Paper Number: 05

Pyrolysis Characteristics of White Pine and Norway Spruce Needles and Properties of Resulting Biochars

Oluwatosin Oginni[1], Connor Crowley[1], Kaushlendra Singh[1], Louis McDonald[2], Tugrul Yumak[3], Edward Sabolsky[3], and Litha Sivanandan[4]

[1]School of Natural Resources, [2]Division of Plant and Soil Science, [3]WVU Extension Service, [4]Mechanical and Aerospace Engineering, West Virginia University, Morgantown, West Virginia, United States

**Correspondence- Kaushlendra.Singh@mail.wvu.edu*

Presented at the USBI Biochar 2018, Wilmington, Delaware

11:40 AM - 12:05 PM, Wednesday, August 22 2018

Presenter
Kaushlendra Singh

Acknowledgements

Funding

1. United States Department of Agriculture McStennis Grant Program (Accession No. 1007044)
2. WV Energy Institute O'Brian Research Award
3. United State Department of Agriculture through Northeast SunGrant Initiative

Oluwatosin Oginni
PhD Candidate
School of Natural Resources

Dr. Tugrul Yumak
Department of Chemistry,
Sinop University, Turkey

Edward Sabolsky
Associate Professor,
Mechanical and Aerospace Engineering

Litha Sivanandan
Associate Professor &
Extension Specialist – Food Safety and Preservation

Louis McDonald
Professor of Environmental Soil Chemistry and Soil Fertility

Biochar/Activated Carbons/Porous Carbons

Wood
Forest Residues
Crop Residues
Manure
Municipal Solid
Waste
Poultry Litter
Undefined Organi
Matter

Feed

Pyrolysis
Gasification

nology

arbons:
ioChars

For combustion
As an absorbent
Soil amendment
atalyst development
Agriculture/Horticulture
Waste water treatment
Electrochemical Devices

Applications

Can any feedstock proce h any technology
produce porous table for all applications?

Characteristics of Porous Carbons as an absorbent

Densities

- Material density
- Bed density
- Particle density

Porosity

- Particle Porosity
- Bulk Porosity

Surface Area

- Internal
- External

Pore Size Distribution

- Macropore > 25 nm
- Mesopore 1nm to 25 nm
- Micropores < 1 nm

Surface Chemistry

- Surface functionalities
- Acidic
- Basic
- Oxygenated groups

Nature of Carbon Surface

- Diamond
- Graphitic
- Amorphous

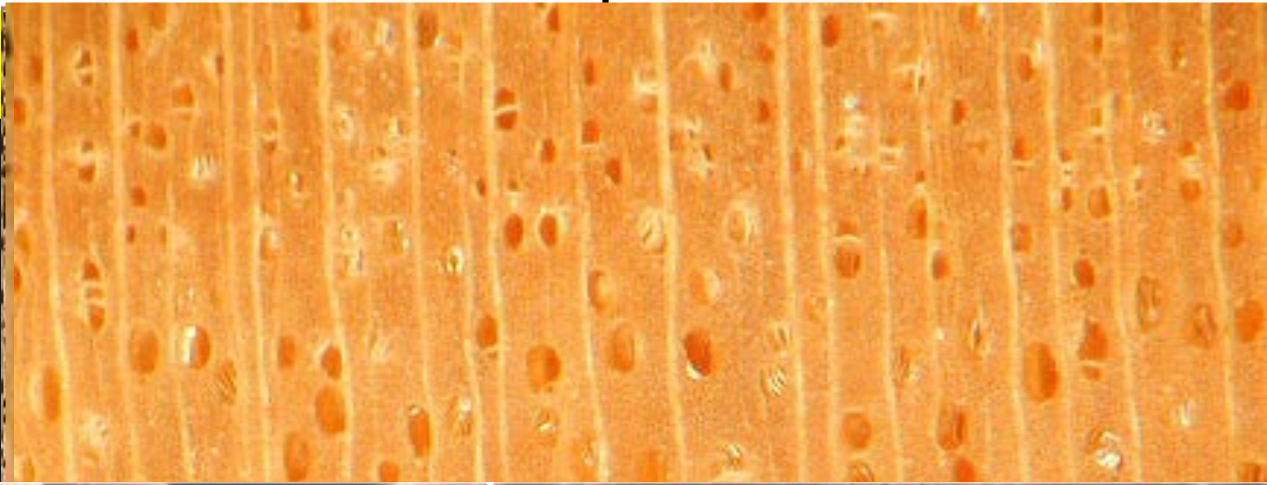
Others

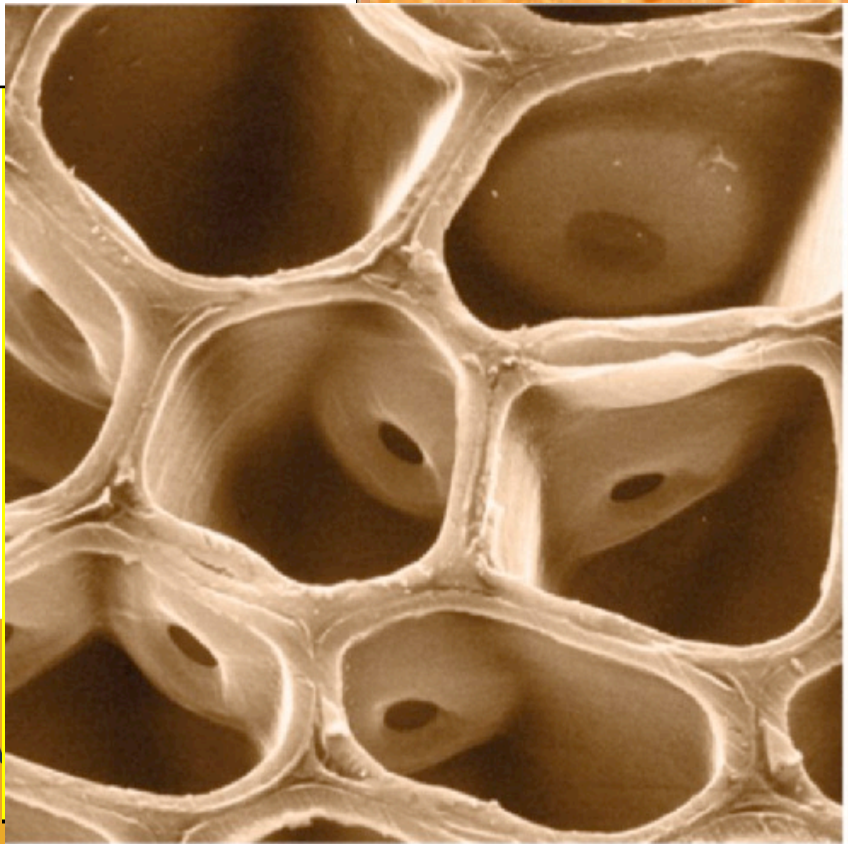
- Surface charge
- Surface energy

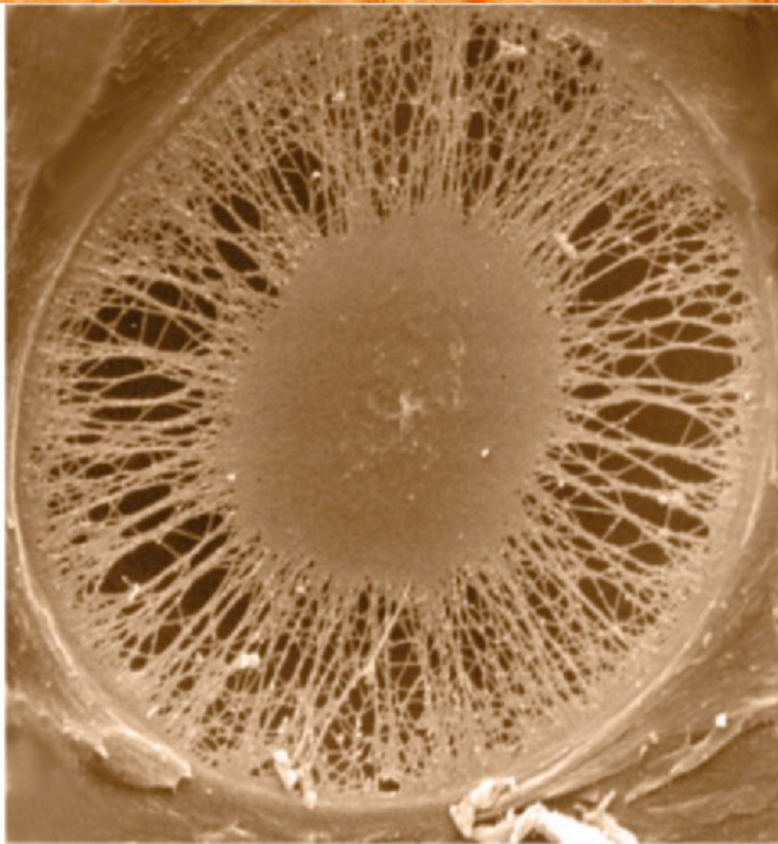
Application: Removal of Acetaminophen from wastewater
Molecule size of acetaminophen: 1.25 nm
Minimum Pore Size Needed: about 2.5 nm or larger
Surface: Partially Graphitic but more disordered carbon surface

Selection of Feedstock is Important

Because we cannot create pore structure totally, otherwise most commercial applications would have use graphite only.







