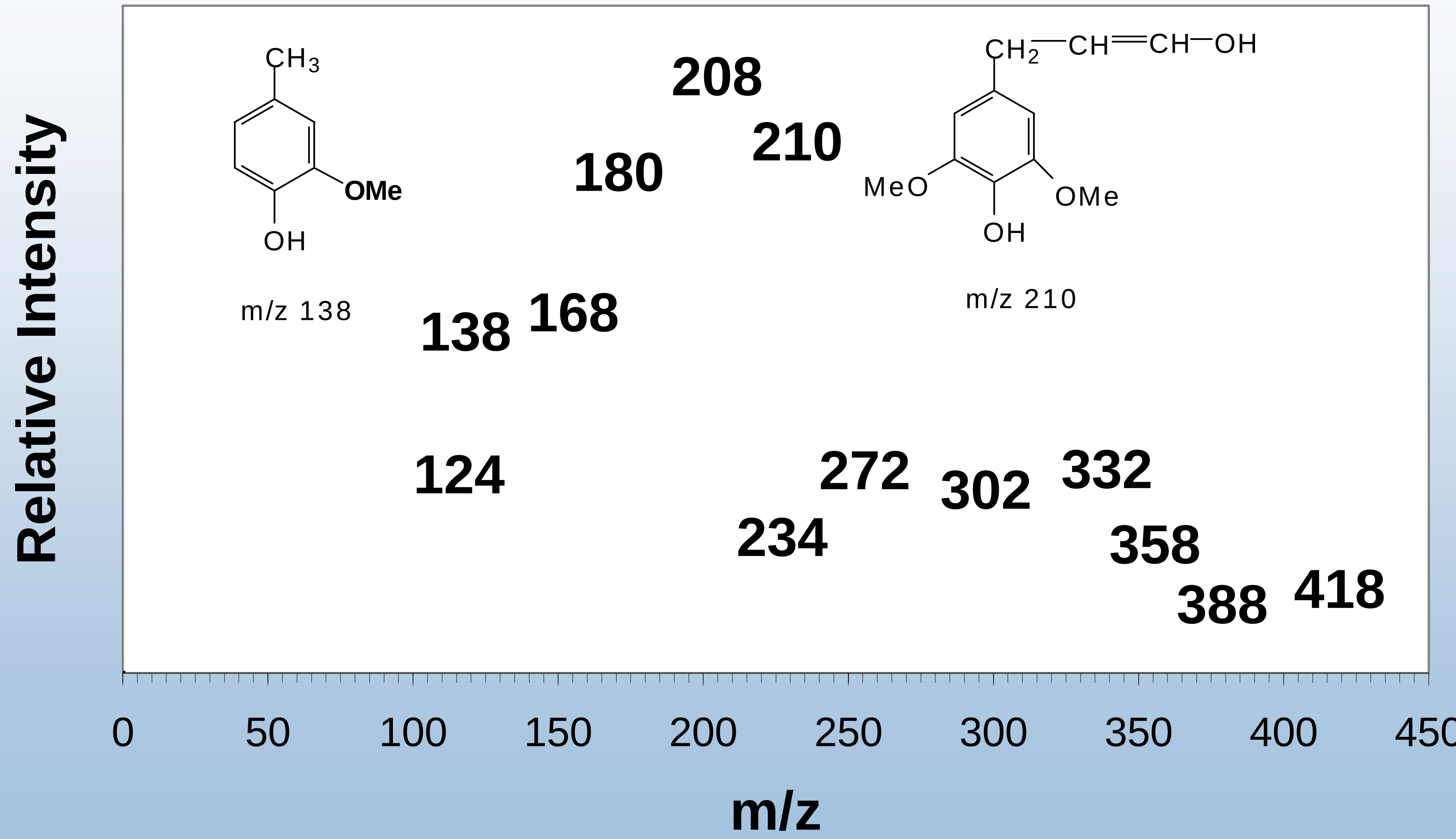
Thermal Severity



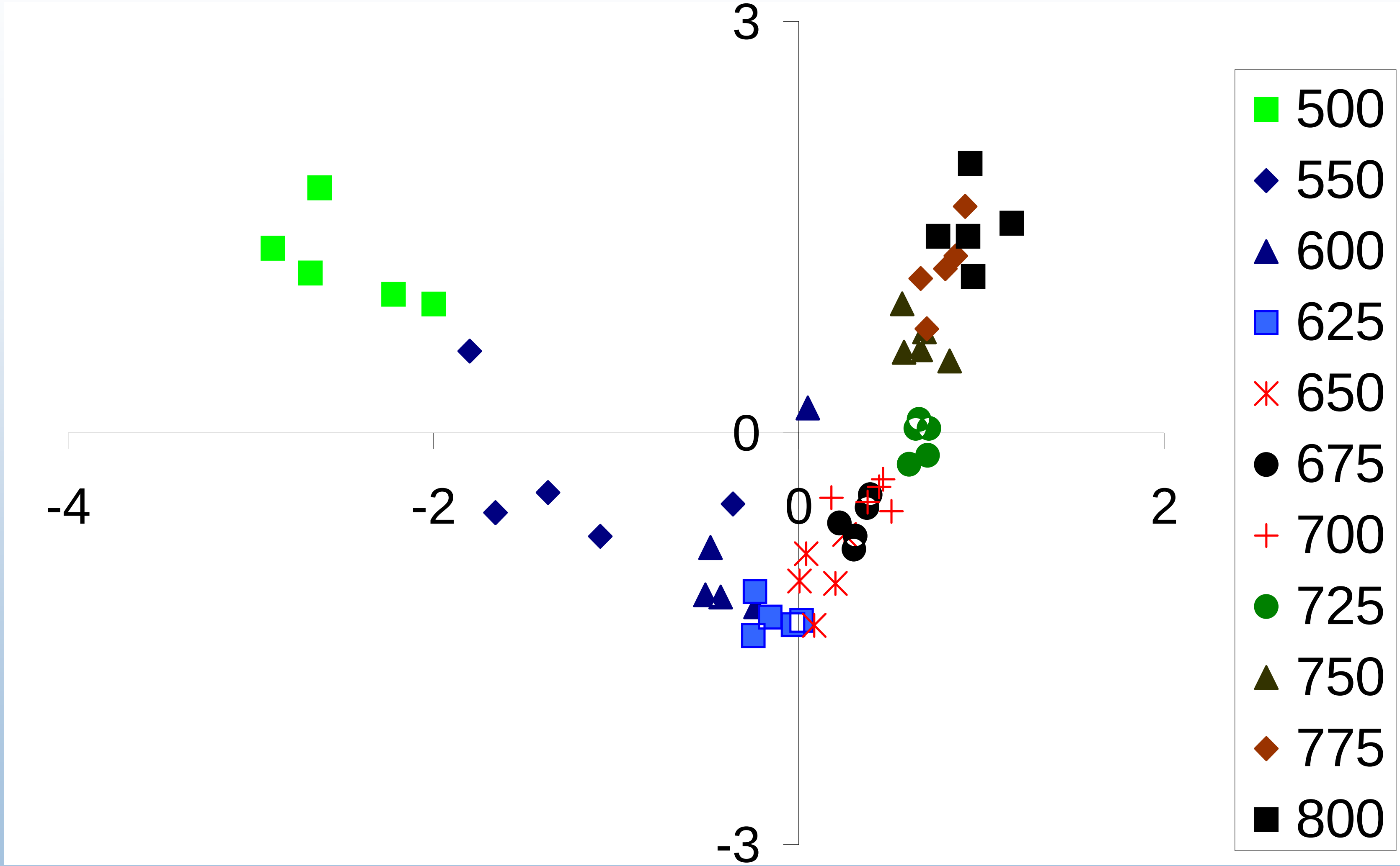
Schematic of Pyrolysis Reactor & NREL's MBMS Sampling System



