



United States  
Department of  
Agriculture

National Institute  
of Food and  
Agriculture



# Mid-Atlantic Sustainable Biomass for Value-added Products Consortium MASBio – Bimonthly Update

## Task Group 3: Value-Added Biomass Products August 9, 2022

A USDA NIFA Funded Grant Project No. 2020-68012-31881



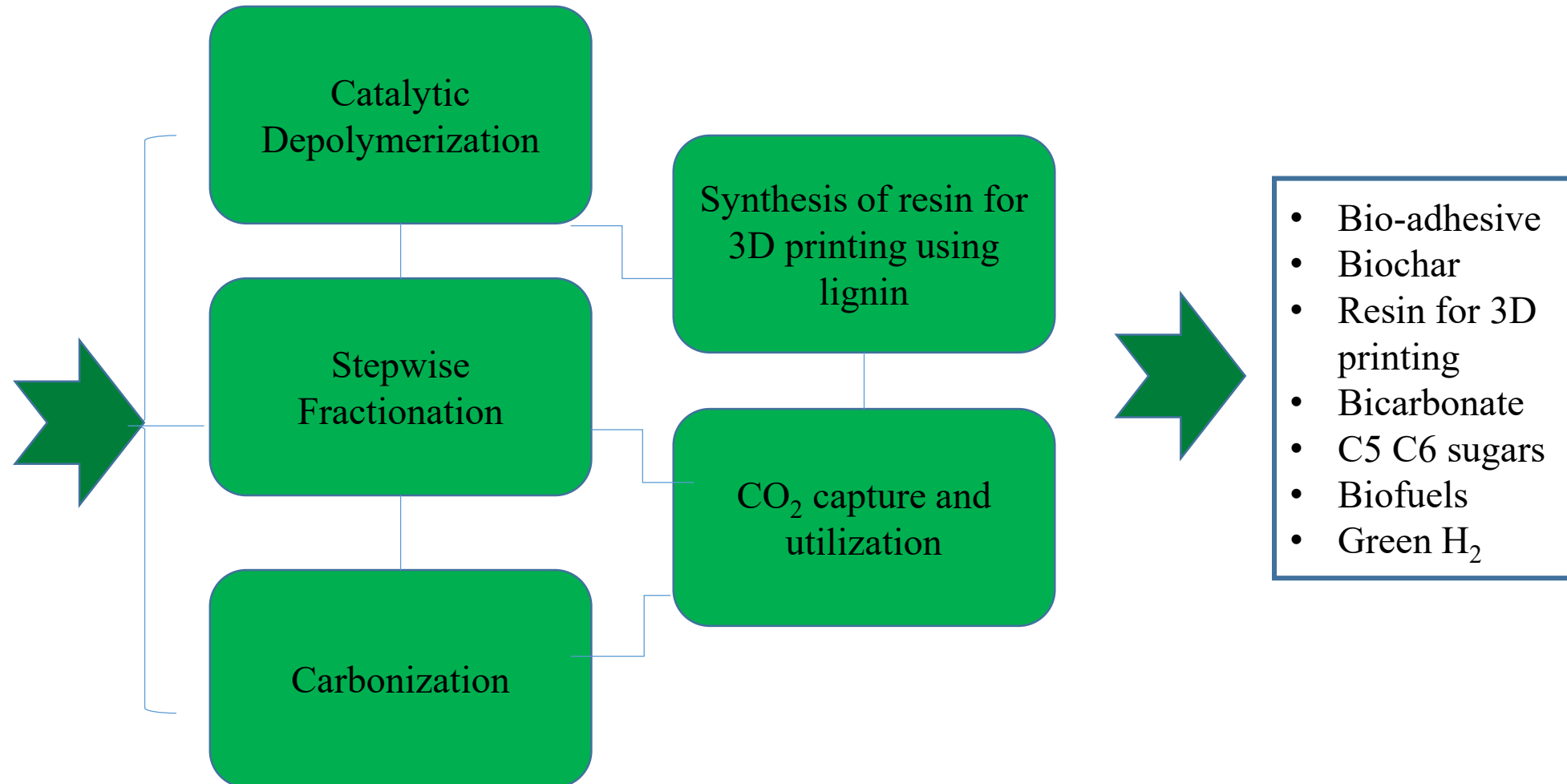
PennState



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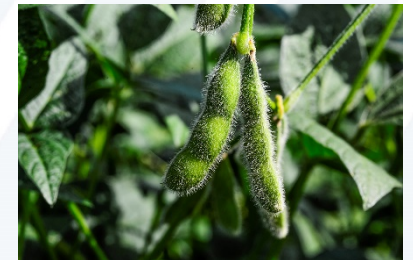
# TG3 Process Flow Diagram



TG3 provides process data to TG5 for LCA and TEA

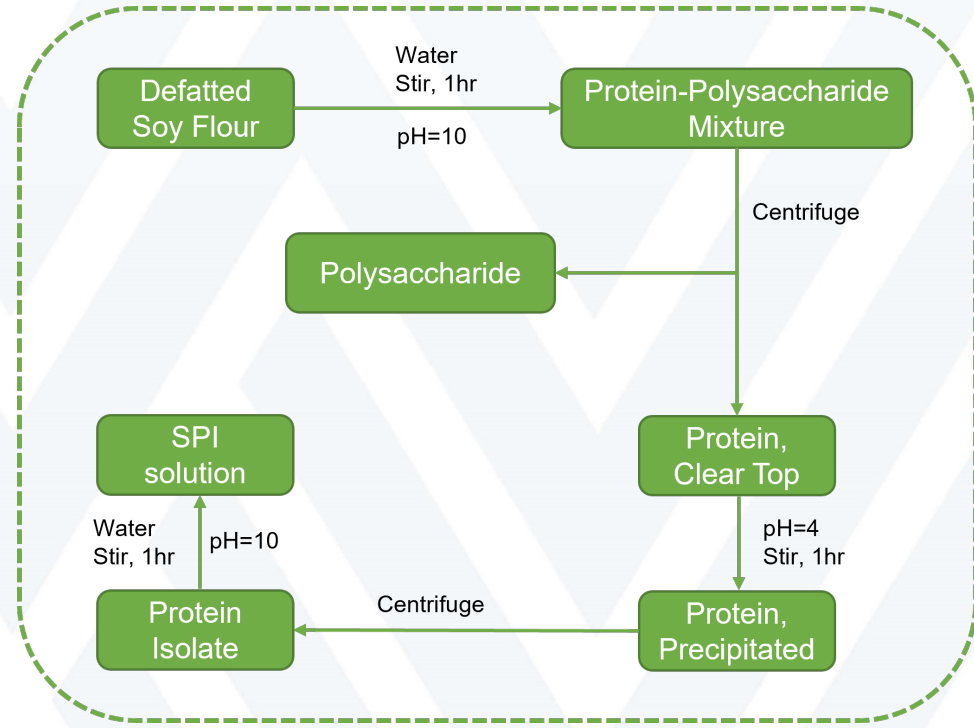
# Bio-adhesive: Research Background

- ❖ Concerns over formaldehyde release from aldehyde-based adhesives
- ❖ Renewable and degradable biobased adhesive from biomass
- ❖ Utilizing abundant lignin residue from forest product industry
- ❖ Challenges being improvements of dispersion, water resistance, and bonding strength



# Soy Protein Isolate and Soy Protein Adhesive

- ❖ Defatted soy flour has ~51% soy protein
- ❖ Soy protein isolate (SPI) can be extracted using the pictured process
- ❖ SPI can be further dissolved to prepare SPI adhesive
- ❖ The adhesive system is water-based and formaldehyde-free

