

**CO₂ Adsorption using Mg-MOF-74/Activated Biochar
Composites Produced from the Pyrolysis of Lignocellulosic
Biomass**

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Degree
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Abstract

Adsorption is a promising carbon capture and storage (CCS) technology with porous solids like activated biochar (AB), graphene oxides (GO), and metal-organic frameworks (MOF) exhibiting different advantages related to separating carbon dioxide (CO₂) from gas mixtures. Accordingly, the synthesis of MOF/GO composites demonstrates synergism between CO₂ adsorption-driving physicochemical characteristics of MOFs and GOs. However, the synthesis of MOF/AB composites has not been explored in the literature to date even though AB shares many physical and chemical similarities with GO. This research project aimed to synthesize MOF/AB composites with appropriate physicochemical characteristics and CO₂ adsorption capacities for adsorbing CO₂ from flue gas and other important industrial gas mixtures using AB derived from lignocellulosic biomass. Biochars were created by pyrolyzing hybrid poplar, loblolly pine, and switchgrass through intermediate pyrolysis at 500°C and used to adsorb CO₂ from a nitrogen gas (N₂) and CO₂ gas mixture. ABs were developed by activating loblolly pine biochar using potassium hydroxide (KOH) through KOH activation at 800°C and used to adsorb CO₂ from a N₂ and CO₂ gas mixture. MOF/AB composites were synthesized by growing magnesium-metal-organic framework-74 (Mg-MOF-74) crystals on loblolly pine AB through solvothermal synthesis at 125°C and used to adsorb CO₂ from a N₂ and CO₂ gas mixture. All biochars had low CO₂ adsorption capacities ranging from 0.17-0.18 mmol/g which was associated with biochars having low specific surface areas, total pore volumes, and alkalinities. Loblolly pine AB had an increased CO₂ adsorption capacity of 0.51 mmol/g compared to 0.18 mmol/g for loblolly pine biochar which was assumed to be connected to loblolly pine AB having a higher specific surface area, total pore volume, and alkalinity and lower average pore width than those of loblolly pine biochar. Mg-MOF-74/loblolly pine AB composites had a higher CO₂ adsorption capacity of 0.59 mmol/g relative to 0.51 mmol/g for loblolly pine AB which was assumed to correspond to Mg-MOF-74/loblolly pine AB composites having a higher amount of micropores than that of loblolly pine AB. Future work will investigate different MOF synthesis methodologies and surface functionalization of MOF/AB composites to improve CO₂ adsorption.

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Abbreviations and Symbols

IEA	International Energy Agency
WEO	World Energy Outlook
BT	Billion Tons
TCF	Trillion Cubic Feet
Tb	Trillion Barrels
MT	Million Tons
BCF	Billion Cubic Feet
Mb	Million Barrels
CO ₂	Carbon Dioxide
Gt	Gigatons
CCS	Carbon Capture and Storage
IPCC	Intergovernmental Panel on Climate Change
GHG	Greenhouse Gas
Mtoe	Million Tons of Oil Equivalent
SAF	Sustainable Aviation Fuel
ASTM	American Society for Testing and Materials
MOF	Metal-Organic Framework
AC	Activated Carbon
H ₂ O	Water
H ₂ O _v	Water Vapor
AB	Activated Biochar
N	Nitrogen
GO	Graphene Oxide
MOF/GO	Metal-Organic Framework/Graphene Oxide
O	Oxygen
MOF/AB	Metal-Organic Framework/Activated Biochar
C	Carbon
H	Hydrogen
db	Dry Basis
KOH	Potassium Hydroxide
ZnCl ₂	Zinc Chloride
H ₃ PO ₄	Phosphoric Acid
P	Phosphorus
Cu	Copper
BTC	1,3,5-Benzenetricarboxylic Acid
Cu-BTC	Copper-Benzene-1,3,5-Tricarboxylate
ZIF	Zeolitic Imidazolate Framework
Zn	Zinc
Zn-ZIF-8	Zinc-Zeolitic Imidazolate Framework-8
Mg	Magnesium
DHTA	2,5-Dihydroxyterephthalic Acid
Mg-MOF-74	Magnesium-Metal-Organic Framework-74
Cu-BTC/GO	Copper-Benzene-1,3,5-Tricarboxylate/Graphene Oxide
Zn-ZIF-8/GO	Zinc-Zeolitic Imidazolate Framework-8/Graphene Oxide

Mg-MOF-74/AB

APA

CH₄

N₂O

O₃

CFC

HFC

GtCO₂-eq

GtCO₂

GDP

CO₂-eq

CDR

BECCS

CCS

CCU

DAC

H₂

O₂

N₂

CO

NO_x

SO_x

EPA

MO

S

F

PSA

TSA

C₃H₃N₂⁻

M-C₃H₃N₂⁻-M

Si-O-Si

IUPAC

HCl

HNO₃

H₂SO₄

NaOH

H₂O₂

KMnO₄

GAC

PAC

C-C

C=C

R-OH

C=O

R-C(=O)-OH

Magnesium-Metal-Organic Framework-74/Activated
Biochar

American Psychological Association

Methane

Nitrous Oxide

Ozone

Chlorofluorocarbon

Hydrofluorocarbon

Gigatons of Carbon Dioxide Equivalent

Gigatons of Carbon Dioxide

Gross Domestic Product

Carbon Dioxide Equivalent

Carbon Dioxide Removal

Bioenergy with Carbon Capture and Storage

Carbon Capture and Storage

Carbon Capture and Utilization

Direct Air Capture

Hydrogen Gas

Oxygen Gas

Nitrogen Gas

Carbon Monoxide

Nitrogen Oxide

Sulfur Oxide

Environmental Protection Agency

Metal Oxide

Sulfur

Fluorine

Pressure Swing Adsorption

Temperature Swing Adsorption

Imidazolate Anion

Metal-Imidazolate-Metal

Silicon-Oxygen-Silicon

International Union of Pure and Applied Chemistry

Hydrochloric Acid

Nitric Acid

Sulfuric Acid

Sodium Hydroxide

Hydrogen Peroxide

Potassium Permanganate

Granulated Activated Carbon

Powdered Activated Carbon

Carbon-Carbon Single

Carbon-Carbon Double

Hydroxyl

Carbonyl

Carboxyl

R-C(=O)-R'	Ketone
dafb	Dry, Ash-Free Basis
UHP	Ultra High Purity
HPLC	High-Performance Liquid Chromatography
UT	University of Tennessee
wb	Wet Basis
HHV	Higher Heating Value
ρ_b	Bulk Density
Mass _{Biomass}	Mass of Biomass
Volume _{Biomass}	Volume of Biomass
ρ_p	Particle Density
He	Helium Gas
ϕ	Bulk Porosity
Al	Aluminum
Ca	Calcium
Fe	Iron
K	Potassium
Mn	Manganese
Ni	Nickel
Si	Silicon
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
HF	Hydrofluoric Acid
H ₃ BO ₃	Boric Acid
DI	Deionized
TGA	Thermogravimetric Analysis
DTG	Derivative Thermogravimetric Analysis
FTIR	Fourier-Transform Infrared
ATR	Attenuated Total Reflection
XRD	X-Ray Diffraction
CI _{Cellulose}	Cellulose Crystallinity Index
A _{Crystalline}	Area of the Cellulose Crystalline Peaks
A _{Amorphous}	Area of the Cellulose Amorphous Peaks
L _{c,Cellulose}	Cellulose Crystallite Size
K _s	Crystallite Shape Factor
λ	Wavelength of the Incident Beam
FWHM	Full Width at Half Maximum
β_{22}	Full Width at Half Maximum of the 22° 2 θ Peak
θ_{22}	Position of the 22° 2 θ Peak
SSA	Specific Surface Area
V _T	Total Pore Volume
BET	Brunauer-Emmett-Teller
P/P ₀	Relative Pressure
Q _M	Nitrogen Gas Monolayer Capacity
N _A	Avogadro's Number
A _{Cross,N2}	Cross-Sectional Area of Nitrogen Gas

M_{N2}	Molar Mass of Nitrogen Gas
$P_{Sat,0.99}$	Saturated Vapor Pressure of Nitrogen Gas at 0.99 Relative Pressure
$V_{N2,0.99}$	Volume of Nitrogen Gas Adsorbed at 0.99 Relative Pressure
$V_{M,N2}$	Molar Volume of Nitrogen Gas
R	Universal Gas Constant
T	Adsorption Temperature
NLDFT	Non-Local Density-Functional Theory
rpm	Revolutions per Minute
$Yield_{Biochar}$	Biochar Yield
$Mass_{Biochar}$	Mass of Biochar
d_γ	Aliphatic Interchain Spacing
θ_γ	Position of the 18° 2 θ Peak
d_{002}	Aromatic Interlayer Spacing
θ_{002}	Position of the 23° 2 θ Peak
L_c	Aromatic Stacking Diameter
L_a	Aromatic Sheet Diameter
N_a	Number of Stacked Aromatic Sheets
β_{002}	Full Width at Half Maximum of the 23° 2 θ Peak
β_{100}	Full Width at Half Maximum of the 43° 2 θ Peak
θ_{100}	Position of the 43° 2 θ Peak
f_a	Aromaticity
$A_{Aromatic}$	Area of the 23° 2 θ Peak
$A_{Aliphatic}$	Area of the 18° 2 θ Peak
GC	Gas Chromatograph
$C_{CO2,In}$	Inlet Carbon Dioxide Concentration
$C_{CO2,Out}$	Outlet Carbon Dioxide Concentration
C_{CO2}	Carbon Dioxide Concentration Ratio
t_A	Adsorption Time
$C_{CO2,A}$	Adsorbed Carbon Dioxide Concentration Ratio
$V_{CO2,A}$	Carbon Dioxide Adsorption Volume
$Q_{CO2,A}$	Carbon Dioxide Adsorption Capacity
F_A	Adsorption Flow Rate
P_A	Adsorption Pressure
m_B	Mass of Biochar in the Adsorption Column
$C_{CO2,D}$	Desorbed Carbon Dioxide Concentration Ratio
$V_{CO2,D}$	Carbon Dioxide Desorption Volume
$Q_{CO2,D}$	Carbon Dioxide Desorption Capacity
F_D	Desorption Flow Rate
P_D	Desorption Pressure
t_D	Desorption Time
ΔQ_{CO2}	Carbon Dioxide Working Capacity
R_A	Regenerability
ANOVA	Analysis of Variance
R-O-R'	Ether

