Carbon Products from the Biorefinery: Graphite and High Surface Area Carbon

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Biorefinery?

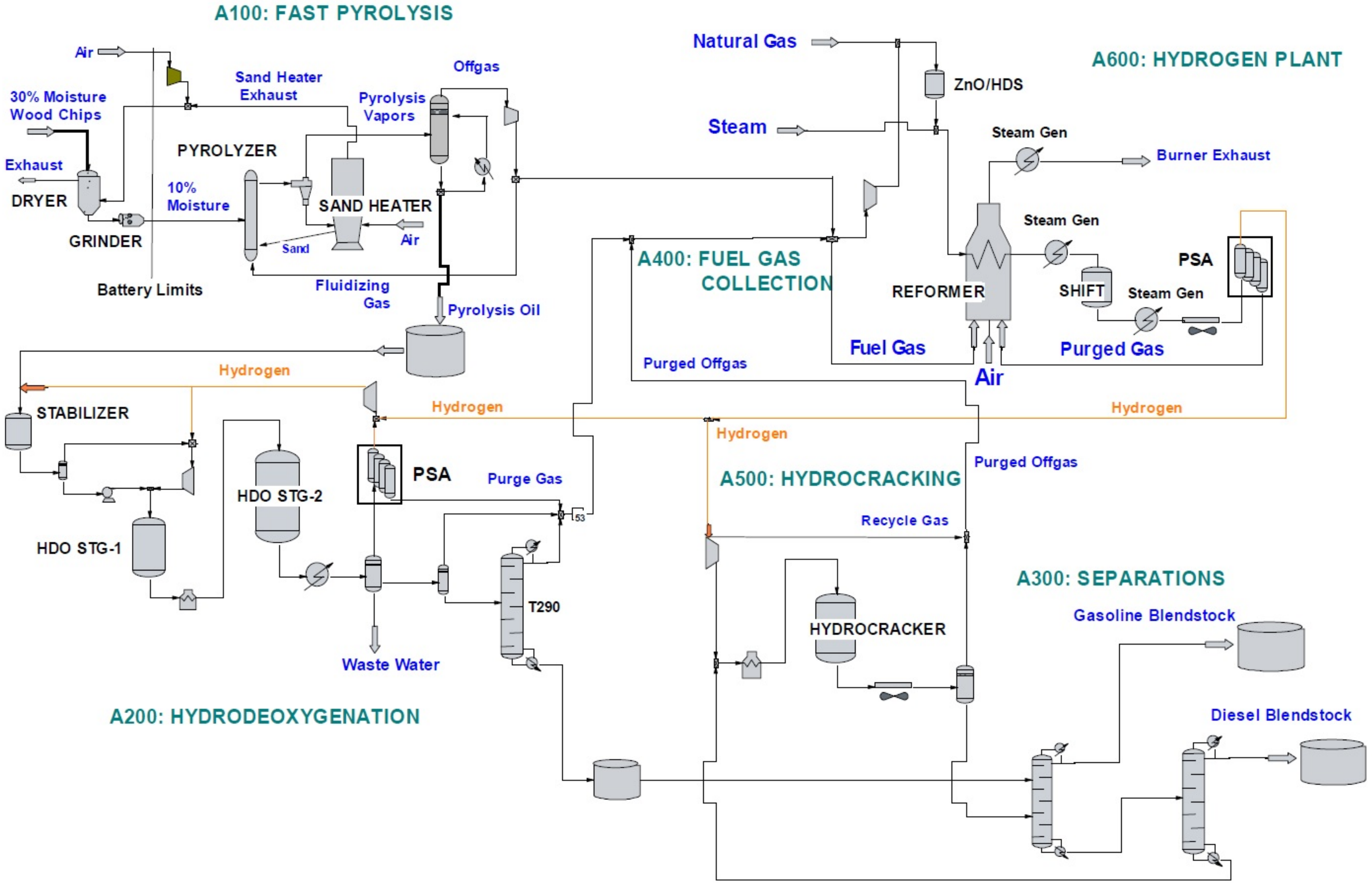
Producing fuel alone will be not be profitable, need a value-added co-product

- **Graphite (Graphene)**
- **Activated Carbon**

Commercial Drivers: Price vs Cost vs Profit

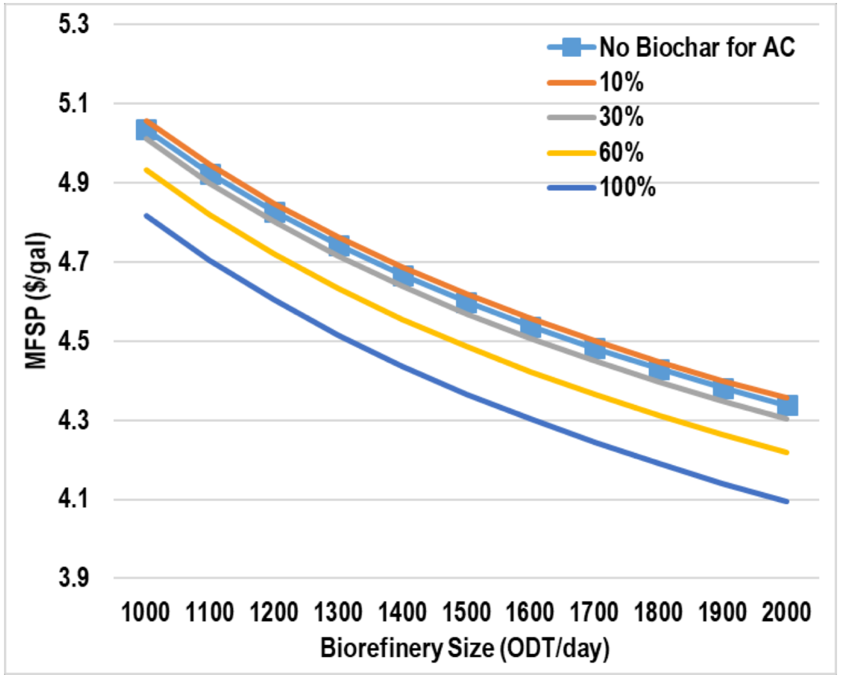
- When talking about ‘value-added’ products the key question is profit, not cost or price
- Many companies also have a potential ‘market value’ hurdle target that they may reach
- ‘Drop-in’ vs ‘Alternative’ – Value can be hard to establish