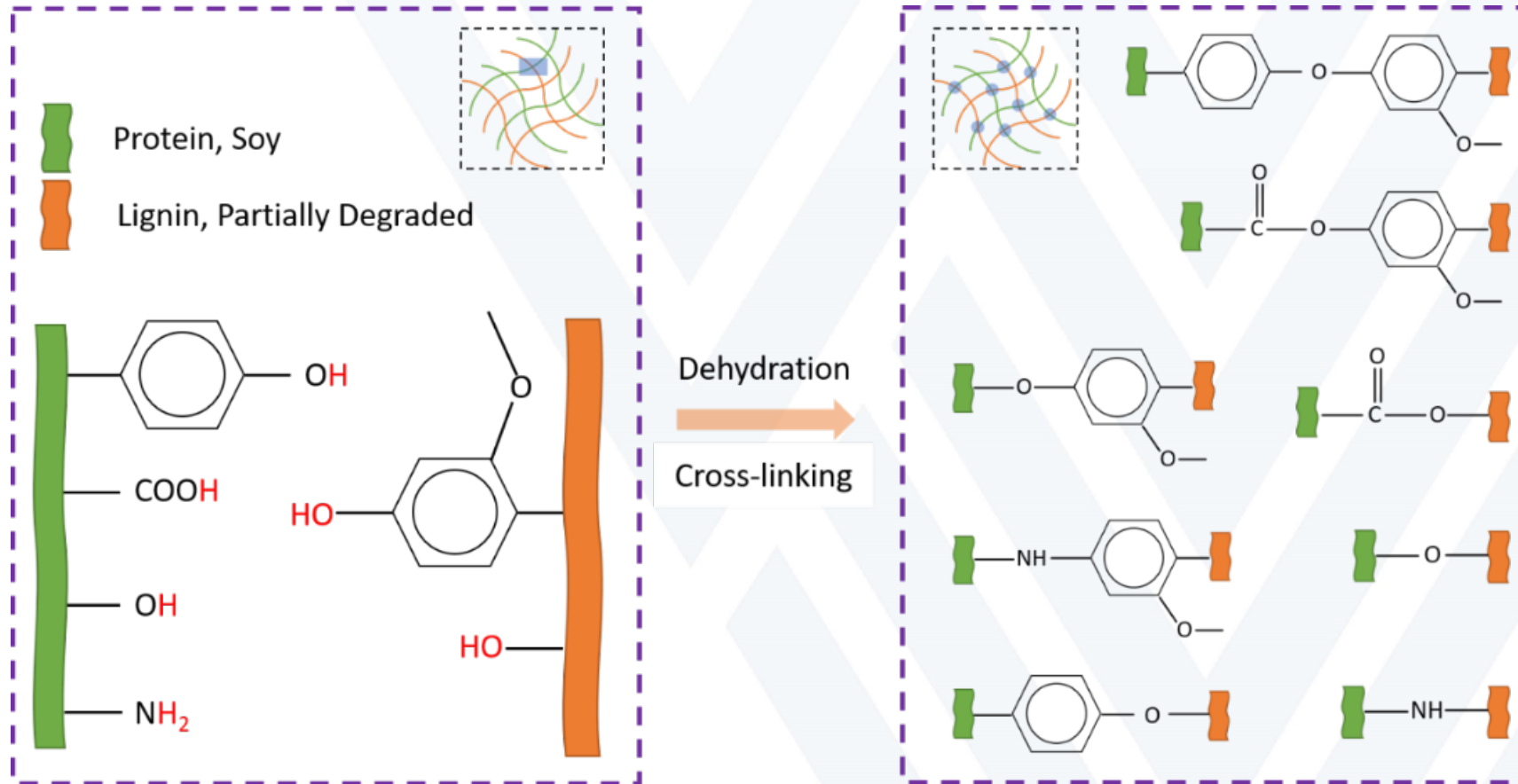


Extraction of SPI



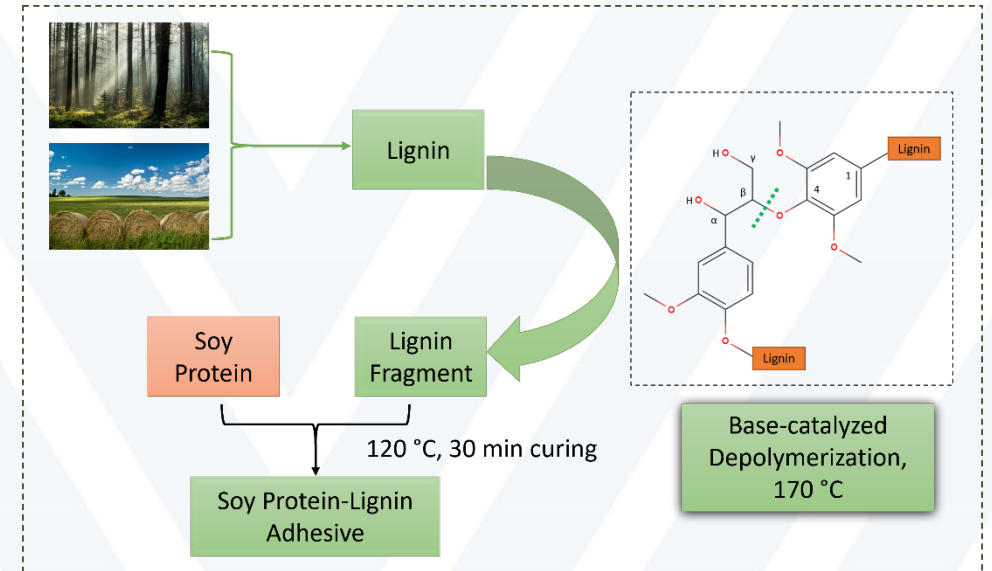
SPI adhesive

# The Reaction Mechanism of Bio-Adhesive



# Lignin Fragments and Soy Protein-Lignin Adhesive

- ❖ Commercial kraft lignin was used to produce partially degraded lignin and resulted bio-adhesive.
- ❖ Mild base-catalyzed depolymerization at 140-200 °C were adopted [1].
- ❖ Lignin derived from biomass was also proven in lab as a similar candidate to prepare bio-adhesive



Autoclave reactor



SPI, Lignin fragment, Bio-adhesive



Lignin extraction for 2 hr at 140 °C



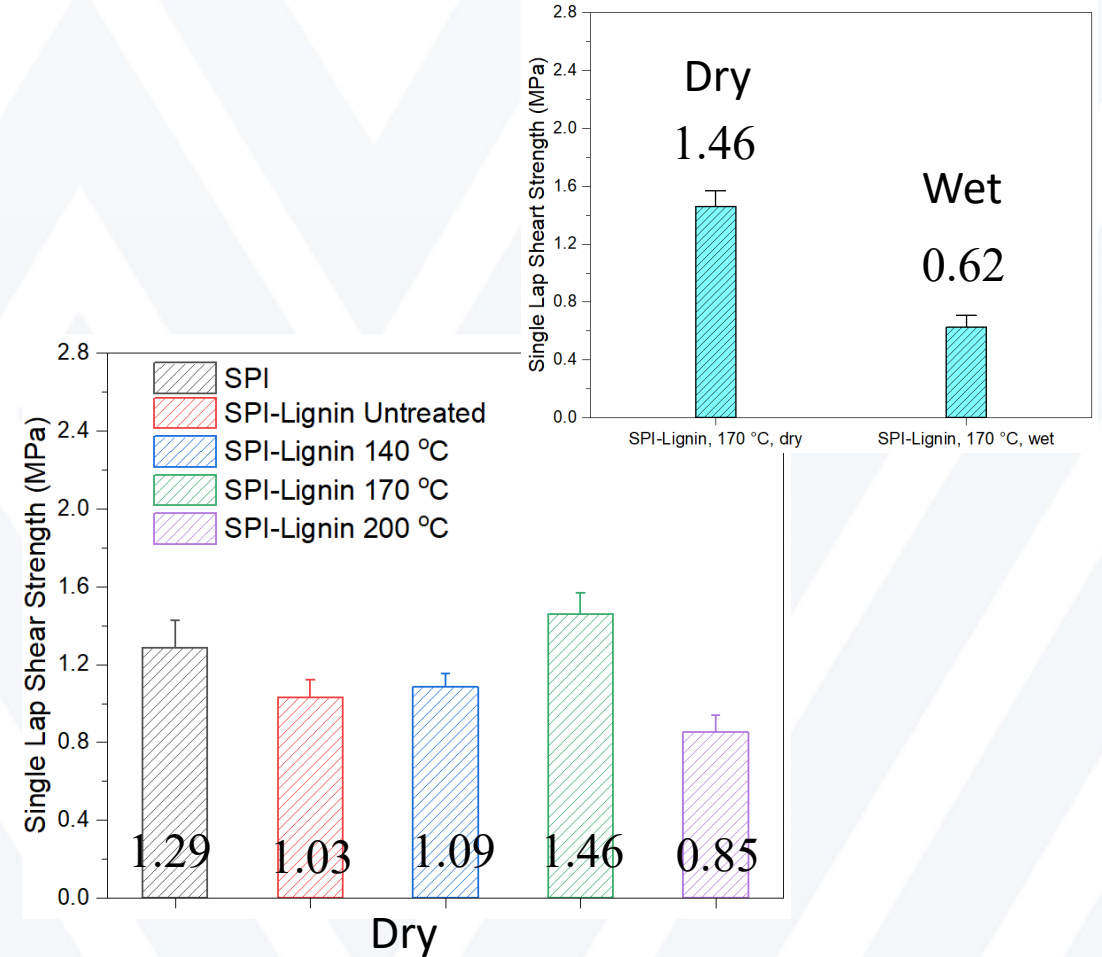
Lignin extraction for 18 hr at 140 °C



Bio-adhesive with lignin extracted from biomass

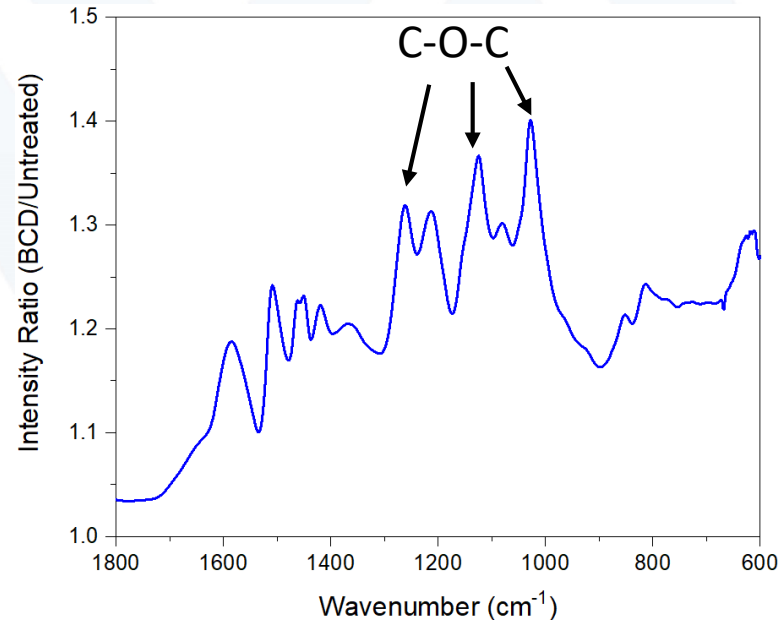
# Bonding Strength: Single Lap Shear Test

