



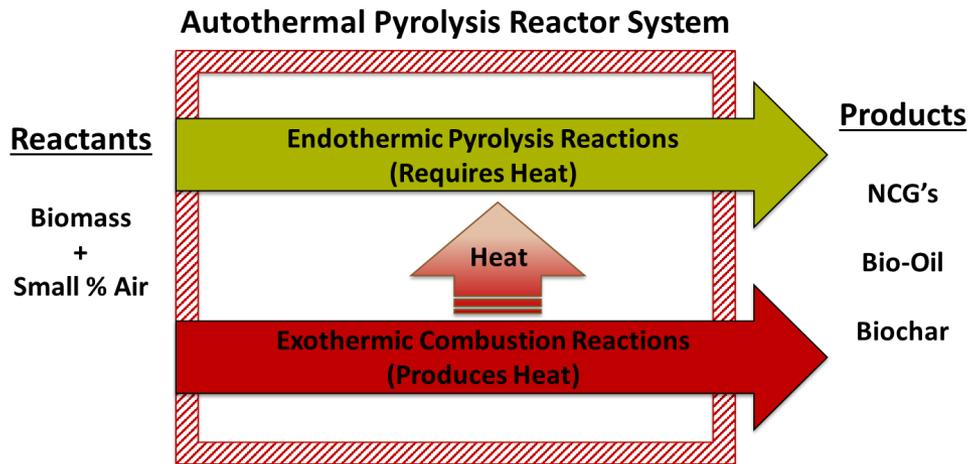
Deriving Kinetics of Autothermal Pyrolysis Partial Oxidation Reactions

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Autothermal Pyrolysis

Part of the pyrolysis products are oxidized to provide energy for endothermic pyrolysis reactions