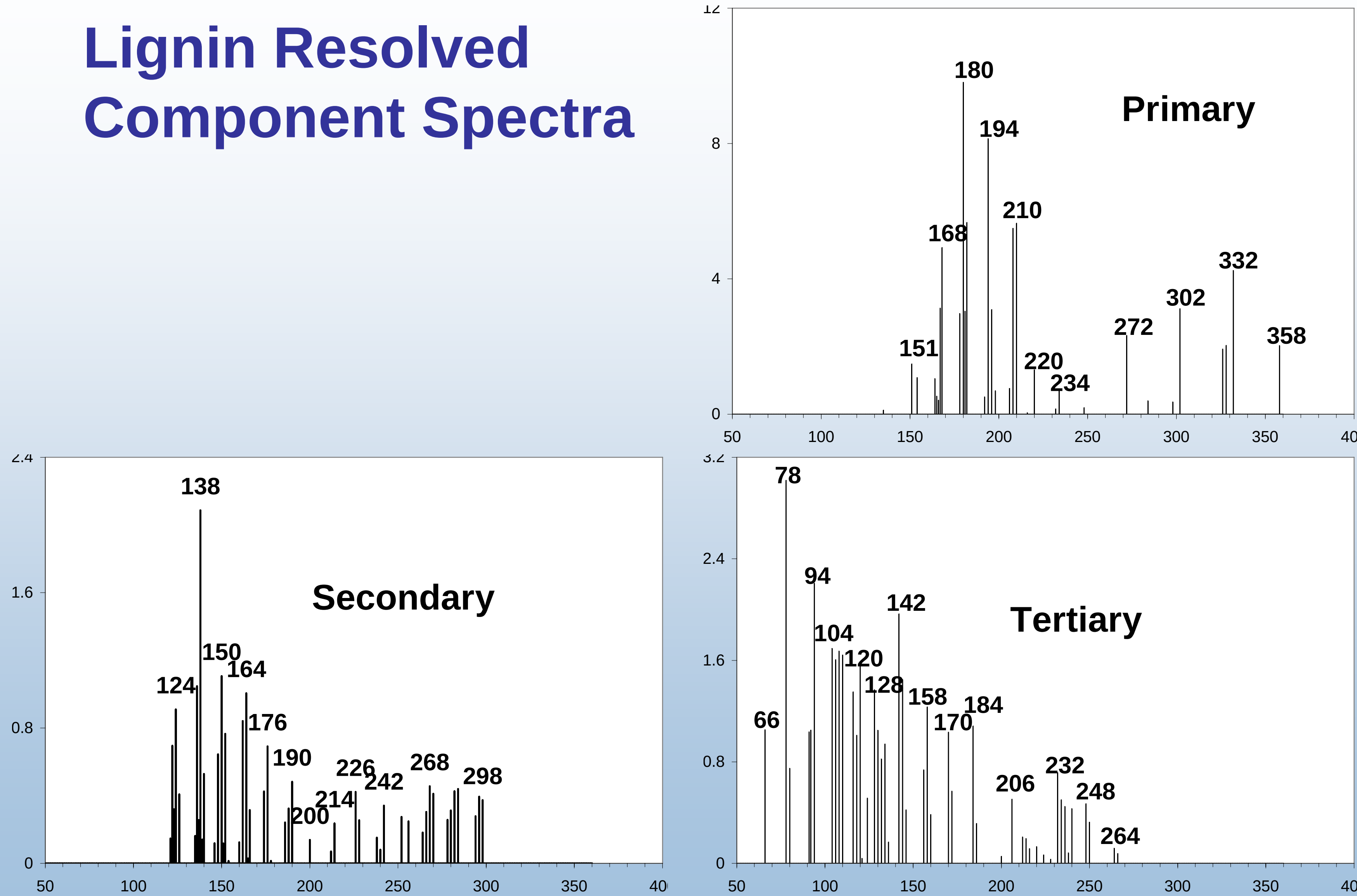
Lignin Pyrolysis 675 ms @ 500 °C



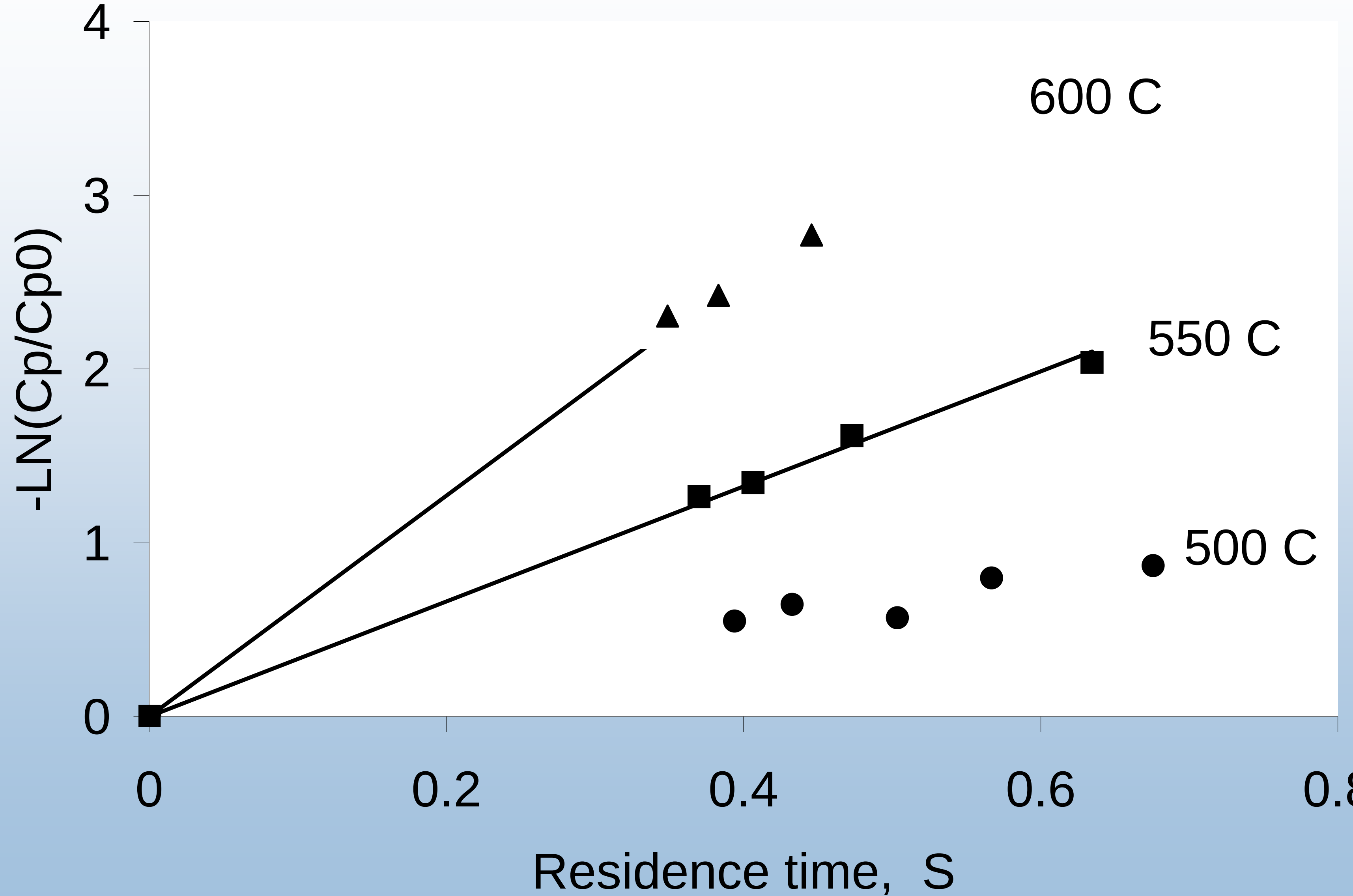
Lignin Pyrolysis Score Plot



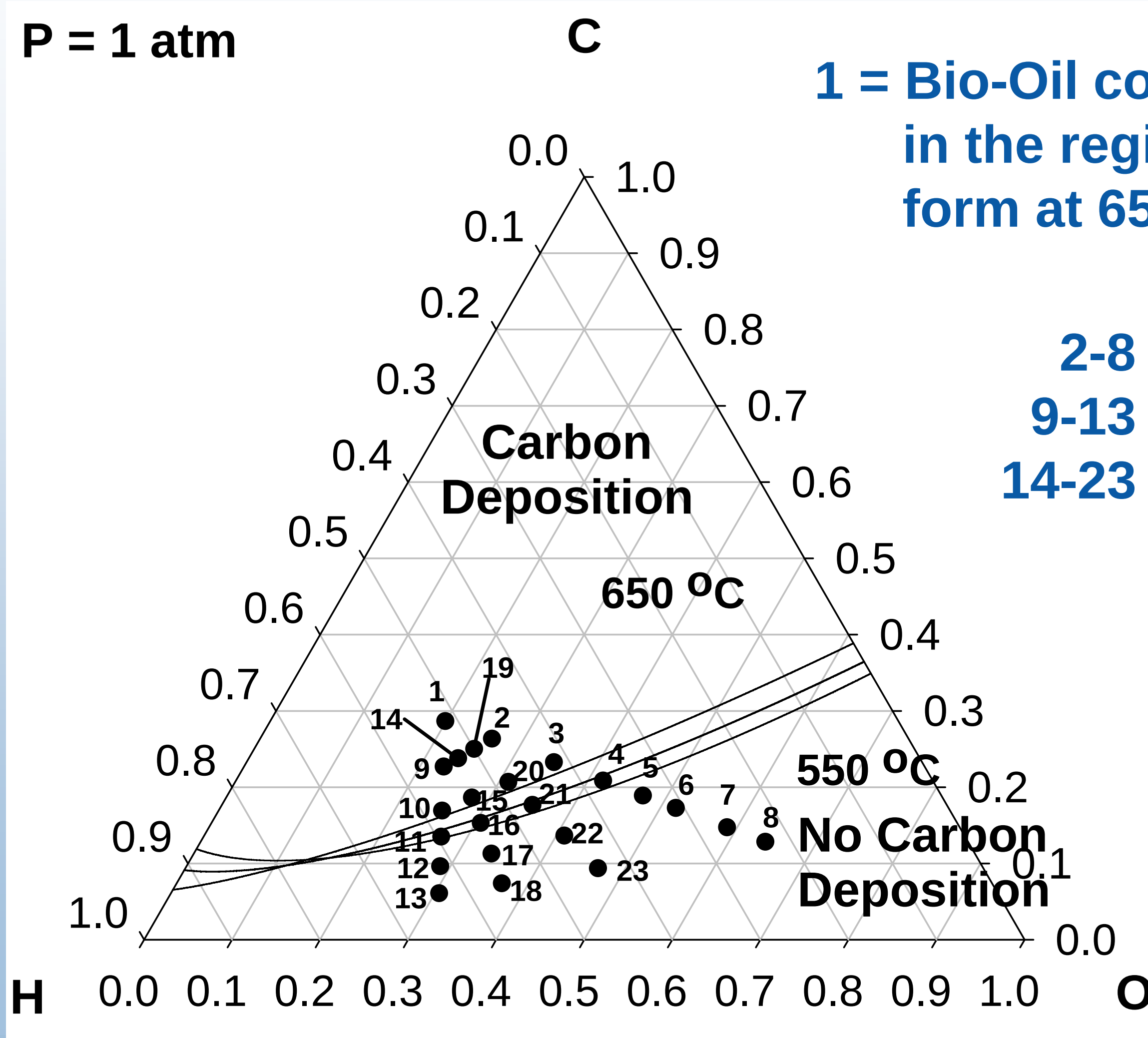
Lignin Resolved Component Spectra



Lignin Empirical Kinetic Model



Equilibrium Modeling Results