- ❖ High lignin loading, ~50 wt.%. Each adhesive was repeated five times for single lap shear strength
- ❖ It is speculated that lignin oligomers formed at 170 °C has the best crosslinking performance with soy protein isolate. The resultant adhesive SPI-D-Lignin has a higher strength than SPI adhesive.
- ❖ Lignin fragments resulted from higher temperatures might decrease the bonding strength
- ❖ Wet strength test: samples were soaked in water for 3 hr at room temperature before test.

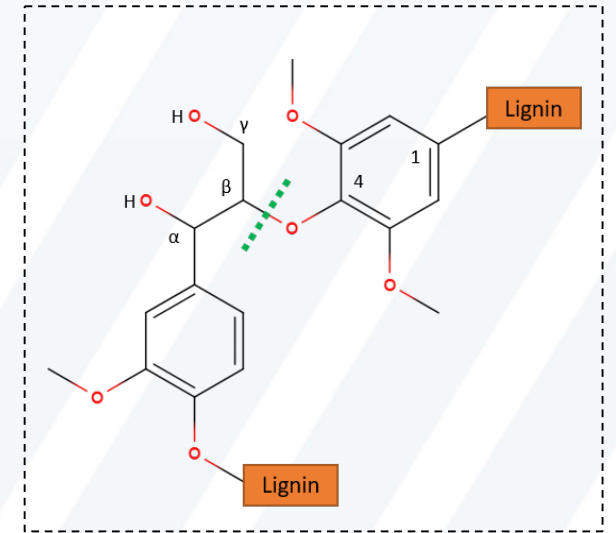


# FTIR Characterization: Degraded Lignin vs Untreated Lignin

- ❖ Transmittance Intensity of C-O-C was visibly changed by observing peaks at 1028, 1214, and 1261  $\text{cm}^{-1}$
- ❖ Direct evidence of cleavage of  $\beta$ -O-4 ether taking place during depolymerization.



FTIR Transmittance Ratio:  
D-lignin/untreated lignin

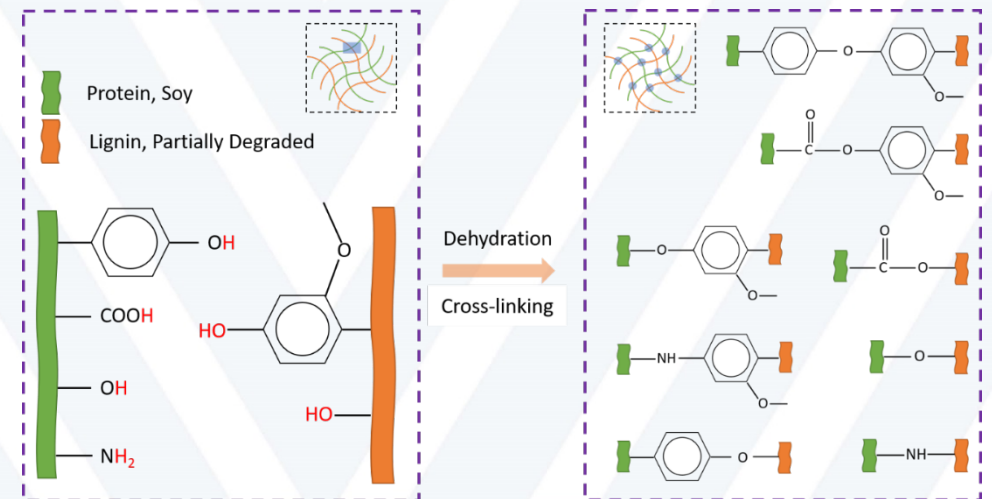
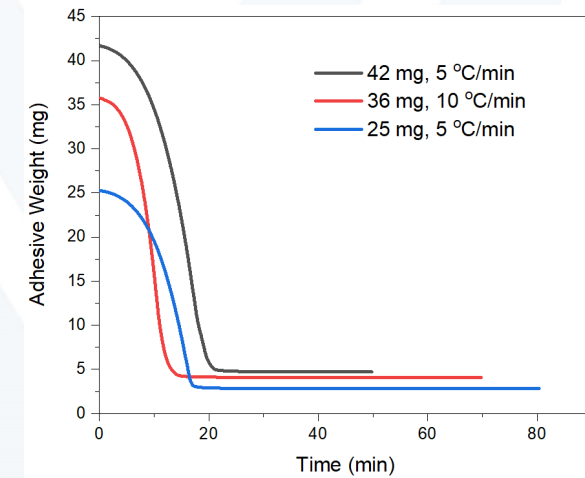


Main reaction for lignin  
depolymerization: cleavage of  
 $\beta$ -O-4 ether



# Curing of Adhesive and Possible Reactions

- ❖ Adhesive is observed to be cured within 25 mins.
- ❖ Measured solid contents is ~11.5%.
- ❖ Possible curing reactions of adhesive: dehydration (ether or ester) and secondary amine forming reactions.



# Lignin comparison

Values in mmol OH per g lignin

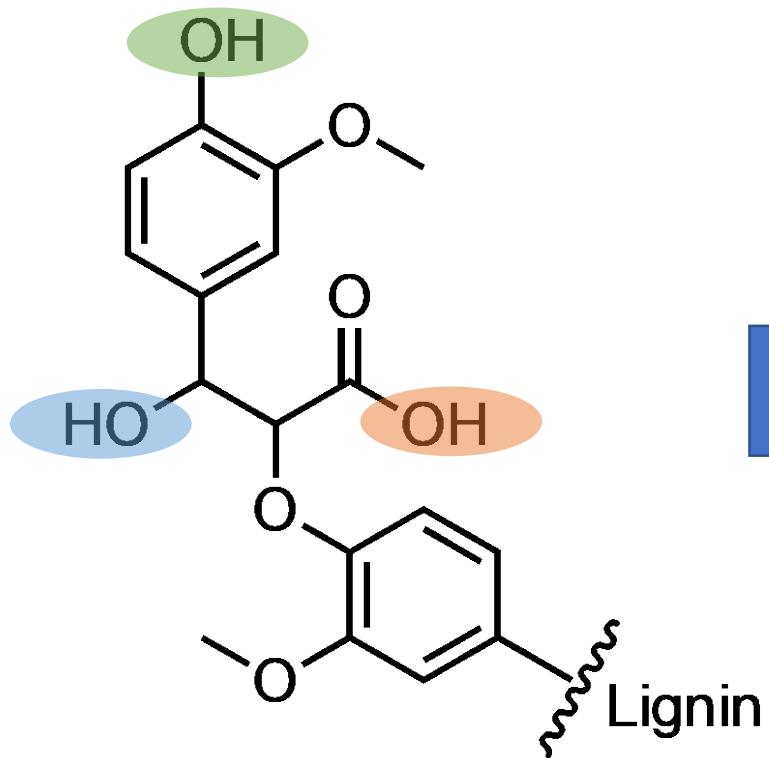
Functional group	Kraft lignin	Hu lignin
Aliphatic OH	3.04	3.64
S-type aromatic	1.46	9.40
G-type aromatic	2.67	8.90
H-type aromatic	0.33	1.27
carboxylic acid	0.48	0.65

The increase in Aliphatic -OH content indicate the high adhesion strength when bonded with protein