Our Research on Porous Carbons- Since 2004- Ongoing

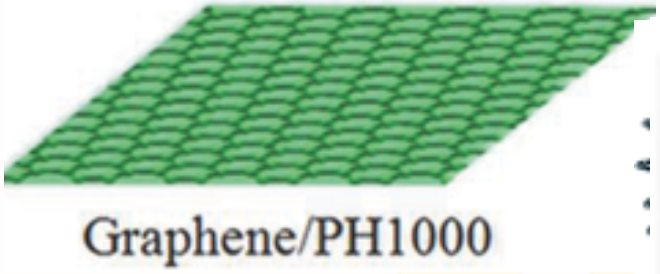
- Poultry Litter Biochars
- Forest Residue Biochars
- Herbaceous Biomass Biochars
- Woody Biomass Biochars
- Selected Forest Materials

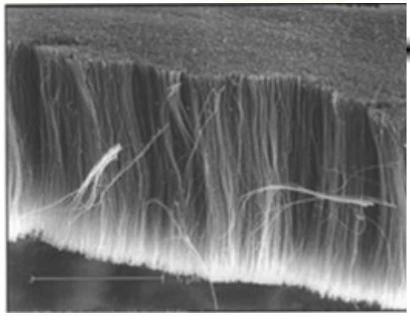
Focused Applications

- As an absorbent for agricultural nutrients and pharmaceutical compounds
- As an electrode material for electrochemical devices

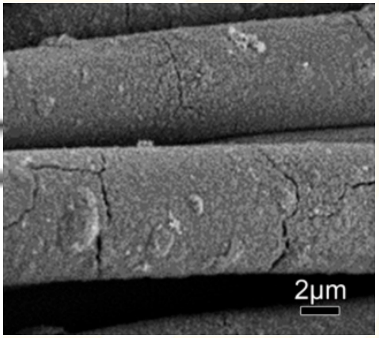
6 research project and 12 published journal articles

Our Search for Porous Carbons for Cost Effective Electrode Materials





carbon nanotubes



carbon fabrics

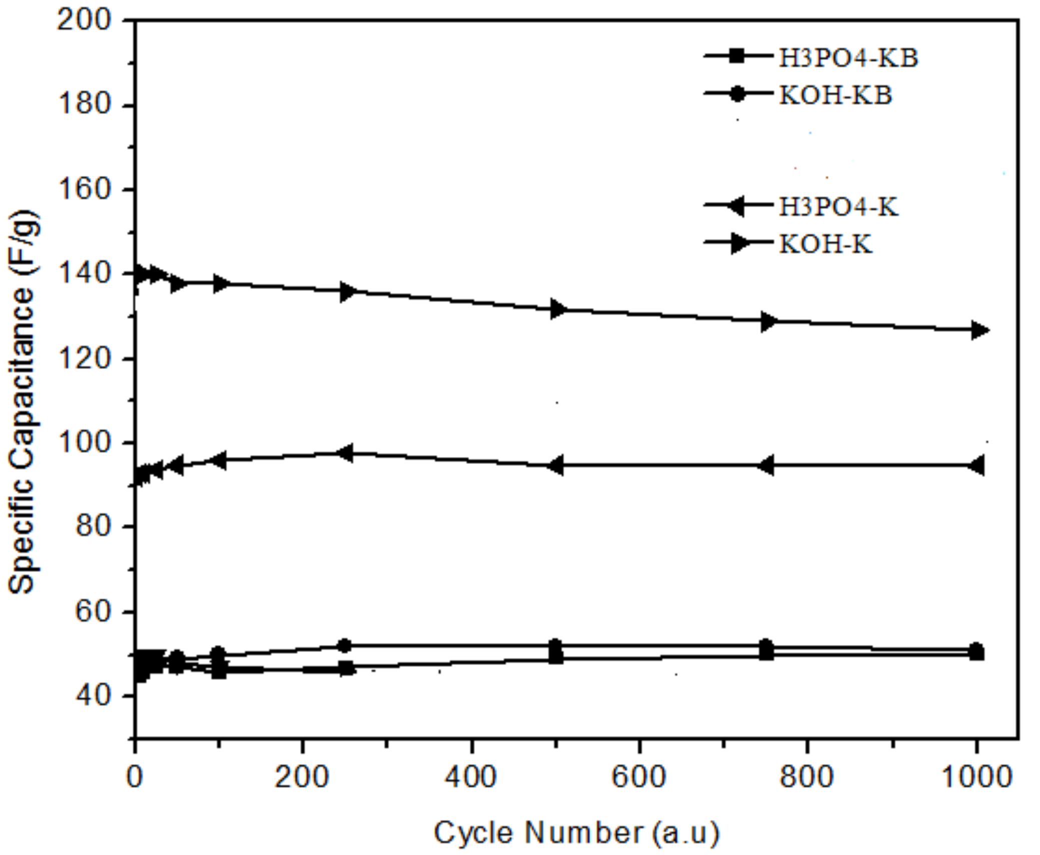
Image (Nanotubes)- Lu, W.; Dai, L., Carbon Nanotube Supercapaci … 010; p Ch. 29.
Image (Nano Horn)- Deshmukh, A. B.; Shelke, M. V., Synthesis an … -Fe_3O_4 nanocomposite supercapacitor electrode. *RSC Advances* **2013,** *3* (44), 21390-21393.
Imange (Carbon Fabric)- Wang, Y.; Tang, S.; Vongehr, S.; Ali Syed, … on Cloth Supercapacitors Based on Highly Processible N-Graphene Doped Polyacrylic Acid/Polyaniline Composites. Scienti

Recent Work: Herbaceous Biomass Crop for Porous Carbon Production

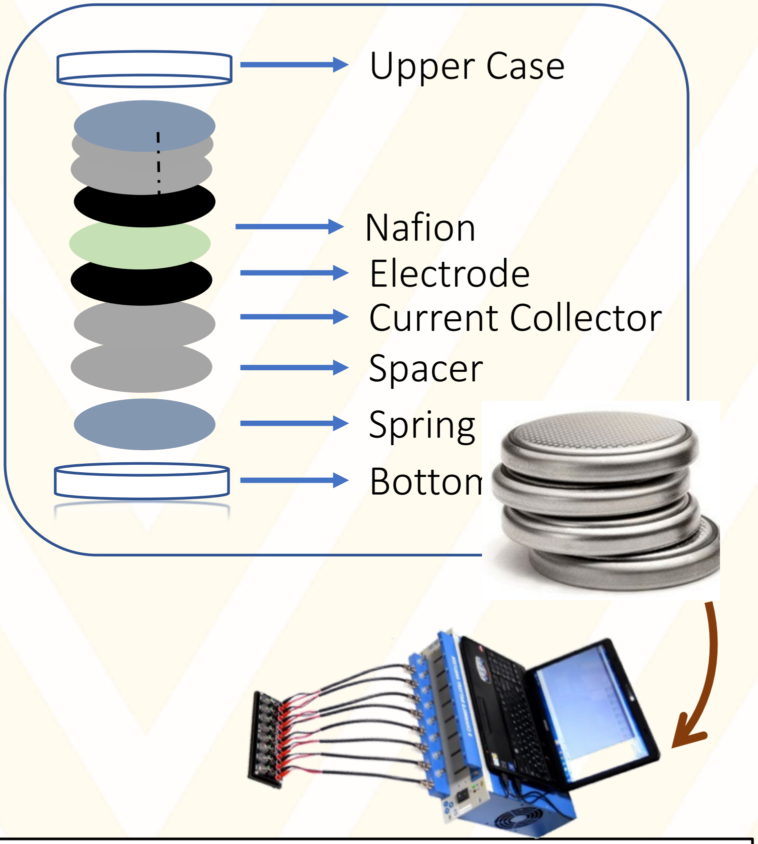
Source	Biomass	Properties	Comment
Ducey et al. [5]	Switchgrass	S_{BET} = 218.7 m^2/g	Steam Activation. Used for soil amendment Cu Sorption
Shim et al. [6]	Miscanthus	S_{BET} = 322 m^2/g	
Kalyani et al. [7]	Turf grass	S_{BET} = 250 m^2/g	Chemical activation ($ZnCl_2$) Used for electrolysis of water for hydrogen production
Our Ongoing Research	Switchgrass	S_{BET} = 1372 m^2/g	Chemical activation (H_3PO_4) Used for electrode materials for energy storage devices

[5] T.F. Ducey, J.A. Ippolito, K.B. Cantrell, J.M. Novak, R.D. Lentz, Addition of activated switchgrass biochar to an aridic subsoil increases microbial nitrogen cycling gene abundances, Applied Soil Ecology, 65 (2013) 65-72.
[6] T. Shim, J. Yoo, C. Ryu, Y.-K. Park, J. Jung, Effect of steam activation of biochar produced from a giant Miscanthus on copper sorption and toxicity, Bioresource Technology, 197 (2015) 85-90.
[7] P. Kalyani, A. Anitha, A. Darchen, Activated carbon from grass – A green alternative catalyst support for water electrolysis, International Journal of Hydrogen Energy, 38 (2013) 10364-10372.

Electrode Performance for Switchgrass-Based Porous Carbons



(2) Supercapacitor Assembly



Upper Case
Nafion
Electrode
Current Collector
Spacer
Spring
Botton

- KOH-activated biomass (KOH-K) showed higher capacitance even after 1000 cycles.
- KOH activation is found to be more effective than H_3PO_4 activation.

Surface Area and Pore Characteristics of Tested Porous Carbons

	BET Surface area (m^2/g)	Micropore volume [a] (cm^3/g)	Cumulative volume [b] (cm^3/g)	Pore diameter [c] (nm)
Biomass	< 5.0	-	-	[illegible]
H_3PO_4-Biomass	1372.9	0.06	[illegible]	[illegible]
KOH-Biomass	1271.7	[illegible]	[illegible]	1.69
KOH-Bio	[illegible]	.22	0.10	1.65
[illegible]	698.0	0.12	0.62	2.74

(a) t-Pl[illegible]icropore volume | **(b)** BJH Desorption cumulative volume of pores between 0.70 nm and 50.0 nm diameter | **(c)** BJH Desorption average pore diameter (4V/A)

We concluded that we need porous carbon with more micropore volume. Find New Feedstock!!!!

- KOH impregnation produced porous carbons with about half of internal pore volume made-up of micropores, whereas, H_3PO_4 produced mostly mesoporous carbons.

Searching for Microporous Carbons

White Pine Needles

Needle Leaves Survive Harsh Winter (-22 to -40°F), Why?

- Possible Reasons:
  - Leaves have sap (mixture of chemicals) that prevent cells from freezing
  - Leaves have lot of micropores that act as safe heaven for sap/liquid and not allowing them to freeze

Needle Leaves Survive Harsh Winter (-22 to -40°F), Why?

Significant depression in the freezing point (ΔT_m) of pure water in small pores may be predicted the Gibbs–Thomson equation [1]. For a pure substance in a cylindrical pore of radius R (nm):

$$\Delta T_m = \frac{51.9}{R}$$

Pores	**Freezing Point**
macropres (>50 nm)	-1.03 °C or 30.14 °F
mesoporoes (>2 nm)	-25.95 °C or -14.71 °F
micropore (<1 nm)	-51.9 °C or -61.42 °F .

Objective

- To compare pyrolysis behavior of White Pine and Norway Spruce needles and investigate characteristics of resulting biochars.