$R-C_nH_{2n+1}$	Alkyl
R-Ar	Aryl
R-O-Ar	Ether Group Between Alkyl and Aryl Groups
B	Boron
Cl	Chlorine
Mo	Molybdenum
R-CH ₃	Methyl
R-C(-H ₂)-R'	Methylene
C=O	Carbon-Oxygen Double
C-O	Carbon-Oxygen Single
C-H	Carbon-Hydrogen
R-C(H ₂)-CH ₃	Ethyl
K ₂ CO ₃	Potassium Carbonate
K ₂ O	Potassium Oxide
KBr	Potassium Bromide
Yield _{Activated Biochar}	Activated Biochar Yield
Mass _{Activated Biochar}	Mass of Activated Biochar
DTGS	Deuterated Triglycine Sulfate
m _{AB}	Mass of Activated Biochar in the Adsorption Column
DMF	<i>N,N</i> -dimethylformamide
SBU	Secondary Building Unit
M-MOF-74	Metal-Metal-Organic Framework-74
Mg ²⁺	Magnesium(II) Ion
Mn ²⁺	Manganese(II) Ion
Fe ²⁺	Iron(II) Ion
Co ²⁺	Cobalt(II) Ion
Ni ²⁺	Nickel(II) Ion
Cu ²⁺	Copper(II) Ion
Zn ²⁺	Zinc(II) Ion
M ₃ O ₃	Divalent Metal Oxide Cluster
C ₈ H ₂ O ₆ ⁴⁻	2,5-dioxidoterephthalate Anion
Mg(NO ₃) ₂ ·6H ₂ O	Magnesium Nitrate Hexahydrate
ACS	American Chemical Society
Yield _{MOF/AB Composite}	Metal-Organic Framework/Activated Biochar Composite Yield
Mass _{MOF/AB Composite}	Mass of Metal-Organic Framework/Activated Biochar Composite
Mass _{Mg(NO3)2}	Mass of Magnesium Nitrate Hexahydrate
Mass _{DHTA}	Mass of 2,5-dihydroxyterephthalic Acid
Mass _{AB}	Mass of Activated Biochar
Yield _{MOF}	Magnesium-Metal-Organic Framework-74 Yield
Mass _{MOF}	Mass of Magnesium-Metal-Organic Framework-74
L _{c,MOF}	Metal-Organic Framework Crystallite Size
β ₁₁₀	Full Width at Half Maximum of the 7° 2θ Peak
θ ₁₁₀	Position of the 7° 2θ Peak
m _{MOF/AB}	Mass of Metal-Organic Framework/Activated Biochar

R-C(-O)-O⁻
LBL

Composite in the Adsorption Column
Carboxylate Ion
Layer-By-Layer

Introduction

Background

As an intrinsic part of everyday life, most people rely on fossil fuels in one way or another to complete their daily goals. From cosmetics and fuels to pharmaceutical drugs and plastics, fossil fuels have shaped large portions of human society because of the vast number of manners in which mankind has harnessed their inherent properties. For instance, the International Energy Agency (IEA) reported in their 2007 annual flagship publication, World Energy Outlook (WEO), that energy created from fossil fuels is still the principal type of energy being used around the world for societal development and that such energy is anticipated to satisfy approximately 84% of the global energy demand in 2030 [1]. However, many individuals strongly believe that this substantial reliance on fossil fuels for energy and other products eventually needs to change for human civilization to continuously expand and thrive. Such beliefs predominantly stem from the knowledge that fossil fuels are natural resources which can only be replenished over millions of years meaning that limited supplies of fossil fuels exist underground at any time. To date, researchers estimate that global reserves of fossil fuels including coal, natural gas, and oil are close to 891.531 billion tons (BT), 6558 trillion cubic feet (TCF), and 1.689 trillion barrels (Tb), respectively. The global acquisition or production rates per day of these different fossil fuels, in order, are also considered to be nearly 21.63 million tons (MT), 326 billion cubic feet (BCF), and 86.81 million barrels (Mb). Consequently, researchers predict that coal, natural gas, and oil global reserves will be depleted by the years 2126, 2068, and 2066, respectively [2].

This pressing circumstance is worsened by the realization that the main pathway used for converting fossil fuels into energy known as combustion releases carbon dioxide (CO_2) into the atmosphere. Normally, the emission of CO_2 would not be alarming since there are many natural processes that fix atmospheric CO_2 into various forms of organic matter for extended periods of time. However, the sheer magnitude and rate at which human-related or anthropogenic activities add CO_2 into the atmosphere vastly outpace these processes resulting in a net accumulation of atmospheric CO_2 . For example, fossil fuels are estimated as being consumed in disparate anthropogenic activities at a global rate of approximately 0.001 Mb per second which suggests that about 29 gigatons (Gt) of CO_2 in total are released per year into the atmosphere. Of this emitted CO_2 , only roughly 6.8 Gt of CO_2 are reclaimed through natural cycles, while the remaining 10.2 Gt of CO_2 are concentrated in the atmosphere [2]. The rate of CO_2 emission into the atmosphere throughout human history has also accelerated since the onset of the Industrial Era which is attributed to the introduction of fossil fuel-powered machinery into human society during this period. The use of this machinery greatly increases the rate of fossil fuel consumption compared to non-mechanical approaches and has significantly amplified the rate of fossil fuel consumption relative to that of pre-industrial times. Furthermore, this accrued atmospheric CO_2 is a major cause of the current global warming phenomenon impacting every country around the world. This crisis threatens to cause significant changes to global land and ocean temperatures which would lead to serious environmental consequences including more frequent and severe natural disasters. Accordingly, there is escalating interest in developing alternative sources of energy to replace fossil fuels and establishing much needed carbon capture and storage (CCS) technologies to remove accumulated CO_2 directly from the atmosphere and capture newly generated CO_2 before it can be emitted into the atmosphere [3][4][5][6][7].

Different types of alternative or renewable energy such as biomass, geothermal, hydroelectric, solar, and wind energies are being investigated to meet global energy demands.

Renewable energy does not involve the emission of more net CO₂ into the atmosphere making many of the disparate kinds of renewable energy ideal replacements for fossil fuels. Moreover, the Intergovernmental Panel on Climate Change (IPCC) has stated that renewable energy must supply an anticipated 70-85% of the global energy demand by 2050 to restrict global warming to only a 1.5°C increase by 2100 compared to pre-industrial times [6]. However, separate varieties of renewable energy have different challenges and opportunities thereby making the use of certain renewable energies only feasible for specific applications and settings. Differing sectors of society also emit various amounts of greenhouse gases (GHG) or different gases including CO₂ into the atmosphere that contribute to global warming which influence the sorts of CCS technologies that can be realistically applied in these areas. Both factors are necessary considerations that must be accounted for when developing new strategies for implementing renewable energy and attempting to reduce CO₂ emissions from a particular portion of society. In terms of the most concerning sectors, the transportation sector is a key area in need of alternatives to fossil fuels. For instance, the IEA emphasized in a report published in 2016 that the transportation sector alone used approximately 2627 million tons of oil equivalent (Mtoe) in 2014 which accounted for nearly 27.9% of the total global energy production. The report also mentioned that global energy consumption in this sector is estimated to increase by a minimum of 80% over the next few decades [8]. Such predictions have led many industry leaders, politicians, and researchers to begin pushing for the incorporation of renewable energy into the transportation sector.

For automobiles, many methods of transitioning from fossil fuels to renewable energy are being researched including manufacturing electric cars and trucks capable of moving using electrical energy stored in batteries and creating biomass-based fuels known as biofuels that can serve as either standalone substitutes for petroleum-derived fuels or as components of petroleum-blended fuels which can both be directly used in the internal combustion engines regularly found in cars and trucks [3][4][5][9]. Yet, despite these efforts, aircrafts cannot currently operate solely using batteries as in the case of electric cars and trucks predominantly because of the lower energy densities of batteries compared to those of conventional jet fuels. This difference implies that the weight of the energy source would increase if batteries were used relative to jet fuels, and therefore, less cargo and passengers would be able to travel per flight [9][10]. Instead, the more favorable strategy for shifting aircrafts from using fossil fuels to renewable energy is to replace these fuels with biomass-based fuels specifically designed for aircrafts referred to as bio-jet fuels or sustainable aviation fuels (SAF). Such biomass-based fuels are produced through both biochemical and thermochemical pathways with the latter encompassing two important thermal decomposition processes known as gasification and pyrolysis. In both processes, biomass experiences thermal degradation at separate temperatures in a partially oxygen-free or completely oxygen-free environment resulting in the production of gaseous, liquid, and solid products commonly called pyrolytic gas or syngas, bio-oil, and biochar, respectively. Afterwards, the major product which is dependent on whether gasification or pyrolysis is performed typically undergoes downstream processing to generate SAFs which have the required physical and chemical or physicochemical properties specified by the American Society for Testing and Materials (ASTM) international standards for allowable jet fuels [3][4][5][9]. In addition, the minor products or byproducts are often transformed into value-added coproducts which are then sold to other industries and manufacturers to help offset the costs of producing SAFs.

Value-added coproducts created from the less desirable byproducts of gasification and pyrolysis assume many different forms and are useful in separate applications across multiple industries. For example, there is growing concern in the energy sector related to the quantities of

CO₂ being emitted into the atmosphere from the combustion of fossil fuels like coal to produce electrical energy in coal-fired power plants. Much of this attention has caused researchers to begin exploring different ways in which CCS technologies can be incorporated into existing coal-fired power plants to effectively capture CO₂. Currently, many distinct techniques for removing CO₂ are being studied in this regard such as absorption, adsorption, cryogenic separation, and membrane separation which each have their own advantages and challenges. However, adsorption is the most promising of these methods for capturing CO₂ from coal-fired power plants because of the low energy requirements and wide range of operating conditions of this process [11]. Additionally, many types of adsorbents or porous solids that adhere atoms, ions, or molecules of gaseous, liquid, or dissolved solid substances known as adsorbates to their surfaces are being investigated including silicas, zeolites, metal oxides, metal-organic frameworks (MOF), and activated carbons (AC), among others. Out of these porous solids, inorganic/organic porous solids such as MOFs are being heavily researched across multiple scientific disciplines for critical applications such as CO₂ adsorption. MOFs exhibit high CO₂ adsorption capacities at atmospheric pressure and room temperature which are beneficial characteristics for CCS technologies within coal-fired power plants. Nevertheless, some researchers stress that MOFs are not suitable for this application since MOFs have high affinities for water (H₂O) which, in the form of water vapor (H₂O_v), normally represents approximately 8-10% by volume of the mixture of gases called flue gas generated from the combustion of coal [11][12].