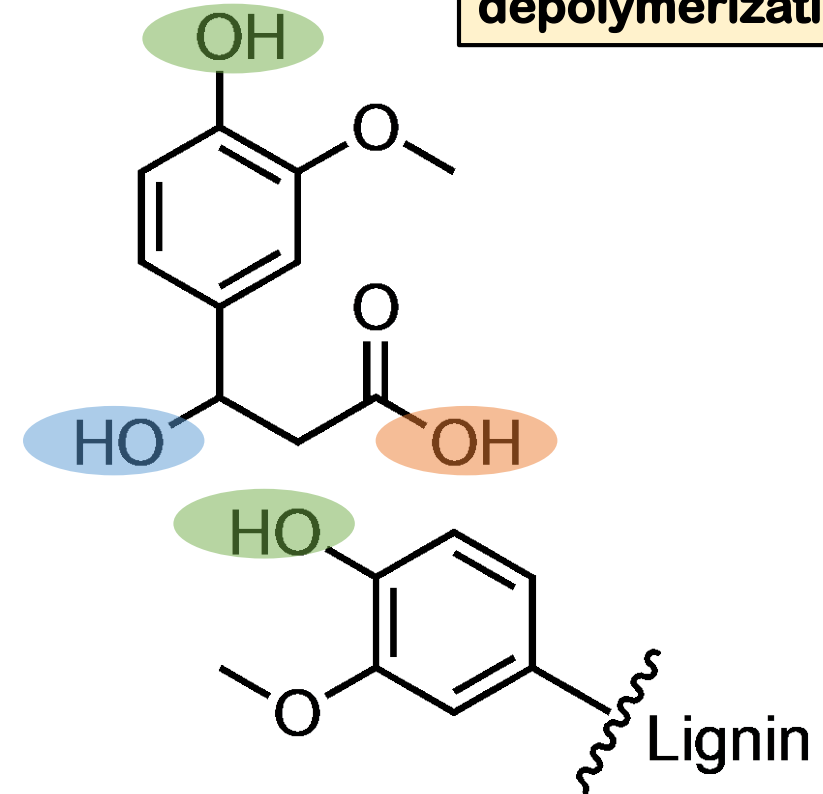


# Understanding $^{31}\text{P}$ NMR of lignin

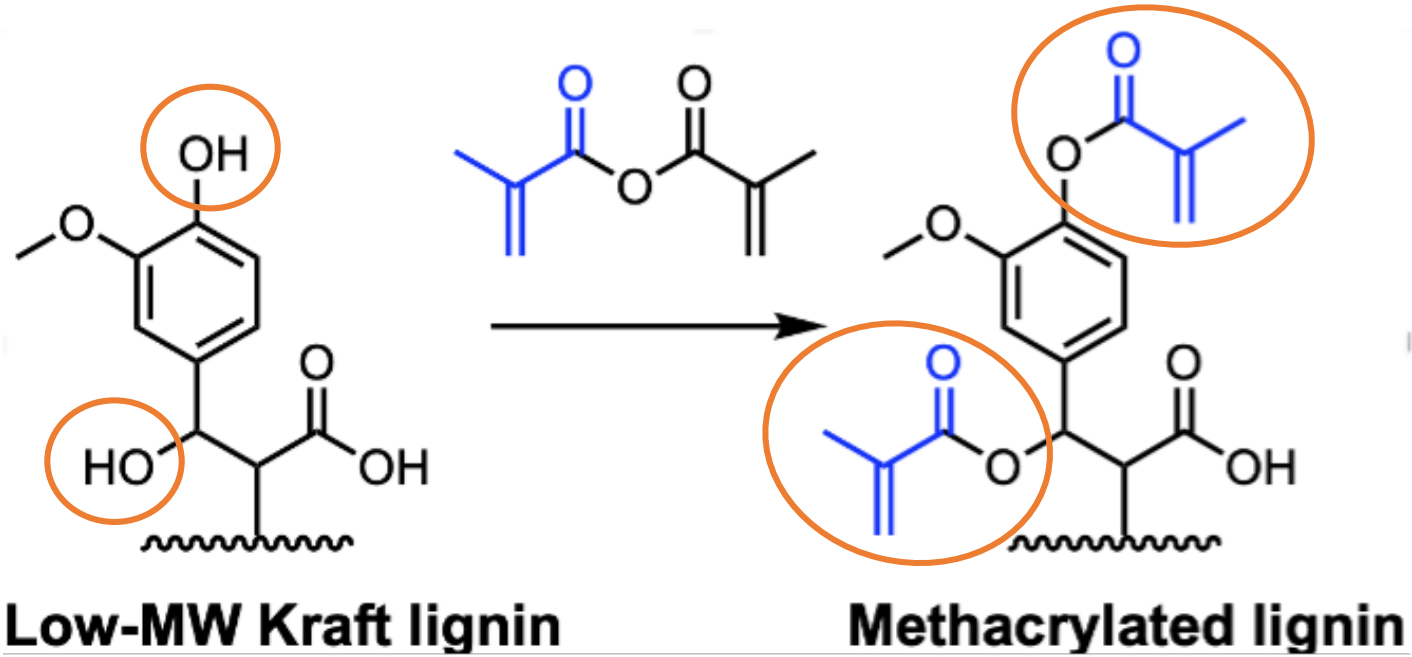
Increase in aromatic  
(G-type) OH groups  
indicates  
depolymerization