Processing and Characterization of Biomass

Sample harvesting

Sample drying

Sample size reduction
<1 mm for Characterization

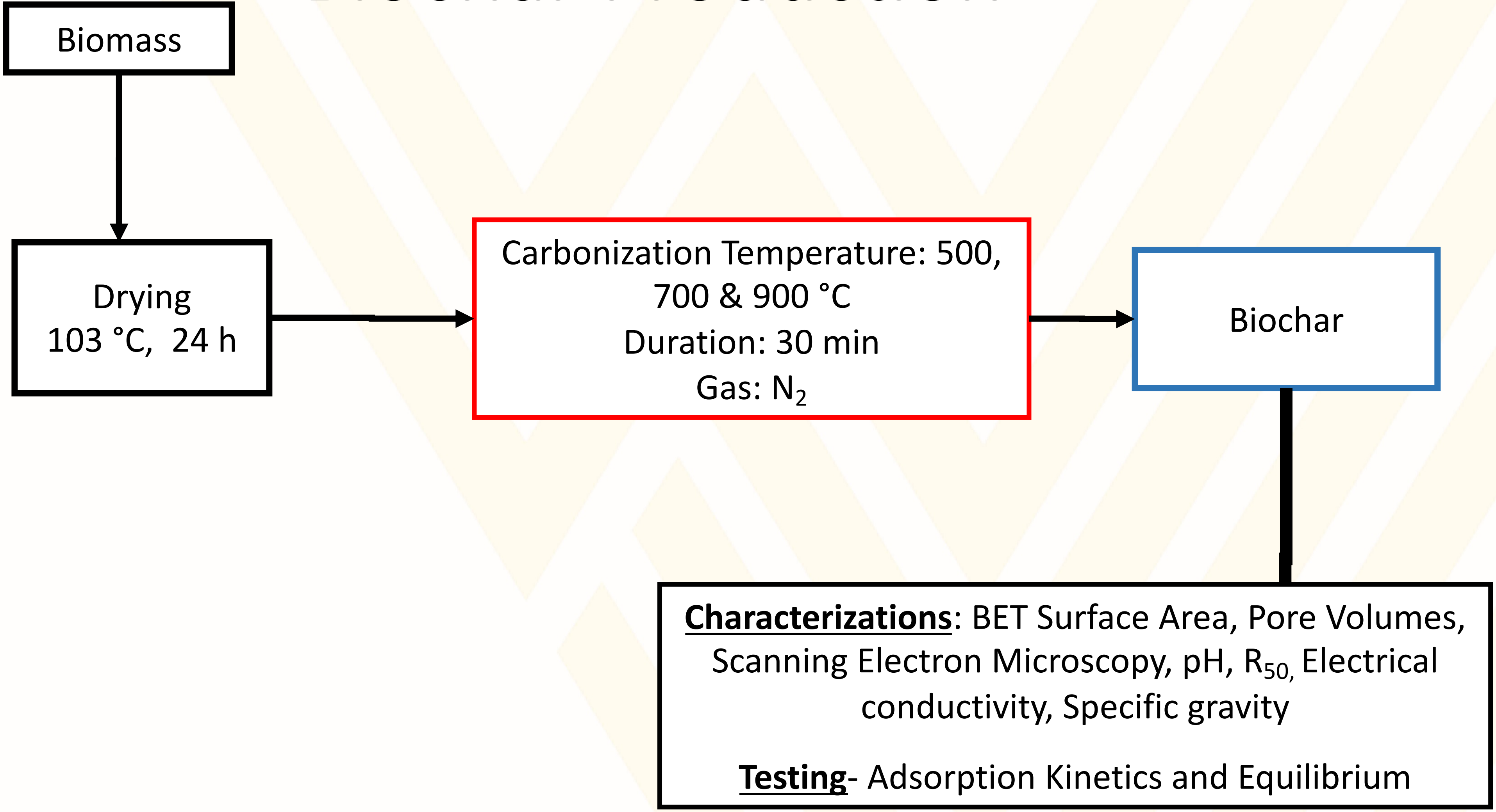
Characterization

Proximate Analysis
Ash, Volatile and Fixed carbon

Ultimate Analysis
Carbon, Hydrogen, Nitrogen, Sulfur, Oxygen

Chemical Composition
Cellulose, Hemicellulose, Lignin, mineral analysis

Biochar Production



Biomass

Drying
103 °C, 24 h

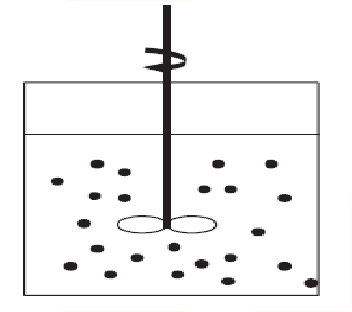
Carbonization Temperature: 500, 700 & 900 °C
Duration: 30 min
Gas: N_2

Biochar

Characterizations: BET Surface Area, Pore Volumes, Scanning Electron Microscopy, pH, R_{50}, Electrical conductivity, Specific gravity

Testing- Adsorption Kinetics and Equilibrium

Testing- Adsorption Kinetics and Equilibrium



Slurry Batch Reactor

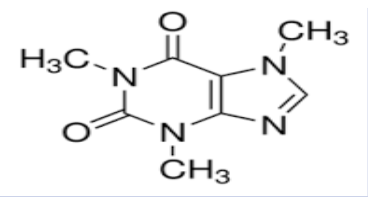
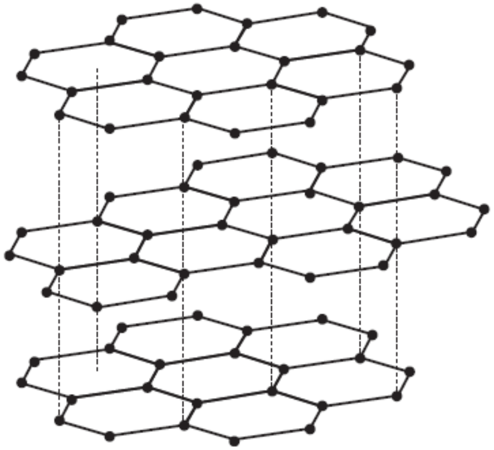
Properties		Caffeine
Molecular structure		
Molecular weight (g/mol)		194.2
Molecular size (nm)		**0.98** x 0.87
Use/category		Stimulant

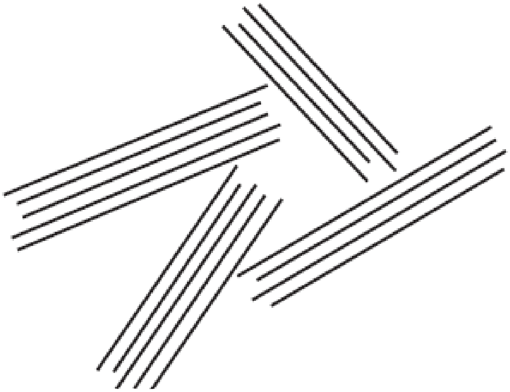
Image Sources:
http://www.thrombocyte.com/is-acetaminophen-a-blood-thinner/
https://www.cbsnews.com/media/things-you-should-know-about-caffeine/

Pore Structure of BioChars

- consists of crystallites with a strongly disturbed graphite structure.
- randomly oriented and interconnected by carbon cross-links.
- The micropores are formed by the voids between the crystallites.
- Slit-like pores are found.



Graphite Crystalline Structure



Randomly Oriented Graphite microcrystallites

How Does BioChars Work?

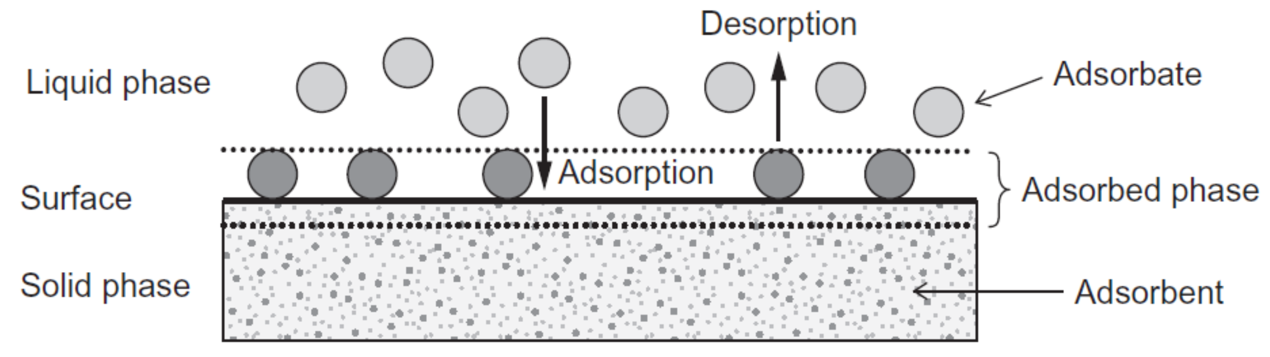


Figure: Basic Single Solute System Adsorption (Worch, 2012)

- Physical Adsorption-
  - It is caused by weak interactions of van der Waals forces (induction forces, dipole-dipole interactions, dispersion forces).

$$H_{ads} < 50\ kJ/mol$$

- Chemical Adsorption-
  - It is caused by chemical reaction between adsorbate and surface sites.

$$H_{ads} > 50\ kJ/mol$$

Sources: Worch, E., *Adsorption technology in water treatment: fundamentals, processes, and modeling*. Walter de Gruyter: 2012

Theoretical Thermodynamic Considerations

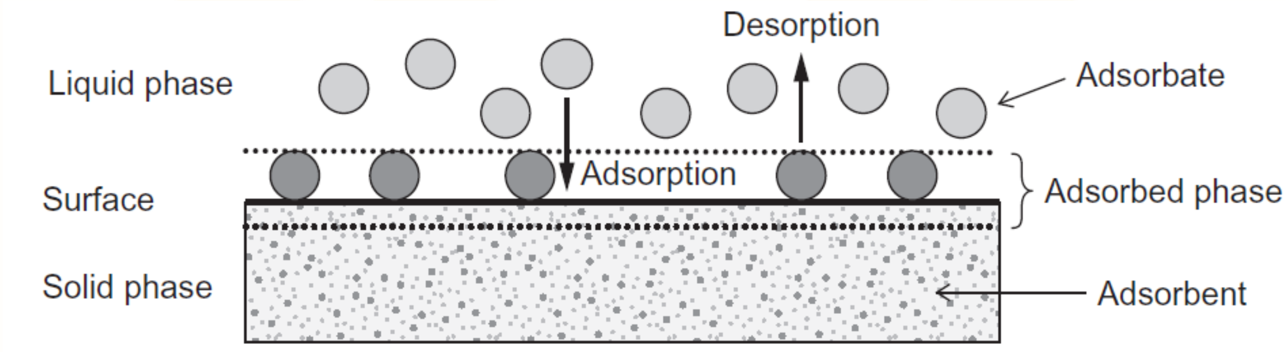


Figure: Basic Single Solute System Adsorption (Worch, 2012)