- **Advantages**

- Heat transfer no longer the bottleneck

- **Challenge**

- Preserve organic yields of bio-oil under partial oxidative conditions

**Autothermal
Pyrolysis**

$$0.08 \leq \phi \leq 0.13$$

Gasification

$$0.20 \leq \phi \leq 0.35$$

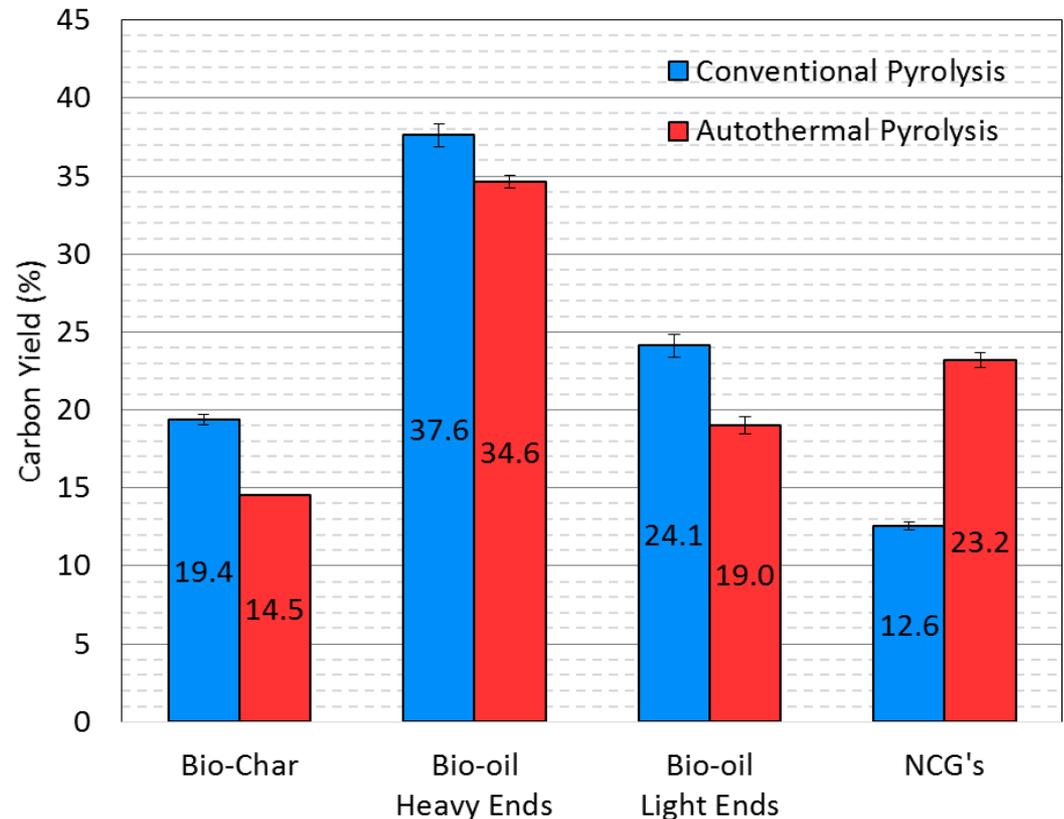
$$\phi = \frac{Air}{Air_{Stoich}}$$

Pyrolysis
 $\phi = 0.00$

Combustion
 $\phi > 1.0$

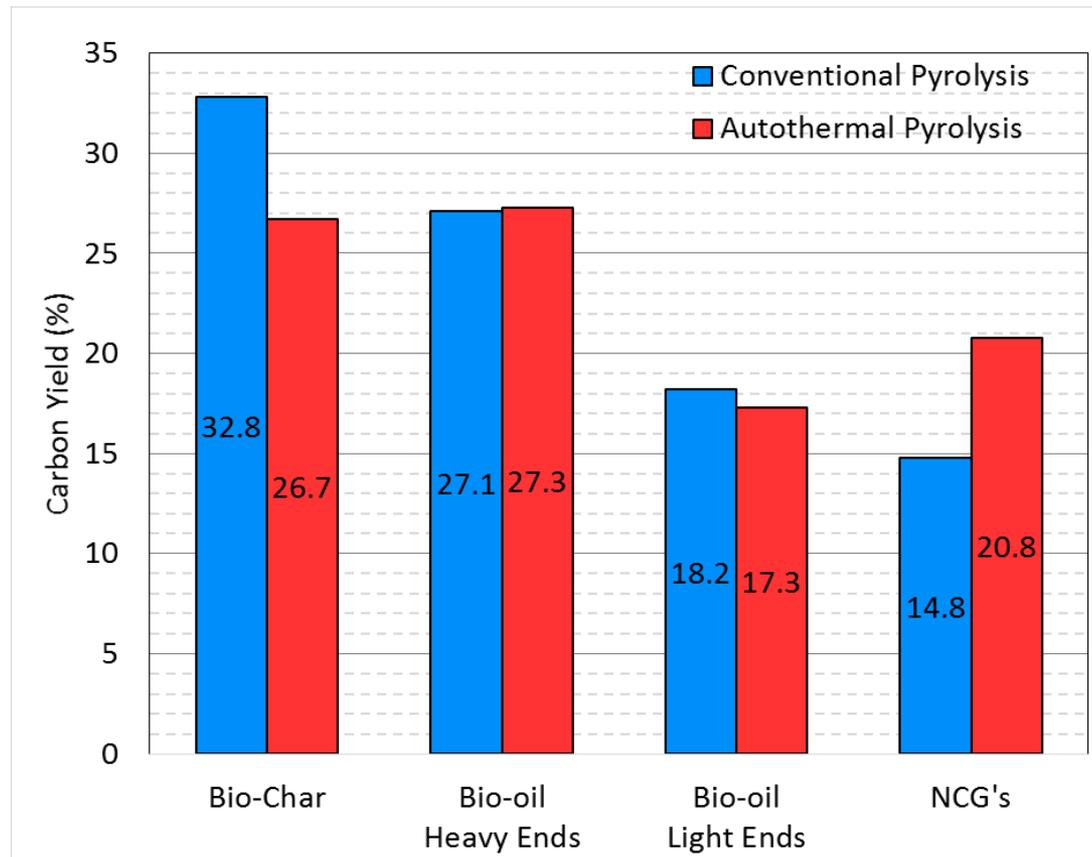
Partial oxidation primarily consumes aqueous phase and bio-char during autothermal pyrolysis (ATP) of red oak

- Heavy Ends
 - Decreased 3.0%
- Light Ends
 - Decreased 5.1%
- Total Bio-Oil Yield
 - (61.7% vs 53.6%)
- Bio-Char
 - Decreased 4.9%
- NCG's
 - Increased by 11.6%
- Equivalence Ratio: 0.1073



Corn stover carbon balance indicates char is primarily oxidized with bio-oil relatively unchanged

- Heavy Ends
 - Increased 0.2%
- Light Ends
 - Decreased 0.9%
- Total Bio-Oil Yield
 - (45.3% vs 44.6%)
- Bio-Char
 - Decreased 6.1%
- NCG's
 - Increased by 6.0%
- Equivalence Ratio: 0.068



Modeling Autothermal Pyrolysis

Determine underlying oxidation reactions in autothermal pyrolysis (ATP)