**PROCESS**

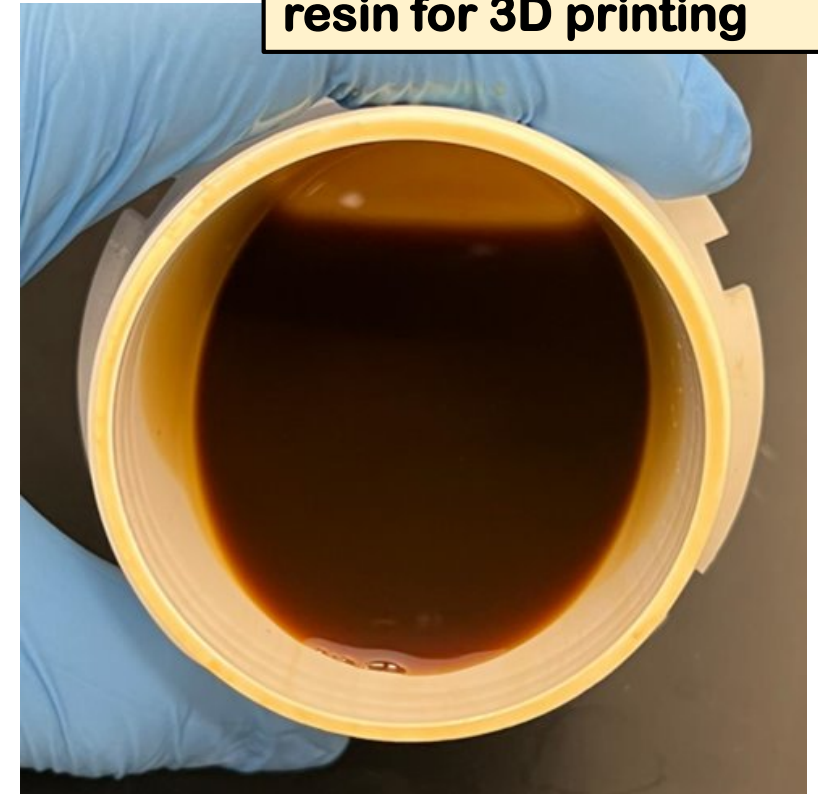


# Modifying Kraft lignin for 3D printing

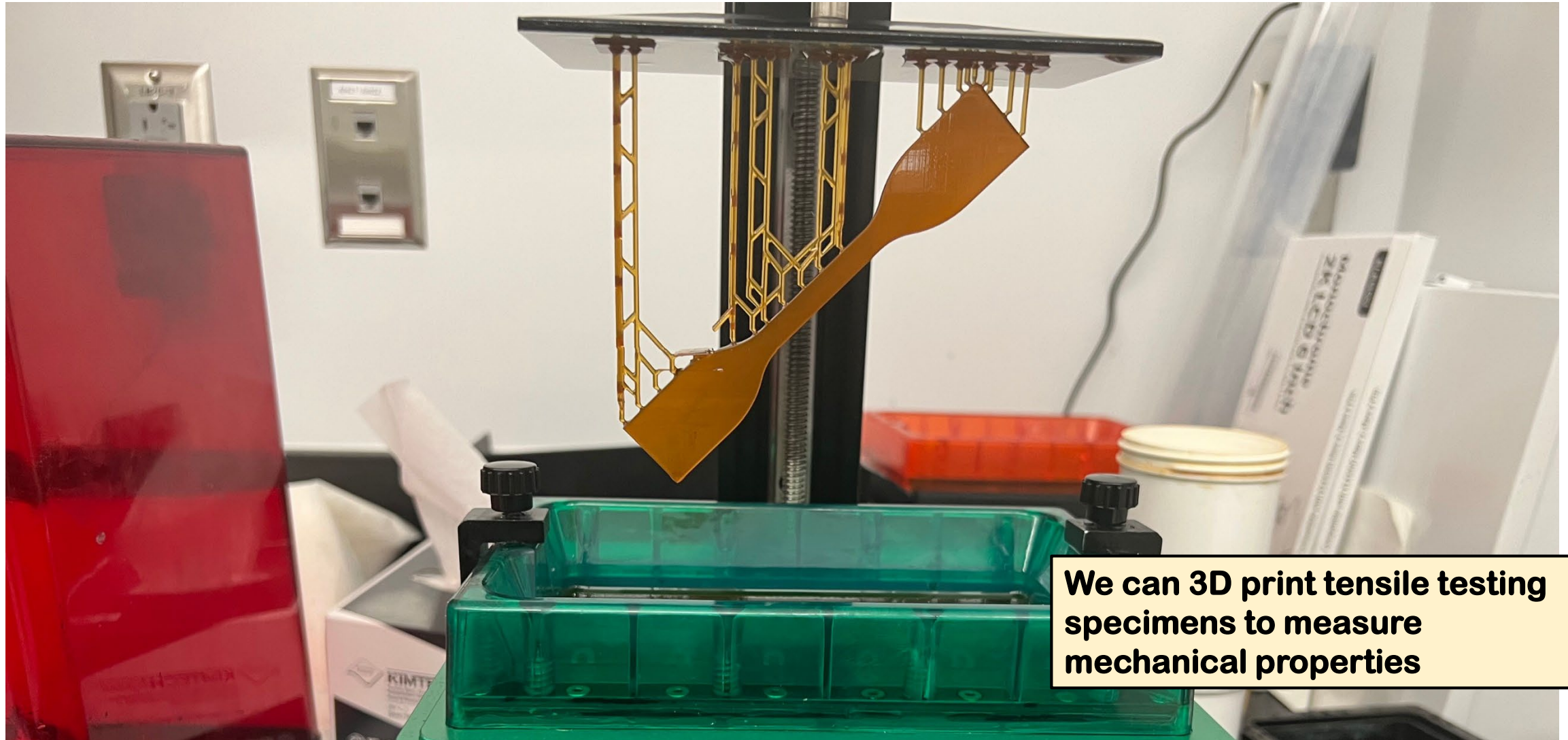


We modify –OH groups (highlighted) with methacrylic anhydride

Soybean-oil based lignin resin for 3D printing



# 3D printing with lignin



### 3.1.2 Stepwise Fractionation

- ✓ The chemical proportions (extractives, lignin, holocellulose) of various-year-harvested logging residues have been completed. Data analysis is in processing
- ✓ Partial results were reported, and aviation fuel conversion will be examined.
- ❖ Presented “**Combustion characteristics and energy properties of torrefied and untorrefied natural-decomposed Red Oak (*Quercus rubra*) forest logging residues**” in the 75th Annual International Conference, Forest Products Society, June 13-16th, Madison, WI, USA.
- ❖ Submitted a manuscript to *Industrial Crops and Products*.

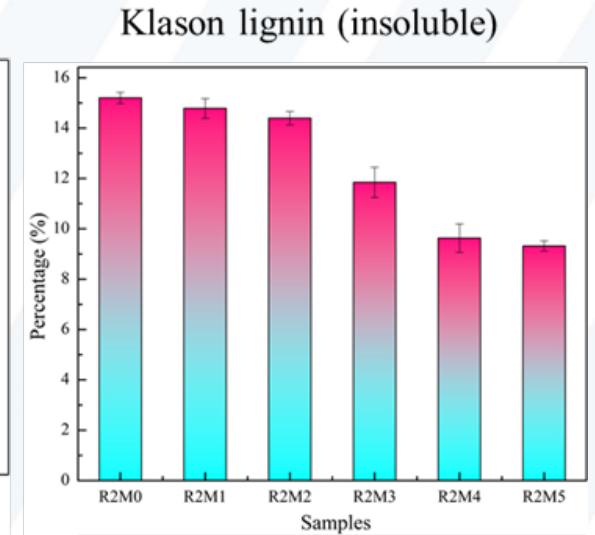
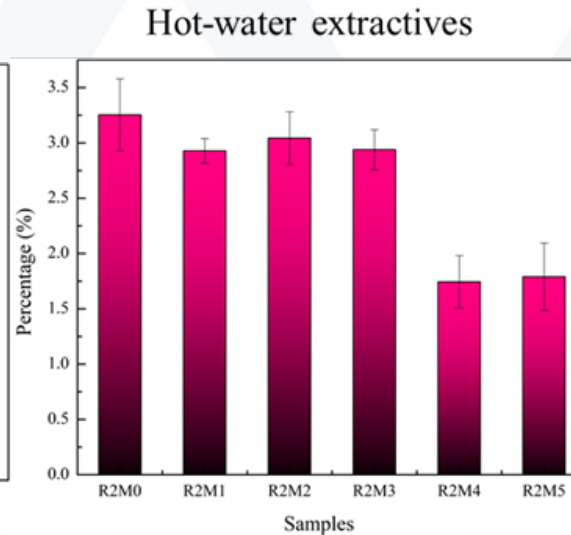
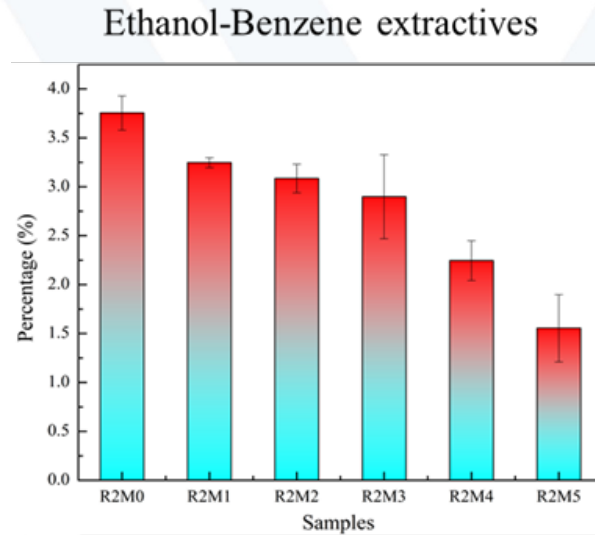
### 3.4 biomass derived carbon products

- ✓ The XRD tests for logging residue hydro-bioproducts have been completed.
- ✓ FTIR and the heavy metal ions adsorption experiments are on going.

## Chemical variations of various-year-harvested hardwood and softwood.

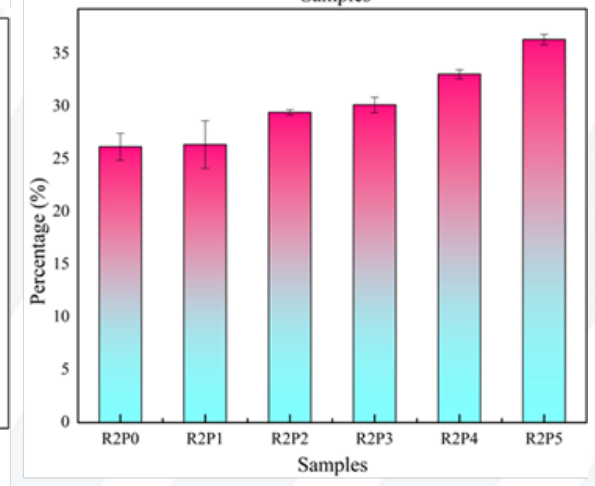
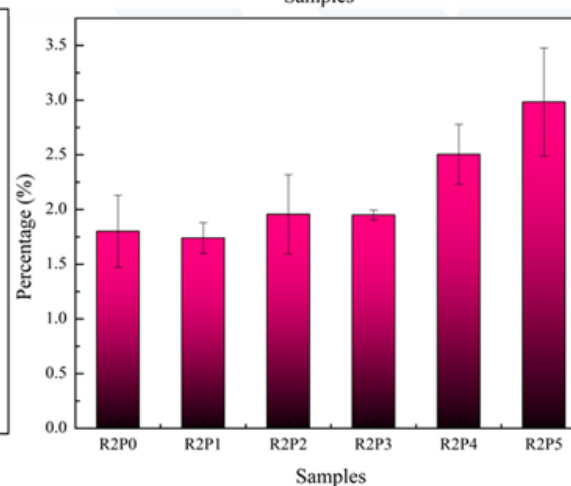
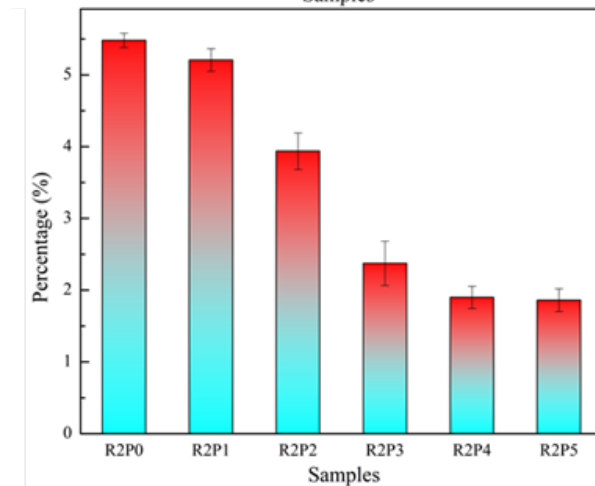
- Chemical extractives of hardwood and softwood decreased with increase after years of harvest.