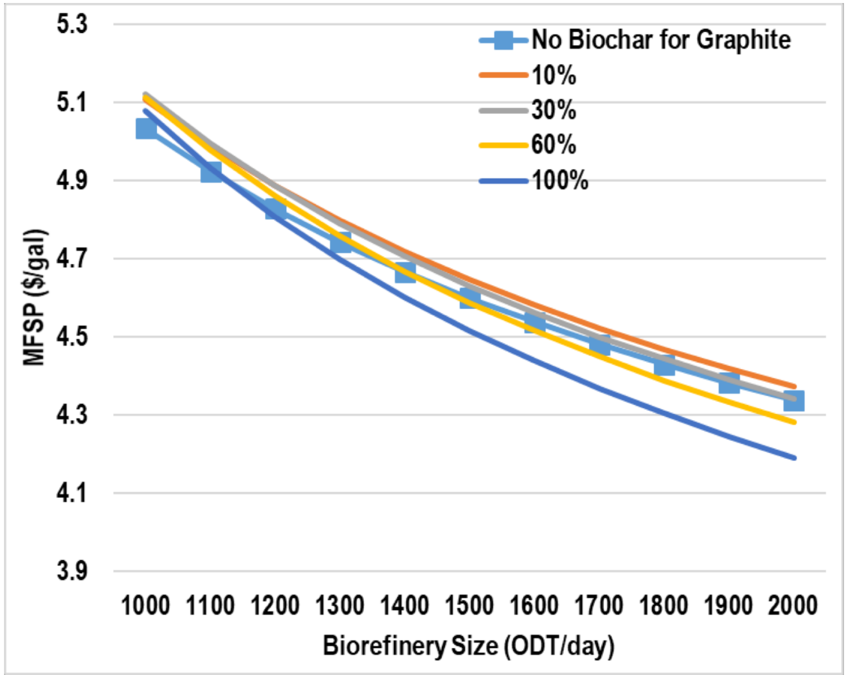
ASPEN Bio-Oil Process Model



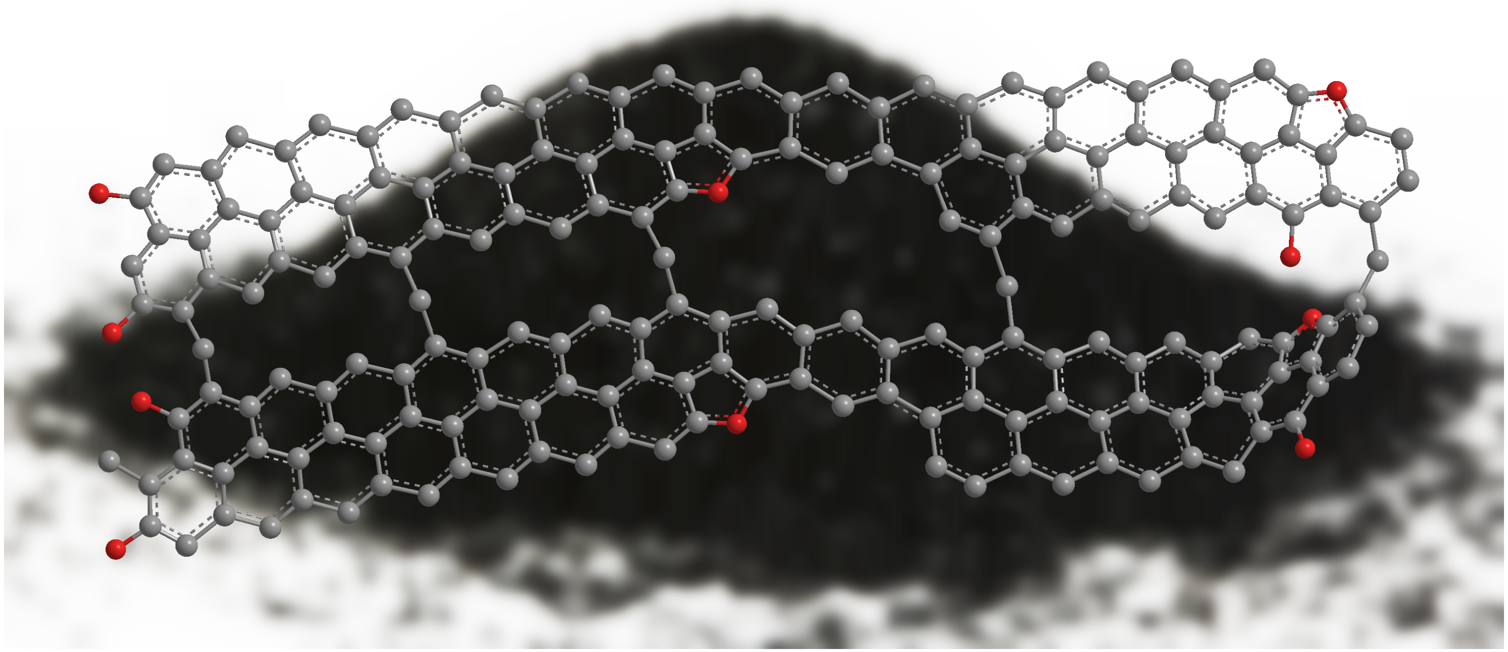
Potential Value-added Products from Biochar

	Activated Carbon Production	Graphite Production
Production yield from biochar (%)	50	10
AC Price ($/ton)	1,100	--
Graphite Price ($/ton)	--	2,500
Capital Costs (mil $)	31.9	20.0
Installed Cost (mil $)	21.0	24.0
Reaction Temp. (℃)	750	1,500



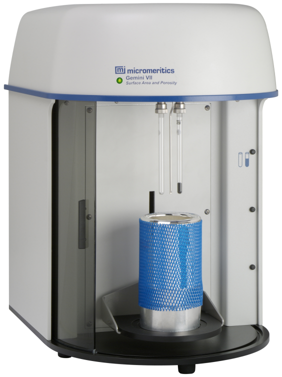


I. Graphite Formation



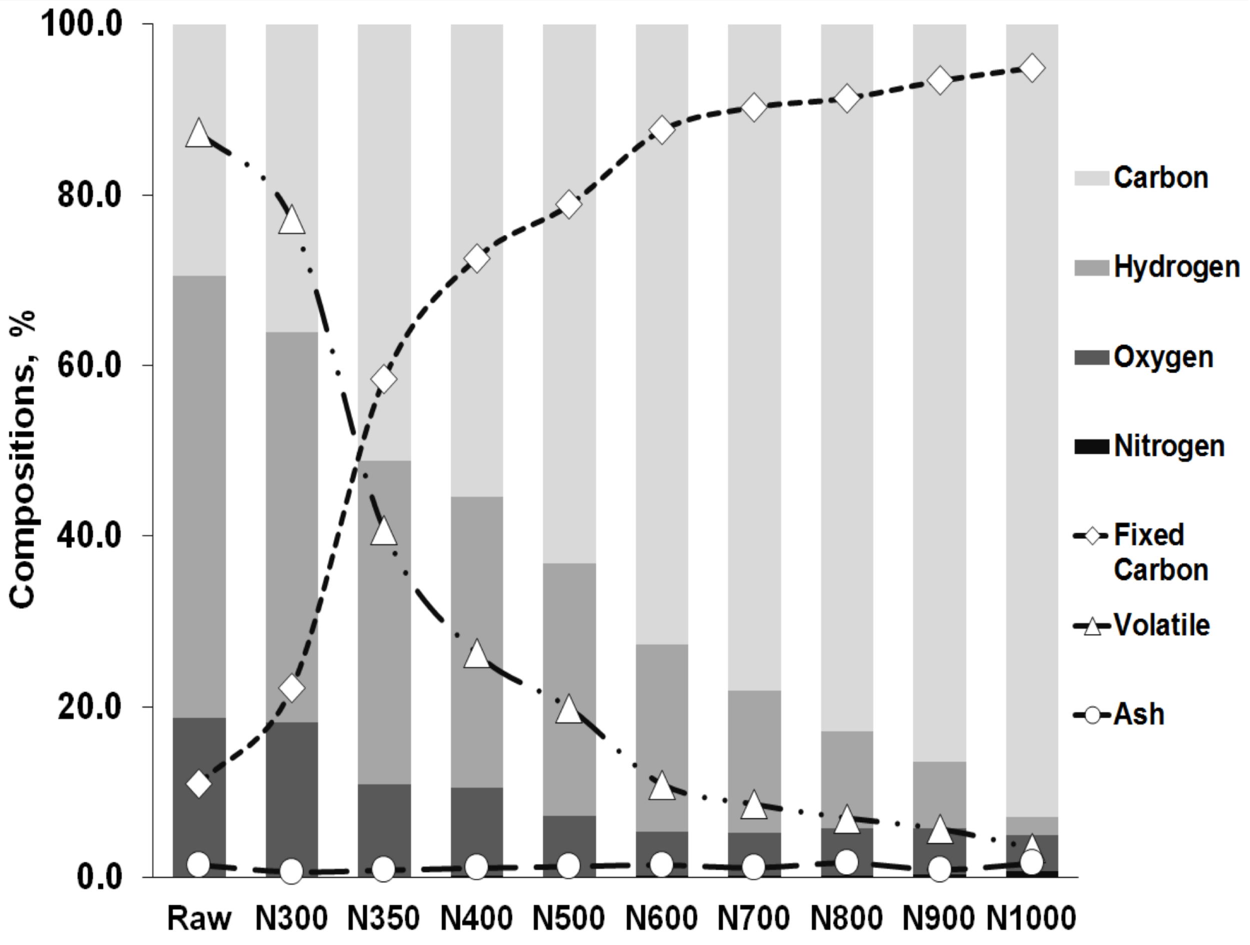
- Biomass derived carbon is inherently complex
- Advanced analytical techniques now offers detailed structural information

Characterization



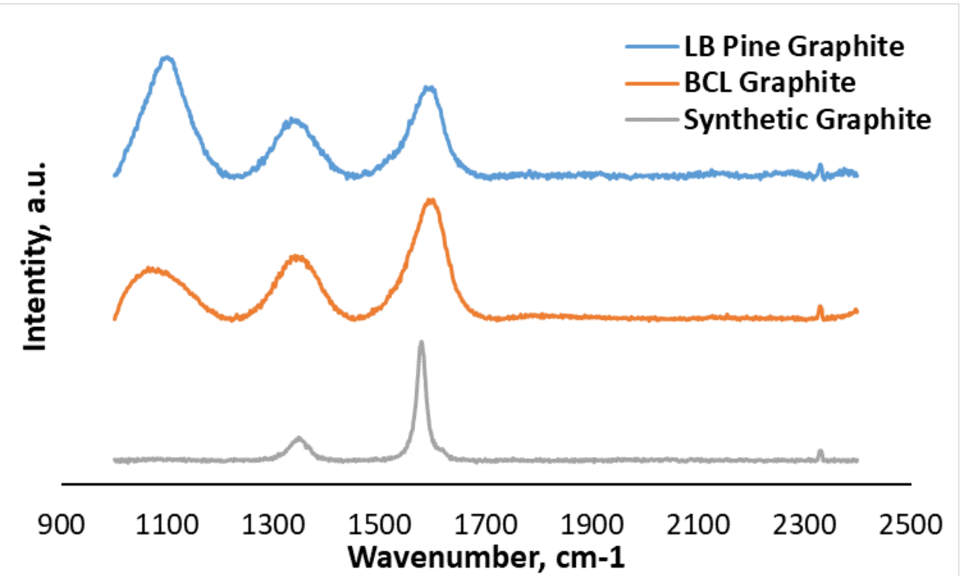
- Proximate and elemental analysis
- BET surface area / pore analysis
- Scanning transmission electron microscopy (STEM)
- Electron energy loss spectroscopy (EELS)
- X-ray diffraction analysis (XRD)