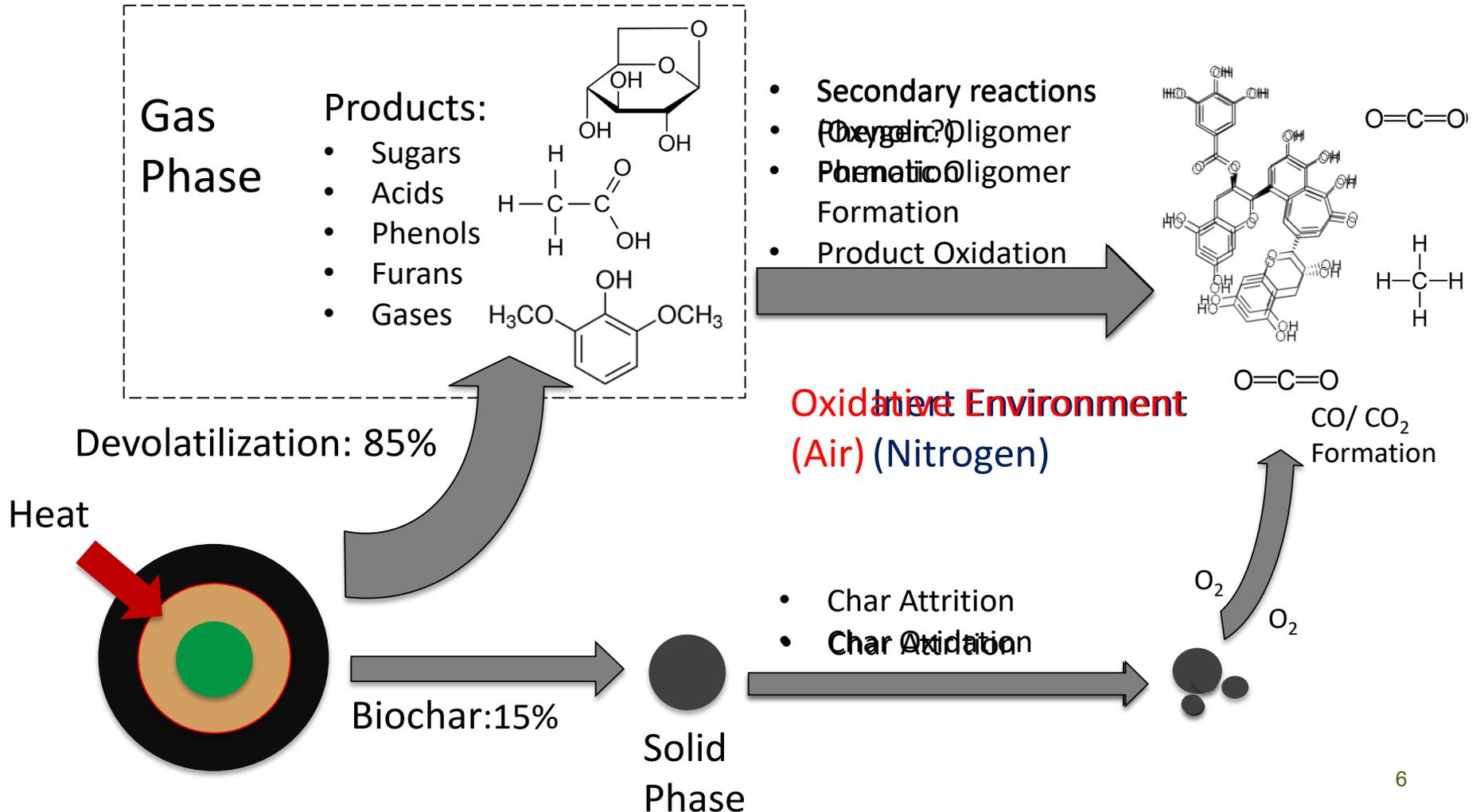
1. Gas-Solid Reactions

- Devolatilization of biomass (i.e. pyrolysis)
- Biochar oxidation (enthalpy for pyrolysis)

2. Gas Phase Reactions

- Oxidation of pyrolysis products (enthalpy for pyrolysis)
- Partial oxidation of products (phenolic oligomer formation)

Oxygen does not interact with solid biomass particle until fully devolatilized



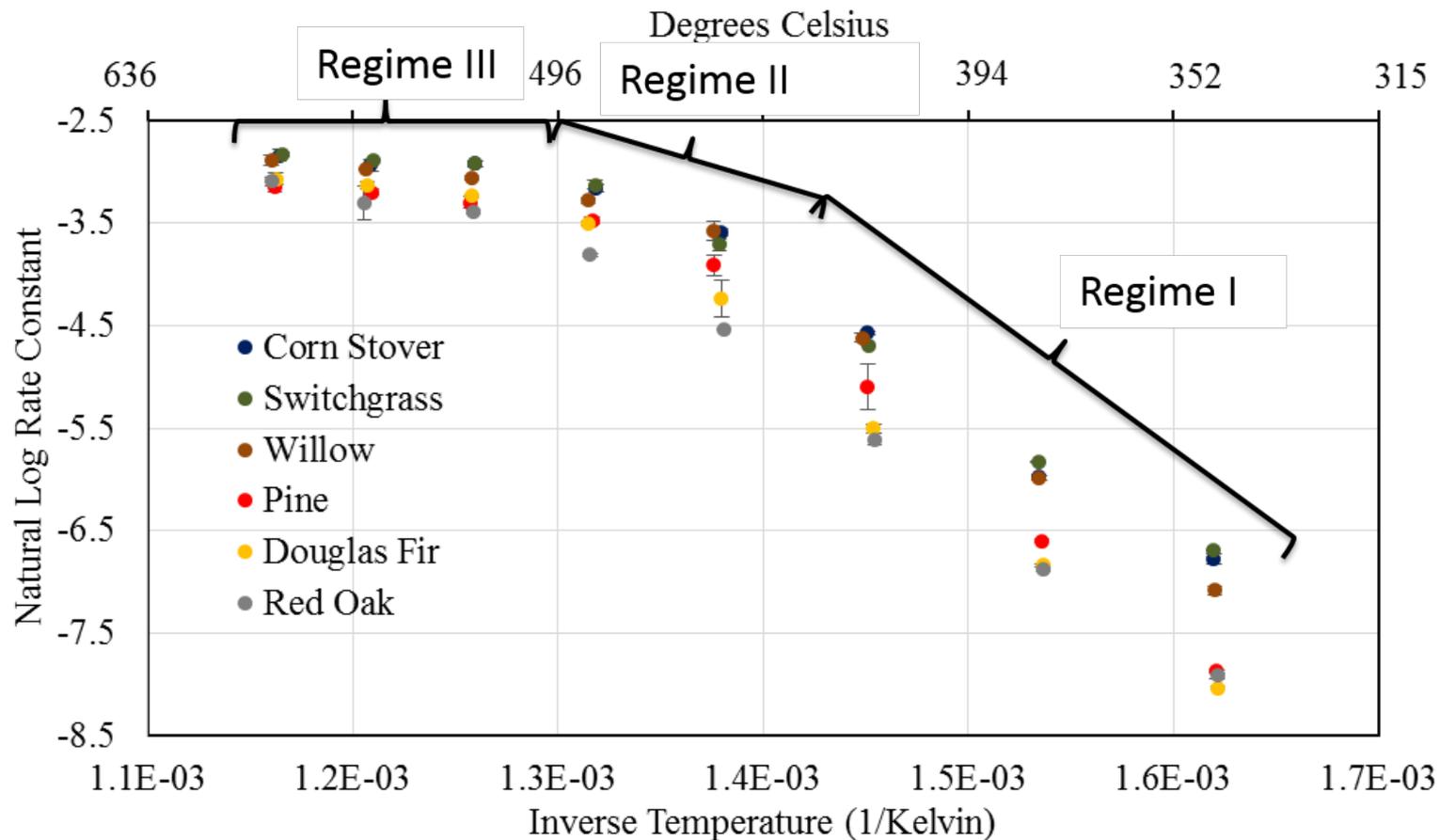
Char reaction kinetics were derived using TGA and fluidized bed experiments

1. Ramp to temperature under nitrogen with stabilization for 5-10 minutes (still nitrogen)
 - Drive off volatile products (~15wt%)
2. Switch sweep gas from nitrogen to air
3. Use mass loss to calculate rate constants
 - Simple Volumetric Model

Feedstock	Douglas Fir	Pine	Red Oak	Willow	Switchgrass	Corn Stover
Proximate Analysis	wt.% (as received)					
Fixed Carbon	62.01	62.00	56.25	48.69	42.44	35.88
Ash	3.91	5.94	6.39	13.31	24.45	30.59
Ultimate Analysis	wt.% (dry basis)					
Carbon	74.33	75.60	71.97	70.66	56.02	51.19