Because of this challenge associated with using MOFs, interest is shifting towards using carbonaceous porous solids or porous carbons like ACs capable of being molded into efficient CO₂ adsorbents which are not ruined by the presence of H₂O_v. The solid coproduct generated from the gasification and pyrolysis of biomass designated as biochar is a suitable candidate for this purpose once the relatively low porosity solid undergoes some form of activation process to establish the porosity needed to effectively separate CO₂ from flue gas. Activated biochars (AB) also have several key advantages over conventional ACs which are still predominantly produced from fossil fuels like coal. For instance, ABs are created from a wider range of precursors or feedstocks such as animal manures, crop remnants, food scraps, forestry residues, municipal solid wastes, and sewage sludges, among others. These porous carbons also have lower feedstock costs compared to those of ACs and are more environmentally friendly since the thermal decomposition of biomass into biochar does not result in significant net additions of CO₂ into the atmosphere [13]. In addition, the CO₂ adsorption capacities of ABs can be further enhanced by functionalizing their porous carbon surfaces and studying their improved CO₂ adsorption performances under a myriad of operating conditions and settings. Many of these studies focus on surface functionalization methods that introduce nitrogen (N) onto porous carbon surfaces which imparts them with surface characteristics that can promote CO₂ adsorption [14]. Therefore, this research project intends to use AB to produce novel AB-based porous solids with suitable CO₂ adsorption capacities for adsorbing CO₂ from gas mixtures.

Problem Statement

AB-based porous solids have several advantageous characteristics that make such adsorbents suitable for adsorbing CO₂ from flue gas. Like ACs, these porous solids have high surface areas, easily altered pore networks, high thermal stabilities, mostly hydrophobic surfaces, adequate chemical stabilities, low energy requirements, high regeneration efficiencies, and low production costs [11]. Furthermore, AB-based porous solids have acceptable CO₂ adsorption capacities at ambient temperatures and low CO₂ concentrations. Yet, like most other porous

carbons, the CO₂ adsorption capacities of these porous solids decrease with increasing temperature. This negative relationship is mostly connected to the subsequent increase in the kinetic energies of the CO₂ molecules in flue gas with increasing temperature which cannot be overcome by the relatively weak physical interactions known as van der Waals interactions that are commonly developed between AB-based porous solid surfaces and CO₂ molecules during adsorption [11]. To overcome this challenge, most researchers change the surface chemistry of porous solids by infusing certain heteroatoms such as N onto AB-based porous solid surfaces through different surface functionalization methods with the aim of forming functional groups or functionalities on their surfaces that are basic and can serve as active sites for the adsorption of acidic CO₂ molecules through relatively strong chemical interactions referred to as acid-base interactions. N is often used for this purpose since the incorporation of N onto porous carbon surfaces increases the electron densities of their carbonaceous structures. These enhanced electron densities magnify the basicities of these porous carbons which lead to improved CO₂ adsorption through the development of widespread acid-base interactions between the newly formed N functionalities on their surfaces and CO₂ molecules [15]. Such chemical interactions have the strength to adsorb CO₂ molecules onto porous solid surfaces at higher temperatures than those compatible with physical interactions which are the dominant interactions between CO₂ molecules and porous solids without basic surface functionalities that are appropriate for adsorbing CO₂. However, AB-based porous solid surface functionalization is a balancing act since the higher interaction strength between CO₂ molecules and basic porous solid surface functionalities can result in higher energy requirements needed to regenerate the porous solids or release the adsorbed CO₂ molecules following adsorption so that the porous solids can be reused over multiple adsorption cycles and, consequently, higher operating costs. The surface functionalization of AB-based porous solids also results in higher production costs related to the reagents, solvents, and energy required to introduce the target functional groups onto their surfaces [11][16].

Instead of surface functionalization, other researchers improve the CO₂ adsorption capacities of porous carbons at higher temperatures by developing mixed porous solids or composites comprised of porous carbons such as graphene oxides (GO) and inorganic/organic porous solids like MOFs which are known as metal-organic framework/graphene oxide (MOF/GO) composites and have the added benefits of both kinds of porous solids. GOs have high atomic densities and amounts of oxygen (O) in the form of different O surface functionalities, while MOFs have low atomic densities and relatively open structures. As such, these contrasting features produce increased dispersive forces in composites formed from both materials which improve CO₂ adsorption onto the surfaces of these composites compared to that onto the surfaces of either of the porous solids individually [17][18]. Moreover, the regular structures of MOFs maintain high degrees of porosity in such composites which facilitate the development of van der Waals interactions between CO₂ molecules and composite surfaces. Meanwhile, the metal ions and organic ligands that form MOFs can serve as active sites depending on their coordination and composition in composite surfaces which promote the creation of acid-base interactions and other chemical bonds between CO₂ molecules and composite surfaces. Researchers have also investigated the impacts of integrating N surface functionalities onto MOF/GO composites to further amplify their CO₂ adsorption capabilities. In certain cases, the addition of such surface functionalities increased the CO₂ adsorption capacities of the composites, yet in others, the incorporation of these surface functionalities caused pore blockages that decreased the CO₂ adsorption capacities of the composites [17][18]. Such findings reveal that the geometries and sizes of surface functionalities must be considered prior to conducting composite surface

functionalization. However, despite different MOF/GO composites having been synthesized and studied in terms of their affinity for adsorbing CO₂, there have not been any studies in the literature to date that have synthesized MOF/AB composites and examined their effectiveness in adsorbing CO₂ from flue gas. Therefore, the composites that have been examined to date are not formed from the most appropriate sort of porous carbon for adsorbing CO₂ from flue gas when considering economic and environmental concerns.

For example, AB is like GO in that both porous carbons are composed of graphene sheet segments which form their surfaces and have various O surface functionalities which may exhibit either acidic or basic behaviors [16][19]. Consequently, the similar physical structures and chemical compositions of AB and GO signify that these porous carbons may behave like one another when added into composites along with MOFs. Yet, despite such similarities, these porous carbons have differences in terms of their production pathways that impact the production costs and sustainability of producing composites with these porous carbons. In terms of production, biochar is normally produced as a byproduct from the pyrolysis of lignocellulosic biomass with the main products being either bio-oil or syngas which can be further processed to form high-value products like biofuels. Biochar is then activated using either a mild oxidizing gas or an inorganic compound to create AB. In contrast, GO is commonly formed in bulk from the oxidation of graphite using different oxidants according to Hummers' method which creates graphite oxide. Graphite oxide is then dispersed in either basic solutions or by sonication in polar solvents to obtain single sheets of graphite oxide referred to as GO [19]. As a result, the production process used to create AB is a much simpler process involving less steps, requiring fewer chemicals, and forming more high-value products than that used to synthesize GO which indicates that producing AB is cheaper and more environmentally friendly than creating GO. These beneficial characteristics make AB the more favorable porous carbon for constructing composites from along with MOFs that are capable of adsorbing CO₂ from flue gas.

Research Goal and Objectives

The goal of this research project is to synthesize metal-organic framework/activated biochar (MOF/AB) composites with suitable physicochemical characteristics and CO₂ adsorption capacities for adsorbing CO₂ from flue gas and other important industrial gas mixtures using AB derived from lignocellulosic biomass. This goal will be accomplished through the following three objectives:

Objective 1: Ascertain the effect of lignocellulosic biomass type using a hardwood, softwood, and grass on physicochemical characteristics of biochar that are known to influence CO₂ adsorption

Objective 2: Create, characterize, and assess the CO₂ adsorption behavior of an AB compared to that of a biochar

Objective 3: Synthesize, characterize, and evaluate the CO₂ adsorption performance of a MOF/AB composite relative to that of an AB

Furthermore, these objectives are supported by the following three hypotheses which will direct the experimental methods, characterization analyses, and statistical procedures used to complete the goal of this research project:

Hypothesis 1 (Objective 1): We hypothesize that the biochar produced from the pyrolysis of a hardwood lignocellulosic biomass will have a higher specific surface area, total pore volume, alkalinity, and CO₂ adsorption capacity than those of the biochars produced from the pyrolysis of softwood and grass lignocellulosic biomasses.

Hypothesis 2 (Objective 2): We hypothesize that the AB created from the activation of a biochar will have a higher specific surface area, total pore volume, alkalinity, and CO₂ adsorption capacity compared to those of a biochar.

Hypothesis 3 (Objective 3): We hypothesize that the MOF/AB composite synthesized from the solvothermal synthesis of a MOF onto an AB will have a higher specific surface area, total pore volume, alkalinity, and CO₂ adsorption capacity relative to those of an AB.

Research Justification

Objective 1

Many different lignocellulosic biomass types, chemical activating agents, and MOFs can be used to achieve this goal. However, in terms of lignocellulosic biomass types, hardwoods, softwoods, and grasses have disparate anatomical and physicochemical characteristics that need to be represented in the lignocellulosic biomass types used to produce biochars for this research project so that the project is comprehensive concerning the sorts of biomasses and biochars being investigated. The three lignocellulosic biomasses chosen to represent each of these differing classes of lignocellulosic biomasses are hybrid poplar, loblolly pine, and switchgrass since these lignocellulosic biomasses are relevant bioenergy feedstocks and regularly studied in thermochemical conversion processes. Moreover, this research project is designed to study biochars that are produced as coproducts during the generation of bio-oil and syngas in thermochemical conversion processes so that this project focuses on adding value to these products. In doing so, these biochars can be transformed into value-added coproducts that can sold to different industries and manufacturers to help offset the operational costs of bioenergy operations that use thermochemical conversion processes and aid in reducing CO₂ emissions from other industrial operations. This measure is going to be realized by thermochemically converting the previously mentioned lignocellulosic biomasses through intermediate pyrolysis at 500°C which is a reasonable type of thermochemical conversion process and operating temperature for obtaining high bio-oil yields [20].

Based on these choices, objective 1 of this research project aims to answer the question of which lignocellulosic biomass, hybrid poplar, loblolly pine, or switchgrass, when used as a feedstock in intermediate pyrolysis at 500°C produces biochar that has the most suitable physicochemical characteristics for adsorbing CO₂ and highest CO₂ adsorption capacity? However, addressing this question is complicated by the significant differences in the physicochemical characteristics of separate biochars that have been reported to affect CO₂ adsorption. Some of the physicochemical characteristics of biochar that are known to affect CO₂ adsorption are specific surface area, total pore volume, average pore size, alkalinity, inorganics content, aromaticity, polarity, and hydrophobicity [13]. For example, biochar with a high specific surface area and total pore volume has more surface available for developing van der Waals interactions with CO₂ molecules which enable CO₂ adsorption, while biochar with a low average

pore size can selectively adsorb CO₂ molecules by excluding other molecules according to physical characteristics which heavily contributes to CO₂ adsorption at low CO₂ partial pressures such as in flue gas. Moreover, biochar with a high alkalinity and inorganics content has more basic active sites available for forming acid-base interactions with CO₂ molecules which facilitate CO₂ adsorption, whereas biochar with a high aromaticity and hydrophobicity and low polarity can selectively adsorb CO₂ molecules by disregarding other molecules based on chemical characteristics which tremendously promotes CO₂ adsorption in the presence of H₂O_v and other gases involved in competitive adsorption [13]. In addition to the complex relationships that these biochar physicochemical characteristics have with CO₂ adsorption, these physicochemical characteristics have significant discrepancies between different biochars that arise from the notable deviations in these physicochemical characteristics between the assorted lignocellulosic biomasses that the biochars are formed from and the separate thermochemical conversion process conditions used to create the biochars. Yet, despite these connections between biochar physicochemical characteristics and CO₂ adsorption, most of these physicochemical characteristics are also influenced by more fundamental physicochemical characteristics of biochar including carbon (C), hydrogen (H), O, inorganics, ash, volatile matter, and fixed carbon contents and pH [21][22].