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i + \sigma\,dA$$

$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,p,n_i}$$

When adsorption takes place:

$$\boldsymbol{\sigma_{ws} - \sigma_{as} = \pi > 0}$$

G= Gibbs Free Energy
S= Entropy
T= Temperature
p= Pressure
ni= Number of moles
A= Surface
V= Volume
µ= Chemical Potential
σ= Surface free energy
ws= Water-Solid interface
as= Adsorbate solution-solid interface
π= Spreading pressure depends on adsorbate amount

For adsorption to take place, change in free energy must be negative:

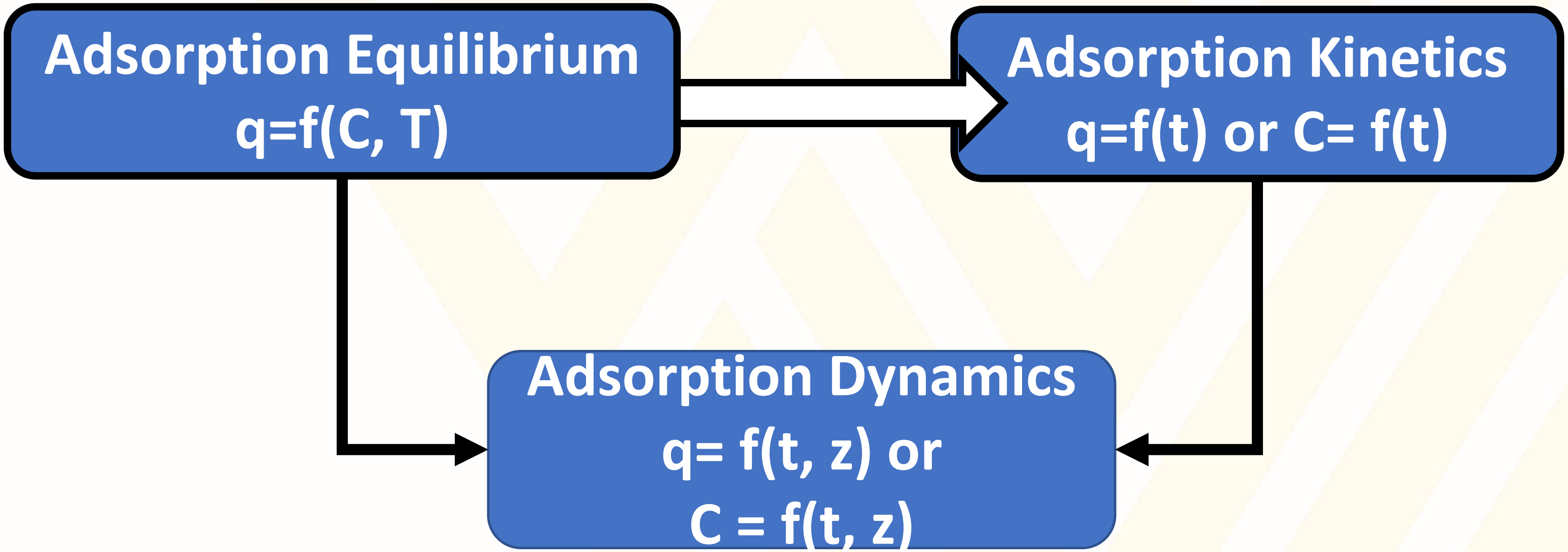
$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} < 0$, since $\Delta S_{ads} < 0$ $\Delta H_{ads} < 0$

Adsorption is a Exothermic process

Sources: Worch, E., *Adsorption technology in water treatment: fundamentals, processes, and modeling*. Walter de Gruyter: 2012

Adsorption Mass Transport Theory

$$\textbf{Adsorbent Loading (q)} = \frac{\boldsymbol{Adsorbed\ Amount}}{\boldsymbol{Asorbent\ Mass}}$$



Adsorption Equilibrium
q=f(C, T)

Adsorption Kinetics
q=f(t) or C= f(t)

Adsorption Dynamics
q= f(t, z) or
C = f(t, z)

Adsorbate Concertation= C; Temperature= T; Space= z; Time= t

Sources: Worch, E., *Adsorption technology in water treatment: fundamentals, processes, and modeling*. Walter de Gruyter: 2012

Adsorption Testing- Single Solute System

Adsorption Kinetics

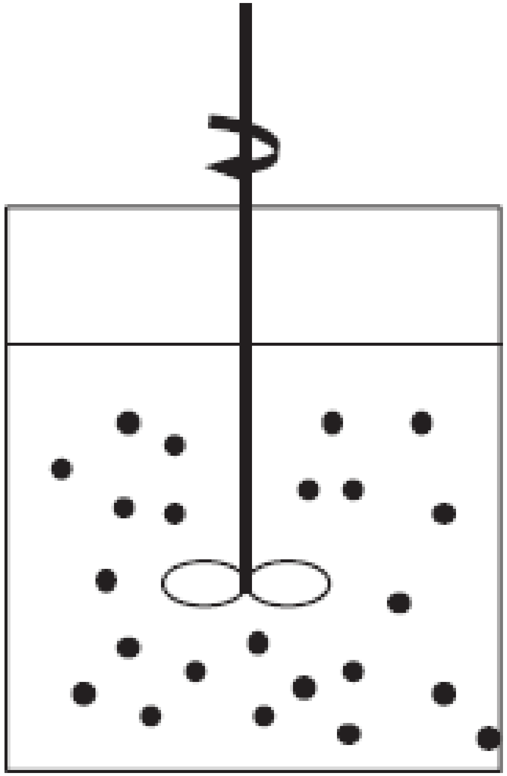
C= f(t)

- Solute Concertation= 40 ppm
- Solution pH= 6.21
- Durations= 0.25, 0.50, 1, 3, 5, 7, and 9 hours
- Temperature= 25 °C
- Adsorbent Loading= 10 mg
- Solution volume= 40 ml

Adsorption Equilibrium

q=f(C, T); T= Constant

- Solute Concentrations (ppm)=10, 20, 30. 40
- Solution pH= 6.21
- Duration = 5 hours
- Temperature = 25 °C
- Adsorbent Loading = 10 mg
- Solution volume = 40 ml



Slurry Batch Reactor

Sources: Worch, E., *Adsorption technology in water treatment: fundamentals, processes, and modeling*. Walter de Gruyter: 2012

Adsorption Kinetics- The pseudo-second order kinetic model

$$q_t = \frac{C_o - C_t}{W} V$$

C_o = initial concentration (ppm),
C_t = concentration at time t (ppm),
V = volume of the adsorbate solution (ml),
W = weight of the activated carbon used (mg), and
q_t= amounts of the adsorbate adsorbed at time t (mg/g)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

q_e= amounts of the adsorbate adsorbed at equilibrium (mg/g),
t= *time (min)*
k_2= equilibrium rate constant (g/mg.min),
k_2 and q_e can be estimated from the intercept and slope, respectively, of the plot of t/q_t versus t,
h= $k_2 . q_e^2$ = the initial adsorption rate (mg/g.min),
$t_{1/2}$ = the time required for the adsorbent to uptake half of the adsorbate amount= $t_{1/2} = \frac{1}{k_2 q_e}$

A.S. Mestre, J. Pires, J.M.F. Nogueira, A.P. Carvalho, Activated carbons for the adsorption of ibuprofen, Carbon, 45 (2007) 1979-1988.

Adsorption Equilibrium

Langmuir isotherm model

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e}$$

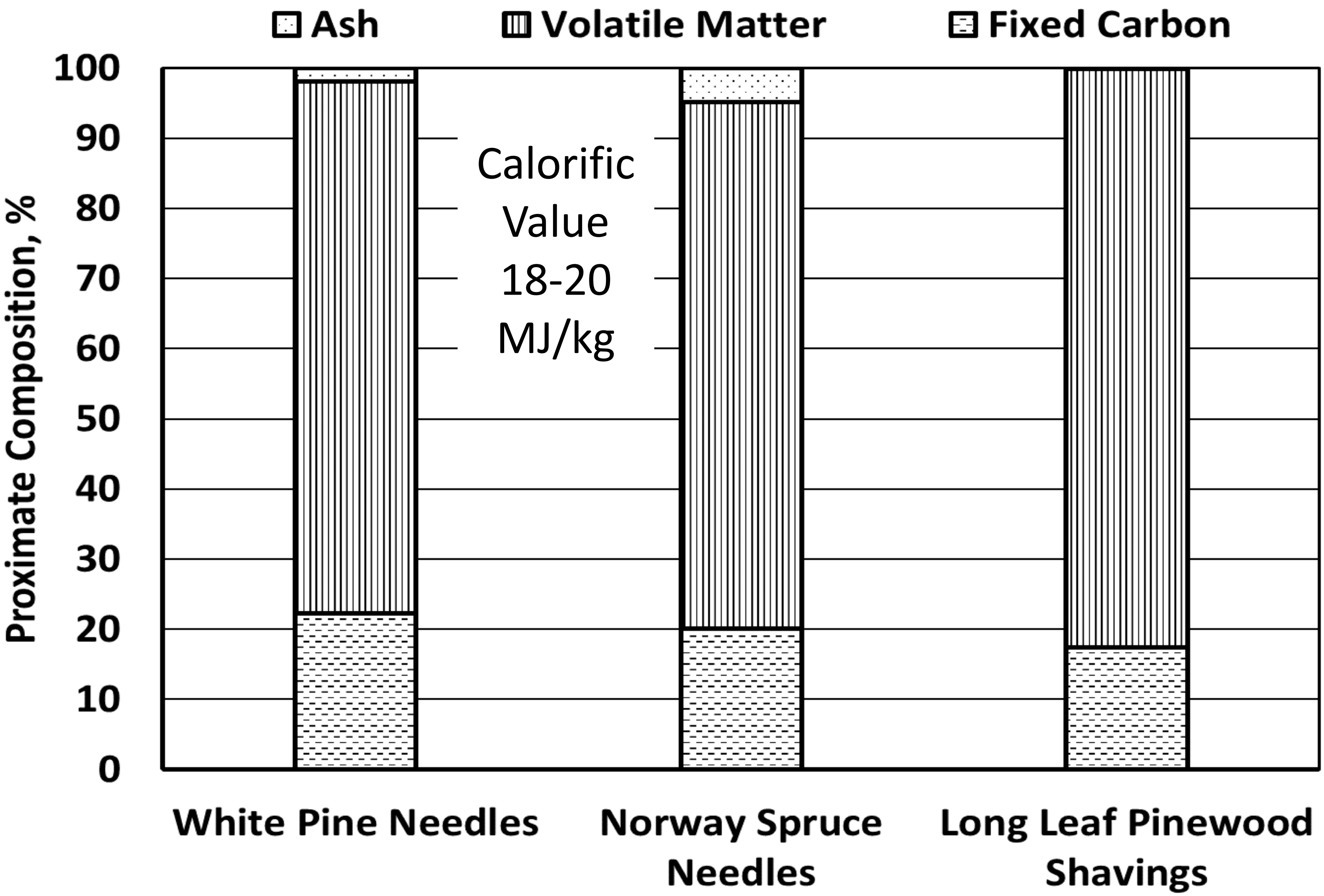
q_e = equilibrium quantity adsorbed (mg/g)
C_e =equilibrium concentration of adsorbate (ppm)
q_m = maximum adsorption capacity (mg/g)
b = Langmuir constant (1/ppm)
q_m and b can be determined from the linear plot of C_e/q_e versus C_e.