TGA results indicate a convergence of oxidation rates at elevated temperatures

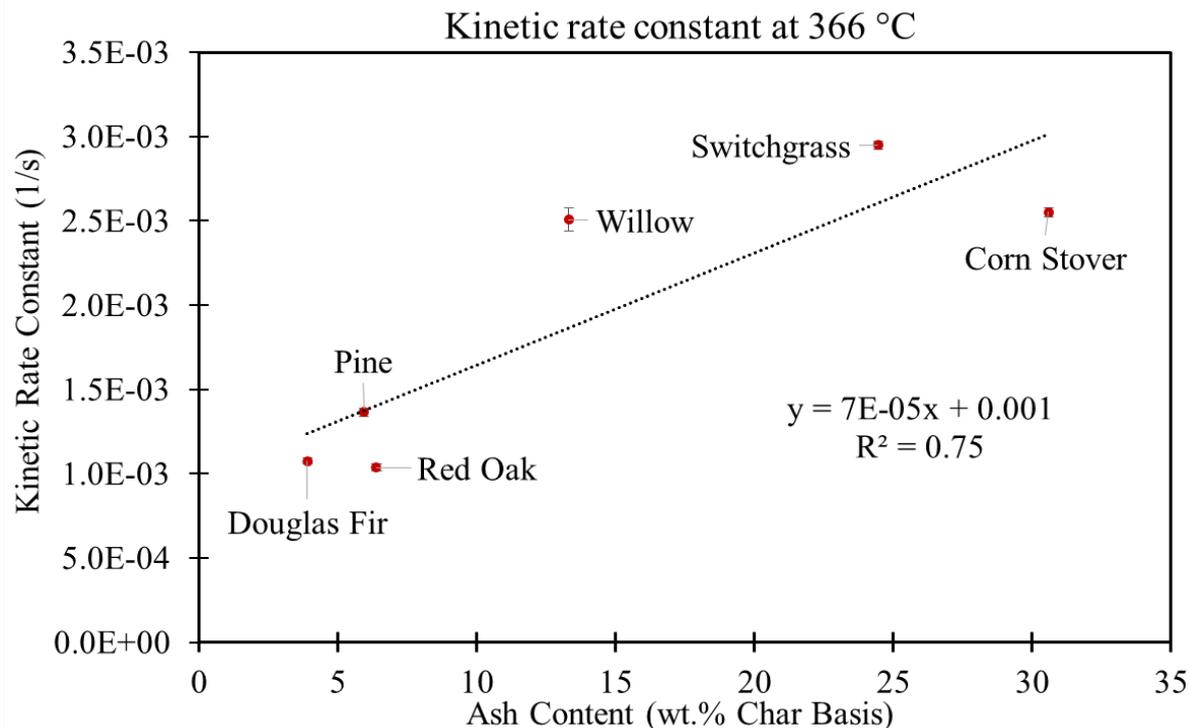
- Demonstrates that at pyrolysis temperatures (400-600 °C) biochar experiences all three regimes of combustion*



*Szekely, J., Evans, J. & Sohn, H. Y. Gas-Solid Reactions. (Academic Press, 1976)

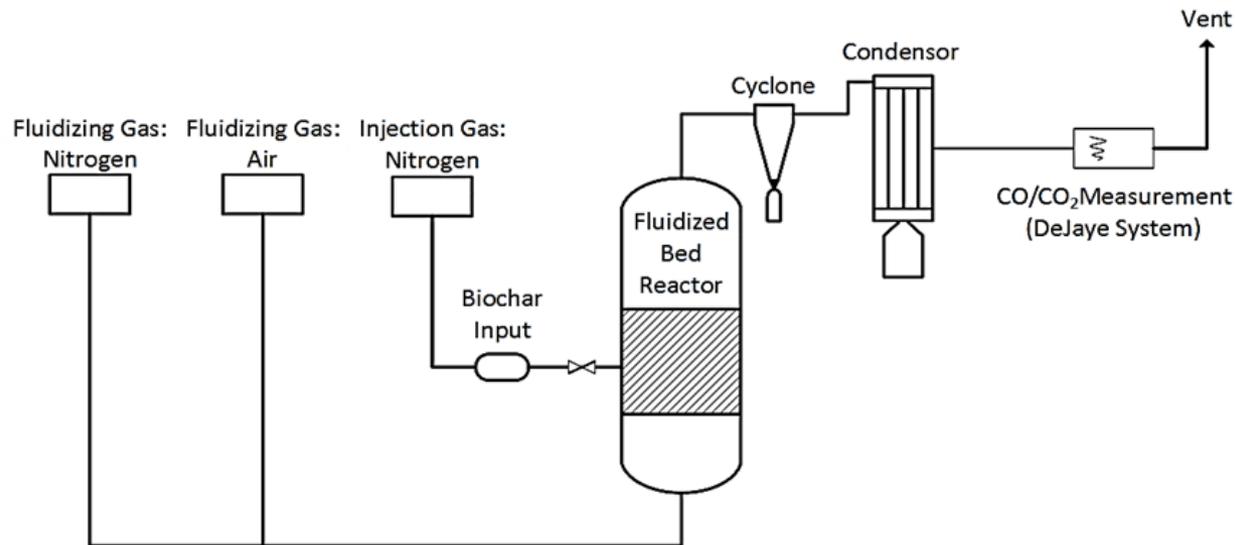
Kinetic rate correlates well with ash content in biochar under kinetically limited regime

- Higher ash chars have reaction rate $\sim x3$ higher than low ash char
- Modest correlation ($R^2 = 0.75$) indicates other factors likely impacting oxidation