In particular, the C, H, and O contents of biochar give indications of the volatile matter and fixed carbon contents of biochar which dictate various aspects of biochar surfaces. Decreases in the volatile matter content present in biochar can signify the creation or enlargement of pores on biochar surfaces which result in increases to the specific surface area, total pore volume, and average pore size of biochar [21][22]. Furthermore, inorganics content provides an indication of the ash content and pH of biochar which control different aspects of biochar surfaces. Increases in the ash content present in biochar and increases in the pH of an aqueous solution containing biochar can imply the addition of alkali, alkaline earth, transition, and rare-earth metals to biochar structures or surfaces which causes increases to the alkalinity of biochar. Increases in the pH of an aqueous solution comprised of biochar can also suggest the introduction of basic biochar surface functionalities which results in increases to the alkalinity of biochar as well [21][22]. Based on these implications, different biochars can be compared in terms of their anticipated effectiveness for adsorbing CO₂ by inspecting the differences in their primary (C, H, O, and inorganics contents) and secondary (ash, volatile matter, and fixed carbon contents and pH) fundamental physicochemical characteristics. Accordingly, C, H, O, inorganics, ash, volatile matter, and fixed carbon contents and pH values of hybrid poplar, loblolly pine, and switchgrass lignocellulosic biomasses and their biochars produced from intermediate pyrolysis at 450 or 500°C are shown in Tables 0.1 and 0.2 on a dry basis (db) and used to predict which of the lignocellulosic biomasses that are chosen for investigation in objective 1 will generate biochar that has the most favorable physicochemical characteristics for adsorbing CO₂ and highest CO₂ adsorption capacity.

The separate primary fundamental physicochemical characteristic values of the various lignocellulosic biomasses and biochars displayed in Table 0.1 suggest that the hybrid poplar biochar has the lowest amount of volatile matter since this biochar has the highest C content and lowest O content. Such findings reveal that the hybrid poplar lignocellulosic biomass may have experienced more devolatilization in the form of dehydration and deoxygenation reactions during intermediate pyrolysis than the loblolly pine and switchgrass lignocellulosic biomasses resulting in C being concentrated in the biochar and substantial amounts of H and O being evolved or removed from the biochar in the form of volatile matter [21][23]. Because of this large evolution of volatile matter from the biochar structure, the hybrid poplar biochar is expected to have the highest specific surface area and total pore volume relative to the loblolly pine and switchgrass

Table 0.1. Primary fundamental physicochemical characteristics of hybrid poplar, loblolly pine, and switchgrass lignocellulosic biomasses and biochars.

Biomass						
	Temperature (°C)	Elemental Analysis (wt. %, db)				Reference
		C	H	O	Inorganics	
Hybrid Poplar	NA	50.4	7.8	39.4	1.1	[24][25]
Loblolly Pine	NA	48.5	5.9	45.2	0.3	[26]
Switchgrass	NA	45.6	5.5	45.7	1.8	[26]
Biochar						
Hybrid Poplar	500	77.0	4.5	12.0	5.6	[24]
Loblolly Pine	450	71.8	3.9	22.7	0.7	[26]
Switchgrass	450	66.5	3.4	15.3	5.9	[26]

NA stands for not applicable.

Table 0.2. Secondary fundamental physicochemical characteristics of hybrid poplar, loblolly pine, and switchgrass lignocellulosic biomasses and biochars.

Biomass						
	Temperature (°C)	Proximate Analysis (wt. %, db)			pH	Reference
		Ash	Volatile Matter	Fixed Carbon		
Hybrid Poplar	NA	3.2	76.1	11.8	NA	[27]
Loblolly Pine	NA	0.3	83.4	9.6	4.7	[26]
Switchgrass	NA	2.7	79.0	9.7	6.1	[26]
Biochar						
Hybrid Poplar	500	7.0	22.7	71.3	10.5	[24]
Loblolly Pine	450	1.4	44.7	52.2	5.1	[26]
Switchgrass	450	13.4	26.3	58.4	9.1	[26]

NA stands for not applicable.

biochars since a significant increase in the quantity of pores present on the hybrid poplar biochar surface likely occurred as volatile matter was evolved. As a result, the hybrid poplar biochar is forecast to have the highest amount of van der Waals interactions developed between the biochar surface and CO₂ molecules during CO₂ adsorption signifying that this biochar has the greatest propensity out of the biochars being researched for adsorbing CO₂. This notion is supported by the disparate secondary fundamental physicochemical characteristic values of the different lignocellulosic biomasses and biochars exhibited in Table 0.2 since the hybrid poplar biochar has the lowest volatile matter content and the highest fixed carbon content denoting that this biochar likely formed the most pores during intermediate pyrolysis.

In addition, the hybrid poplar biochar has a high inorganics content as illustrated in Table 0.1 which conveys that the hybrid poplar lignocellulosic biomass structure and surface may have contained high amounts of alkali, alkaline earth, transition, and rare-earth metals that were mostly retained following intermediate pyrolysis by the hybrid poplar biochar and only slightly less than those preserved by the switchgrass biochar. Consequently, the hybrid poplar biochar is predicted to have the highest number of acid-base interactions created between the biochar surface and CO₂ molecules during CO₂ adsorption signaling that this biochar has the greatest aptitude out of the biochars being studied for adsorbing CO₂. This proposition is reinforced by the separate secondary fundamental physicochemical characteristic values of the assorted lignocellulosic biomasses and biochars shown in Table 0.2 since the hybrid poplar biochar has a high ash content and the highest pH indicating that this biochar likely formed a high quantity of basic surface functionalities during intermediate pyrolysis in addition to keeping many of the different inorganics originally held by the hybrid poplar lignocellulosic biomass. And even though these projections were based on physicochemical characteristics of biochars obtained through the intermediate pyrolysis of hybrid poplar, loblolly pine, and switchgrass lignocellulosic biomasses at 450-500°C, the implications of the differences in the fundamental physicochemical characteristics of these biochars are anticipated as being applicable to biochars created from the intermediate pyrolysis of these same lignocellulosic biomasses at 500°C. Therefore, the hybrid poplar biochar is expected to have the most suitable physicochemical characteristics for adsorbing CO₂ and highest CO₂ adsorption capacity among the biochars being analyzed in this research project.

Objective 2

Concerning chemical activating agents, there is a large assortment of chemical activating agents that have been used to activate biochars to create ABs for adsorbing CO₂ under different adsorption conditions. For example, potassium hydroxide (KOH) is a commonly used chemical activating agent that penetrates into biochar structures and transforms parts of these structures into volatile matter that is then evolved from biochar structures at higher temperatures creating new pores and widening existing pores in biochar surfaces [13][28][29][30]. AB created through KOH activation has an increased specific surface area, pore volume, pore size, amount and assortment of basic O surface functionalities, and surface basicity which assist in CO₂ adsorption. However, despite these improvements, the formation of micropores in biochar surfaces through KOH activation is the most important aspect of using this chemical activating agent since the presence of substantial amounts of micropores in AB surfaces have been associated with significantly increased CO₂ adsorption [13][28][29][30]. Similarly, zinc chloride (ZnCl₂) is another frequently used chemical activating agent that, like KOH, perforates into biochar structures and changes pieces of these structures into volatile matter that is then released from biochar structures at higher temperatures forming new pores and enlarging existing pores in biochar surfaces [28][31]. Yet,

ZnCl₂ usually enters biochar structures more uniformly than KOH and produces hierarchical pore networks composed of macro-, meso-, and micropores. AB formed through ZnCl₂ activation has an increased specific surface area, pore volume, and pore size which help in CO₂ adsorption but this AB also has an increased amount and collection of acidic O surface functionalities and surface acidity which hinder CO₂ adsorption [28][31]. Apart from KOH and ZnCl₂, phosphoric acid (H₃PO₄) is a regularly used chemical activating agent that behaves in a similar manner to KOH and ZnCl₂ in terms of how H₃PO₄ infiltrates biochar structures and alters sections of biochar structures generating new pores and broadening existing pores in biochar surfaces [28][32][33]. H₃PO₄ seeps into biochar structures and constructs hierarchical pore networks containing macro-, meso-, and micropores akin to those established using ZnCl₂ while also introducing phosphorus (P) onto biochar surfaces. AB produced through H₃PO₄ activation has an increased specific surface area, pore volume, and pore size which promote CO₂ adsorption but this AB also has an increased amount and variety of acidic P surface functionalities and surface acidity which inhibit CO₂ adsorption [28][32][33]. Since these chemical activating agents create ABs that have high specific surface areas and pore volumes, each of the chemical activating agents previously detailed displays promise for producing ABs that have improved CO₂ adsorption behaviors compared to those of biochars. To designate a chemical activating agent to produce an AB with for this research project, the CO₂ adsorption capacities of multiple ABs synthesized using different chemical activating agents including KOH, ZnCl₂, and H₃PO₄ under comparable pyrolysis and activation conditions and at similar adsorption conditions are illustrated in Table 0.3 and used to decide as to which of the chemical activating agents that are suitable for exploration in objective 2 will make an AB that has the most favorable physicochemical characteristics for adsorbing CO₂ and higher CO₂ adsorption capacity relative to those of a biochar.