Freundlich Isotherm Model

$$lnq_e = lnK_f + \frac{1}{n} lnC_e$$

K_f = strength of adsorption
n = energetic heterogeneity of adsorbent surface
The values of n and K_f can be obtained from the slope and intercept of the linear plot of $\ln q_e$ versus lnCe.

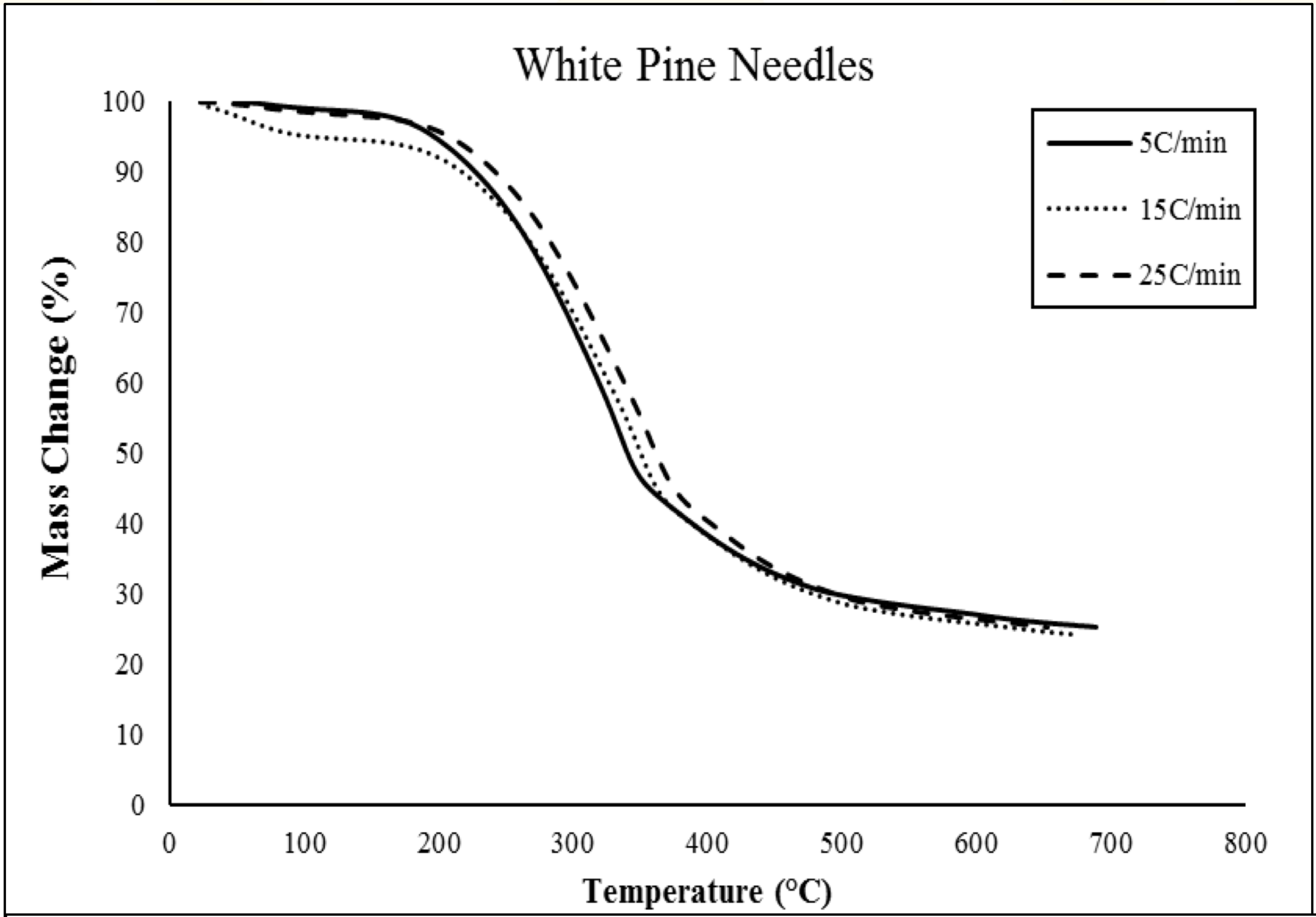
Results- Biomass Characterization



Calorific Value 18-20 MJ/kg

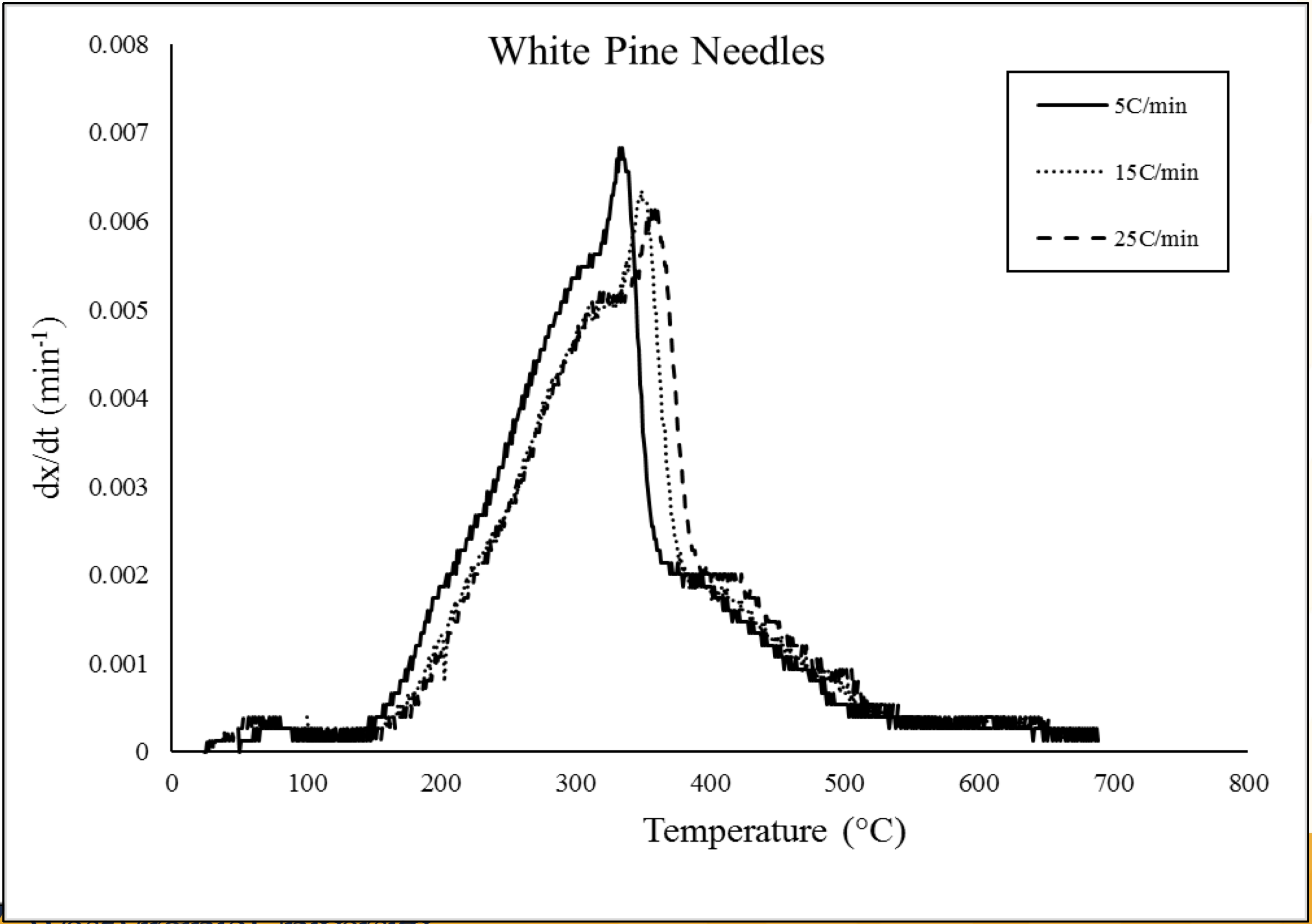
Source for Longleaf Pine Data: Little, A. D. 1916. The Utilization of Wood. The Journal of Industrial and Engineering Chemistry 8 (Part 1): 102-104.