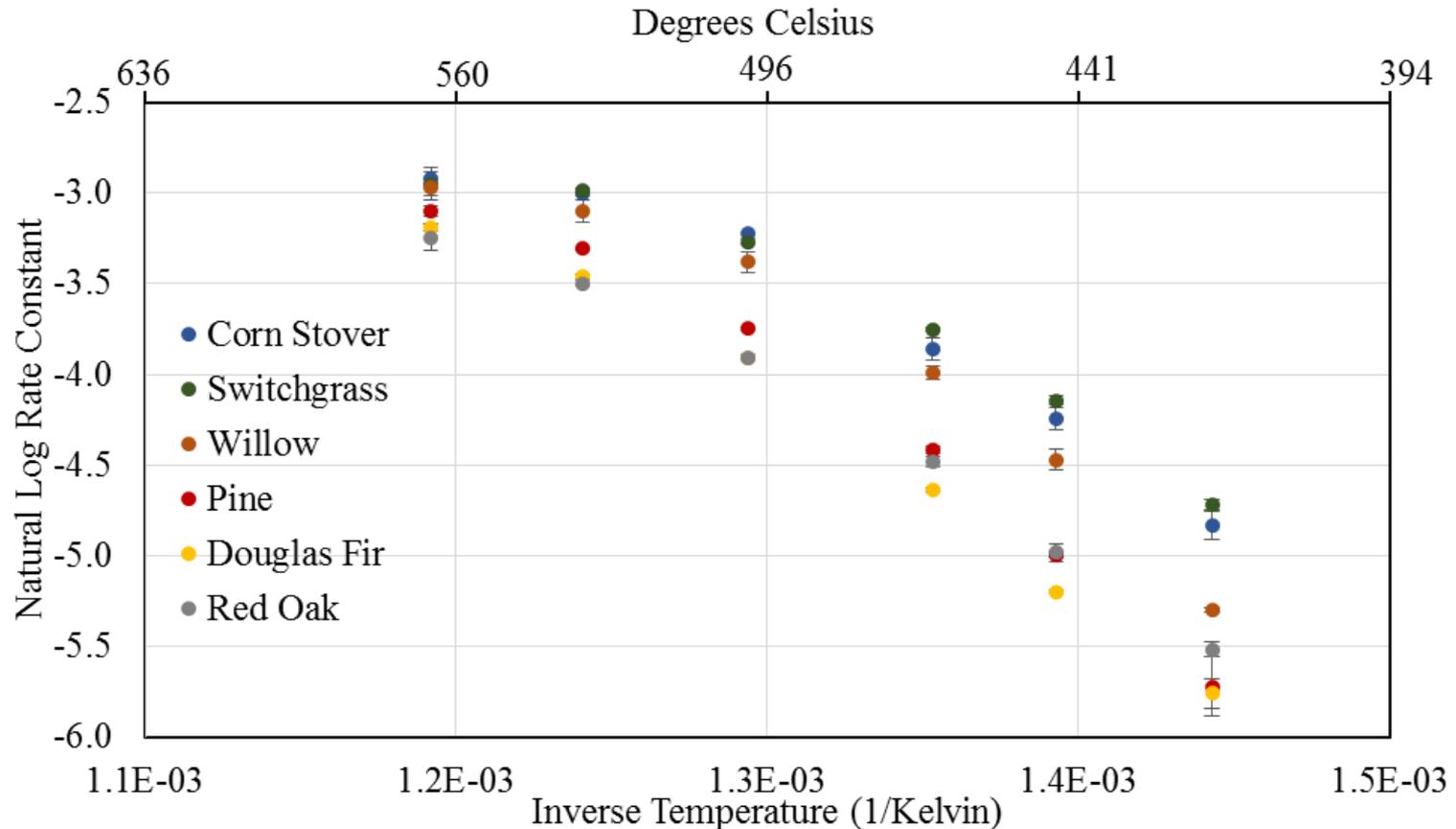


Fluidized bed allows for isothermal oxidation tests of sieved biochar

- Fluidized bed operated at near isothermal conditions
 - Fluidize with 3.5 SLPM air
 - Pneumatically inject 100 milligrams of sieved (600-850 micron) biochar
- DeJaye System measured CO/CO₂ every second allowing for transient combustion experiments
- Reactor kept isothermal at six temperatures to derive reaction kinetics