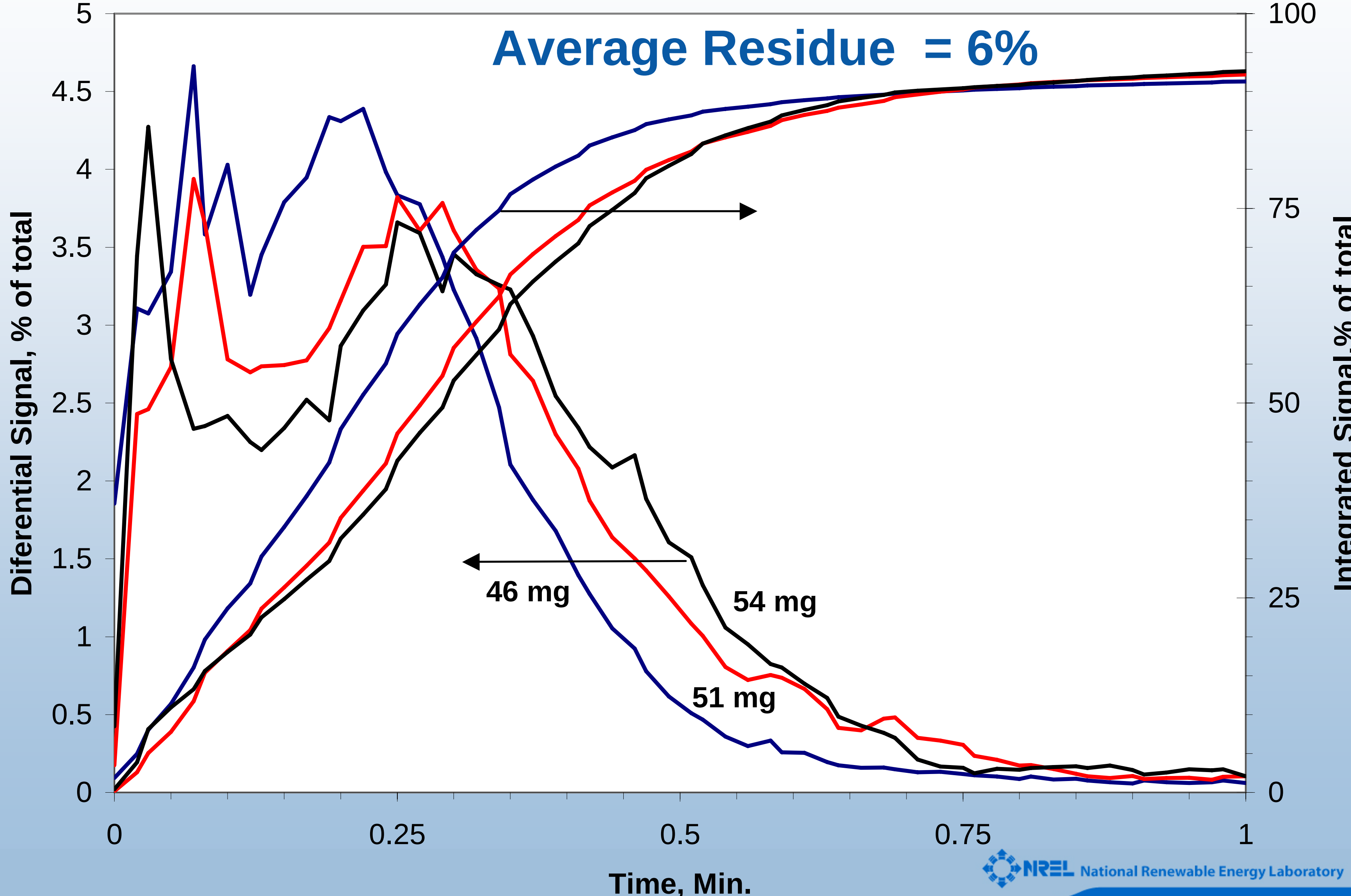


1 = Bio-Oil composition, which lies in the region where carbon will form at 650 C

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

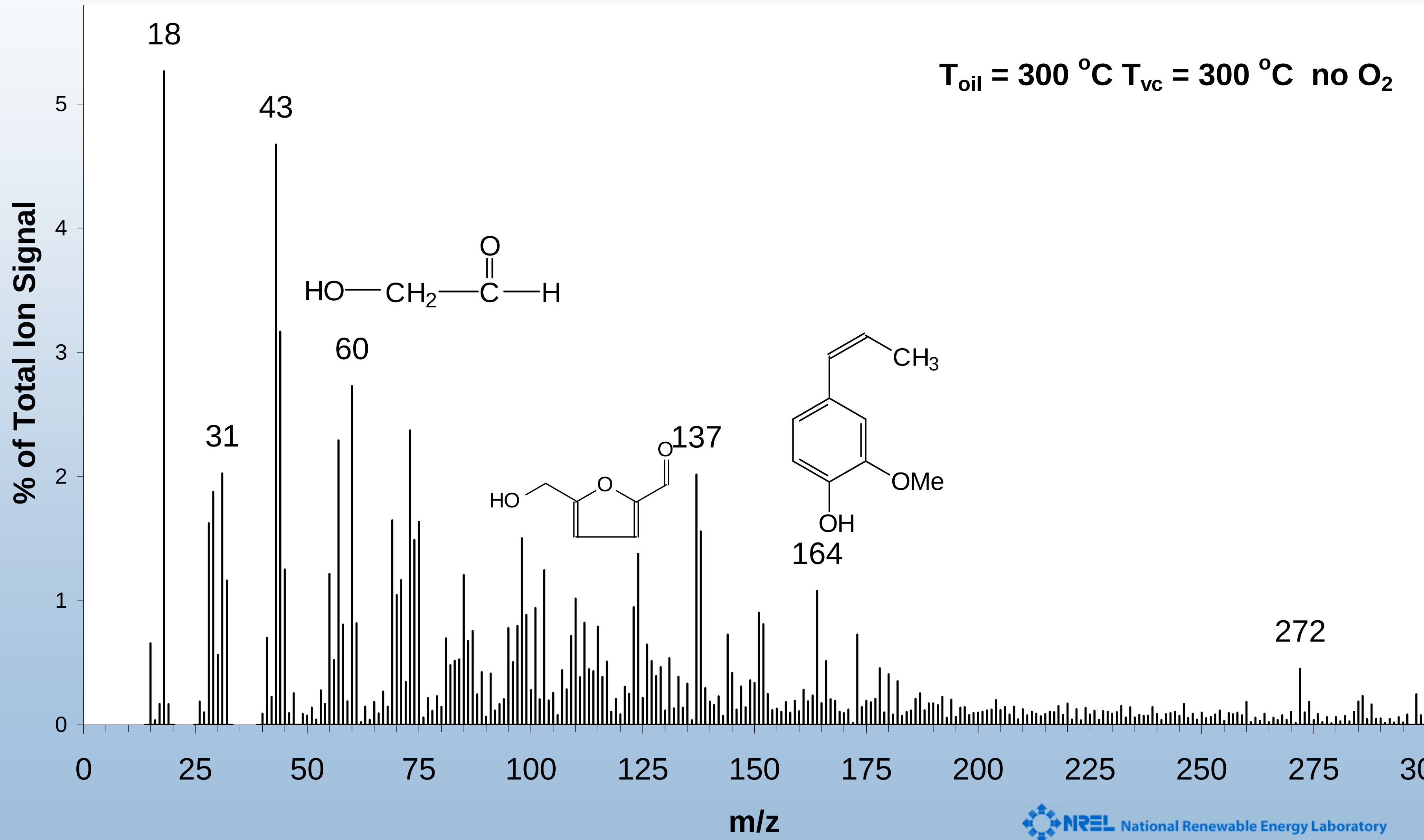
Goal is to identify the thermodynamic and kinetic domains for deposit free operation