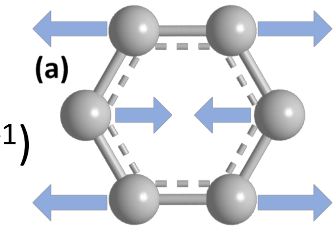
Composition Analysis



- Elemental and fixed carbon increase as the temperature increases (300℃ ~350℃)
- Elemental oxygen and hydrogen and volatile decrease
- Ash content and nitrogen content remain relatively constant

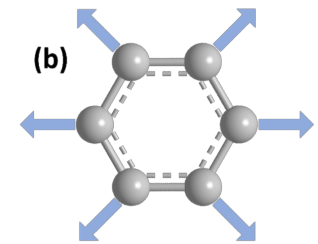
Raman Spectroscopy





G band (1,500 – 1,630 cm^{-1})

- E_{2g} symmetry
- In-plane bond-stretching motion of sp^2 bonding
- Does not require a polyaromatic sp^2 structure



D band (1,355 cm^{-1})

- A_{1g} symmetry
- Breathing mode of poly aromatic sp^2 structure
- always requires a sp^2 benzene ring structure

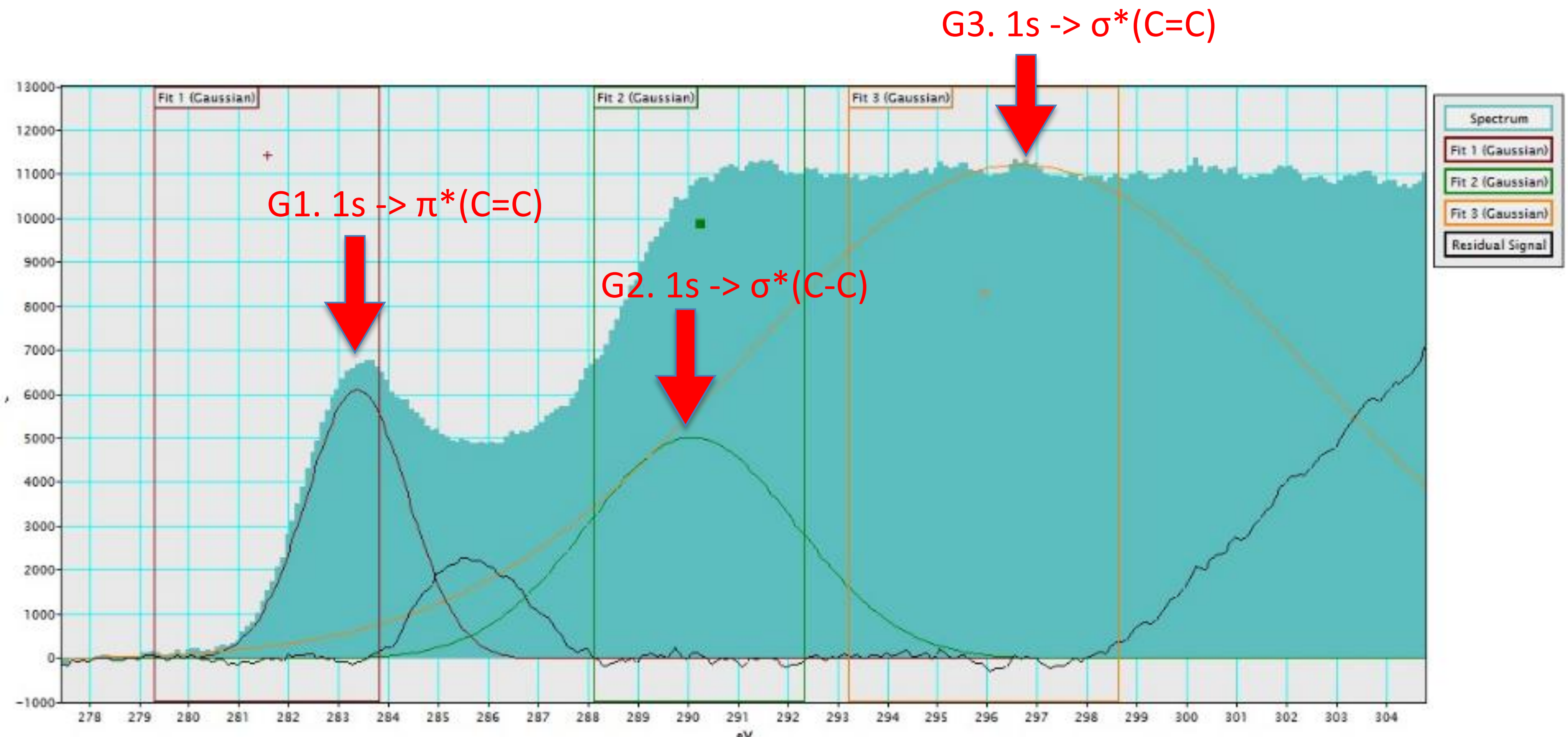
$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a}$$

$$L_a = \frac{C(\lambda) \times I(G)}{I(D)}$$

Calculated layer coherence length (L_a)

- **LB pine graphite**: 822.89 nm
- **BCL graphite**: 1005.19 nm
- **Synthetic graphite**: 2710.58 nm

EELS Calculation of the Carbon sp^2 Content



Electron energy-loss near-edge structure

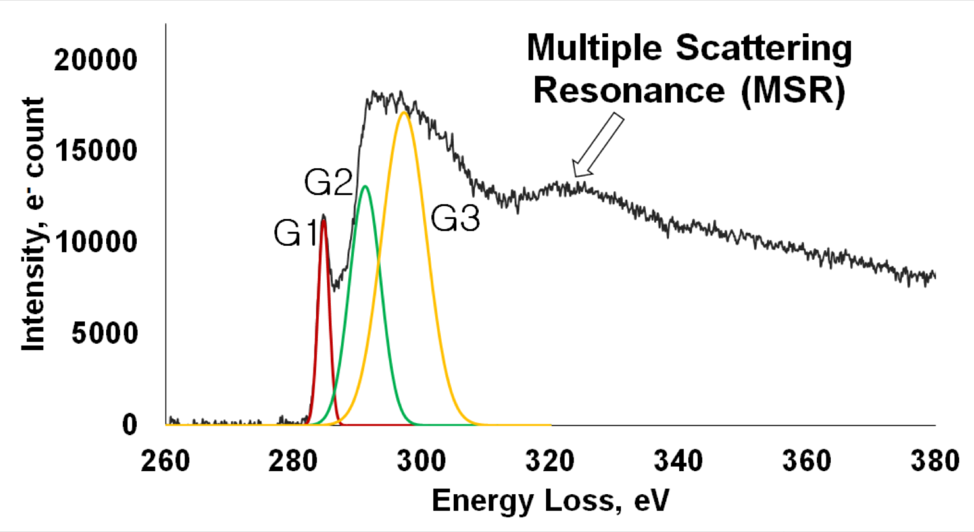
1s -> π* peak is detected at 285 eV (C double bond)

1s -> σ* peak is detected at 292 eV (C single bond)

1s -> σ* peak is detected at 298 eV (C double bond)