The different CO₂ adsorption capacities of the assorted ABs exhibited in Table 0.3 indicate that AB made from eucalyptus lignin biochar and KOH has the highest CO₂ adsorption capacity. However, this discovery is unexpected since AB created from giant reed biochar and ZnCl₂ has the highest specific surface area which is significantly higher than that of eucalyptus lignin KOH AB. As previously mentioned, specific surface area is directly connected to CO₂ adsorption on AB surfaces since increasing specific surface area through the creation of new pores or expansion of existing pores increases the formation of van der Waals interactions between AB surfaces and CO₂ molecules which enhances CO₂ adsorption. Based on this relationship, giant reed ZnCl₂ AB should have the highest CO₂ adsorption capacity instead of having a CO₂ adsorption capacity that is notably lower than that of eucalyptus lignin KOH AB. This disparity suggests that there is a drastic difference in the surface chemistries of these ABs which is affecting CO₂ adsorption on their surfaces. As noted prior, surface basicity is also directly related to CO₂ adsorption on AB surfaces since increasing surface basicity through the development of new basic surface functionalities or transformation of existing surface functionalities increases the creation of acid-base interactions between AB surfaces and CO₂ molecules which promotes CO₂ adsorption. Therefore, this inconsistency between the specific surface areas and CO₂ adsorption capacities of eucalyptus lignin KOH and giant reed ZnCl₂ ABs implies that eucalyptus lignin KOH AB surfaces contain a significant amount and variety of basic O surface functionalities created through KOH activation which increase the surface basicity of this AB and remarkably improve CO₂ adsorption on this AB. In contrast, giant reed ZnCl₂ AB surfaces encompass a considerable quantity and assortment of acidic O surface functionalities formed through ZnCl₂ activation which increase the surface acidity of this AB and markedly worsen CO₂ adsorption on this AB.

Table 0.3. Specific surface areas and CO₂ adsorption capacities of different activated biochars produced with potassium hydroxide, zinc chloride, and phosphoric acid at comparable pyrolysis, activation, and adsorption conditions.

Activated Biochar	Chemical Activating Agent	Pyrolysis / Activation / Adsorption Temperature (°C)	Specific Surface Area (m ² /g)	CO ₂ Adsorption Capacity (mmol/g)	Reference
African Palm Shell	KOH	600/850/25	1250	4.4	[31][34][35]
African Palm Stone	H ₃ PO ₄	NA/450/0	1092	3.7	[34][36]
Coconut Shell	KOH	500/650/25	1593	4.5	[34][37]
Coconut Shell	H ₃ PO ₄	NA/450/0	1322	3.7	[34][36]
Eucalyptus Lignin	KOH	365/700/0	1647	6.0	[34][38]
Giant Reed	KOH	NA/600/25	1122	3.6	[28][39]
Giant Reed	ZnCl ₂	NA/500/25	3298	2.2	[28][40]
Spruce Lignin	KOH	380/700/0	1380	3.8	[34][38]
Whitewood	KOH	500/775/25	1400	1.8	[13][41]

NA stands for not applicable.

Such an extreme difference in the CO₂ adsorption behaviors of ABs reflects the influence that chemical activating agent selection has on the physicochemical characteristics and CO₂ adsorption capacities of ABs. Accordingly, the chemical activating agent designated to produce an AB with is KOH because an AB created from KOH is anticipated to have more advantageous physicochemical characteristics for adsorbing CO₂ and a higher CO₂ adsorption capacity than those of a biochar and an AB made from either ZnCl₂ or H₃PO₄. This expectation is mostly attributed to the knowledge that ZnCl₂ and H₃PO₄ introduce acidic O and P surface functionalities onto AB surfaces, respectively, which magnify the surface acidities of these ABs and diminish CO₂ adsorption on such ABs. Following this designation, objective 2 of this research project seeks to answer the question of how does the creation of an AB through activation using KOH alter the physicochemical characteristics and CO₂ adsorption behavior of a biochar? However, answering this question is difficult because there have not been many studies to date that have sought to activate hybrid poplar, loblolly pine, or switchgrass biochars through KOH activation to create an AB for CO₂ adsorption. Nevertheless, assuming that the physicochemical characteristics and CO₂ adsorption capacities of each of these biochars experience changes during KOH activation to produce an AB similar to those of the physicochemical characteristics and CO₂ adsorption capacities of the different biochars previously examined, the creation of an AB through KOH activation should improve the physicochemical characteristics linked to CO₂ adsorption and CO₂ adsorption capacity of a biochar. Consequently, an AB created through activation using KOH is expected to have the most favorable physicochemical characteristics for adsorbing CO₂ and higher CO₂ adsorption capacity relative to those of a biochar.

Objective 3

Regarding MOFs, several assorted MOFs have already been used to create highly efficient MOF/GO composites for adsorbing CO₂ under disparate adsorption parameters. For instance, the MOF composed of metal ions and organic ligands in the forms of copper (Cu) cations and 1,3,5-benzenetricarboxylic acids (BTC), respectively, otherwise known as copper-benzene-1,3,5-tricarboxylate (Cu-BTC) is an easily synthesized and stable MOF that has a low production cost. Furthermore, MOF/GO composites synthesized from the solvothermal synthesis of Cu-BTC onto GO have appropriate physicochemical characteristics for adsorbing CO₂ and high CO₂ adsorption capacities [17]. Other than conventional MOFs like Cu-BTC, zeolitic imidazolate frameworks (ZIF) are a subclass of MOFs comprised of different metal ions and organic ligands in the form of imidazoles oriented in structures similar to those of zeolites. Of the different kinds of ZIFs that have been synthesized, the ZIF composed of metal ions and organic ligands in the forms of zinc (Zn) cations and imidazoles, respectively, where the Zn cations are each tetrahedrally coordinated by four imidazoles commonly referred to as zinc-zeolitic imidazolate framework-8 (Zn-ZIF-8) is a high surface area MOF that has high thermal and chemical stabilities. Additionally, MOF/GO composites synthesized from the solvothermal synthesis of Zn-ZIF-8 onto GO have favorable physicochemical characteristics for adsorbing CO₂ and high CO₂ adsorption capacities [18]. Aside from Cu-BTC and Zn-ZIF-8, the MOF composed of metal ions and organic ligands in the forms of magnesium (Mg) cations and 2,5-dihydroxyterephthalic acids (DHTA), respectively, typically designated as magnesium-metal-organic framework-74 (Mg-MOF-74) is a high CO₂ adsorption capacity MOF that shows great promise for CO₂ adsorption. Yet, there are not many studies in the literature to date that have synthesized MOF/GO composites from the solvothermal synthesis of Mg-MOF-74 onto GO and analyzed the changes to the physicochemical characteristics associated with CO₂ adsorption and CO₂ adsorption capacity of Mg-MOF-74 and

GO [42][43]. Because these MOFs have suitable physicochemical characteristics for CO₂ adsorption and high CO₂ adsorption capacities, each of the MOFs previously reviewed shows promise for synthesizing MOF/AB composites that have refined CO₂ adsorption performances compared to those of ABs. To select a MOF to synthesize a MOF/AB composite with for this research project, the CO₂ adsorption capacities of multiple porous solids and composites including GO, Cu-BTC, Zn-ZIF-8, Mg-MOF-74, copper-benzene-1,3,5-tricarboxylate/graphene oxide (Cu-BTC/GO), and zinc-zeolitic imidazolate framework-8/graphene oxide (Zn-ZIF-8/GO) at similar adsorption conditions are presented in Table 0.4 and used to forecast as to which of the MOFs that are acceptable for investigation in objective 3 will produce a MOF/AB composite that has the most favorable physicochemical characteristics for adsorbing CO₂ and higher CO₂ adsorption capacity compared to those of an AB.

The disparate CO₂ adsorption capacities of GO and the different MOFs and MOF/GO composites shown in Table 0.4 signify that Mg-MOF-74 has the highest CO₂ adsorption capacity. This result is surprising since the MOF/GO composite synthesized from Cu-BTC has a higher CO₂ adsorption capacity than those of Cu-BTC and GO individually that is significantly lower than that of Mg-MOF-74 despite Cu-BTC/GO and Mg-MOF-74 having similar specific surface areas. Consequently, this variation implies that the Mg cations in Mg-MOF-74 form stronger chemical interactions with CO₂ molecules relative to those generated with the Cu and Zn cations in Cu-BTC and Zn-ZIF-8 which amplifies CO₂ adsorption onto Mg-MOF-74 surfaces compared to that onto Cu-BTC and Zn-ZIF-8 surfaces. Similarly, Mg-MOF-74 has a significantly higher CO₂ adsorption capacity than those of Cu-BTC/GO and Zn-ZIF-8/GO which indicates that a MOF/GO composite synthesized from Mg-MOF-74 will have an even higher CO₂ adsorption capacity than those of GO and Mg-MOF-74 individually. Such an enormous contrast in the CO₂ adsorption performances of GO, MOFs, and MOF/GO composites demonstrates the effect that MOF preference has on the physicochemical characteristics and CO₂ adsorption capacities of MOF/GO composites. Therefore, the MOF selected to synthesize a MOF/AB composite with is Mg-MOF-74 since a MOF/AB composite synthesized from Mg-MOF-74 is predicted to have more beneficial physiochemical characteristics for adsorbing CO₂ and a higher CO₂ adsorption capacity than those of an AB and a MOF/AB composite synthesized from either Cu-BTC or Zn-ZIF-8. This projection is largely ascribed to the understanding that Mg-MOF-74 has an extremely high CO₂ adsorption capacity and is forecast to synthesize a MOF/AB composite that has exceptional CO₂ adsorption performance assuming that the presence of AB has a similar impact as that of GO on the physicochemical characteristics and CO₂ adsorption capacity of MOF/AB and MOF/GO composites, respectively, during composite synthesis. According to this selection, objective 3 of this research project seeks to answer the question of how does the synthesis of a Mg-MOF-74/AB composite change the physicochemical characteristics and CO₂ adsorption performances of an AB? However, this question is tough to answer since there have not been any studies to date that have sought to synthesize Mg-MOF-74 through a solvothermal synthesis onto hybrid poplar, loblolly pine, or switchgrass ABs to produce a magnesium-metal-organic framework-74/activated biochar (Mg-MOF-74/AB) composite for CO₂ adsorption let alone synthesize a MOF onto AB to produce a MOF/AB composite. Regardless, assuming that the similar physical structures and chemical compositions of GO and AB ensure that the physicochemical characteristics and CO₂ adsorption capacities of each of these ABs and Mg-MOF-74 experience changes during composite synthesis to produce a MOF/AB composite akin to those of the physicochemical characteristics and CO₂ adsorption capacities of the various MOF/GO composites previously inspected, the synthesis of a Mg-MOF-74/AB composite through solvothermal synthesis should synergize the

Table 0.4. Specific surface areas and CO₂ adsorption capacities of graphene oxide, different metal-organic frameworks, and separate metal-organic framework/graphene oxide composites at comparable adsorption conditions.

Porous Solid	Adsorption Temperature (°C)	Specific Surface Area (m ² /g)	CO ₂ Adsorption Capacity (mmol/g)	Reference
GO	30	9	1.1	[18]
Cu-BTC	25	892	2.1	[17]
Zn-ZIF-8	30	1318	0.7	[18]
Mg-MOF-74	25	1174	8.6	[42][43]
Cu-BTC/GO	25	1080	2.6	[17]
Zn-ZIF-8/GO	30	NM	0.5	[18]

NM stands for not measured.

physicochemical characteristics associated with CO₂ adsorption and CO₂ adsorption capacities of an AB and MOF. As such, a MOF/AB composite synthesized through solvothermal synthesis using Mg-MOF-74 is expected to have the most favorable physicochemical characteristics for adsorbing CO₂ and higher CO₂ adsorption capacity compared to those of an AB.