Hardwood: Red maple

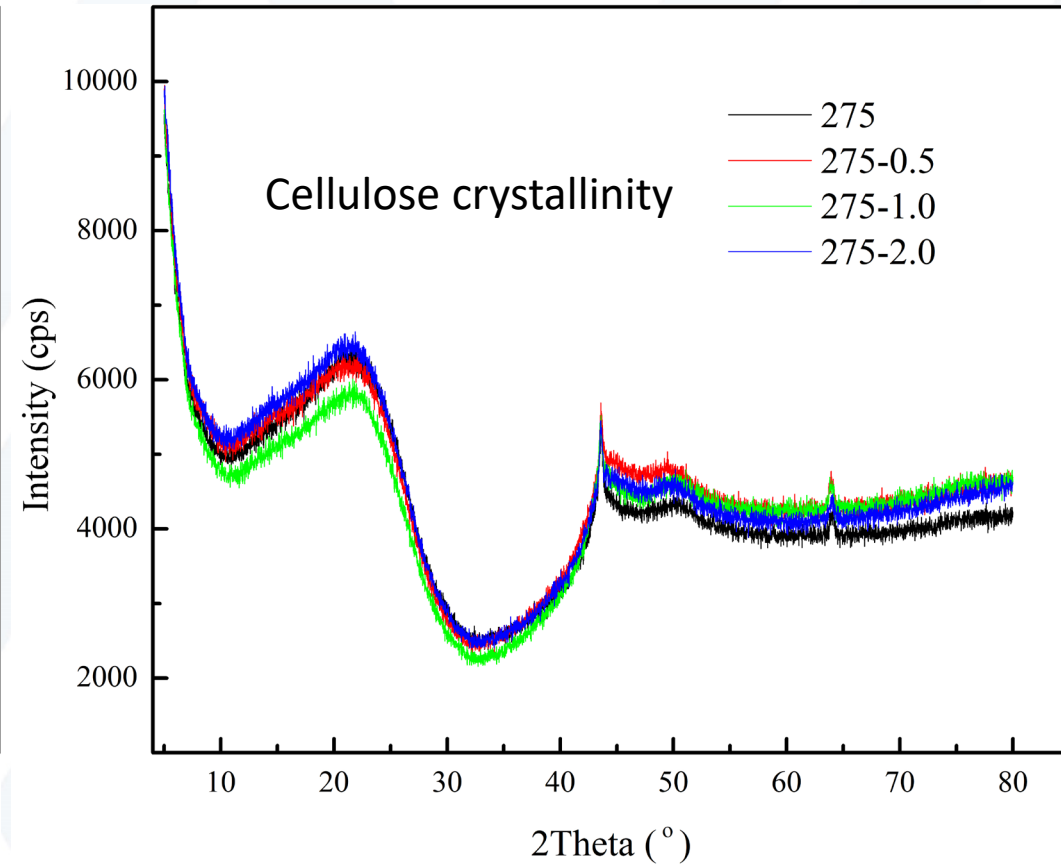
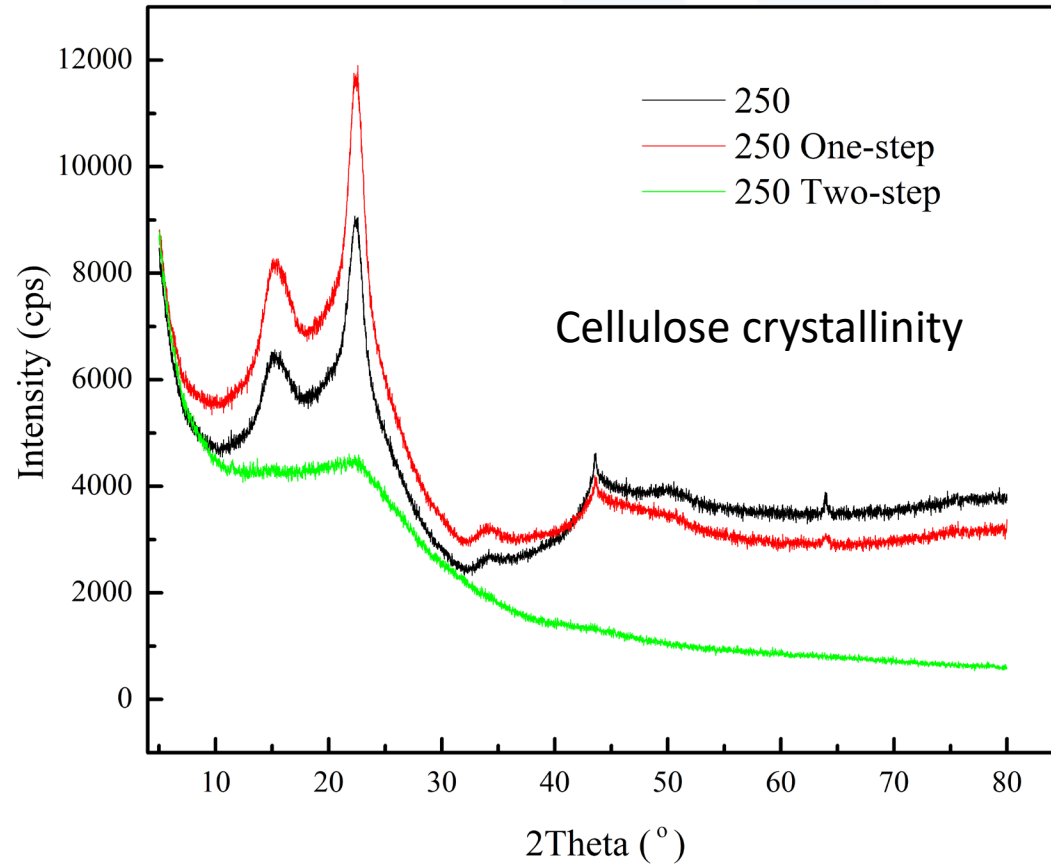


- Hot-water extractives for softwood and hardwood demonstrates an opposite trend.