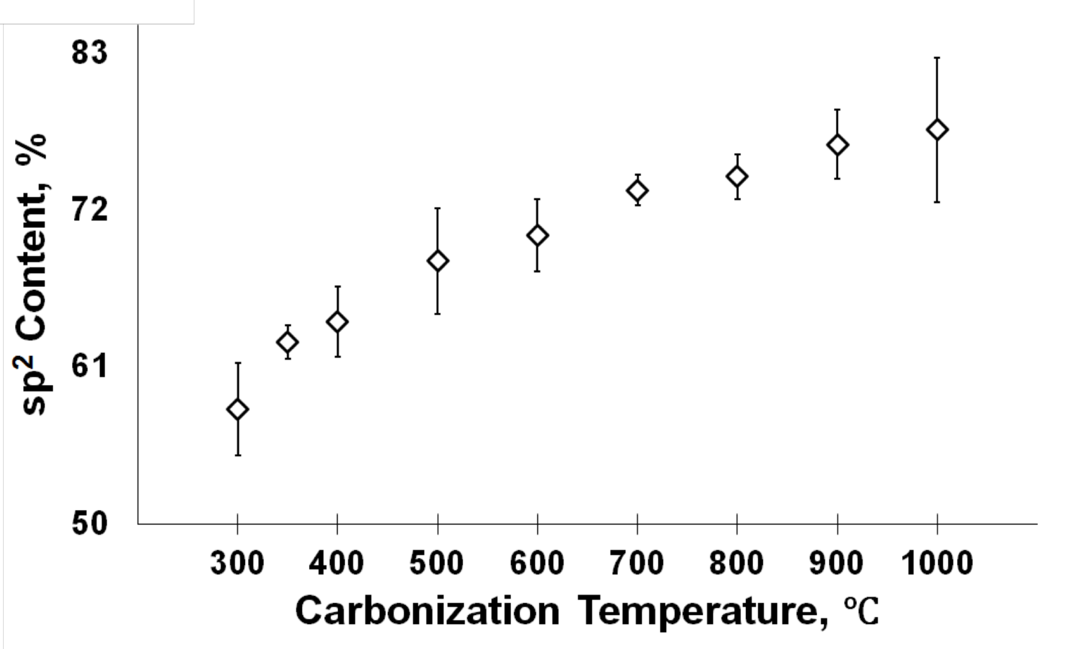
Marriott, (2014). Investigating the structure of biomass-derived non-graphitizing mesoporous carbons by electron energy loss spectroscopy in the transmission electron microscope and X-ray photoelectron spectroscopy. *Carbon.*

EELS Analysis – sp^2 content



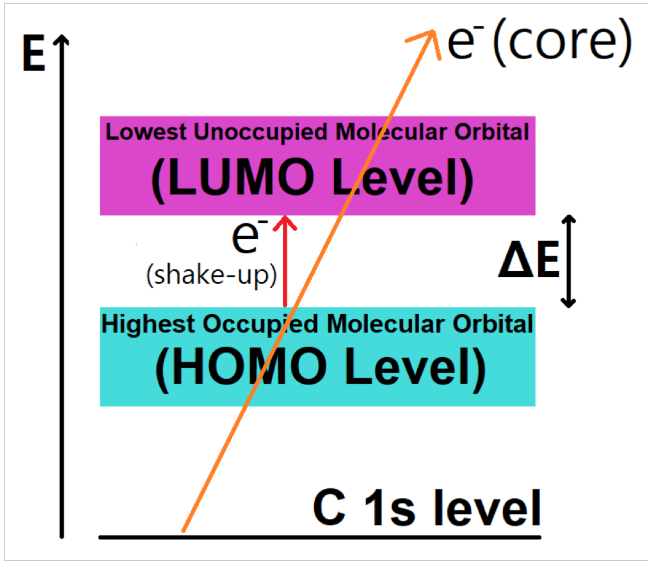
- Three major transitions of carbon core electron
- Area ratio of G1 over (G1+G2+G3) indicates sp^2 content of biochar

- The sp^2 content increases as temperature goes up



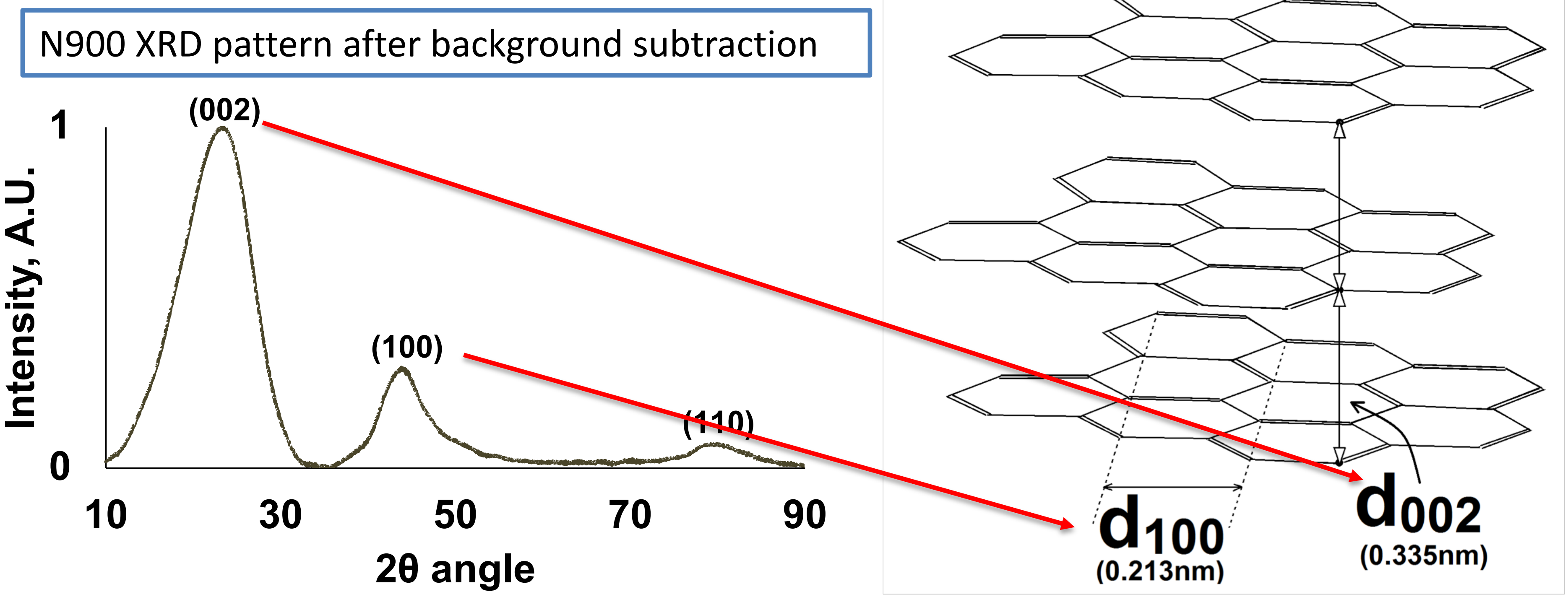
XPS Analysis

	c-c, c=c, c-H 284.6 eV	c-o 286.2 eV	c=o 287.6 eV	coo 289.1 eV	pi-pi* shake up, 290.6
N300	82.6	8.4	7.5	1.4	0.0
N350	85.9	7.6	4.9	1.1	0.6
N500	83.2	7.9	5.8	2.1	1.0
N700	86.4	9.1	2.3	1.2	1.1
N300-AC	71.0	10.1	6.8	3.3	8.8
N350-AC	70.3	10.0	5.1	3.0	11.5
N500-AC	68.6	12.9	4.1	3.4	11.0
N700-AC	62.7	12.5	3.3	2.5	18.9



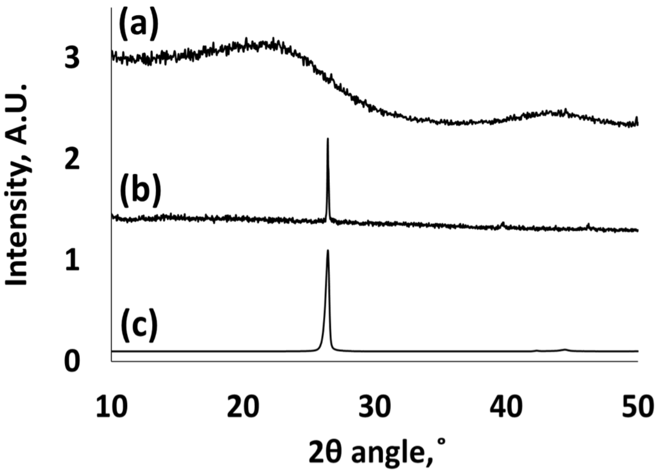
- Other than carbon and carbon-oxygen signals, pi-pi* transition occurs during the XPS measurement
- The pi-pi* transition is related to HOMO to LUMO transition of electron which is related to the size of energy gap

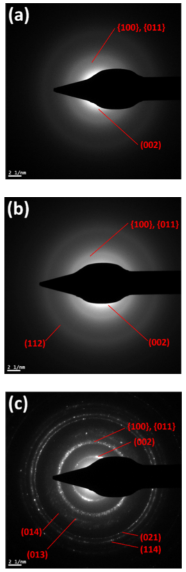
XRD Analysis



- With 2θ angle and full width at half maxima, the plane reflection interlayer spacing **(Bragg's law)** and layer coherence length **(Scherrer equation)** can be calculated