Organization

The thesis is organized as follows. In Chapter 1, a literature review is provided which summarizes topics related to CCS, adsorption on porous solids, characteristics of porous solids, and types of porous solids. In Chapter 2, an investigation into objective 1 of this research project is presented which covers the introduction, materials and methods, results and discussion, and conclusions related to discovering which lignocellulosic biomass of those researched produces biochar that has the most suitable physicochemical characteristics for adsorbing CO₂ and highest CO₂ adsorption capacity. In Chapter 3, a study into objective 2 of this research project is portrayed which details the introduction, materials and methods, results and discussion, and conclusions related to uncovering how the physicochemical characteristics and CO₂ adsorption behavior of biochar are changed when biochar is activated using KOH to create an AB. In Chapter 4, an exploration into objective 3 of this research project is displayed which recounts the introduction, materials and methods, results and discussion, and conclusions related to determining how the physicochemical characteristics and CO₂ adsorption performances of an AB are transformed when Mg-MOF-74 is synthesized onto an AB to produce a Mg-MOF-74/AB composite. In Conclusions and Future Work, a synopsis of the conclusions of Chapters 2-4 is given which critiques the appropriateness of using MOF/AB composites to adsorb CO₂ from flue gas and other important industrial gas mixtures and a statement discussing the future work that should be conducted related to this research project is supplied. Apart from the contents of each chapter, the thesis contains both chemical reactions and mathematical formulas. Chemical reactions are denoted using the number of the chapter that the reaction is presented in as R1.1, R1.2, R1.3, R2.1, R2.2, R2.3...etc. in curly brackets, whereas mathematical formulas are indicated using the number of the chapter that the formula is revealed in as F1.1, F1.2, F1.3, F2.1, F2.2, F2.3...etc. in parentheses. In addition, the thesis is written using the American Psychological Association (APA) 7th edition citation and format style with in-text citations shown in square brackets.

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Chapter 1. Literature Review

1.1 Introduction

1.1.1 Natural Variability and Anthropogenic Climate Change

The existence of anthropogenic climate change is a heavily debated topic amongst both the public and scientific community. Such discussions are largely motivated by the increasing frequency and severity of natural disasters occurring worldwide that are uncommon for both the regions and seasons in which these catastrophes transpire relative to those in historical records. Some individuals and organizations attribute these abnormal climatic phenomena to the natural variability of Earth's climate. This view is founded on the observation that Earth's climate naturally varies from year to year and across much longer time periods as well. In this context, natural variability refers to irregularities in climatic characteristics such as precipitation and temperature caused by nonhuman factors that develop from one year to another. In some situations, natural forces create deviations in climatic parameters from their long-term average states resulting in changes to the mean states of climatic features that ultimately transform Earth's climate. This naturally induced transformation is classified as climate change. The forces that naturally alter Earth's climate can be either external or internal to Earth's climate system. Examples of external forces that govern Earth's climate include changes in the Sun's characteristics, discrepancies in Earth's orbit around the Sun, and volcanic eruptions. These external events naturally shift the state of Earth's climate over long timespans and are the driving forces behind the glacial and interglacial periods that Earth's climate cycles between. In contrast, instances of internal forces that vary Earth's climate consist of interactions between the atmosphere and ocean such as those that occur during tropical storms. Such internal occurrences transform Earth's climate over much shorter timeframes compared to external forces [1]. However, despite the existence of natural climate change, others argue that the bizarre climatic events that have unfolded recently are the result of human-induced or anthropogenic alterations to different climatic variables such as increased global surface temperatures. In most cases, the elevated surface temperatures that are being observed worldwide are well outside of the typical conditions of their respective regions and seasons. Such divergences support the notion that anthropogenic climate change in the form of increased global surface temperatures, commonly called global warming, is occurring.

1.1.2 Observed Changes to Earth's Climate

To uncover the factors that initiated and continue to affect the ongoing global warming, the Intergovernmental Panel on Climate Change (IPCC) published a report in 2014 on the state of climate change science and detailed recently observed changes to Earth's climate system. These observations included alterations to climatic characteristics of Earth's atmosphere, oceans, and cryosphere. For instance, the IPCC found that Earth's atmosphere has been drastically changed since Earth's surface grew progressively warmer across each decade from 1983-2012 and these surface temperatures were warmer than any previous decade since 1850. Moreover, these researchers highlighted that the global average combined land and ocean surface temperature exhibited a linear warming of 0.85°C throughout 1880-2012 with almost every region around the world having experienced increasing surface temperatures from 1901-2012 compared to those reported in their historical records [2]. The IPCC also mentioned that average precipitation over the Northern Hemisphere mid-latitude land areas has likely increased since 1901 and increased with a much higher likelihood relative to 1951. Aside from alterations to Earth's atmosphere, the report indicated that Earth's oceans have been notably modified as well since the global ocean temperature of the upper 75 m experienced a warming of 0.11°C per decade from 1971-2010 and

the global ocean surface water pH decreased by 0.1, which corresponds to a 26% increase in acidity relative to the global ocean surface water pH at the beginning of the Industrial Age [2]. In addition to changes to Earth's oceans, the IPCC announced that Earth's cryosphere has been significantly transformed over the last two decades since the rates of ice mass loss from both the Antarctic and Greenland ice sheets increased over 1992-2011 and 2002-2011, respectively. The report revealed that in the Northern Hemisphere the extent of snow cover decreased by 1.6% per decade for March and April and by 11.7% per decade for June over 1967-2012 [2]. Meanwhile, the IPCC discovered that the global average sea level has been elevated partially because of the thermal expansion of Earth's oceans and mass loss from Earth's glaciers. The global average sea level was determined to have risen by 0.19 m from 1901-2010 with approximately 75% of this increase being explained by the ocean thermal expansion and glacier mass loss previously highlighted [2].

1.1.3 Solar Irradiance, Aerosols, and Greenhouse Gases

With these observations in mind, the report then discussed potential causes for these modifications to Earth's climate. As previously mentioned, Earth's climate system typically experiences perturbations because of various natural forces whose effects on Earth's climate are evaluated according to their respective change on the energy stored in Earth's climate system or radiative forcing. In terms of natural climate influences, the IPCC emphasized in their report that changes in solar irradiance were only responsible for close to 2% of the total radiative forcing in 2011 compared to 1750 and that the radiative forcing of aerosols from volcanic eruptions throughout 1750-2011 was calculated to be nearly -0.9 W/m^2 indicating that aerosols had a cooling effect on Earth's climate system [2]. Consequently, these findings suggest that changes in solar irradiance and atmospheric aerosol concentrations cannot account for the recently observed transformations to Earth's climate since solar irradiance had a minimal influence on Earth's climate system relative to other factors and the temperature of Earth's surface steadily increased despite atmospheric aerosols cooling Earth's climate system. Apart from these natural forces, certain gases present in Earth's atmosphere govern how radiation from the Sun is distributed throughout Earth's atmosphere and at Earth's surface. These gases are commonly called greenhouse gases (GHG) since they produce a greenhouse effect on Earth's atmosphere by absorbing and emitting radiant energy transmitted from the Sun which can effectively warm Earth's climate system when a certain amount of radiation is stored in Earth's atmosphere by these gases. Prominent GHGs include water vapor (H_2O_v), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3), chlorofluorocarbons (CFC), and hydrofluorocarbons (HFC), among others. Upon further inspection of potential climate change driving factors, the IPCC found that atmospheric concentrations of GHGs including CO_2 , CH_4 , and N_2O have substantially increased since 1750 by as much as 40, 150, and 20%, respectively [2]. Such increases are largely attributed to different anthropogenic activities that emit GHGs into Earth's atmosphere which have been continuously performed since the beginning of the Industrial Age. Subsequently, in the report compiled by the IPCC, the total anthropogenic radiative forcing over 1750-2011 was computed to be 2.3 W/m^2 and recognized as having increased more rapidly since 1970 relative to that of previous decades [2]. This result includes the effect of GHGs introduced into Earth's atmosphere through anthropogenic means and supports the perception that anthropogenic forces have had and continue to have a warming effect on Earth's climate system.

1.1.4 Anthropogenic Emissions and Atmospheric CO₂ Accumulation

Along with increased radiative forcing, the IPCC learned that total annual anthropogenic GHG emissions continually increased over 1970-2010 with a larger increase having occurred between 2000-2010, despite the growing number of climate change mitigation policies in effect. Additionally, this increase in total annual anthropogenic GHG emissions between 2000-2010 was recorded as being in the amount of 10 gigatons of CO₂ equivalent (GtCO₂-eq) with 47, 30, 11, and 3% of this increase being ascribed to the energy, industry, transportation, and building sectors, respectively [2]. Such findings justify the need to identify which anthropogenic GHGs pose the most serious threat to Earth's climate system based on which of these GHGs is the dominant GHG being emitted by these sectors. As a result, the IPCC determined that CO₂ was the largest single contributor to the anthropogenic radiative forcing that occurred over 1750-2011 and to the more rapid increase since 1970. Furthermore, the researchers calculated that the cumulative anthropogenic CO₂ emissions during 1750-2011 equaled $2,040 \pm 310$ gigatons of CO₂ (GtCO₂) and stressed that approximately half of these emissions were released into the atmosphere within the past 40 years. In terms of individual anthropogenic operations, the IPCC specified that cumulative CO₂ emissions from fossil fuel combustion, cement production, and flaring have nearly tripled since 1970, whereas those from forestry and other land use have increased by an estimated 40% [2]. Despite these results, some individuals and organizations argue that these figures are not alarming since CO₂ is removed from Earth's atmosphere by different carbon repositories or sinks such as Earth's oceans, soil, and vegetation that store CO₂ in natural carbon cycles. However, the IPCC's report gauged that only about 40% of the anthropogenic CO₂ emissions accumulated over 1750-2011 have been retained in Earth's atmosphere while nearly 30% have been absorbed by Earth's oceans resulting in the ocean acidification previously noted. Moreover, the anthropogenic CO₂ emissions from fossil fuel combustion and other important industrial processes accounted for roughly 78% of the total GHG emission increase across 1970-2010 and represented a similar proportion of the increase over 2000-2010 [2].