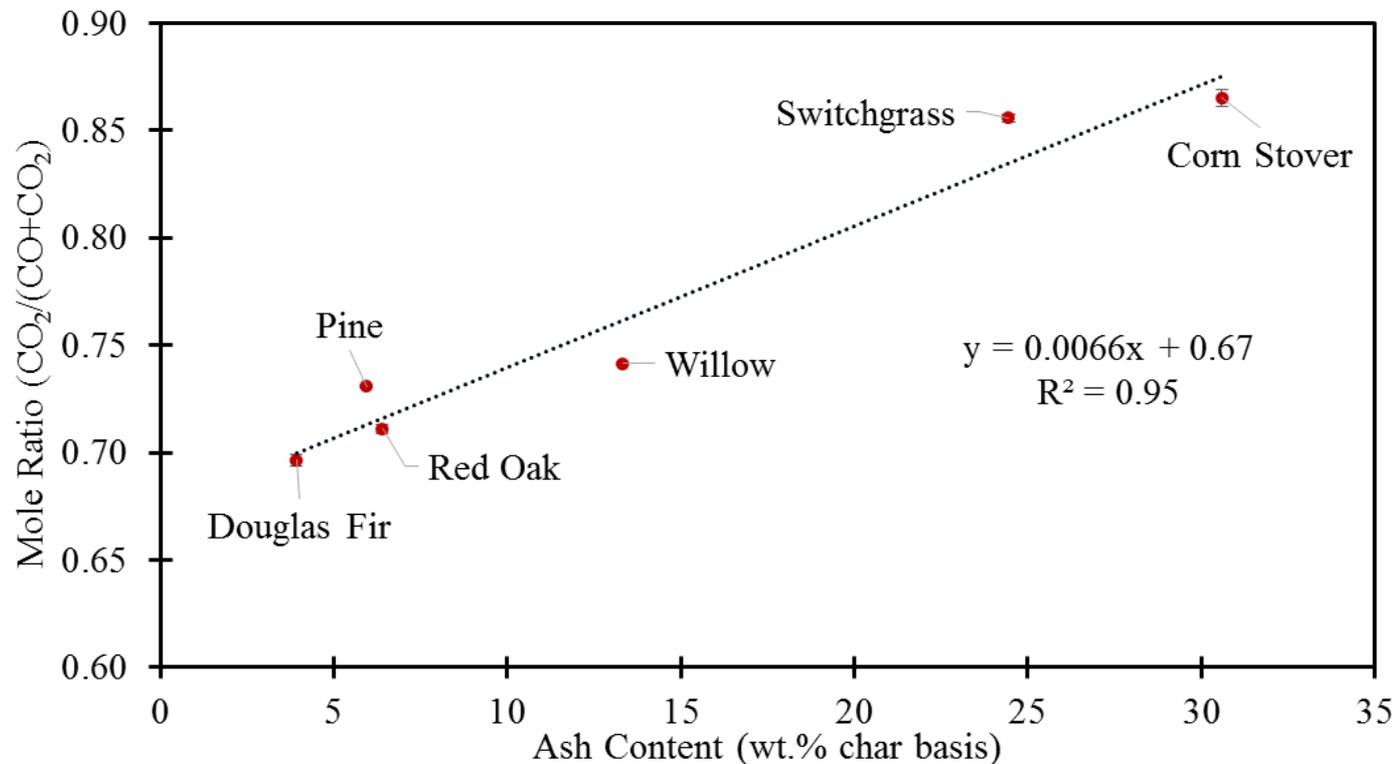


Fluidized bed results have a similar Arrhenius plot to TGA experiments with a convergence in rates at higher temperatures



CO₂ formation had a strong correlation with inorganic content in biochar

- Ash content and inorganic sites can promote CO₂ formation*



*Dupont, C. *et al.* How inorganic elements of biomass influence char steam gasification kinetics. *Energy* **109**, 430–435 (2016).

Faster kinetic rate and higher CO₂ formation supports experimental work with autothermal pyrolysis of corn stover and red oak

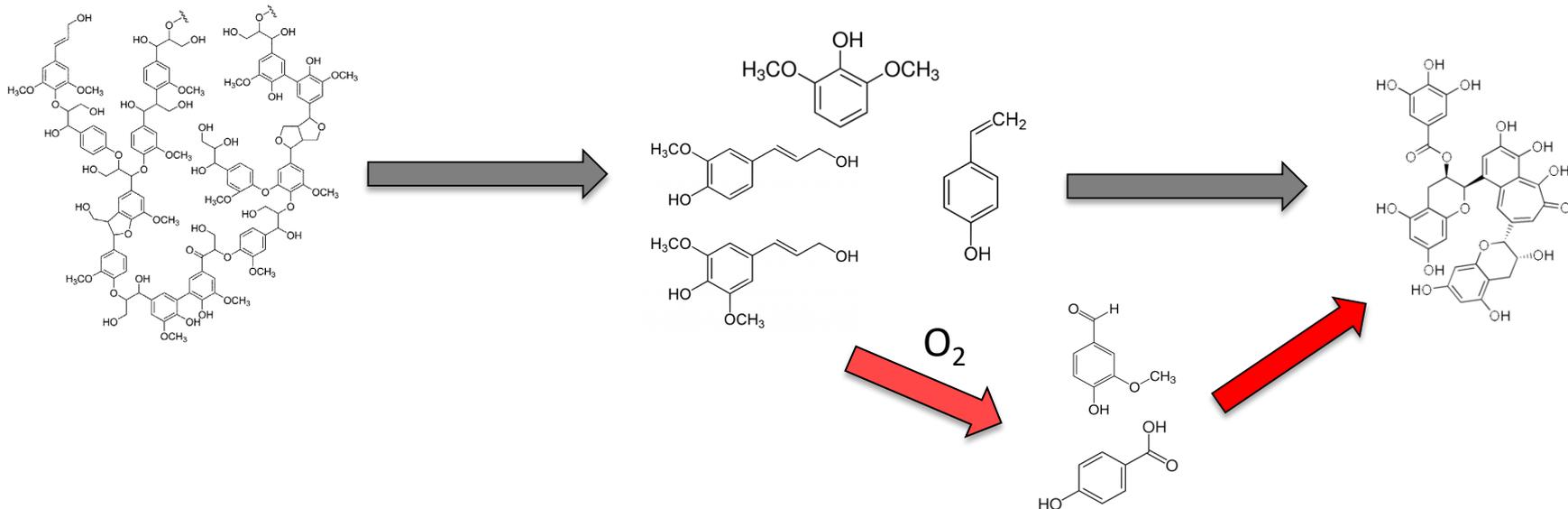
- 1M HCl washed chars reduced CO₂ formation at 500 °C
- CO₂ formation agrees with previous correlation (predicted 0 wt.% ash would have 0.67 CO₂ formation-'y intercept')

Feedstock	Mole Ratio CO ₂ /(CO+CO ₂)		Percent Change
	Unwashed	HCl Washed	
Corn Stover	0.87	0.68	-22.0%
Switchgrass	0.86	0.66	-23.1%
Red Oak	0.71	0.62	-12.2%

- Char oxidation studies support autothermal pyrolysis observations
 - Oxidation to CO₂ would release more energy than CO oxidation (-393 kJ/mol vs -110 kJ/mol)
 - Char would be preferentially consumed in autothermal pyrolysis of corn stover (faster kinetic rate)
 - Higher CO₂ formation would release more energy per mole of oxygen
 - Explains difference in equivalence ratios (0.107 red oak vs 0.067 corn stover)

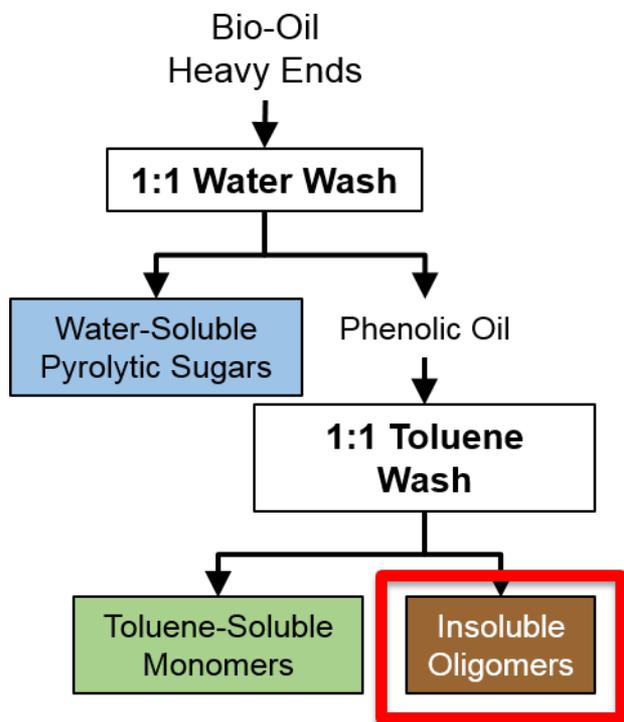
Partial oxidation of lignin derived phenolic compounds during autothermal pyrolysis