Softwood: Red pine



## XRD results for logging residues-based hydro-bioproducts

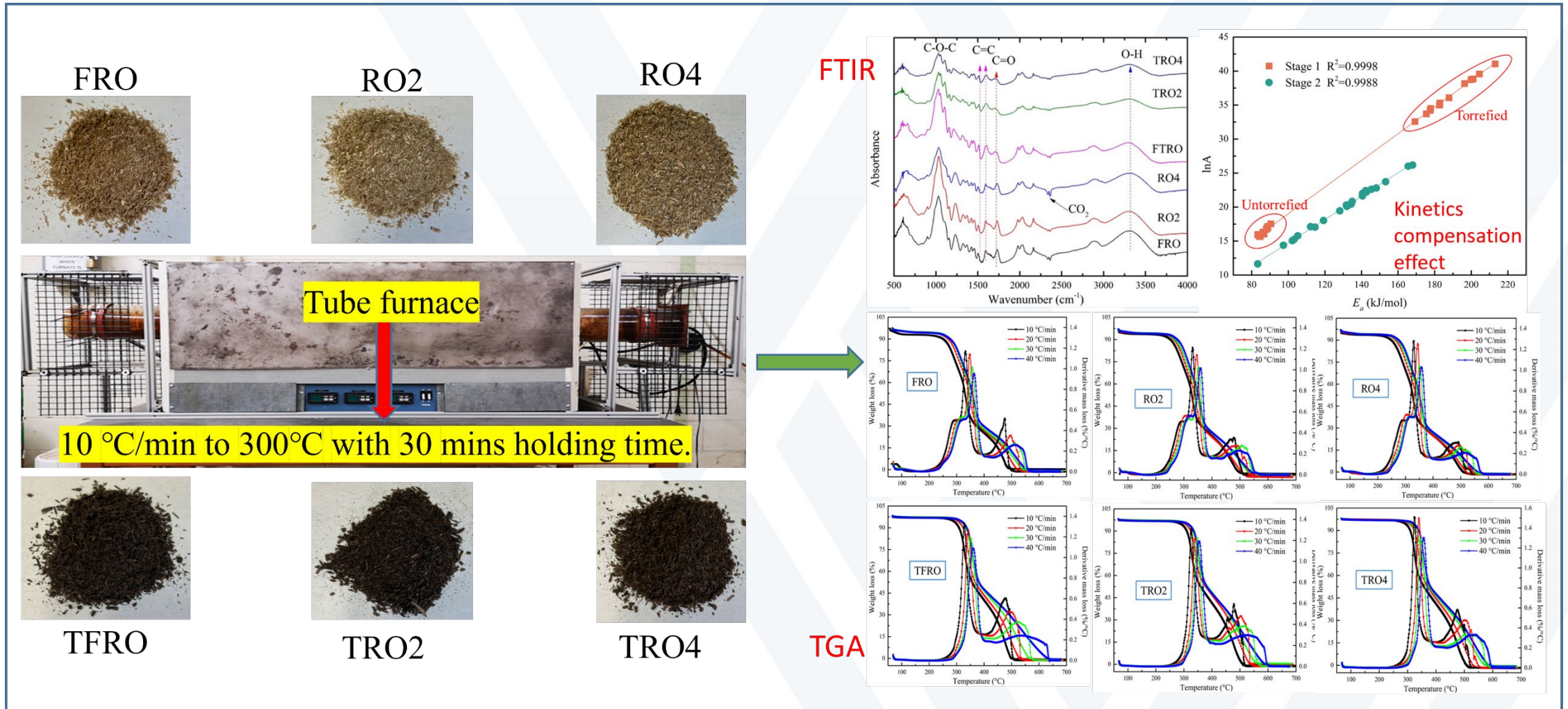


- One- and two-step  $\text{KMnO}_4$  hydrothermal modified red maple logging residues under 250 °C.
- Different concentrations  $\text{KMnO}_4$  hydrothermal modified red maple logging residues treated under 275 °C.

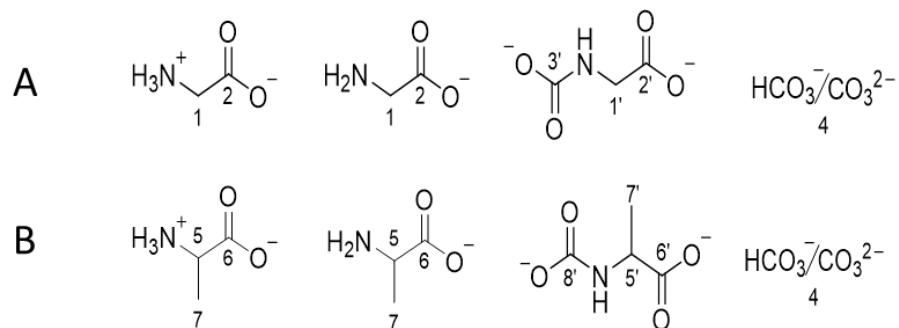


# The submitted manuscript – Combustion characteristics of the torrefied and untorrefied red oak forest logging residues

Graphical abstract

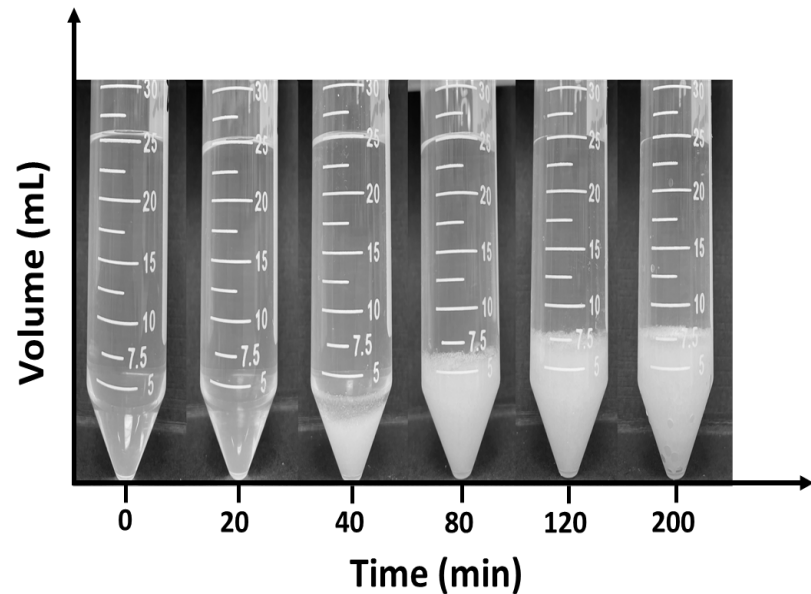


## □ Role of amino acid glycine (Gly) in Gly-K<sub>2</sub>CO<sub>3</sub> solvent system



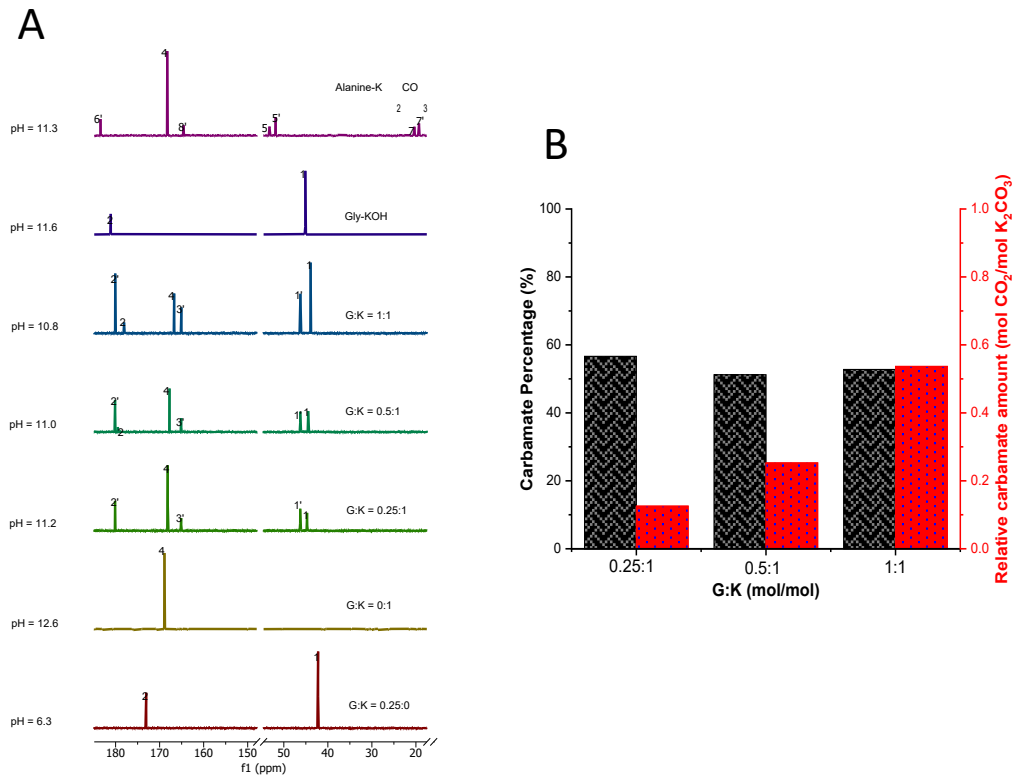
**Figure 1.** The structures of species in **(A)** Gly-K<sub>2</sub>CO<sub>3</sub> and **(B)** alanine-K<sub>2</sub>CO<sub>3</sub> solvent systems.

- In this report period, we examined the role of the two amino acids (i.e., glycine or Gly and alanine) in amino acid-K<sub>2</sub>CO<sub>3</sub> solvents.
- The rationale of studying this solvent system was that K<sub>2</sub>CO<sub>3</sub> may be used to replace KOH and the former is relatively easier to obtain.
- Figure 1 shows the possible chemical species that may be presented upon reacting with CO<sub>2</sub>.



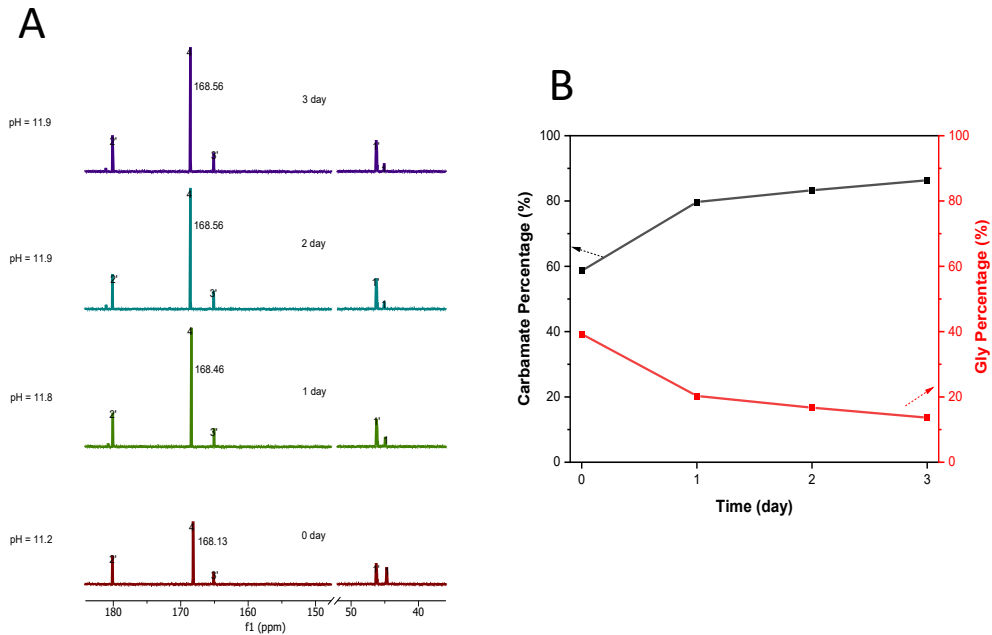
**Figure 2.** Phase separation in Gly- $\text{K}_2\text{CO}_3$  solvent ( $\text{CO}_2$  flow rate: 300 sccm, 293 K) at different reaction time (Gly: $\text{K}_2\text{CO}_3$  = 0.25:1).