XRD Lattice Parameters

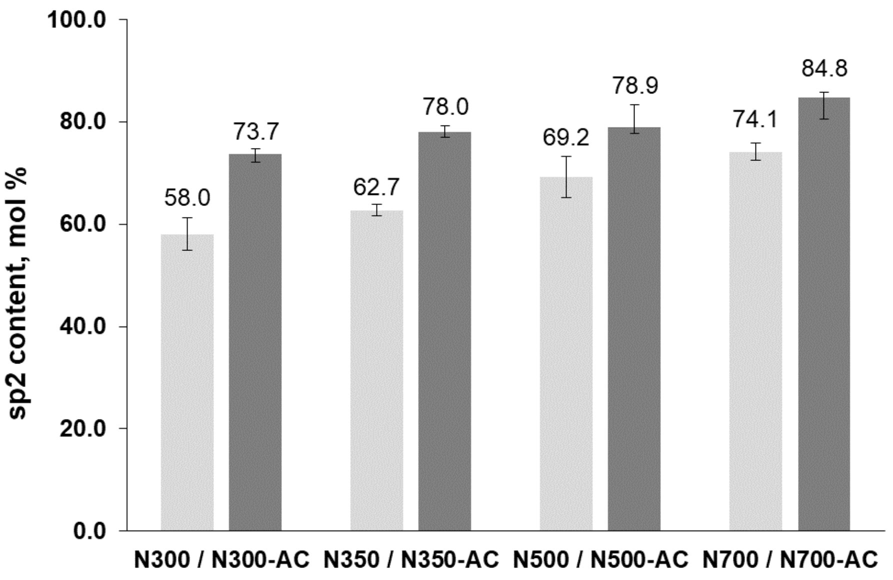


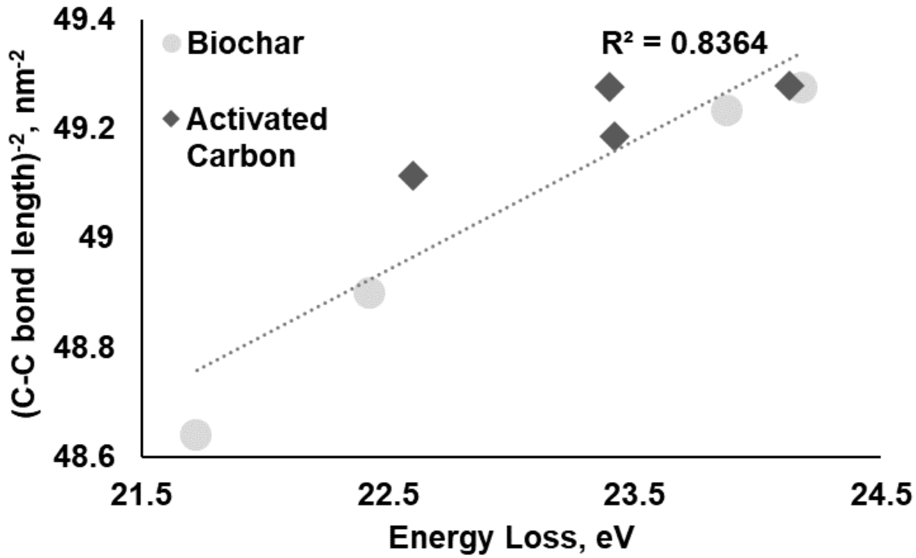


- Comparison of biochar/biomass graphite/natural graphite
- Lattice parameters were calculated and crystalline cluster sizes were calculated by Scherrer equation
- Electron diffraction patterns become larger and clearer as the structure has higher orderings

	N800	Biomass Graphite			Natural Graphite
Measurement Temperature	25°C	1500°C	1600°C	Cooled to 25°C	25°C
a (Å)	N/A	2.658	2.671	2.619	2.465
c (Å)	N/A	7.020	7.049	6.735	6.734
La (Å)	23.5	331.5	368.0	369.0	316.6
Lc (Å)	8.3	158.3	175.9	176.3	235.8
d_{002} (Å)	4.046	3.510	3.524	3.368	3.367
$\bar{g}$ (%)	N/A	N/A	N/A	84.12	84.83