Results- Thermo-Chemical Decomposition Behavior



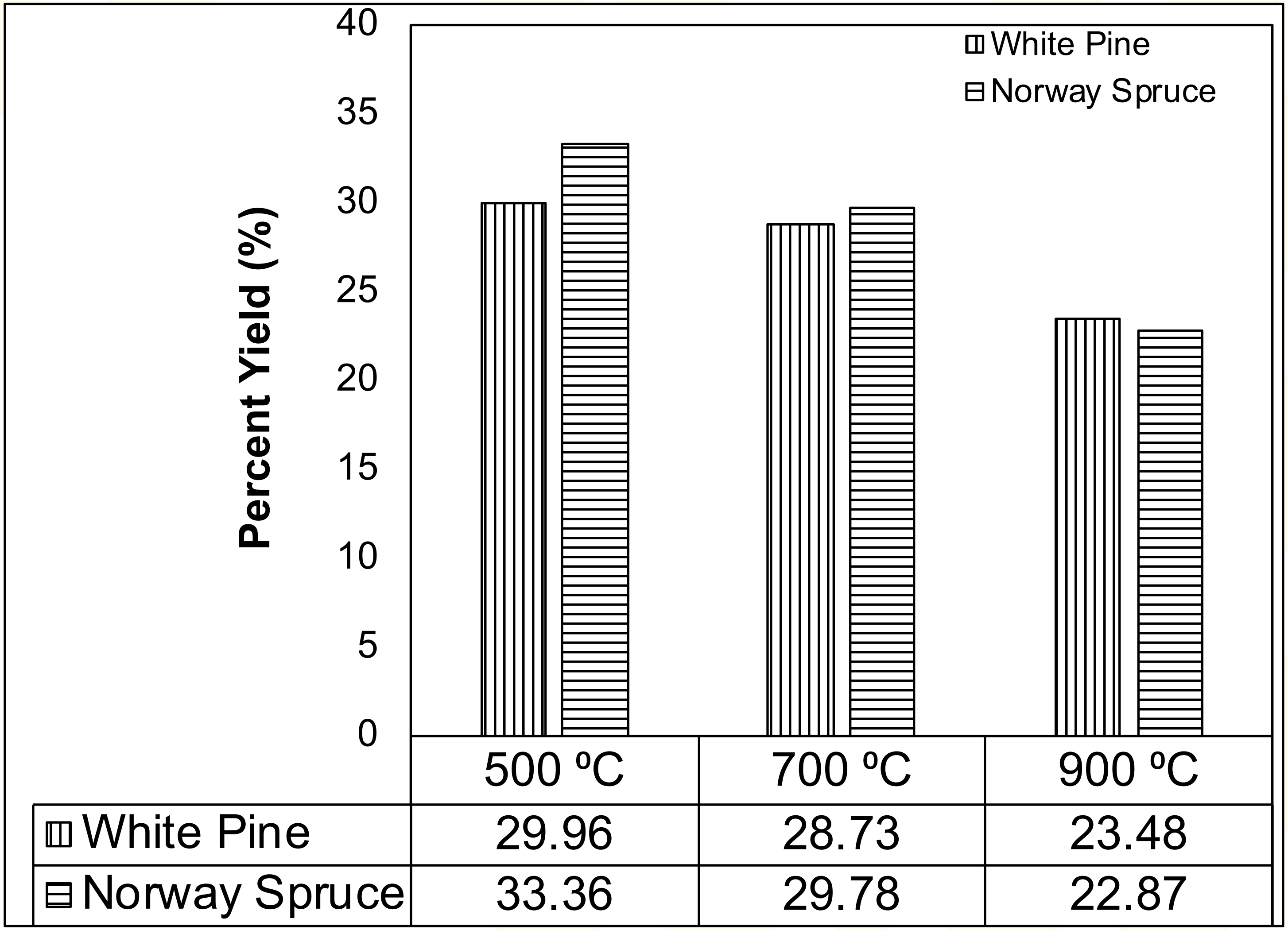
- Both biomass appears to be producing 25-26% biochars and lost 75% of their mass during heating.
- Heating faster or slower does not appear to have much effect on biochar yields or mass loss.

Results- Thermo-Chemical Decomposition Behavior



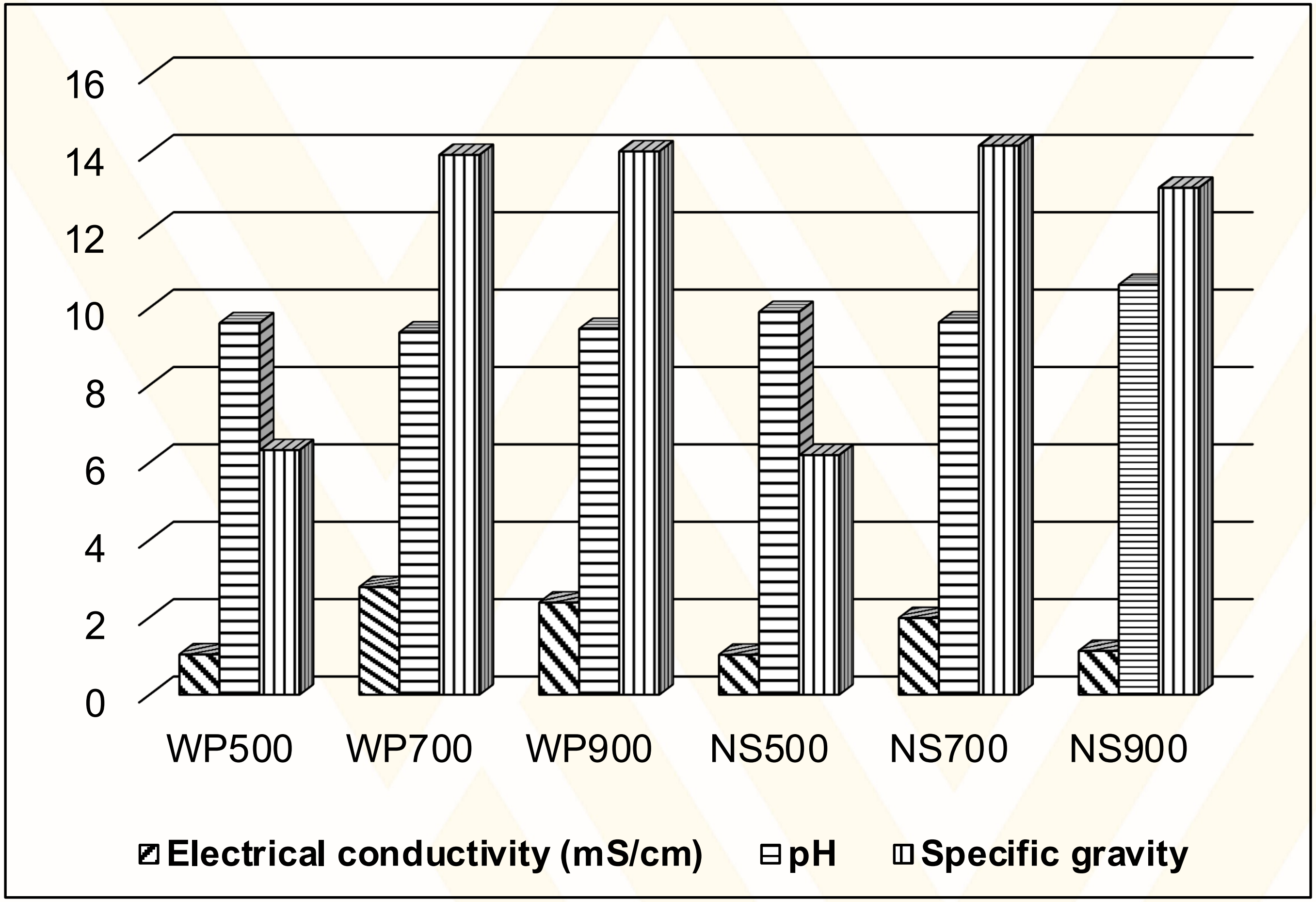
Raveendran, K., Ganesh, A., & Khilar, K. C. (1996). Pyrolysis characteristics of biomass and biomass components. *Fuel*, *75*(8), 987-998.

Results- Pyrolysis Biochar Yields



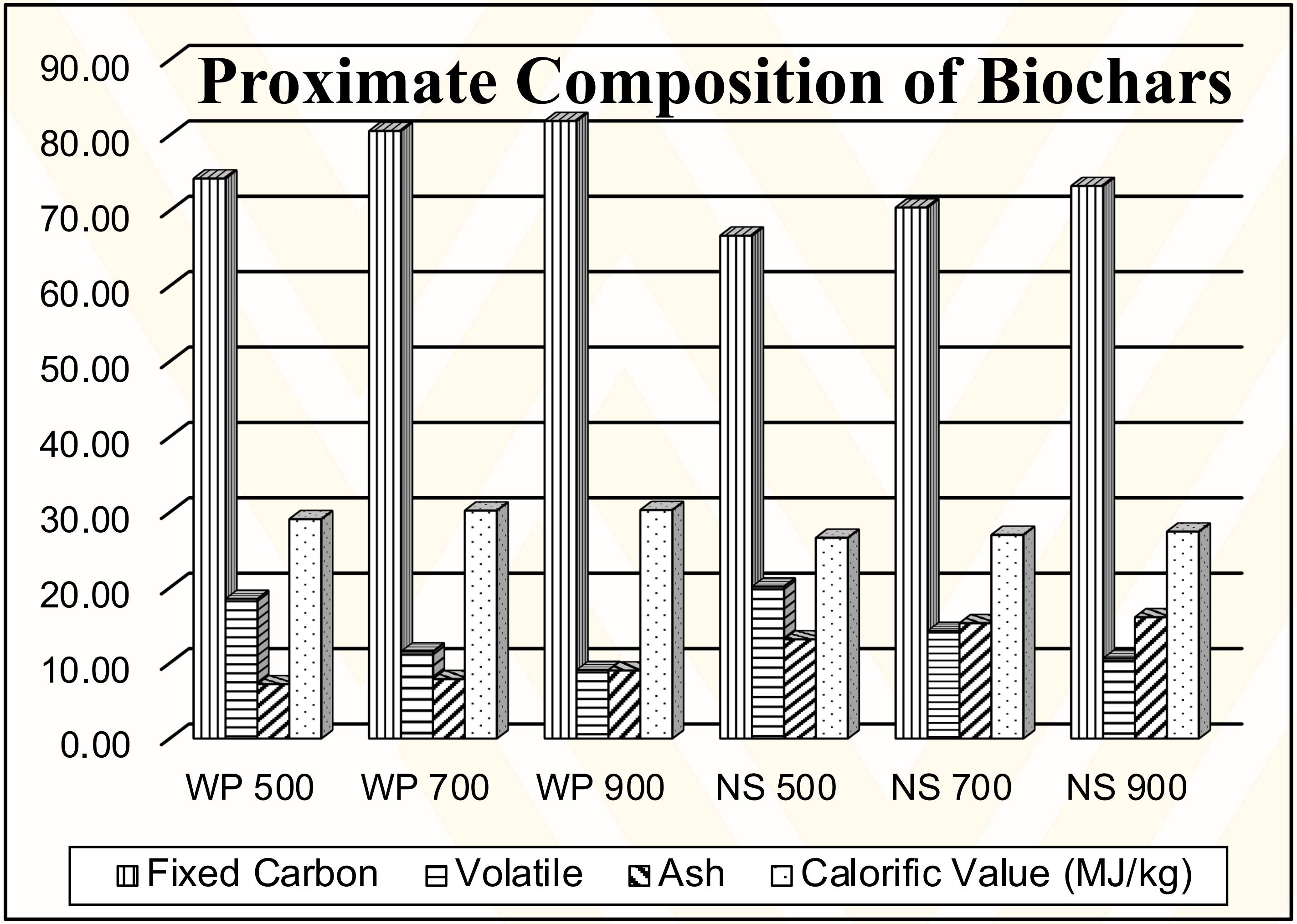
	500 ºC	700 ºC	900 ºC
▥ White Pine	29.96	28.73	23.48
▤ Norway Spruce	33.36	29.78	22.87

Results- Biochar Characteristics



- pH of the biochars showed that they are alkaline in nature. This is a good indicator that the biochars will be good for amending acidic soils.