Bio-Oil Film Volatilization – 400 ºC



Bio-Oil Film Volatilization

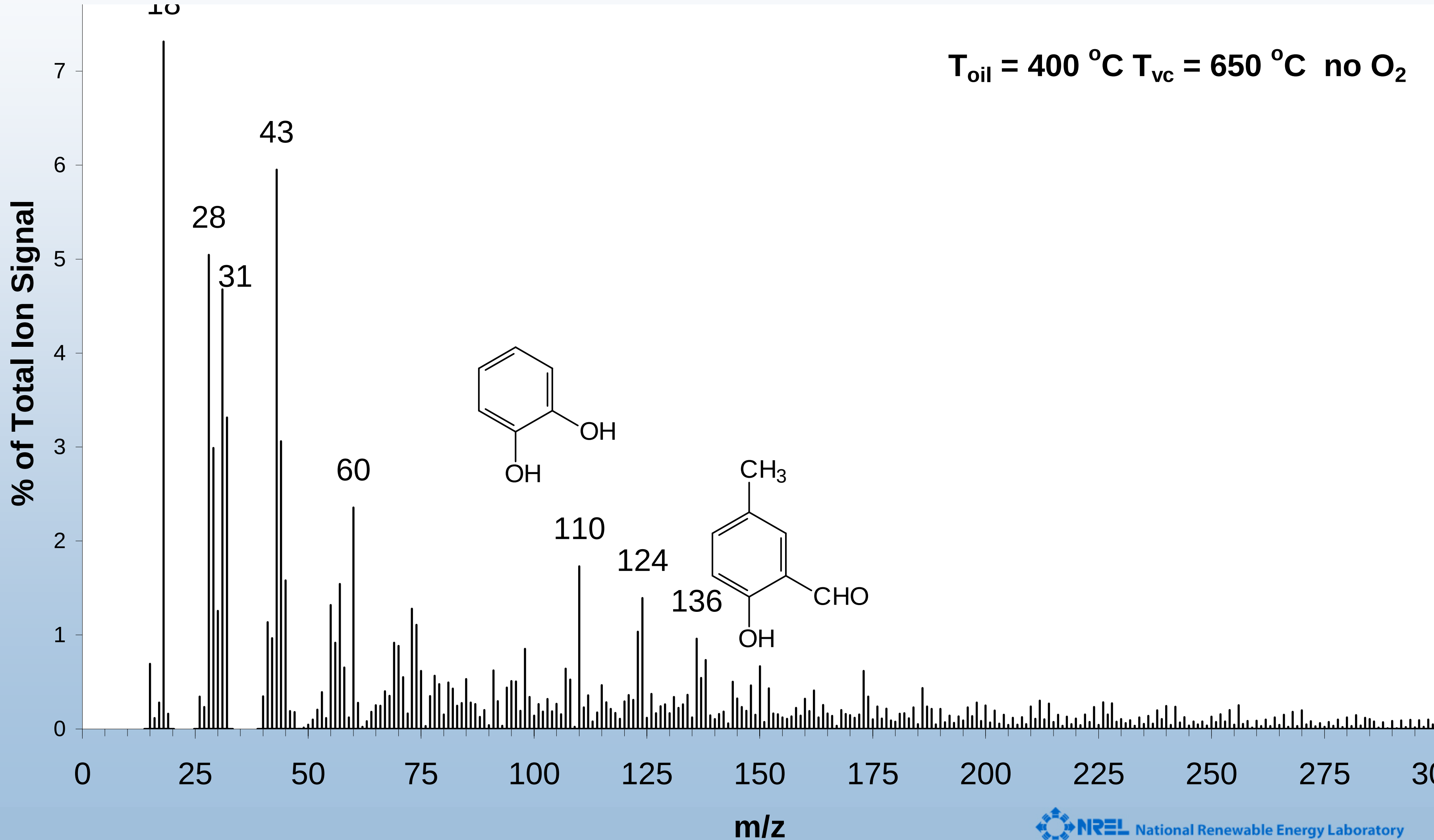
MBMS Bio-Oil Spectrum



National Renewable Energy Laboratory

Bio-Oil Film Volatilization

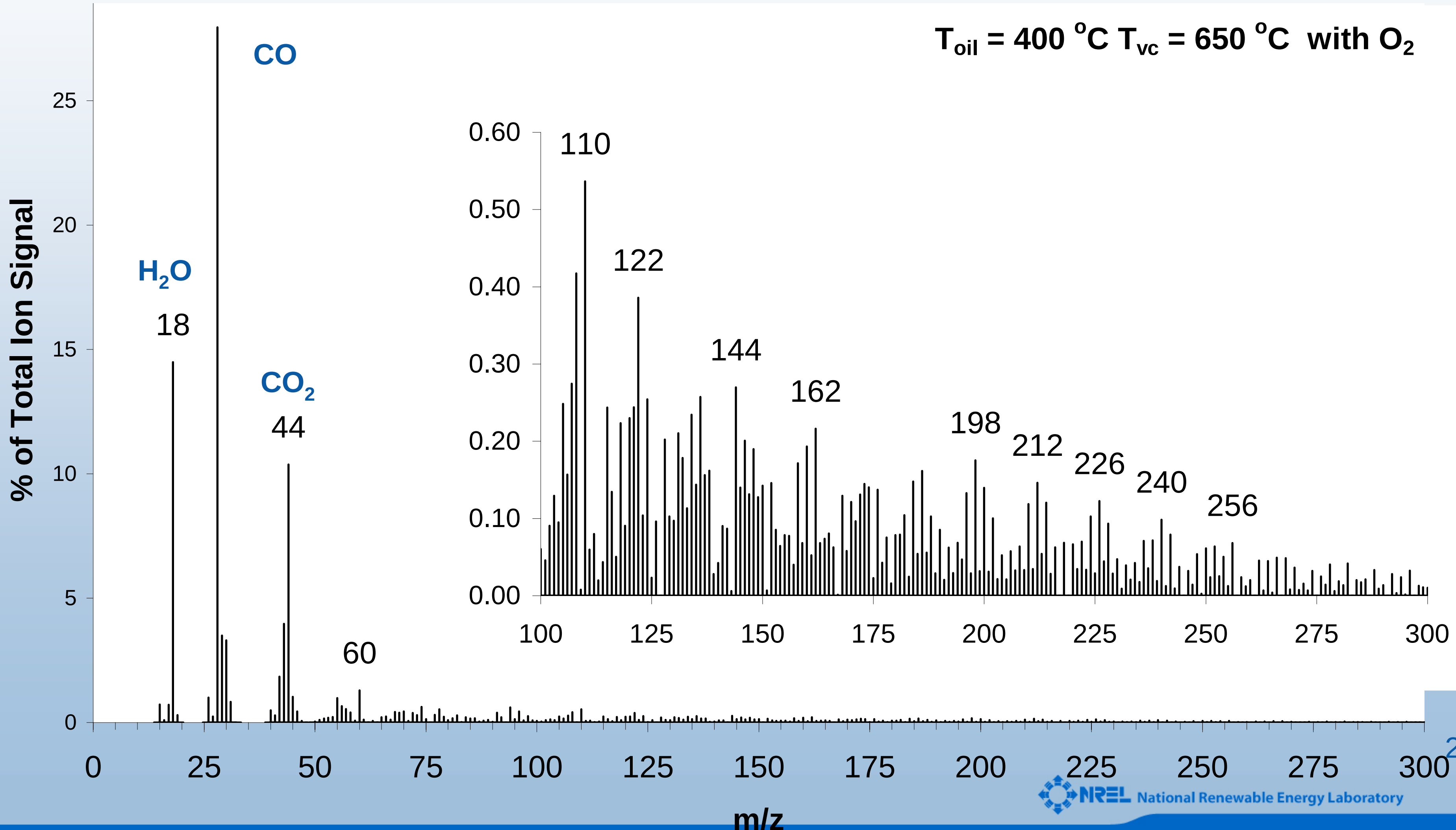
Cracking 0.5 s @ 650 C



NREL National Renewable Energy Laboratory

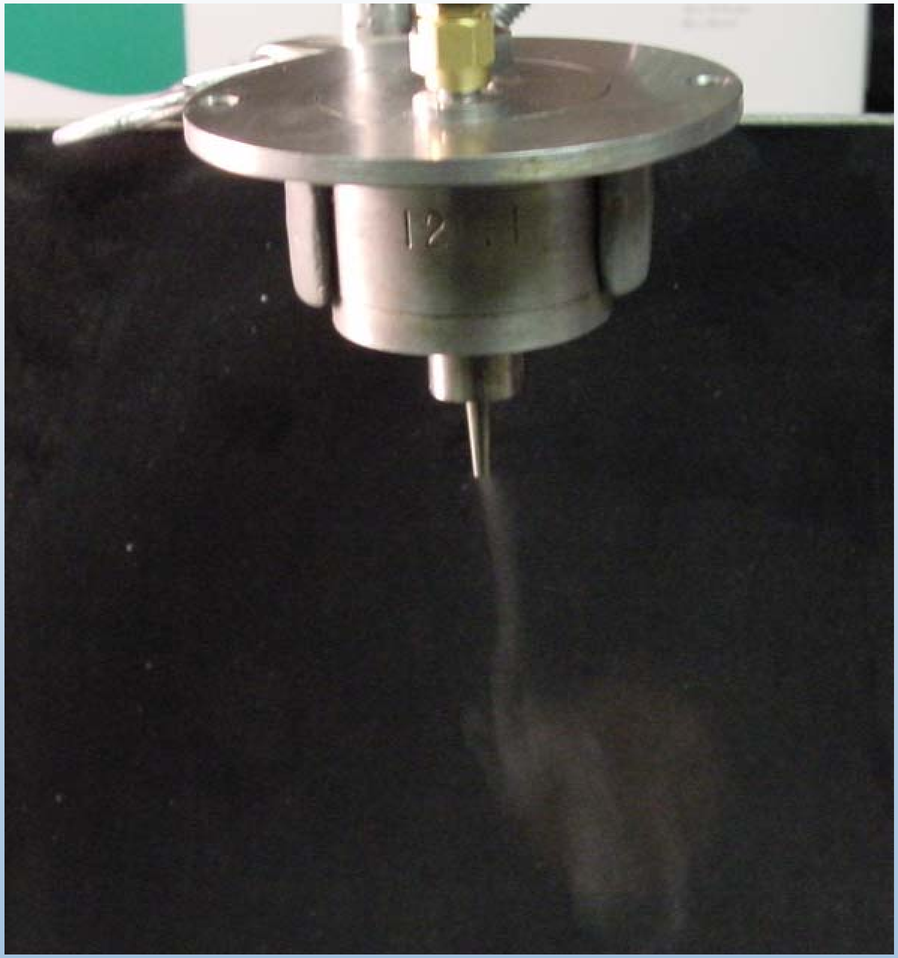
Bio-Oil Film Volatilization

Oxidative Cracking 0.5 s @ 650 C

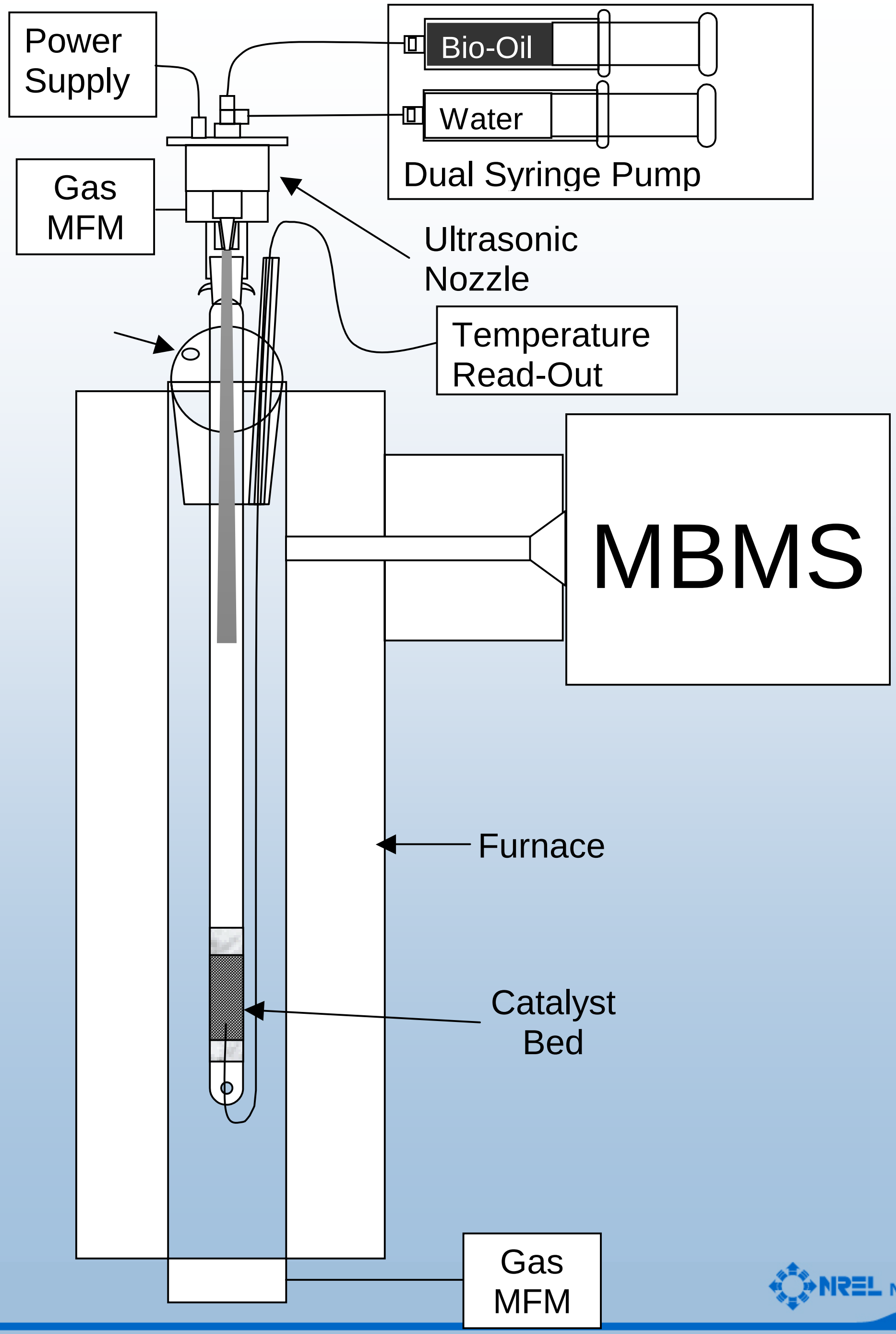


NREL National Renewable Energy Laboratory

Ultrasonic Nozzle

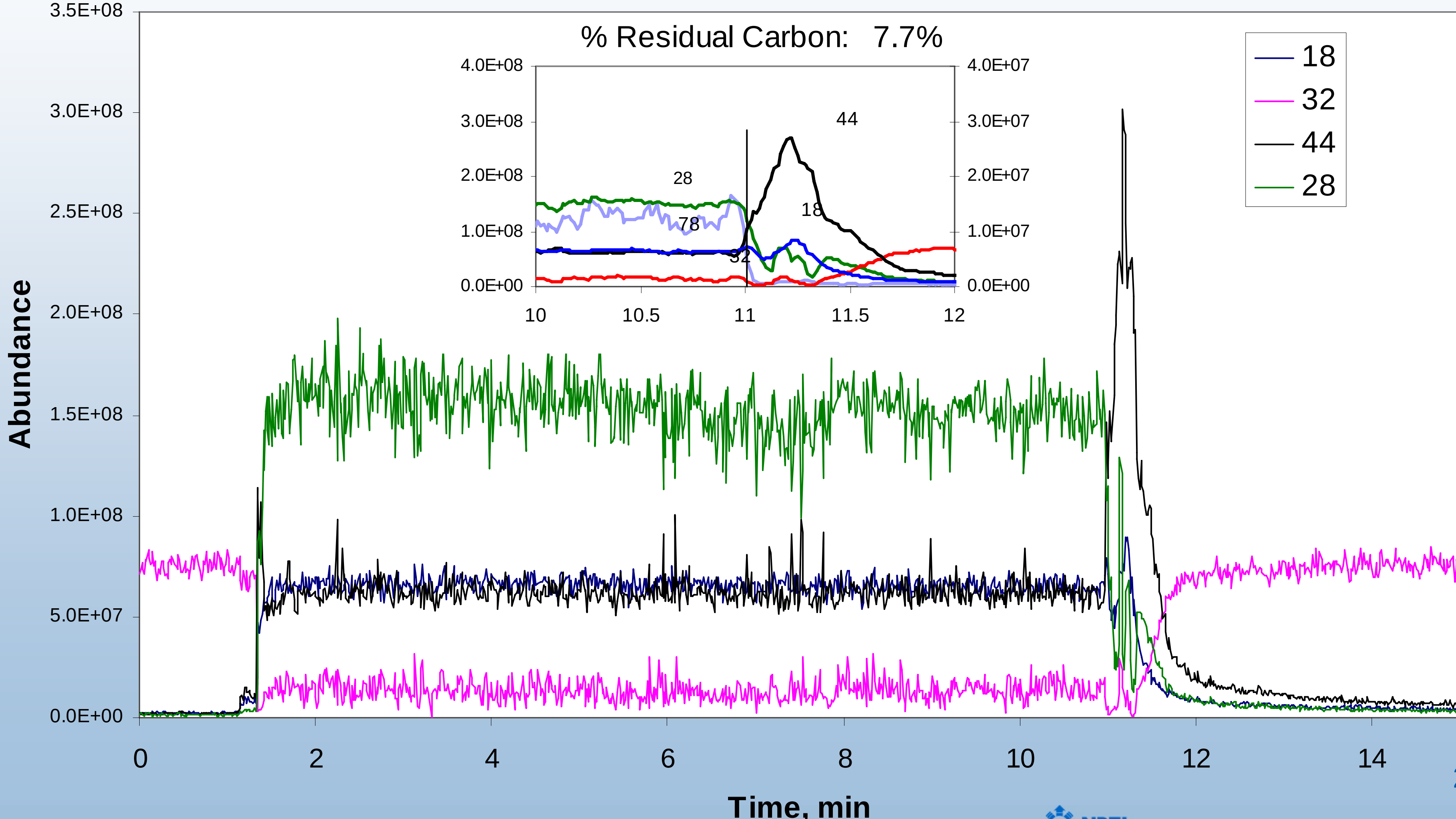


- Generating a fine mist at 0.3g/min