- A phase-separation phenomena was observed in the Gly- $\text{K}_2\text{CO}_3$  solvent system.
- With increasing  $\text{CO}_2$  reaction time, the formation of a white solid phase increased.



**Figure 3.** (A) <sup>13</sup>C NMR spectra of Gly-K<sub>2</sub>CO<sub>3</sub> solvents before CO<sub>2</sub> bubbling with different Gly:K ratios, and Gly, Gly-KOH, K<sub>2</sub>CO<sub>3</sub>, and alanine-K<sub>2</sub>CO<sub>3</sub> (Alanine:K<sub>2</sub>CO<sub>3</sub> = 0.25:1) solvents; pH of the solvents was presented on the left. (B) Carbamate percentage and carbamate amount of Gly-K<sub>2</sub>CO<sub>3</sub> solvents with different Gly:K<sub>2</sub>CO<sub>3</sub> ratios.

- The results showed that only peaks 1 and 2 representing Gly appeared in the pure Gly solvent and only peak 4 representing HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> showed in the pure K<sub>2</sub>CO<sub>3</sub> solvent. Compared to the Gly and K<sub>2</sub>CO<sub>3</sub> solvent controls, three new peaks (1', 2', and 3') representing carbamate appeared in all Gly-K<sub>2</sub>CO<sub>3</sub> solvents.
- Similarly, in the K<sub>2</sub>CO<sub>3</sub>-alanine solvent, peaks 5', 6', 7', and 8' representing alanine-formed carbamate were observed.
- The carbamate percentage in the Gly-K<sub>2</sub>CO<sub>3</sub> solvents (Gly:K<sub>2</sub>CO<sub>3</sub> = 0.25:1, 0.5:1, 1:1) was about the same (i.e., 52%), and the relative carbamate amount increased with increasing Gly level.



**Figure 4.** (A) <sup>13</sup>C NMR spectra at various storage time after solvent preparation but before CO<sub>2</sub> bubbling (Gly:K<sub>2</sub>CO<sub>3</sub> = 0.25:1); pH of the solvents was indicated on the left. (B) Carbamate% and Gly% of Gly-K<sub>2</sub>CO<sub>3</sub> solvents at various storage time.

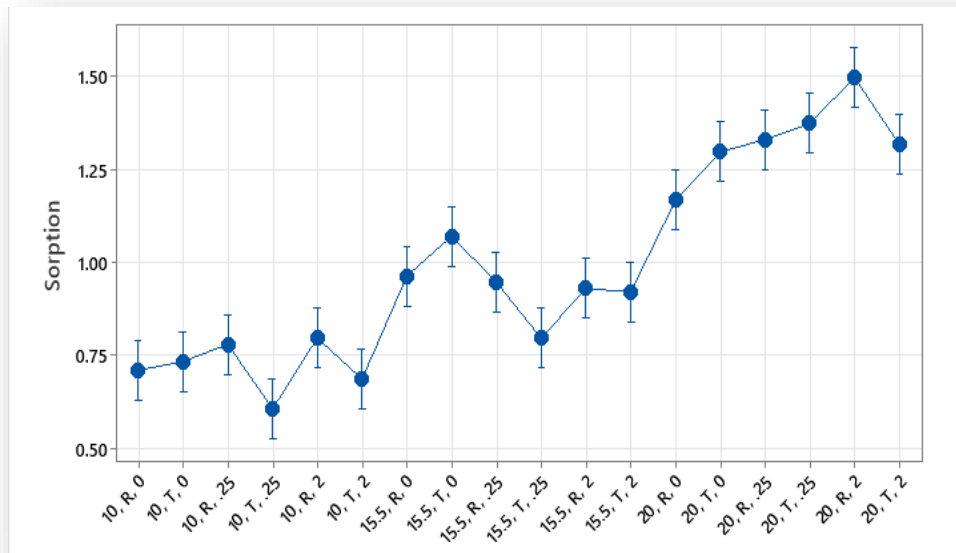
- The <sup>13</sup>C NMR spectra (**Figure 4A**) showed that peak 4 representing HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> shifted from 168.13 ppm to 168.56 ppm with increase of storage time from 0 to 3 days.
- The carbamate% (**Figure 4B**) increased sharply after 1-day storage followed by a slow increase trend with increasing solvent storage time, while the Gly% decreased with increasing solvent storage time.
- **Major finding:** for the first time, our studies showed the formation of carbamate without presence of CO<sub>2</sub>.
- **New reaction pathways identified:** In the K<sub>2</sub>CO<sub>3</sub> + Gly solvent, carbonate hydrolyzed into bicarbonate and hydroxide, Gly reacted with bicarbonate to form carbamate in the absence of CO<sub>2</sub>. In the presence of CO<sub>2</sub>, Gly further reacted with CO<sub>2</sub> to form carbamate. As a result, Gly significantly enhanced the CO<sub>2</sub> absorption kinetics and a high CO<sub>2</sub> loading (0.62 mol CO<sub>2</sub>/mol K<sub>2</sub>CO<sub>3</sub>) was achieved.

# Task #3.4: Biomass Derived Carbon Products

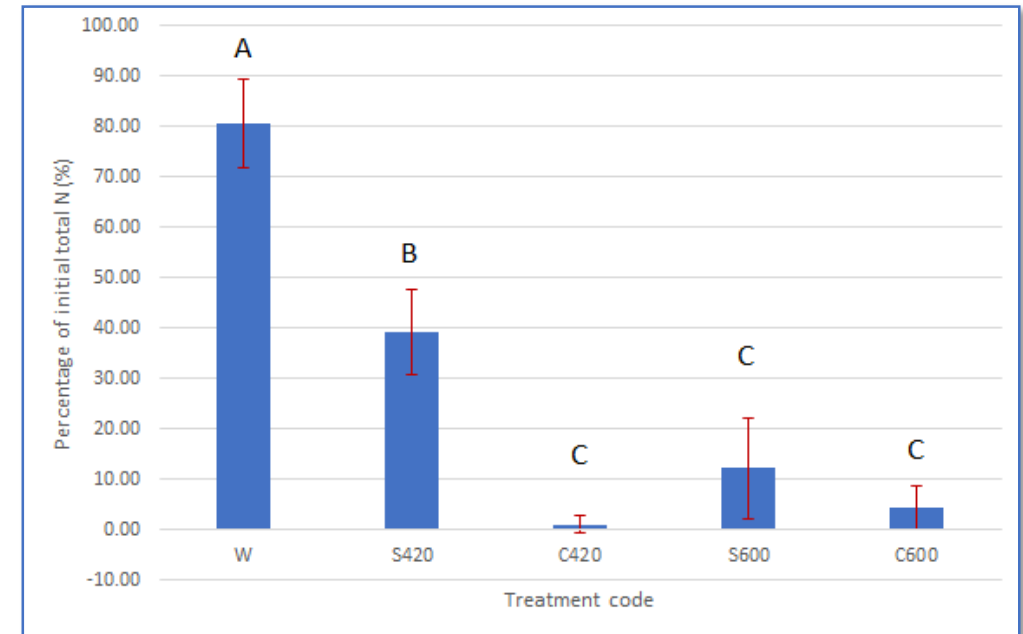
- First set of denitrifying bioreactor trials completed.
- Different degrees of pyrolysis showing notable differences in system performance



Lab Scale Bioreactor



Sorption Capacity ( $\text{mg g}^{-1}$ ) for biomass samples treated at three contaminant levels, two thermal treatment levels, and three alkaline treatment levels.



Bioreactor Nitrogen Concentration After 36 Hours.

# Task #3.4: Biomass Derived Carbon Products

- Examining sorption capacity vs thermal severity, for optimization of process conditions in carbonized product manufacture
- End objective: utilization in denitrifying bioreactors and engineered runoff treatment structures

$$\text{Thermal Severity } (\Delta RMF) = A * \exp * (-E_a / RT) * \Delta t$$

Where

A = Pre-exponential factor (s<sup>-1</sup>)

E<sub>a</sub> = Activation energy (J/mol)

R = Universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>)

T = Torrefaction temperature (K)

Δt = residence time (s)