Results- Biochar Characteristics



Results- Biochar Characteristics

Harvey classification of Biochar Thermal Recalcitrance

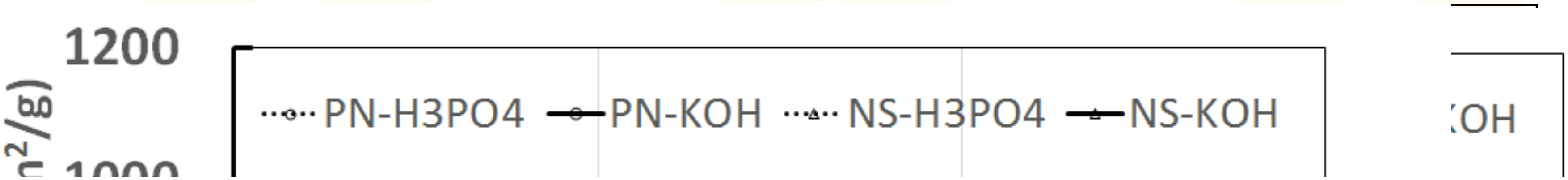
Thermal Recalcitrance	Class C	Class B	Class A
R_{50}	Highly susceptibility to biodegradation	Some susceptibility to biodegradation	Minimal susceptibility to biodegradation
	< 0.50	$0.50 < R_{50} < 0.70$	> 0.70

Table 1: Thermal Recalcitrance values (R_{50}) of Biochars

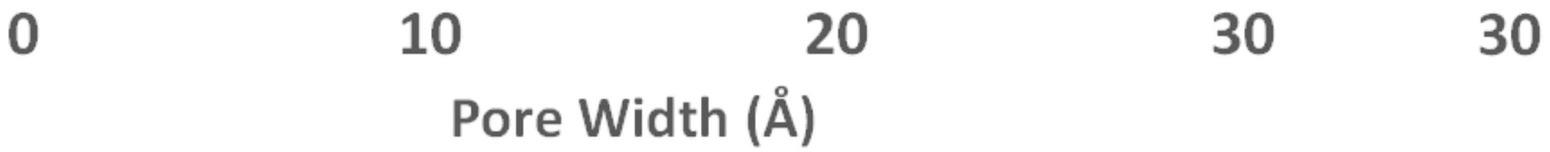
Pyrolysis Temp (°C)	White Pine	Norway Spruce
500	0.50	0.47
700	0.53	0.49
900	0.64	0.51

Harvey, Omar R., et al. "An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars)." *Environmental science & technology* 46.3 (2012): 1415-1421.

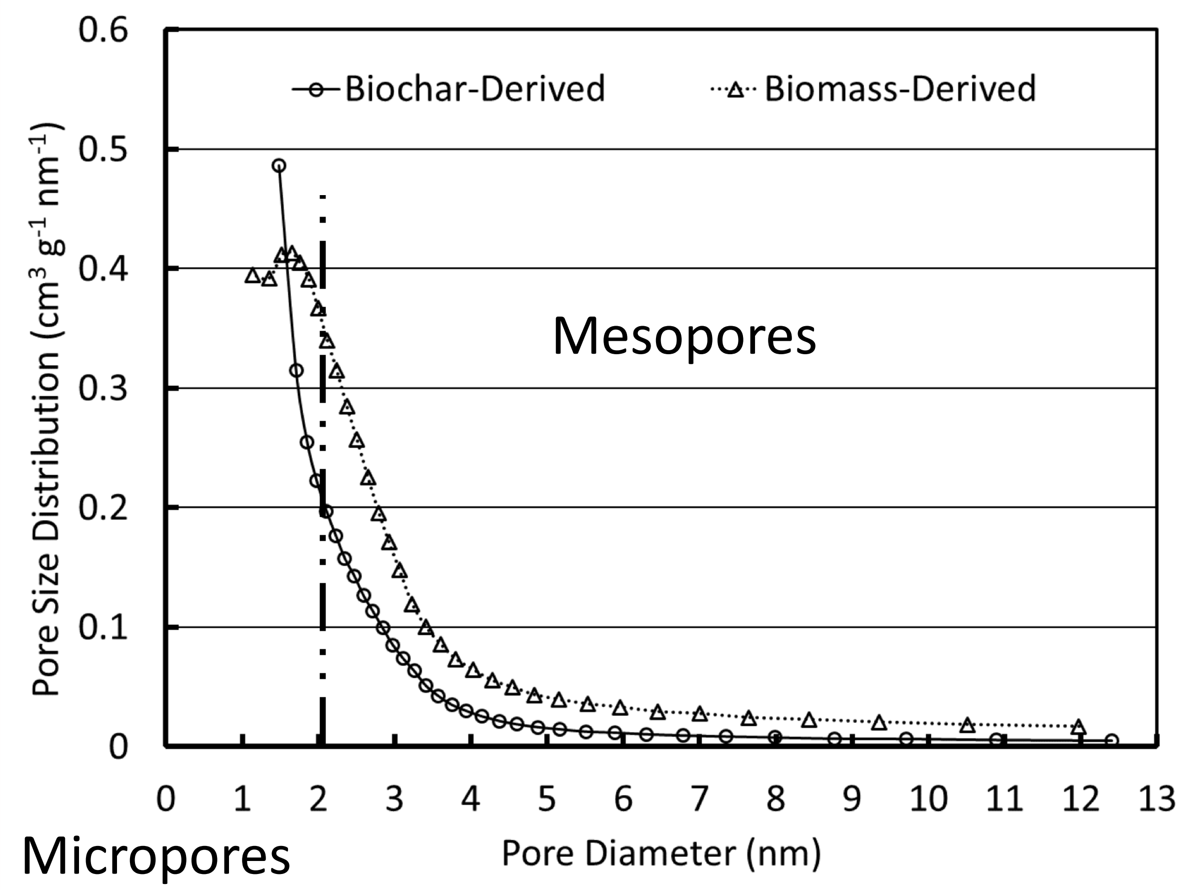
Results- Pore Characteristics of Biochars

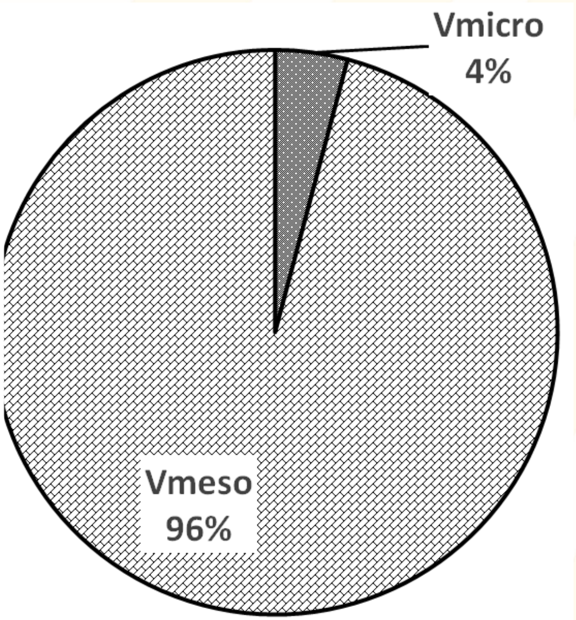


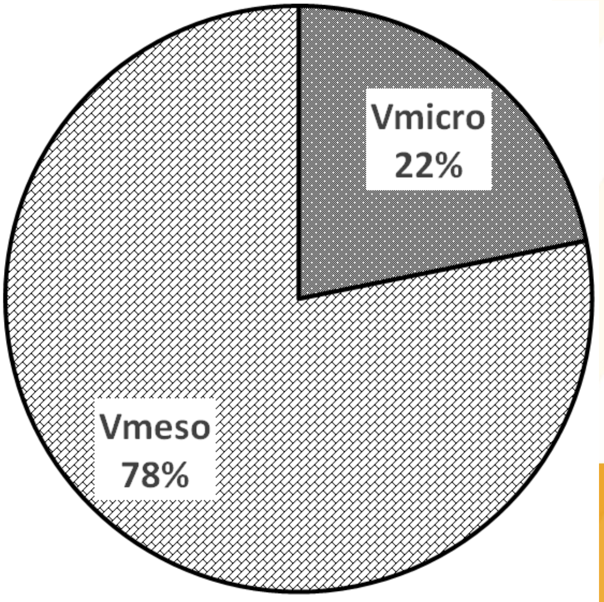
97-99% pores were made-up of micropores



Switchgrass Biochar's Pore Characteristics

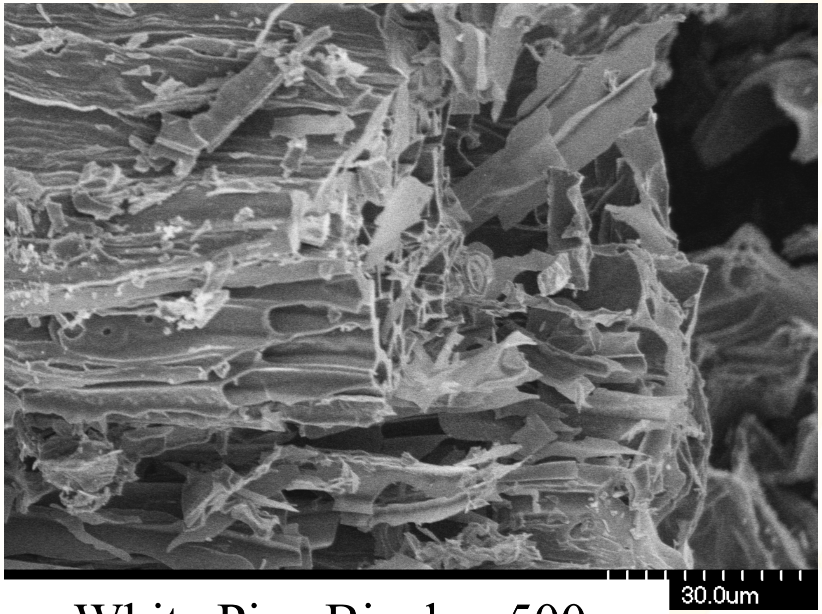




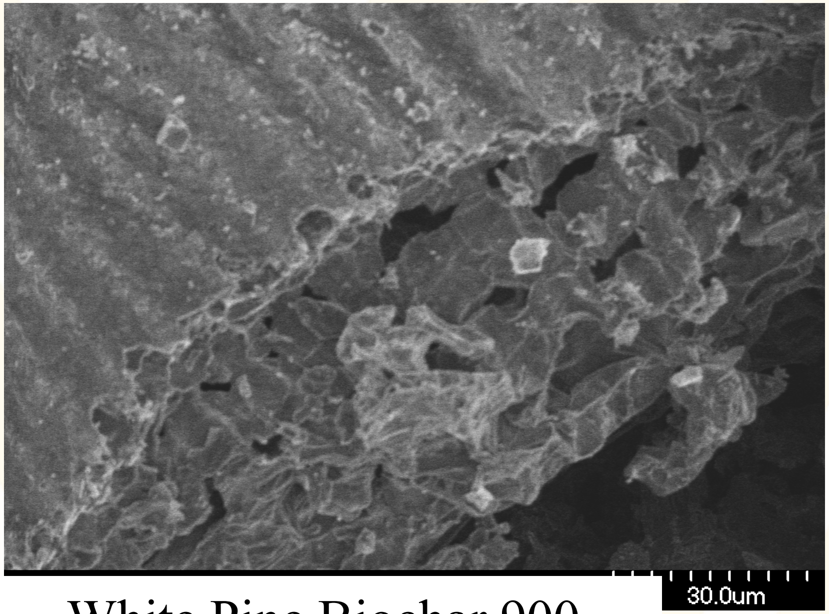


For effective adsorption, the pore diameter of the activated carbon has to be 1.7 to 2 times bigger than the adsorbate dimension.