- Enables steady liquid feed at low rates


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

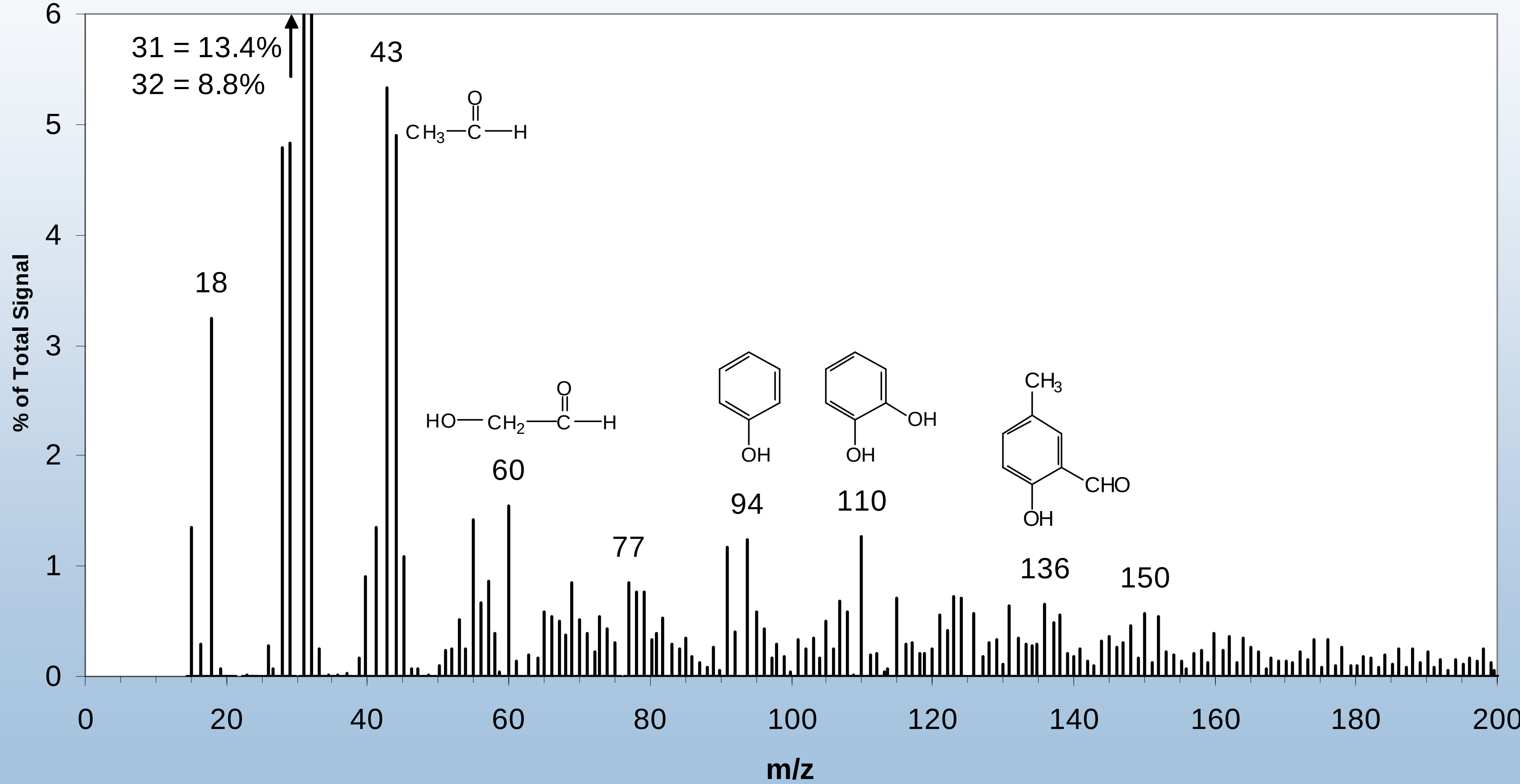
Ultrasonic Nebulizer

Oxidative Cracking 0.5 s @ 650 C



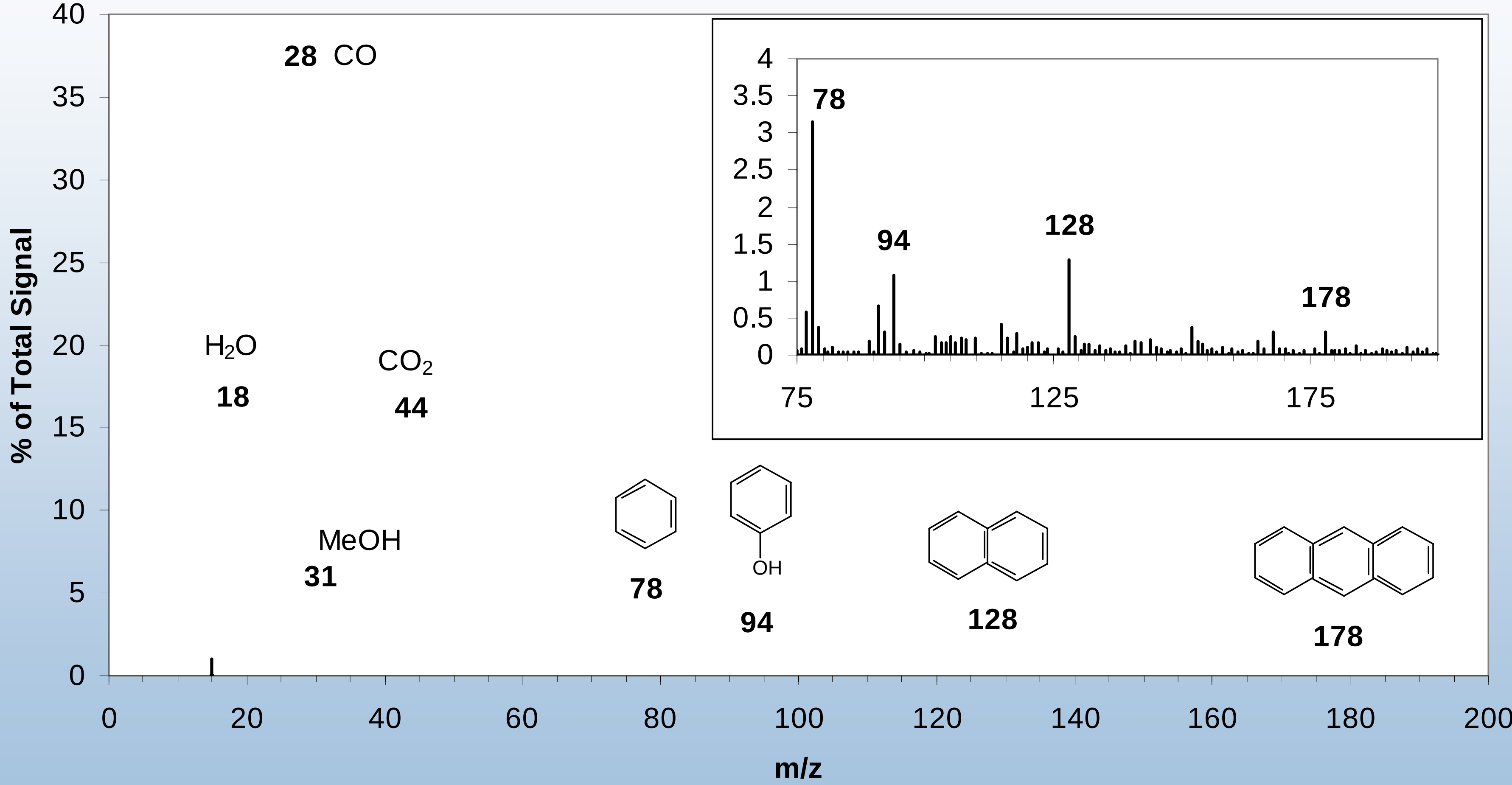
Ultrasonic Nebulizer

Thermal Cracking 0.5 s @ 650 C



Ultrasonic Nebulizer

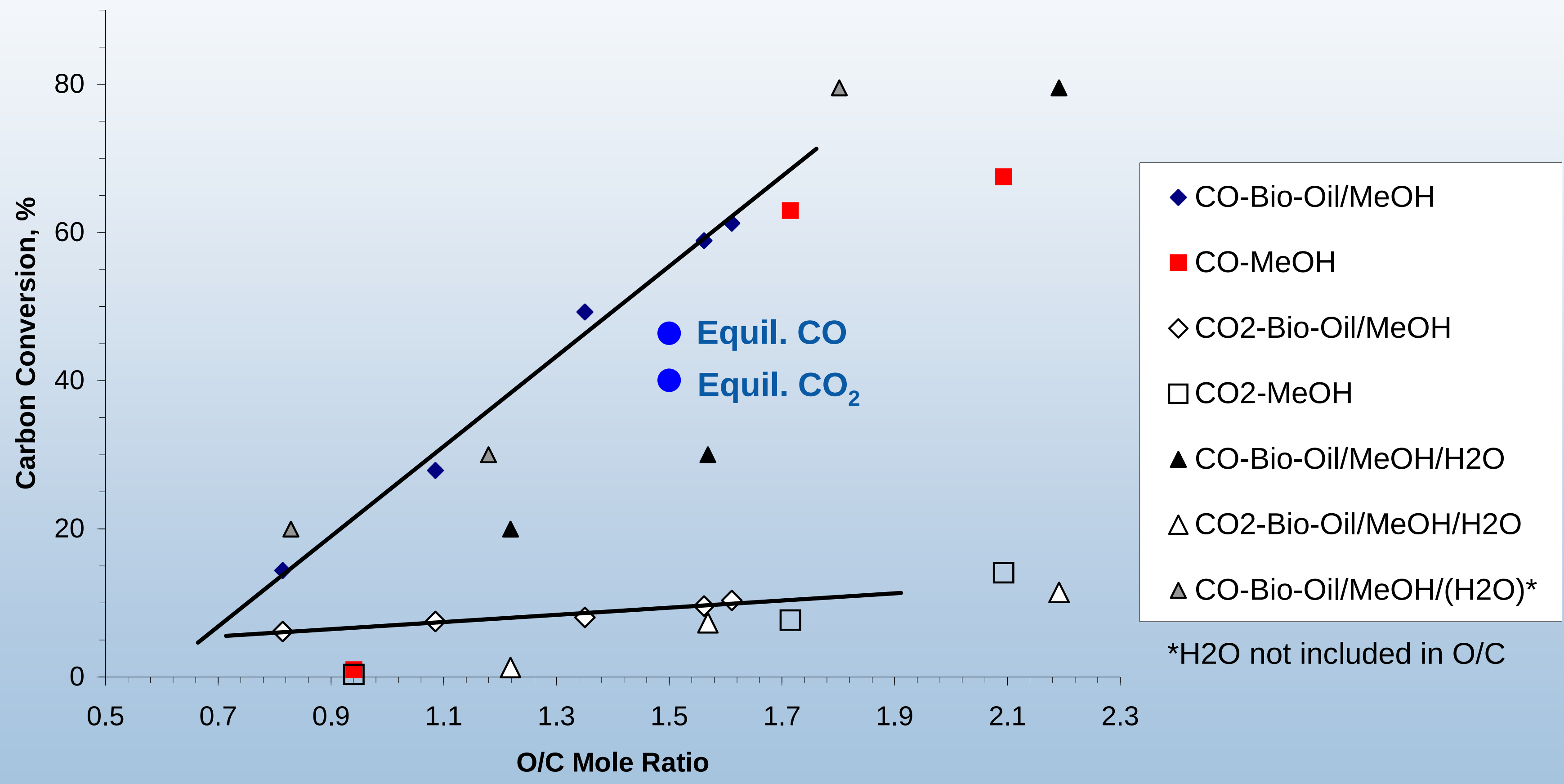
Oxidative Cracking 0.5 s @ 650 C



National Renewable Energy Laboratory

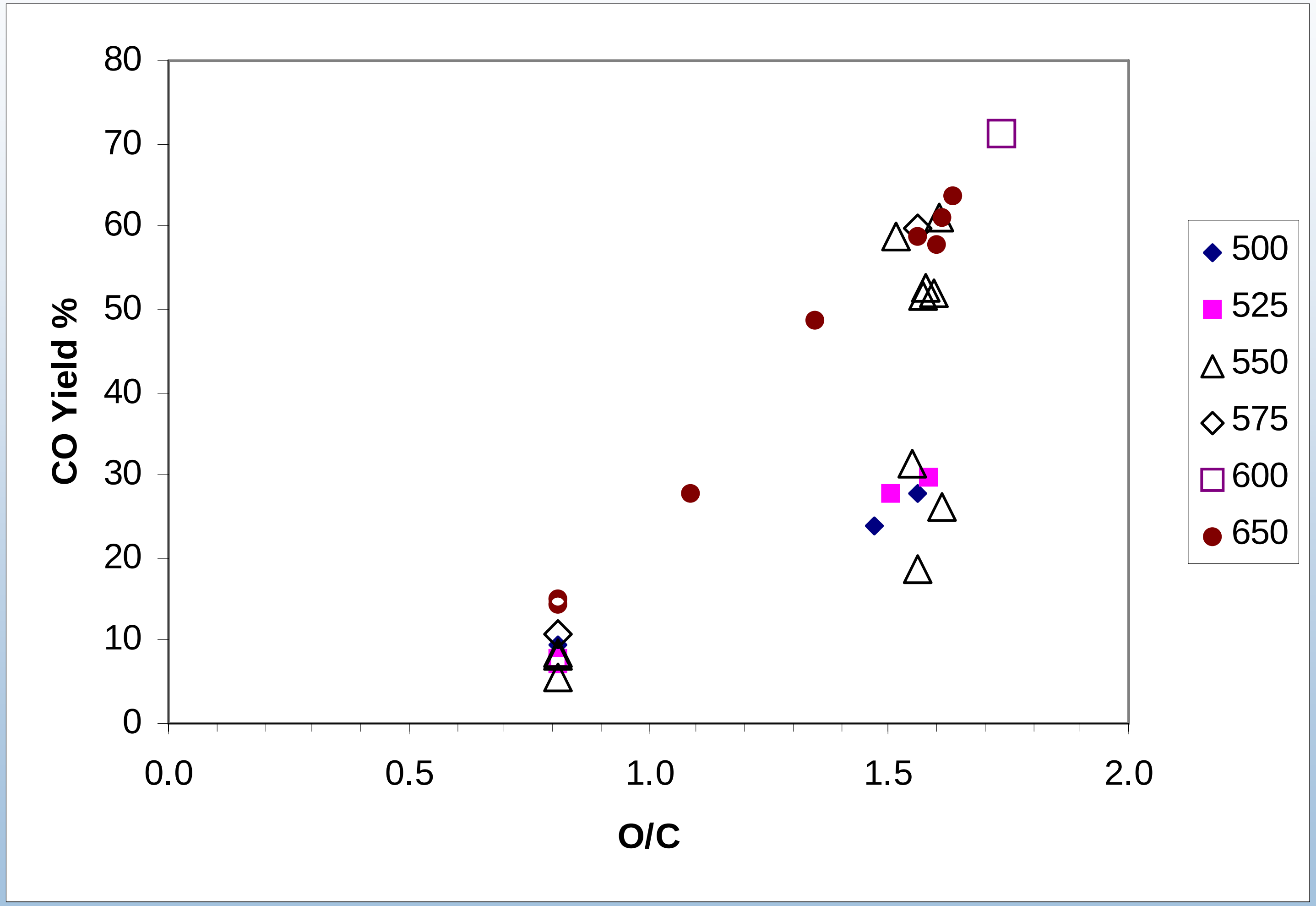
Carbon Conversion

Oxidative Cracking 0.5 s @ 650 C

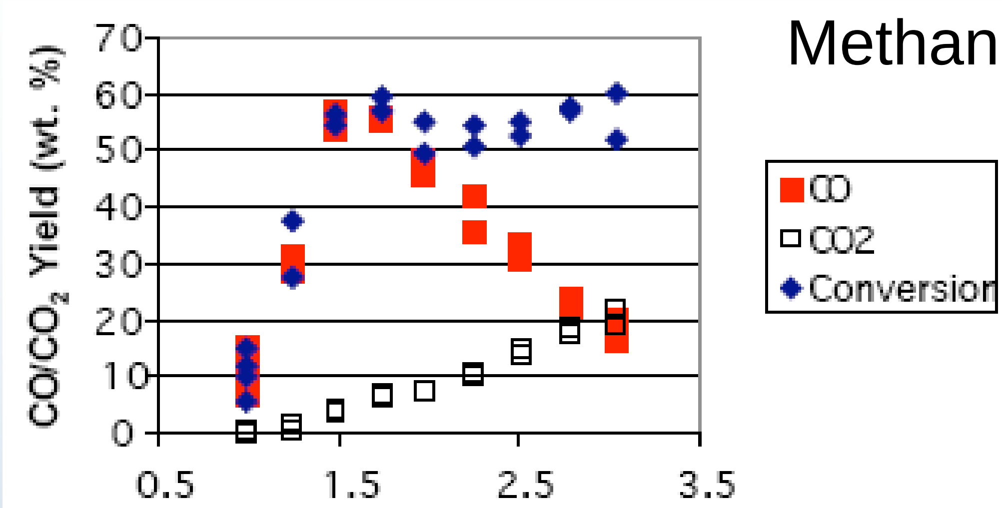


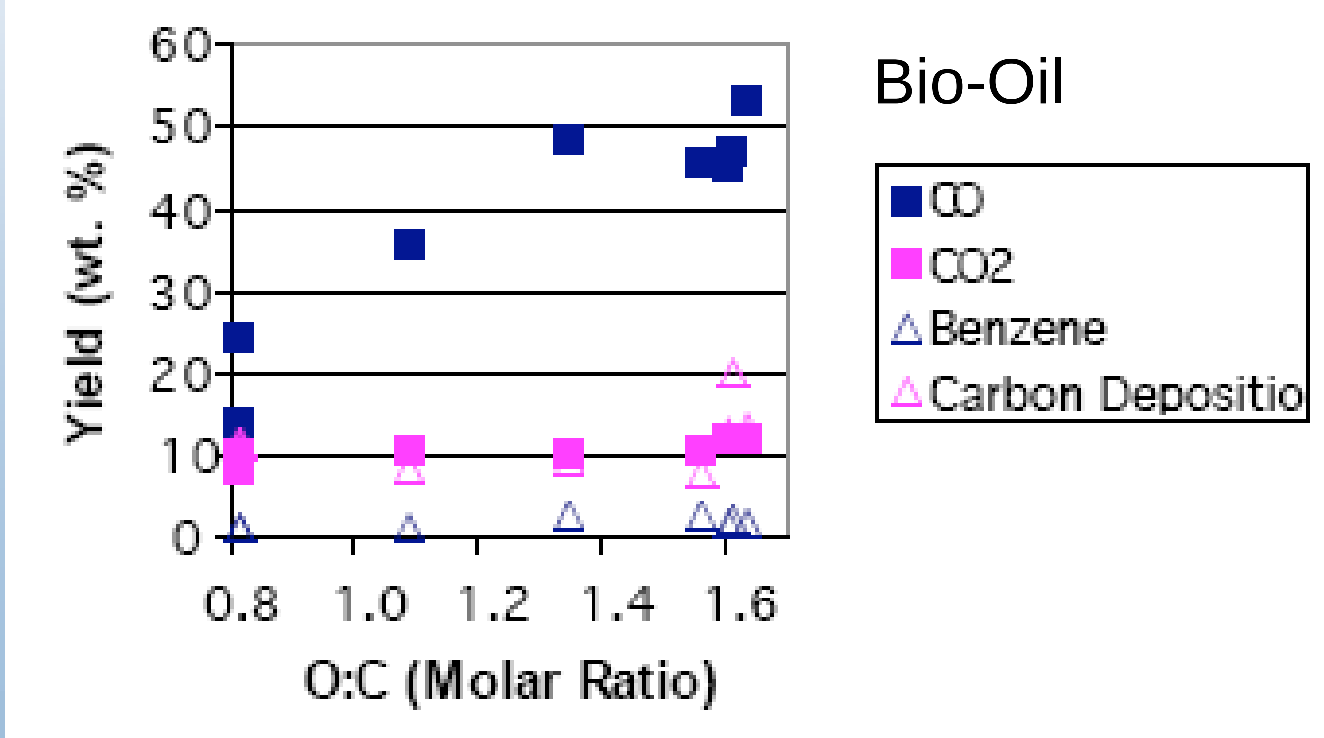