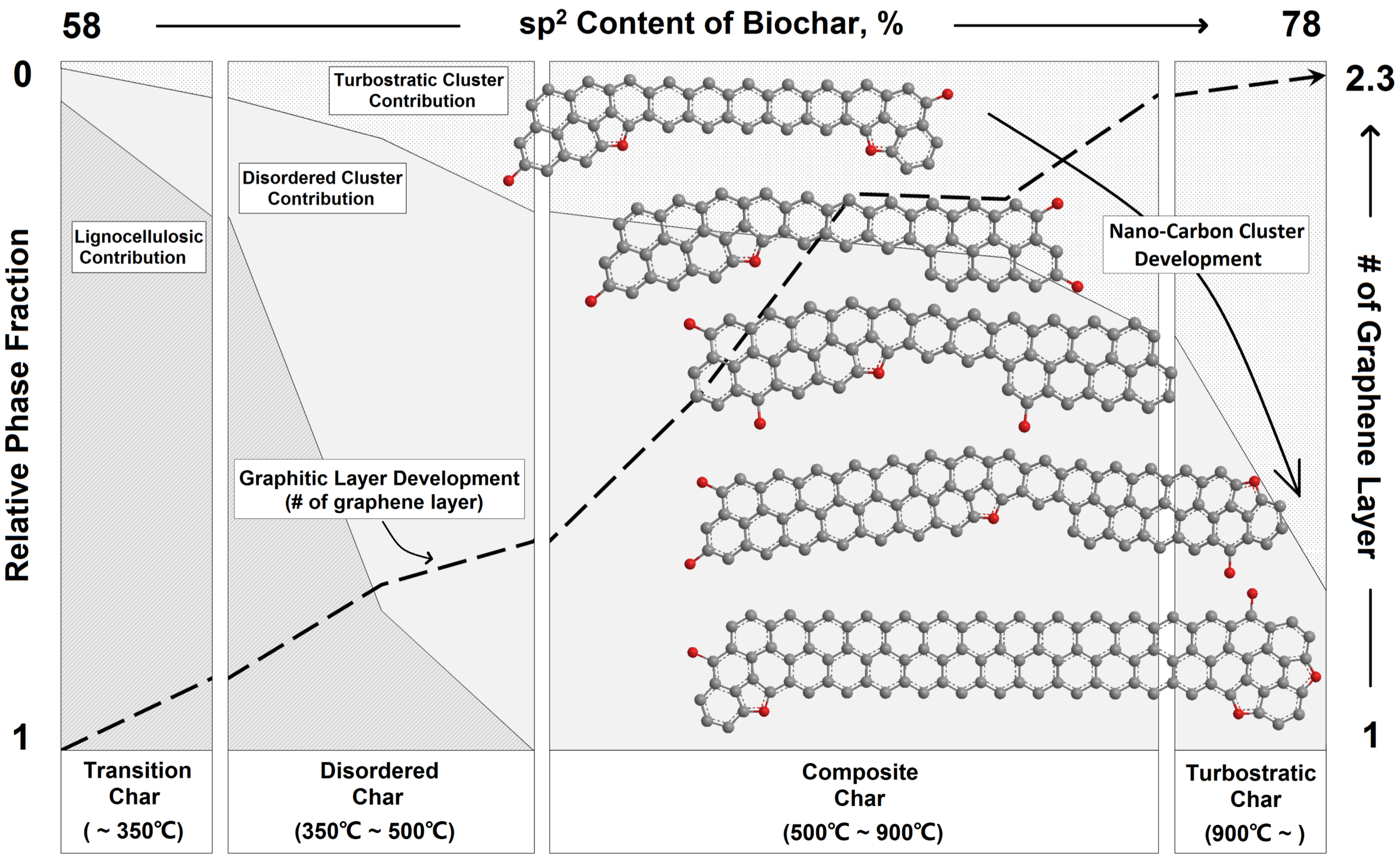
EELS Analysis



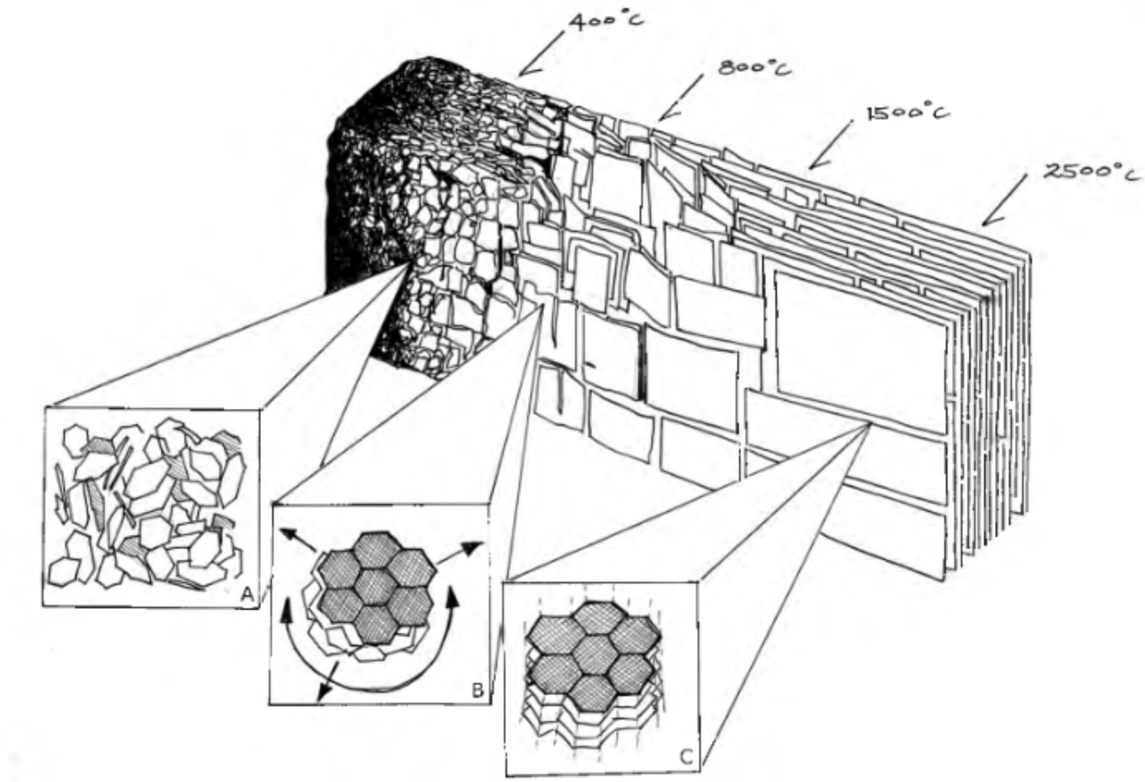


- The sp^2 content increased after activation
- Bulk plasmon excitation energy – C-C bond length relationship was also confirmed

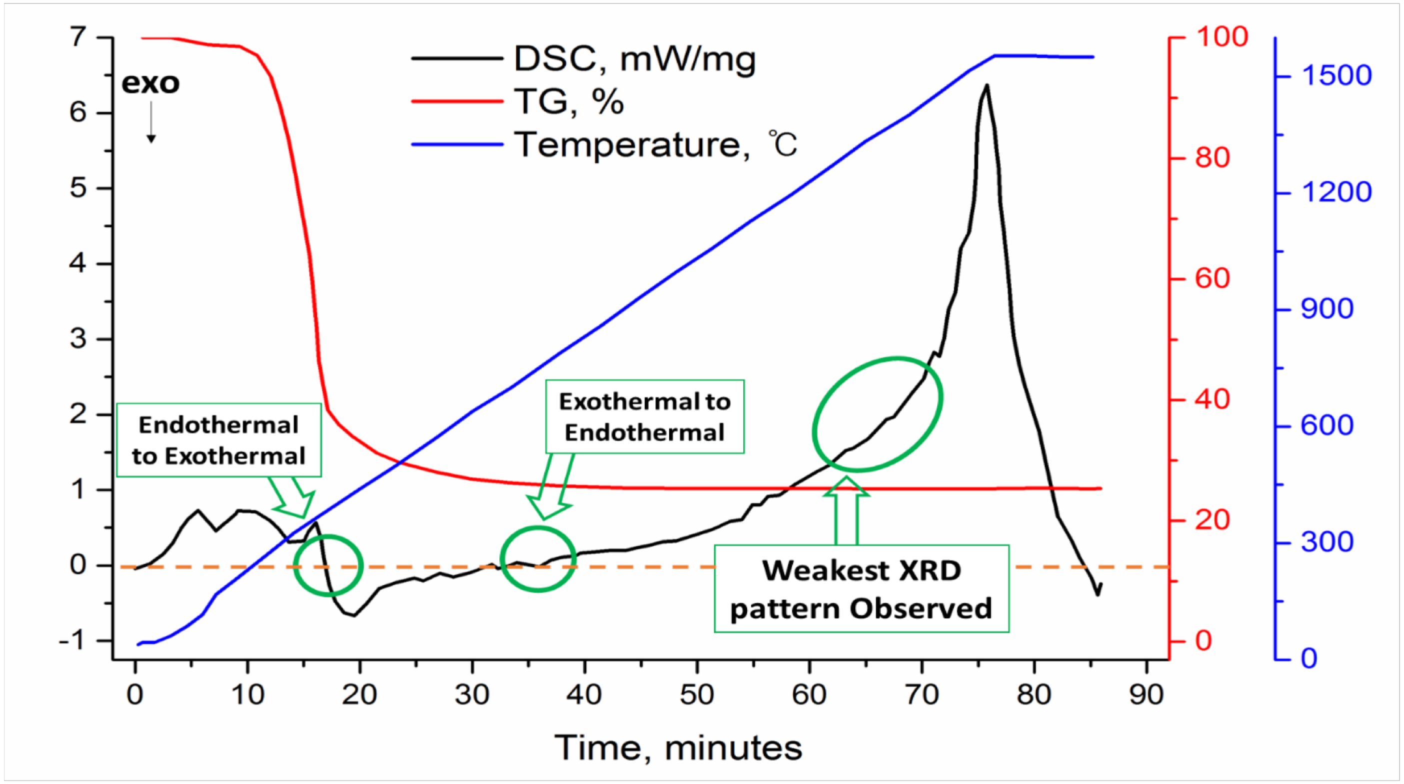
Biochar Development Model



II. Graphite Formation Kinetics



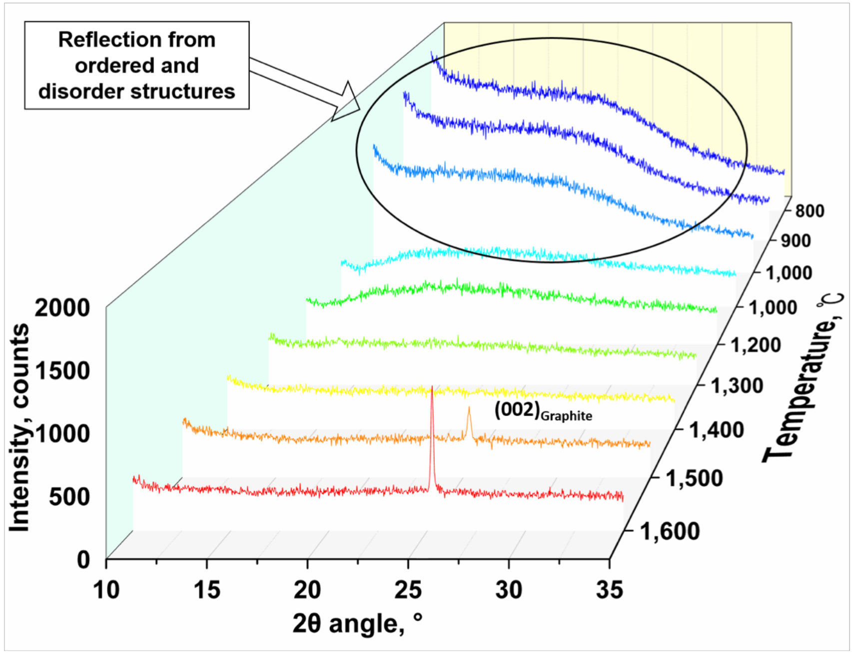
Thermal Analysis, DSC and TGA



Heat Flow measured by Differential Scanning Calorimetry

- Below 300°C - **(endothermic)** degradation of biomass components (cellulose, hemicellulose, lignin)
- 300°C ~ 850°C - **(exothermic)** formation of disordered biochar
- 850°C ~ 1,550°C - **(endothermic)** formation of graphitic stacking (huge endothermic peak)

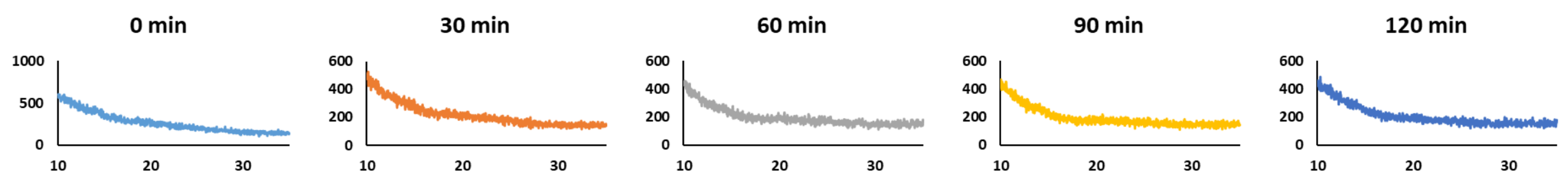
High Temperature XRD



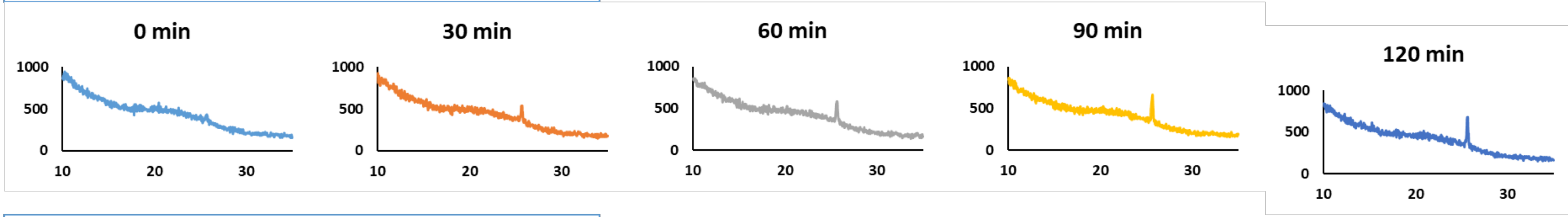
- A question from the preliminary exam
- Is formation of graphitic (002) stacking related to temperature or thermal treatment time?
- Details of graphitization kinetics of loblolly pine and lignin are studied