CO₂ emissions from anthropogenic ventures like fossil fuel combustion and other important industrial processes have and will continue to be increasingly detrimental to Earth's climate system if countries and societies worldwide continue to develop without appropriate adjustments to these and other practices. For instance, the increases in anthropogenic CO₂ emissions from fossil fuel combustion were observed by the IPCC to be primarily related to global economic and population growth with the contribution from the latter over 2000-2010 being close to that of the past three decades, while that of the former had sharply soared. In addition, the increases in anthropogenic CO₂ emissions from these two factors dwarfed the CO₂ emissions reductions during this same period from advances in the energy intensity of the gross domestic product (GDP) [2]. Such revelations support the call for removing CO₂ from Earth's atmosphere and enhancing the prevention of CO₂ being emitted into Earth's atmosphere from anthropogenic practices. Without these provisions being put into effect and strictly enforced, the IPCC has projected in their report that the global average peak surface temperature of Earth's climate system is likely to increase anywhere from 0.8-2.5°C per trillion tons of carbon released into Earth's atmosphere as CO₂. Shockingly, the global average surface temperature has already been predicted to increase in the range of 0.3-0.7°C during 2016-2035 relative to 1986-2005 [2]. The IPCC has also anticipated that more frequent and prolonged heat waves, more frequent and intense extreme precipitation events, further ocean acidification and warming, and continued global average sea level rise will occur in Earth's climate system throughout the 21st century. Yet, the societal risks associated with these climate change phenomena have been estimated to only become moderate to

high if the global average surface temperature reaches 1-2°C above that of Earth's climate system prior to the Industrial Age [2]. Therefore, these estimations put forth by the IPCC are spurring many governments, industry leaders, organizations, political figures, and scientists to advocate for and implement adaptation and mitigation strategies to remove CO₂ and other GHGs from and prevent the emission of CO₂ and other GHGs into Earth's atmosphere to avoid the serious societal risks linked to a 2°C global average surface temperature increase. Among the different options currently available for achieving this goal, the IPCC indicated that projected adaptation and mitigation scenarios capable of maintaining atmospheric CO₂ equivalent (CO₂-eq) concentrations at or below 450 ppm by 2100 were likely to avert global warming from causing the global average surface temperature to exceed a 2°C increase over the 21st century relative to that of Earth's climate system before the Industrial Age. Additionally, the projected adaptation and mitigation scenarios that satisfied this criterion relied significantly on the availability and widespread deployment of CO₂ removal (CDR) practices and technologies and more sustainable industrial practices and technologies such as bioenergy with carbon capture and storage (BECCS) production processes and afforestation operations by the second half of the 21st century [2].

1.2 Carbon Capture and Storage

1.2.1 Carbon Capture Technology for Fossil Fuel Combustion

Along with the development and deployment of BECCS production processes, carbon capture and storage (CCS) and carbon capture and utilization (CCU) technologies are being incorporated into multiple important industrial operations such as fossil fuel combustion for energy generation, cement and petrochemical manufacturing, and iron and steel refining [3]. The aim of integrating CCS and CCU technologies into these long-standing operations is to mitigate their harmful effects on the current climate crisis by capturing CO₂ from these point sources and either sequestering or storing the captured CO₂ underground or transforming the captured CO₂ into different value-added products to prevent the addition of further anthropogenic CO₂ emissions into Earth's atmosphere [4]. To accomplish this objective, the IPCC has distinguished three distinct stages in CCS and CCU processes, namely the separation, transportation, and storage or utilization of CO₂, that must be applied and optimized to establish successful CCS and CCU processes [3]. However, the application and optimization of some of these stages is not occurring without difficulties. While both the transportation and storage or utilization of CO₂ are encountering obstacles in their implementation, the separation of CO₂ faces the largest challenge by far since this stage in CCS and CCU processes accounts for approximately two thirds of the entire process cost [3][5]. Most of this expense is related to the difficulty in effectively separating CO₂ from gas mixtures that are generated from fossil fuel combustion and other important industrial processes since such gas mixtures typically have low CO₂ concentrations and other characteristics that are unfavorable for CO₂ separation. Moreover, the process cost associated with CO₂ separation increases as the CO₂ concentration in a gas mixture decreases with direct air capture (DAC) processes being the most expensive CO₂ separation processes of interest while simultaneously involving the gas mixture with the lowest CO₂ concentration that needs CO₂ separation, air [6]. Therefore, researchers are focused on creating CCS and CCU technologies that can separate CO₂ in large quantities from gas mixtures with low CO₂ concentrations and have low process costs.

In terms of carbon capture from fossil fuel combustion for energy generation operations such as those that occur in coal-fired power plants, three different types of carbon capture technologies, that is pre-combustion, post-combustion, and oxy-fuel combustion carbon capture

systems, are being studied for removing CO₂ from fossil fuel combustion operations under assorted conditions and at different locations throughout these operations. In greater detail, pre-combustion carbon capture encompasses the gasification of coal in a water-gas shift reactor to produce hydrogen gas (H₂) and CO₂ at high pressures. The H₂ is then used for energy generation while the CO₂ is separated from this gas mixture before the gasified coal undergoes combustion [5][7]. This kind of carbon capture has a significant advantage over the other two carbon capture technologies in that the gas mixture created from the gasification of coal contains a high CO₂ concentration with few additional components which allows for simple and cheap CO₂ separation. As a result, new coal-fired power plants that are being developed are anticipated to operate using pre-combustion carbon capture [6]. In contrast, post-combustion carbon capture involves the separation of CO₂ from the gas mixture formed from the combustion of coal. This gas mixture is commonly referred to as flue gas and is composed of multiple different components in varying concentrations that are produced at high temperatures and low pressures close to atmospheric pressure which results in complex and expensive CO₂ separation [5][7]. Unlike the previous carbon capture technologies, oxy-fuel combustion carbon capture requires the combustion of coal in oxygen gas (O₂) instead of air which results in the production of a gas mixture like flue gas except that the gas mixture has a higher CO₂ concentration. The higher CO₂ concentration is linked to the lack of nitrogen gas (N₂) typically included in the air used for combustion within the combustion environment which greatly simplifies and cheapens CO₂ separation since the gas mixture that is generated is also devoid of N₂ [5][7]. Yet even though both pre-combustion and oxy-fuel combustion carbon capture have clear benefits in terms of CO₂ separation ease and cost, post-combustion carbon capture is acquiring greater attention. This growing interest is mostly related to post-combustion carbon capture systems being more easily retrofitted onto existing coal-fired power plants which currently contribute to a greater extent of the total quantity of anthropogenic CO₂ being emitted into Earth's atmosphere than that from the coal-fired power plants still in development [3][6][7].

1.2.2 Flue Gas and Post-Combustion Carbon Capture Technology

Despite the increasing attention, the composition and properties of the flue gas generated from the combustion of coal impart important restrictions on post-combustion carbon capture systems that are viable for CO₂ separation. For example, the flue gas produced from coal-fired boilers contains an estimated 72-77% N₂, 12-14% CO₂, 8-10% H₂O_v, and 3-5% O₂ as well as low amounts of carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x), and particulate matter. Pollution control systems that perform denitrogenation, desulfurization, and filtration are incorporated into coal-fired power plants downstream of the furnace outlet as a means of lowering or removing most of the contaminants and hazardous substances occupying lower proportions of flue gas to meet Environmental Protection Agency (EPA) emissions guidelines. This gas mixture also typically exits the furnace at a temperature of 1,200°C which gradually decreases to close to 150°C as flue gas travels from the furnace outlet through the pollution control systems to the flue or stack before being emitted into Earth's atmosphere [8]. Therefore, post-combustion carbon capture systems must not only selectively separate CO₂ from the other gases that compose flue gas to carry out decarbonization but also effectively perform CO₂ separation in the presence of high temperatures anywhere from 150-1,200°C. To overcome these challenges, a variety of different separation methods including absorption, adsorption, cryogenic separation, and membrane separation are being used to develop post-combustion carbon capture systems [3]. Historically, post-combustion carbon capture in industrial operations has involved the application of chemical absorption systems otherwise known as amine or wet scrubbing systems that use alkanolamine

solvents as absorbents to selectively separate CO₂ from flue gas. Such systems separate CO₂ from flue gas by passing flue gas through a piece of equipment known as an absorber that contains an alkanolamine solvent at slightly elevated temperatures of nearly 40°C [9]. During this process, basic amine functional groups on alkanolamine molecules present within the solvent react with weakly acidic CO₂ molecules found in flue gas resulting in the formation of intermediates known as zwitterions or molecules containing equal amounts of positively and negatively charged functional groups. Each zwitterion intermediate is then deprotonated by either a H₂O_v molecule in flue gas or an amine functional group on a different alkanolamine molecule present in the solvent which forms either a bicarbonate anion and protonated amine or a carbamate anion and protonated amine, respectively [9][10][11]. Once the solvent becomes rich with bicarbonate and carbamate anions, the remaining flue gas is released out of the absorber and the CO₂-rich solvent is regenerated for subsequent use by sending the spent solvent to another piece of equipment called a stripper that contains H₂O_v at elevated temperatures of approximately 100-120°C [9]. Through this process, H₂O_v molecules react with bicarbonate and carbamate anions in the spent solvent stripping CO₂ molecules from the solvent and simultaneously regenerating bicarbonate and carbamate anions back into alkanolamine molecules with basic amine functional groups that can react with CO₂ molecules again. The regenerated solvent is then returned to the absorber for further use while the vapor mixture containing H₂O_v and CO₂ is sent to a condenser where H₂O_v is condensed out of the vapor mixture leaving behind concentrated CO₂. After this process, the concentrated CO₂ is fed to a compressor to increase the pressure that the CO₂ is under so that the CO₂ can be transported through a pipeline for either storage or utilization [9][10]. However, despite how effective amine or wet scrubbing systems are at separating CO₂ from flue gas, these systems have multiple disadvantages which limit their continued use such as high equipment corrosivity, high susceptibility to oxidative degradation, high energy requirements for solvent regeneration, and serious health risks related to amine exposure, among others [3][4][6][9][12].