Carbon Conversion

Oxidative Cracking 0.5 s @ 500-650ºC



Oxidative Cracking - Methanol vs Bio-Oil

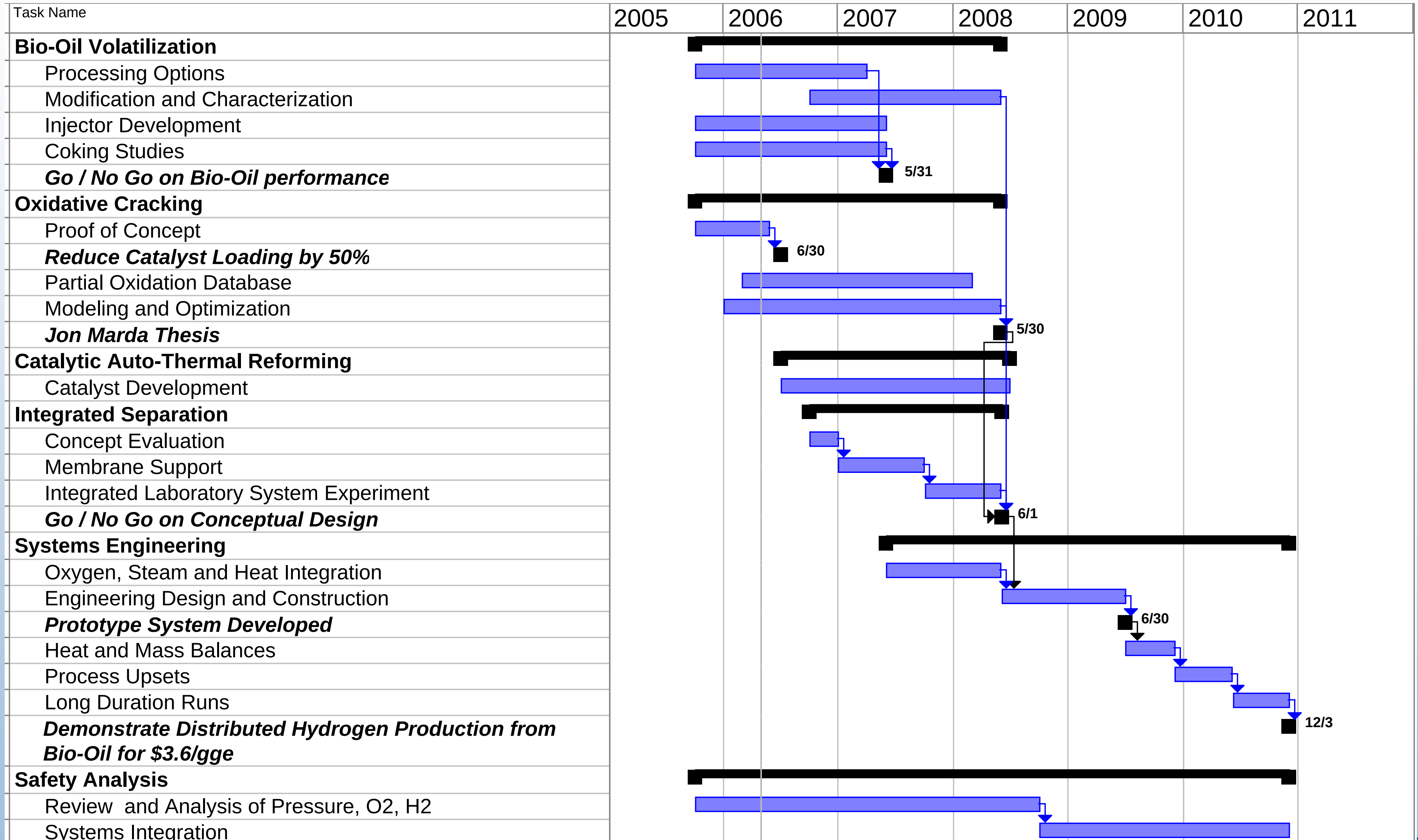




Process Comparison

	Fluid Bed	Staged
Bio-Oil Organics %	80	78
MeOH %	0	10
water,wt%	20	18
C	45	44.2
H	7.9	8.4
O	47.1	47.4
H/C	2.1	2.3
O/C	0.8	0.8
H2 production rate, kg/day	1500	1500
H2 Yield, wt%	11.9	11.9
Conversion efficiency,%	70	70
Bio-Oil Feed Rate, kg/hr	525	525
Feed C feed rate, kg/hr	236	232
O2 feed rate, kg/hr	0	246
Ratios with O2		
H/C(H2Ofree)	1.5	1.7
O/C(H2Ofree)	0.5	1.3
Starting H2O/C	0.30	0.27
H2O/C after Oxcrack	0.30	0.75