- Phenolic oligomers form during biomass fast pyrolysis through recombination/condensation of phenolic monomers^{1,2}

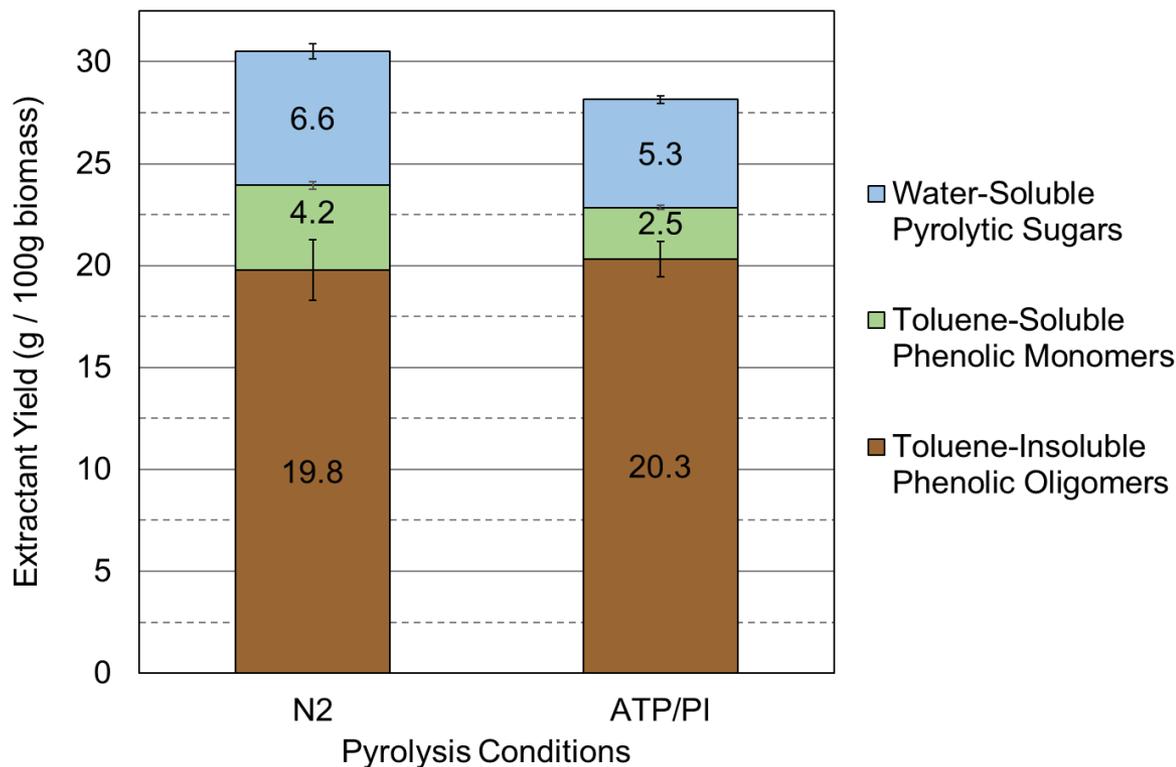


- Partial oxidation of $-OH$ groups would result in higher concentration of carbonyl groups³

Red Oak phenolic oligomers appear to be least sensitive to partial oxidation conditions



Liquid-Liquid Extractions of Bio-Oil Heavy Ends



³¹P NMR and ¹³C NMR of phenolic oligomers measured detectable amount of oxidation

- ³¹P NMR measured a 11% relative decrease in hydroxyl groups on a phenolic oligomer basis

	δ (ppm)	Phenolic -OH, mmol g PO ⁻¹	
		Non-Oxidative	Oxidative
Aliphatic-OH	150.0-145.5	1.28	1.31
C5 substituted β -5	144.7-142.8	1.20	1.04
Condensed 4-O-5	142.8-141.7	0.74	0.65
Phenolic OH 5-5	141.7-140.2	0.33	0.30
Guaiacyl phenolic OH	140.2-139.0	1.02	0.88
Catechol type OH	139.0-138.2	0.73	0.57
P-hydroxyl-phenyl OH	138.2-137.3	0.30	0.23
Acid-OH	136.6-133.6	0.27	0.26
Summation		5.87	5.24

- ¹³C NMR measured noticeable increase in carbonyls with autothermal produced phenolic oligomers

	δ (ppm)	% of Carbon Bonds	
		Non-Oxidative	Oxidative
Carbonyl	215.0-166.5	2.68	3.06
Aromatic C-O Bond	166.5-142.0	17.30	19.25
Aromatic C-C	142.0-125.0	39.49	36.20
Aromatic C-H	125.0-95.8	13.18	14.05
Aliphatic C-O	95.8-60.8	2.90	2.89
Methoxly-Aromatic	60.8-55.2	15.43	16.37
Aliphatic C-C	55.2-0.0	9.02	8.18

Conclusions and Future Work

Conclusions

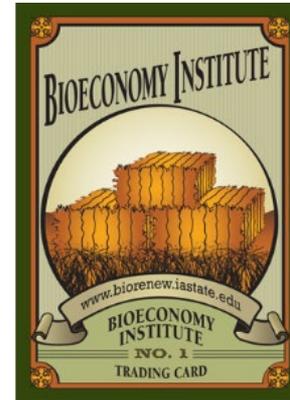
- Ash content an important parameter when modeling char oxidation under autothermal conditions
 - Increases reaction rate and enhances CO₂ formation
- Analysis of phenolic oligomers suggests subtle but detectable amount of oxidation during autothermal pyrolysis
 - Increase in carbonyls and decrease in total hydroxyl groups indicates oxidation