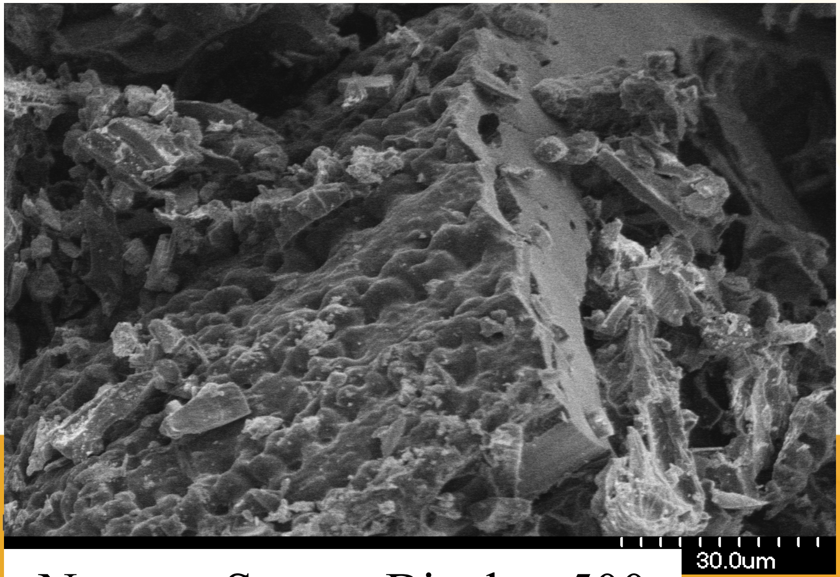
Results- Ultrastructure of Biochars



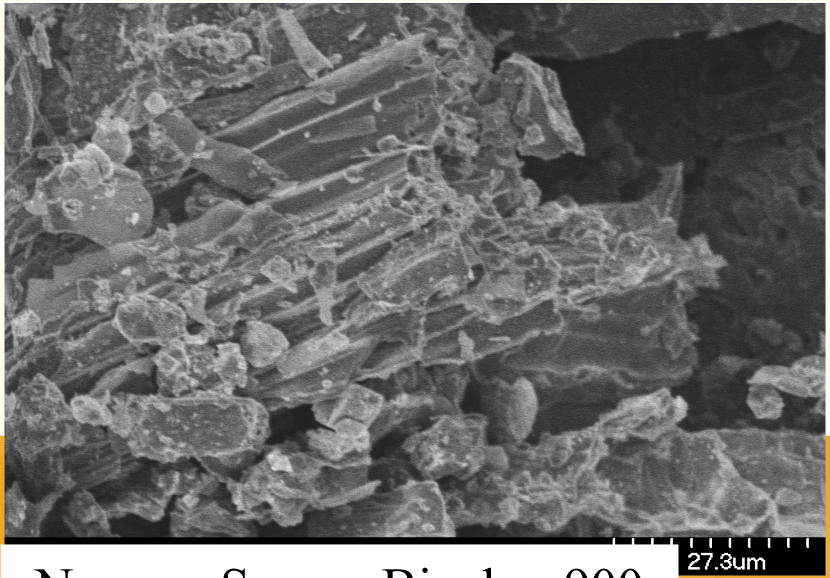
White Pine Biochar 500



White Pine Biochar 900

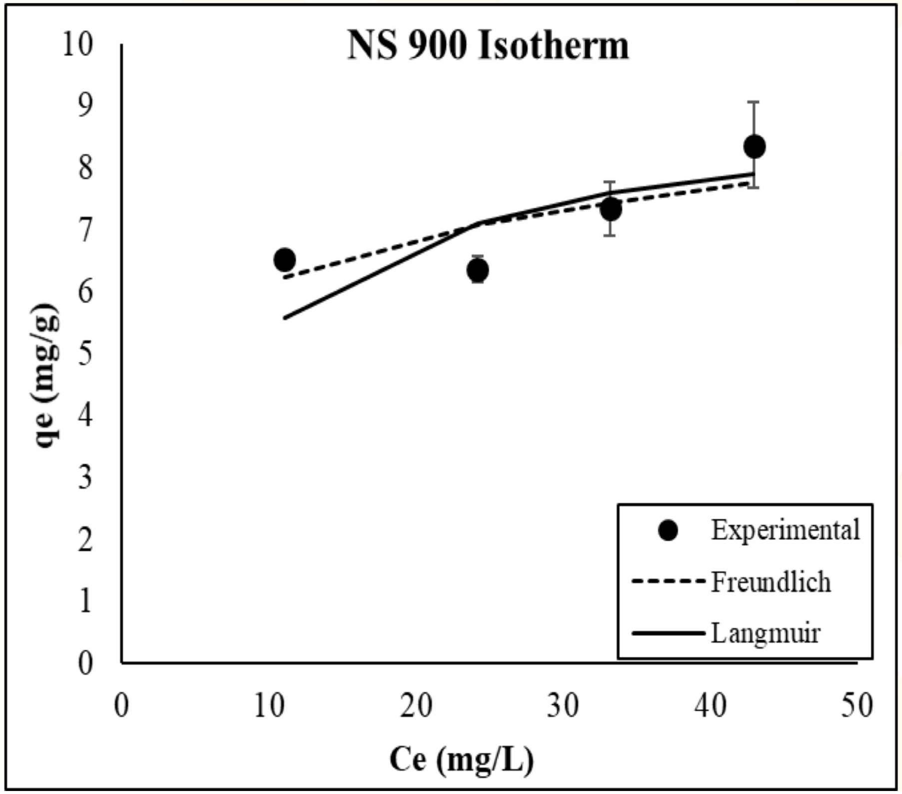


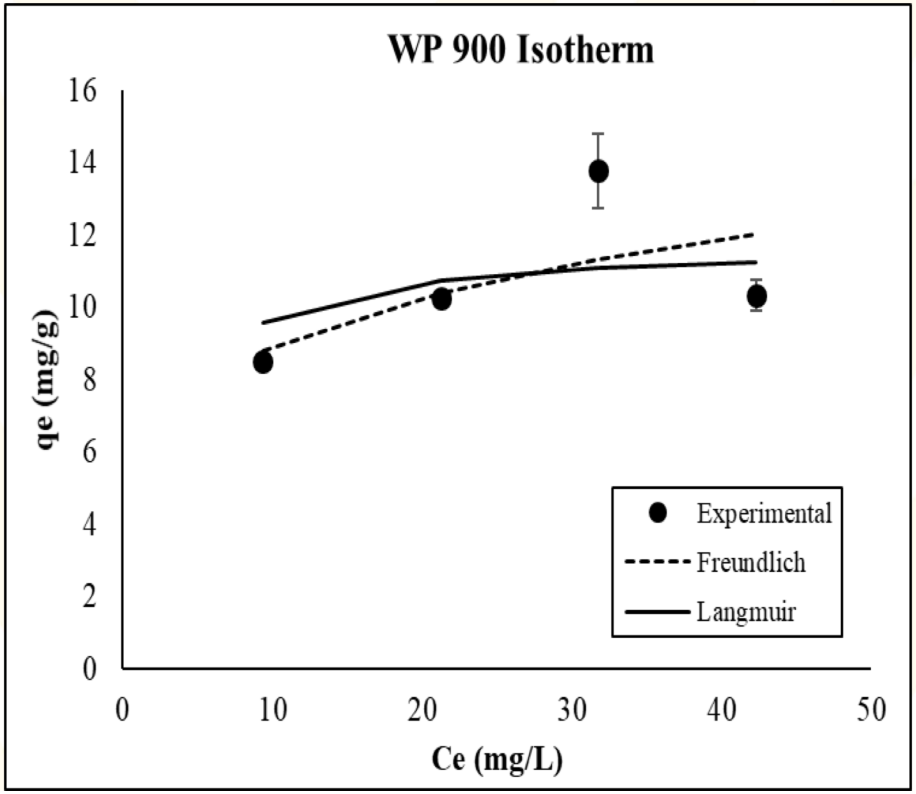
Norway Spruce Biochar 500



Norway Spruce Biochar 900

Results- Adsorption Equilibrium- Caffeine





- Langmuir isotherm model provides the better fit for the adsorption of caffeine than the Freundlich model.
- The Langmuir isotherm model assumes the surface of the activated carbon is energetically homogenous and that a monolayer surface coverage is formed with no interactions between the molecules adsorbed

Results- Adsorption Kinetics

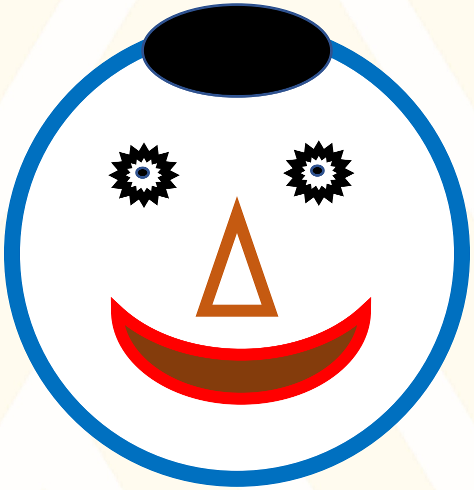
t 1 1

Switchgrass-Derived Biochars had caffeine absorption of 140.85 mg/g, 14 times higher

Take Home Message:

Carefully select feedstock that is suitable to produce porous carbons for the intended application.

Thank you for your undivided attention!!!!!



**Email-*
Kaushlendra.Singh@mail.wvu.edu