Loblolly Pine

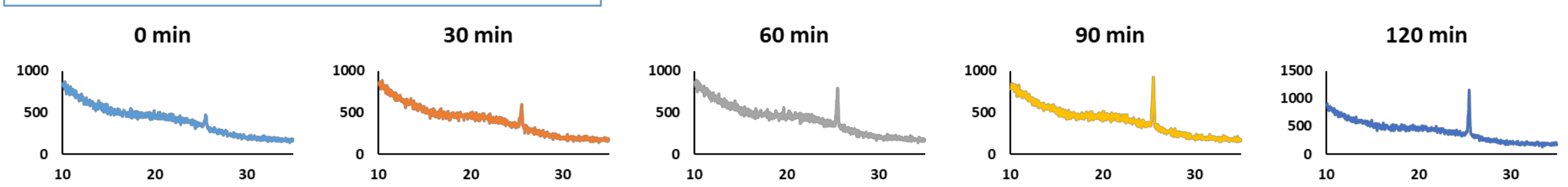
LB Pine Graphite (holding for 2hr at 1,400°C)



LB Pine Graphite (holding for 2hr at 1,438°C)



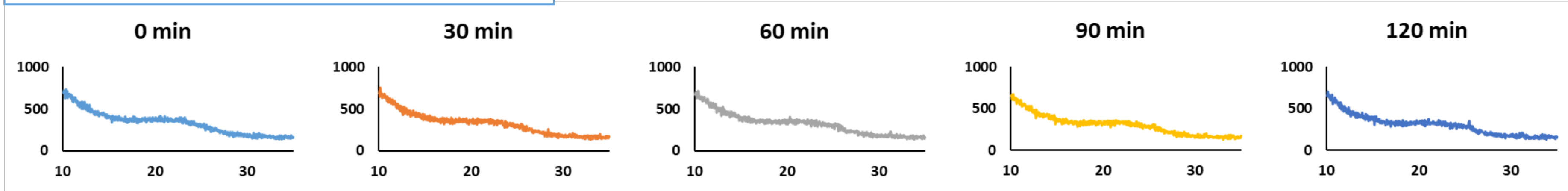
LB Pine Graphite (holding for 2hr at 1,450°C)



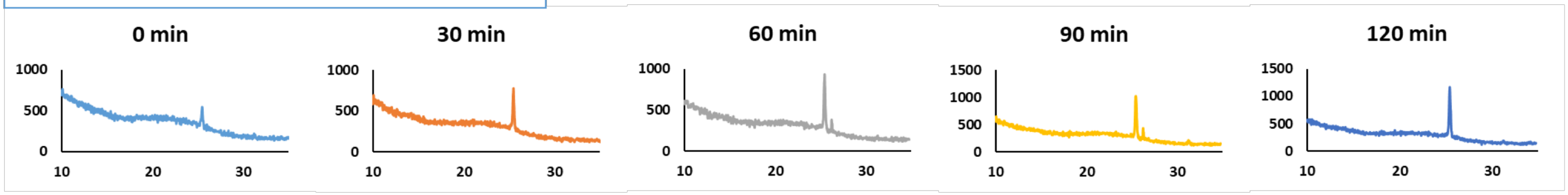
- Formation of graphitic stacking was not found until reaching 1,438 °C

Bio Choice Lignin

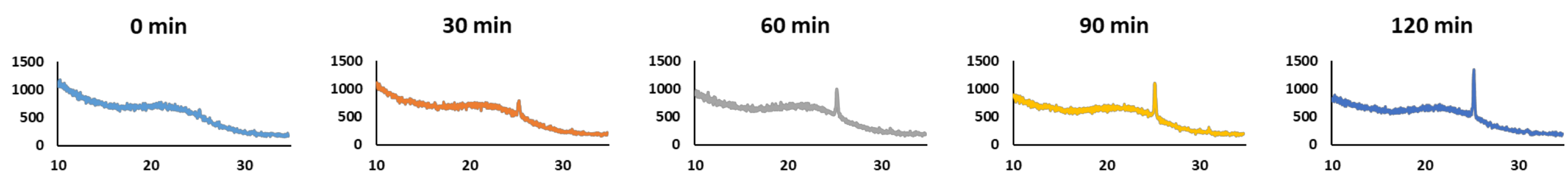
BCL Graphite (holding for 2hr at 1,438°C)



BCL Graphite (holding for 2hr at 1,475°C)

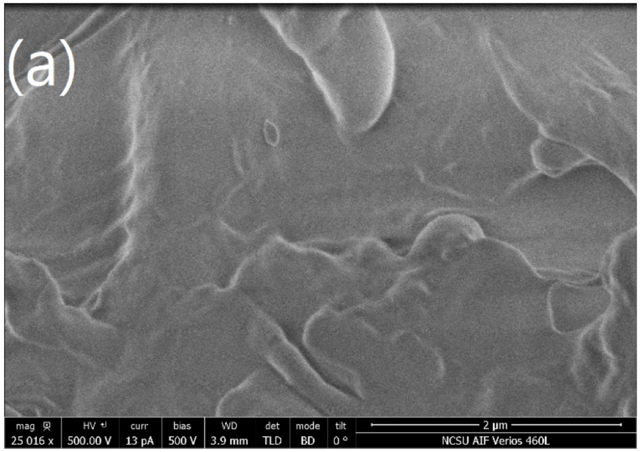


BCL Graphite (holding for 2hr at 1,500°C)