Water addition, Kg/hr	**1668**	**407**
Catalyst load, kg	**1734**	**430**
Temperature, C	**800**	**600**
Reactor diameter, M	1.03	0.31
Reactor height, M	6	5
Catalyst reactor volume, L	5029	372
Cracking reactor volume, L	0	130
Vaporizer, L	0	130
Total reactor volume, L	**5029**	**632**

Project Timeline



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	•Catalysis Integration in FY07 by working with DOE funded team

Technical Challenges

- Bio-Oil Volatilization
  - Management of residue
- Oxidative Homogeneous Cracking
  - High Reactivity but Unexpected Aromatics
- Catalyst System Design and Performance
- Carbon Deposit Removal and Catalyst Regeneration Management
- Process Energy Integration
- Integrated Hydrogen Separation

Complementary Projects

- Chevron Bio-oil Feedstock Effects
  - Bio-oils produced from a variety of feedstocks
  - Performance in staged auto-thermal reforming
  - Determine effect of major and trace constituents
- USDA/DOE Bioenergy Initiative
  - ISU, Cargill, NREL, ORNL, Eprida, USDA ARS
  - Corn Stover Pyrolysis for H2, NH3, Bio-carbon based soil amendments
  - NREL: Bio-oil characterization and reforming
- DOE Biomass Program
  - Bio-oil Stabilization and Derivatization