Future Work

- Improvement of gas phase kinetics
 - Current reaction mechanism have limited validation at autothermal pyrolysis conditions

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 - NREL and ORNL
 - AICHE Rapid Institute

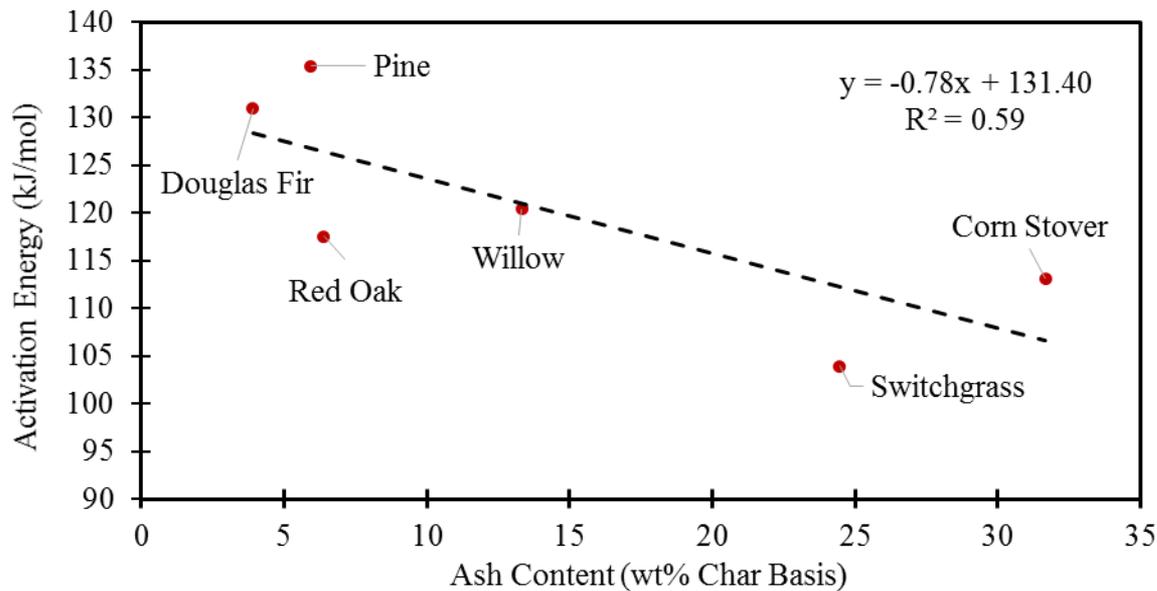


Questions?

Supplemental Slides

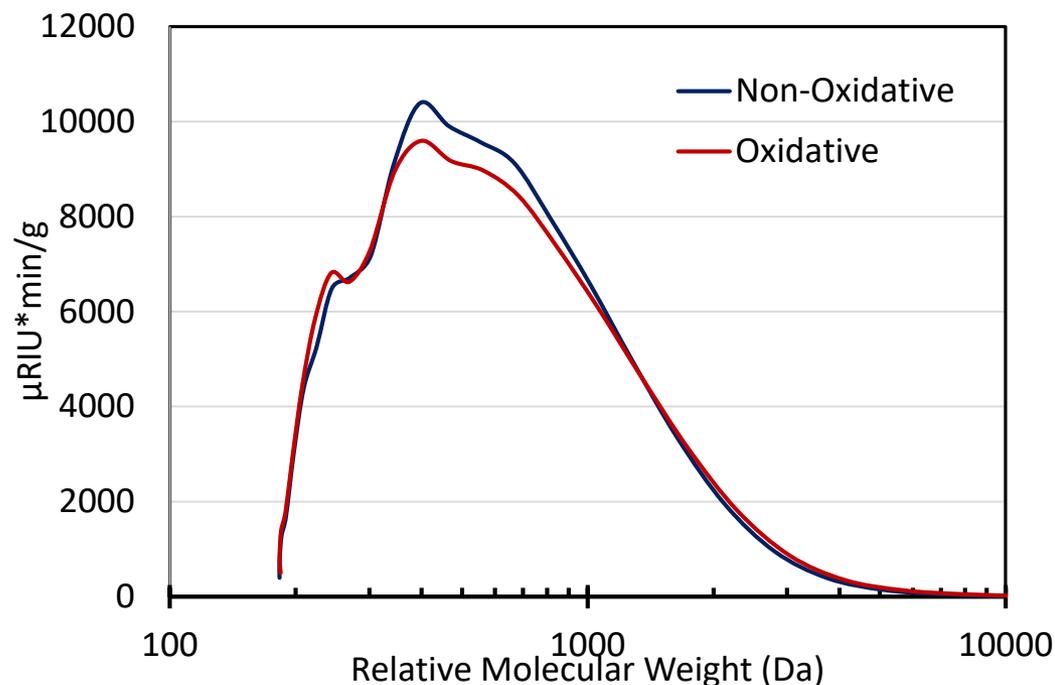
Activation Energy and Pre-Exponential Factors

Feedstock	Pre-Exponential Factor (1/s)	Activation Energy (kJ/mol)
Douglas Fir	3.76E+07	131
Pine	1.08E+08	135
Red Oak	3.12E+06	118
Willow	1.24E+07	120
Switchgrass	7.09E+05	104
Corn Stover	3.75E+06	113



GPC of phenolic oligomers showed no discernable difference between operating conditions

- Molecular weight was nearly identical between the autothermal and conventionally produced phenolic oligomers
- Suggest limited oxidative environment neither inhibits nor promotes polymerization reactions



Pyrolysis Condition	M_w (Da)	M_n (Da)	Dispersity Index (M_w/M_n)
Non-Oxidative	595	390	1.52
Oxidative	591	378	1.56