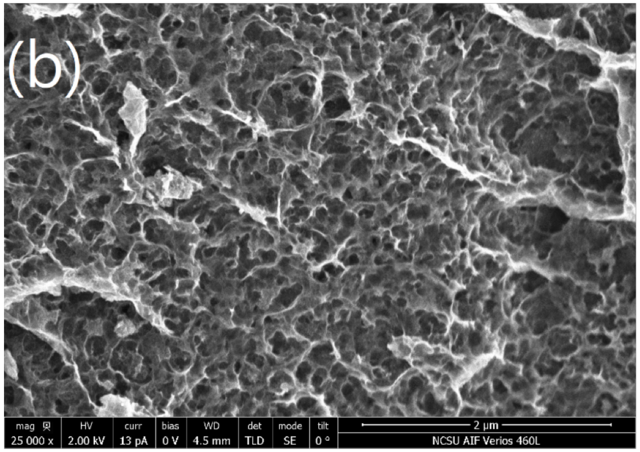


- Formation of graphitic stacking was not found until reaching 1,475 °C

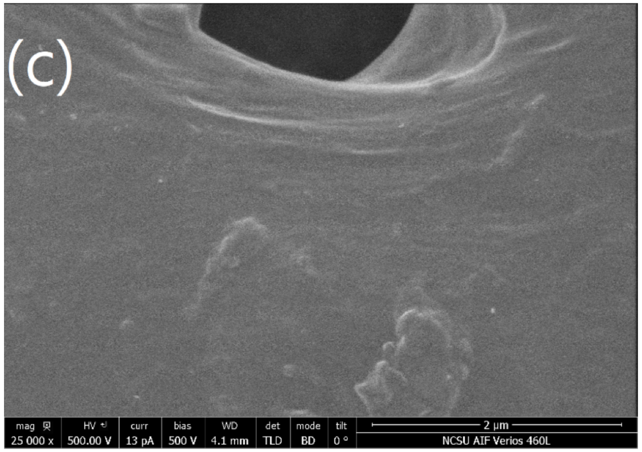
III. Biochar vs Activated Carbon



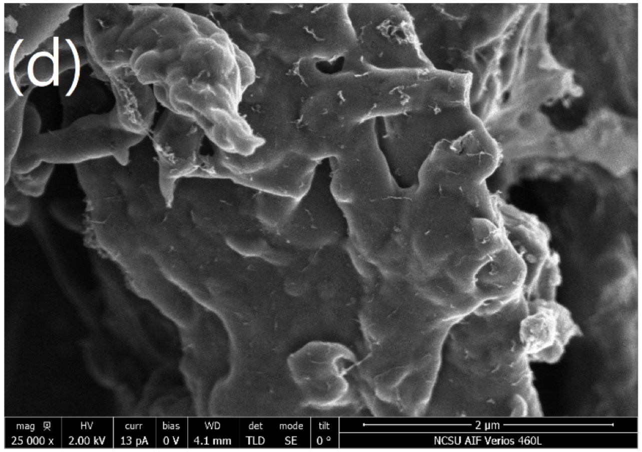
N300



N300-AC

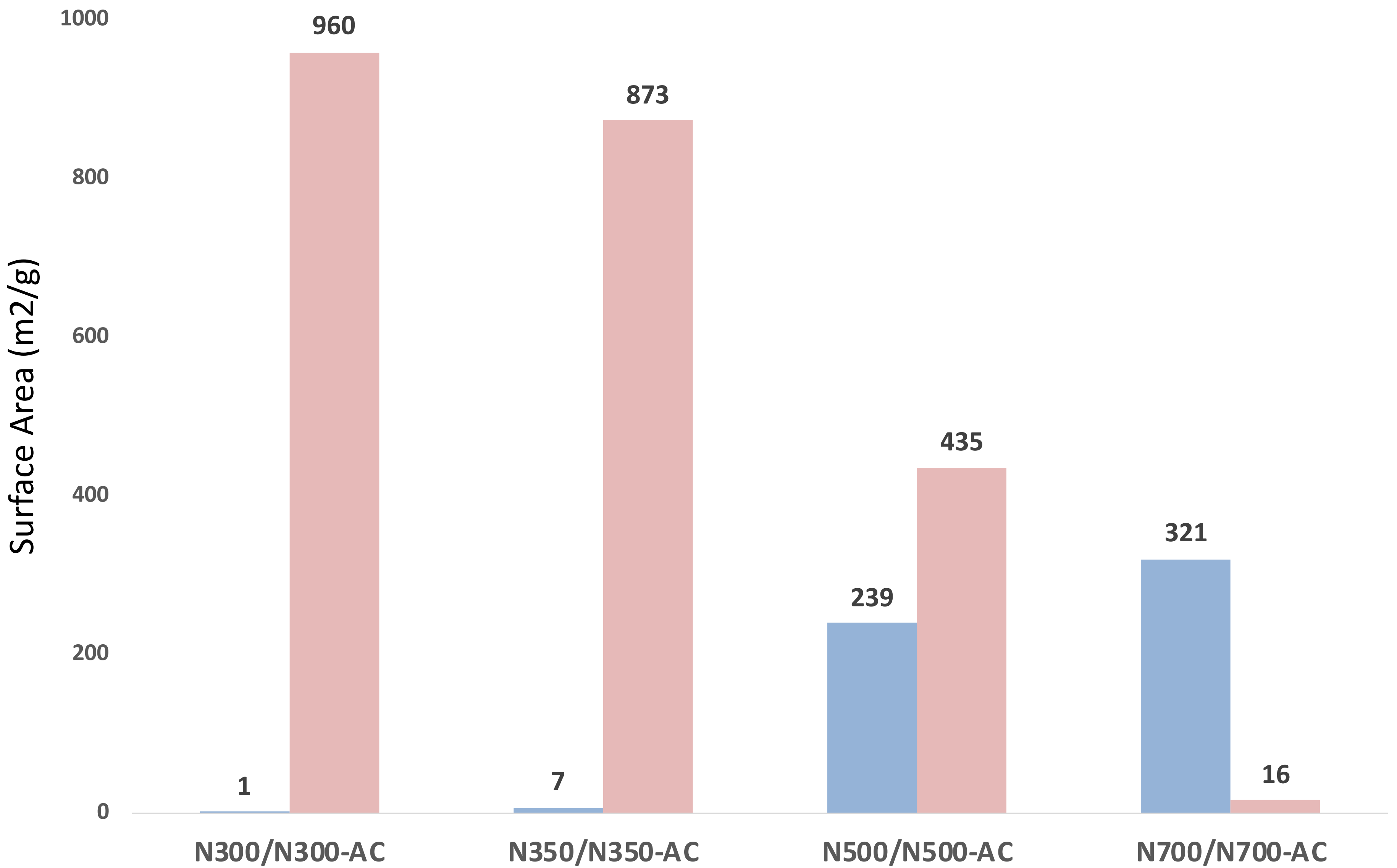


N700

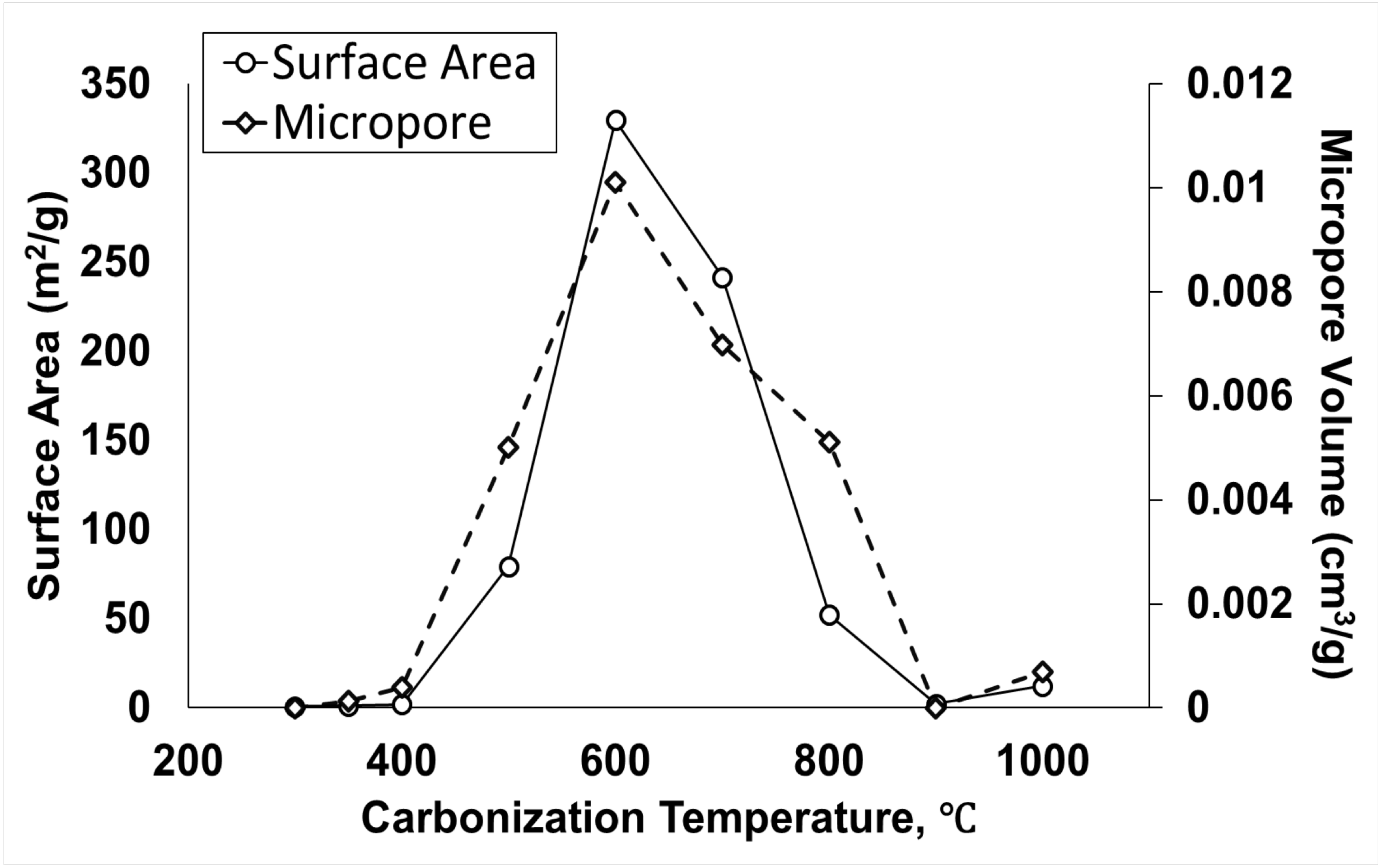


N700-AC

BET Surface Area



BET Surface Area / Micropore



- Bell shaped curve as a function of carbonization temperature
- Intense thermal treatment destroys the structure of carbon

Conclusions

- *Biomass can be used to produce ordered graphite structures*
- *The source (structure) of biomass matters*
- *Graphite formation requires a complex set of chemical and morphological changes*
- *The 'value' of graphite depends on production costs, and performance in specific applications*
- *The performance of activated carbon is also dependent on the biomass source and processing conditions*

USDA
United States Department of Agriculture
National Institute of Food and Agriculture

IBSS
Southeastern Partnership for
Integrated Biomass Supply Systems