Apart from this traditional approach, physical absorption separates CO₂ from flue gas by dissolving CO₂ molecules into a solvent like that used in chemical absorption, except that physical interactions between molecules in the solvent and CO₂ molecules in flue gas drive absorption instead of chemical interactions. However, this separation method is more advantageous than chemical absorption since the physical interactions between molecules in the solvent and CO₂ molecules in flue gas are weaker than the chemical interactions developed during chemical absorption. Consequently, physical absorption requires less energy to regenerate the solvent for subsequent use compared to that needed in chemical absorption. Yet, despite this benefit, physical absorption is not recommended for separating CO₂ from gas mixtures with low CO₂ partial pressures like flue gas which means that this separation method is not acceptable for separating CO₂ from flue gas [6]. As previously mentioned, chemical absorption separates CO₂ from flue gas by dissolving CO₂ molecules into a solvent through chemical interactions between molecules in the solvent and CO₂ molecules in flue gas. Most solvents used in chemical absorption contain molecules with amine functional groups which impart the detrimental features previously discussed onto this separation method. To combat some of these hindrances, current research on chemical absorption is focused on developing high-pressure and hybrid systems, new solvents, and redesigned stripping process configurations [10]. One of the more promising solutions is the use of biphasic solvents which are homogenous solvents that become heterogenous once they absorb CO₂ or experience a temperature change which forms CO₂-rich and CO₂-lean phases in these solvents. This unique characteristic of biphasic solvents alleviates part of the high energy requirement normally needed for solvent regeneration since only the CO₂-rich phases of these

solvents undergo regeneration and the high CO₂ partial pressure of these phases decreases the amount of heat and work needed for stripping and compression, respectively [9][10]. Nevertheless, research into the use of such solvents is still new meaning that the technical and economic feasibilities of applying biphasic solvents to separate CO₂ from flue gas need further investigation before their widespread implementation can be achieved. On the other hand, cryogenic separation separates CO₂ from flue gas by cooling flue gas below the condensation temperature of CO₂ through refrigeration which causes CO₂ molecules to condense out of flue gas. However, refrigerating flue gas to this point requires a high amount of energy that is comparable to that needed for solvent regeneration in chemical absorption [3]. This high energy requirement makes cryogenic separation unsuitable for separating CO₂ from flue gas. In contrast, membrane separation separates CO₂ from flue gas by passing flue gas through a membrane that physically and chemically interacts with CO₂ molecules. This separation method is more cost-effective than chemical absorption because of the solid state and faster separation kinetics of the membranes used in membrane separation which are more advantageous than the liquid state and slower separation kinetics of the solvents used in chemical absorption. Additionally, membrane separation has other beneficial attributes including modular system design, compact configuration, and operational flexibility [13]. However, this separation method is pressure-dependent meaning that certain differences in pressure are required to separate CO₂ from flue gas effectively. This stipulation poses a serious challenge since flue gas is produced at low pressures near atmospheric pressure and has a low CO₂ concentration which indicate that a high amount of energy must be supplied during membrane separation to create a pressure gradient capable of forcing flue gas through the membrane and separating CO₂ at the same time [14]. Consequently, this high energy requirement makes membrane separation unfavorable for separating CO₂ from flue gas like many other separation methods. Because of the various downsides of these separation methods, research efforts are shifting towards using adsorption to develop post-combustion carbon capture systems that can be incorporated into coal-fired power plants. This separation method is also preferred over other available options because of the different advantages afforded to the overall carbon capture process by using adsorption such as easier application across a wider range of operating pressures and temperatures, lower energy requirements, and a lower process cost, among others [3].

1.3 CO₂ Adsorption

1.3.1 Adsorption Process

Adsorption is a natural surface phenomenon where the concentration of a substance at the boundary layer or interface of different phases increases compared to that in each phase because of surface forces that are created when different phases are in contact with one another. This phenomenon occurs at the interfaces of gas, liquid, and solid phases such as gas-liquid, gas-solid, liquid-liquid, and liquid-solid interfaces, yet gas-solid interfaces are the main interfaces of interest for CO₂ adsorption in important industrial operations [15][16][17][18]. In terms of CO₂ adsorption at a gas-solid interface, the substance in the gas phase, CO₂, that increases in concentration at the interface or is adsorbed is known as the adsorptive prior to adsorption and the adsorbate after adsorption, whereas the substance in the solid phase that the adsorptive is adsorbed onto is referred to as the adsorbent. At this interface, an adsorbent is in contact with the bulk phase of the CO₂ adsorptive forming an adsorption system known as the interfacial layer. The interfacial layer consists of two sections, namely 1.) the portion of the CO₂ adsorptive in the force field of the adsorbent surface and 2.) the surface of the adsorbent. During CO₂ adsorption, CO₂ adsorptive

molecules accumulate in the interfacial layer as surface forces are created and attract CO₂ adsorptive molecules to the adsorbent surface where the CO₂ adsorptive molecules are adsorbed until the adsorption system reaches an equilibrium state [15][16]. Once equilibrium is achieved, the adsorption system eventually undergoes desorption to separate the CO₂ adsorbate molecules from the adsorbent surface. Desorption is a natural surface phenomenon where the concentration of a substance at the interface of different phases decreases relative to that of each phase because of surface forces that are removed when different phases are in contact with one another. During CO₂ desorption, CO₂ adsorbate molecules dissipate from the interfacial layer as surface forces are removed and release CO₂ adsorbate molecules from the adsorbent surface so that the CO₂ adsorbate molecules are desorbed until the adsorption system reaches an equilibrium state [15]. Adsorption hysteresis is a natural phenomenon where the attraction of adsorptive molecules to the adsorbent surface during adsorption differs from the release of adsorbate molecules from the adsorbent surface during desorption. Prior to CO₂ desorption, CO₂ adsorbate molecules can also enter the bulk phase of the adsorbent past the adsorbent surface through CO₂ absorption which is a different phenomenon from CO₂ adsorption [15]. Absorption is a natural phenomenon where the concentration of a substance in the bulk phase of a liquid or solid increases because of forces that are formed when different phases are in contact with one another. With regard to CO₂ absorption at a gas-solid interface, the substance in the gas phase, CO₂, that increases in concentration in the bulk phase of a solid or is absorbed is known as the absorptive prior to absorption and the absorbate after absorption, while the substance in the solid phase that the absorptive is absorbed into is referred to as the absorbent. In some cases, CO₂ adsorption and absorption occur simultaneously with CO₂ adsorptive molecules being attracted to the adsorbent surface and becoming adsorbed through CO₂ adsorption as CO₂ adsorbate molecules are moving into the bulk phase of the absorbent and becoming absorbed through CO₂ absorption, and in others, both phenomena are indistinguishable from each other [15].

1.3.2 Adsorption Mechanisms

Concerning the mechanisms that influence this process, CO₂ adsorption occurs when the interaction potential energy between CO₂ adsorptive molecules and the adsorbent surface is equal to the work needed to transition the CO₂ adsorptive molecules into CO₂ adsorbate molecules. This interaction potential energy is composed of the adsorbate-adsorbate and adsorbate-adsorbent interaction potential energies between CO₂ adsorbate molecules and CO₂ adsorbate molecules and the adsorbent surface, respectively. However, the potential energies of CO₂ adsorbate-adsorbate interactions are often insignificant compared to those of CO₂ adsorbate-adsorbent interactions and therefore usually disregarded [19]. Apart from these interactions, there are three classes of CO₂ adsorbate-adsorbent interactions involved in CO₂ adsorption, namely dispersion, electrostatic, and chemical bond interactions. The creation of these different types of interactions when the bulk phase of the CO₂ adsorptive is in contact with the adsorbent determines whether CO₂ adsorption occurs through physical or chemical means with adsorption that occurs through dispersion and electrostatic interactions being designated as physical adsorption or physisorption and adsorption that progresses through chemical bond interactions being referred to as chemical adsorption or chemisorption [3][6][7][15][16][17][19][20][21]. For CO₂ physisorption, the interaction potential energy is comprised of the dispersion and repulsion interaction energies and electric field and induced dipole or induction, electric field and permanent dipole, and electric field gradient and quadrupole interaction energies that develop between CO₂ adsorbate molecules and the adsorbent surface. The dispersion and repulsion interaction energies are nonspecific because these interaction

energies are developed when CO₂ adsorbate molecules interact with any adsorbent surface. In contrast, the electric field and induced dipole or induction, electric field and permanent dipole, and electric field gradient and quadrupole interaction energies are specific since these interaction energies are produced when CO₂ adsorbate molecules interact with an adsorbent surface that contains atoms with charges or ions which create electric fields on the adsorbent surface [19]. Moreover, the nonspecific interactions are nonelectrostatic and chiefly affected by the polarizabilities of CO₂ and the adsorbent surface with higher polarizabilities causing increased nonspecific interaction energies. The induction interactions are also largely governed by these polarizabilities. Conversely, the specific interactions are electrostatic and mostly influenced by the charges and van der Waals radii of the atoms that form the adsorbent surface or surface atoms with higher surface atom charges and lower surface atom van der Waals radii creating increased specific interaction energies [19]. Regardless of the differences between these interactions, dispersion and electrostatic interactions control the attraction of CO₂ adsorptive molecules to the adsorbent surface throughout CO₂ physisorption. These intermolecular interactions are commonly discussed together and typically referred to as van der Waals interactions. Depending on the strength of these intermolecular interactions, CO₂ physisorption can result in monolayer or multilayer adsorption where either a single layer or multiple layers of CO₂ adsorptive molecules are adsorbed onto the adsorbent surface, respectively [20]. The formation of multiple layers of CO₂ adsorbate molecules on the adsorbent surface is possible since van der Waals interactions can affect multiple CO₂ adsorbate molecules simultaneously. Nevertheless, van der Waals interactions are relatively weak intermolecular interactions compared to chemical bonds which means that CO₂ physisorption is more effective at lower temperatures since CO₂ adsorptive molecules at lower temperatures have lower kinetic energies and can be more easily attracted to the adsorbent surface through van der Waals interactions. The weak nature of these intermolecular interactions also means that CO₂ physisorption is a reversible process at lower temperatures because CO₂ adsorbate molecules need lower amounts of energy to overcome the van der Waals interactions keeping them adsorbed on the adsorbent surface and facilitate CO₂ desorption [3][6][7][15][20][22].

For CO₂ chemisorption, the interaction potential energy is constituted of only the chemical bond interaction energy that develops between CO₂ adsorbate molecules and the adsorbent surface. The chemical bond interaction energy is specific since this interaction energy is formed when CO₂ adsorbate molecules interact with an adsorbent surface that contains ions or functional groups which can develop covalent bonds with CO₂ [7][15][16][17][19][20][23]. Furthermore, this specific interaction is principally regulated by the strength of the covalent bond created between CO₂ and an ion or functional group on the adsorbent surface or surface ion and functional group with a stronger covalent bond producing an increased specific interaction energy. The main chemical bonds made between CO₂ adsorbate molecules and surface ions or functional groups are acid-base interactions since CO₂ is a weak Lewis acid that can react with surface ions and functional groups which are Lewis bases [3][6][7][20][21]. As such, acid-base interactions dictate the attraction of CO₂ adsorptive molecules to the adsorbent surface throughout CO₂ chemisorption. Yet, unlike CO₂ physisorption, CO₂ chemisorption can only result in monolayer adsorption where a single layer of CO₂ adsorptive molecules is adsorbed onto the adsorbent surface [20]. The production of only a single layer of CO₂ adsorbate molecules on the adsorbent surface is possible because chemical bonds can only affect a single CO₂ adsorbate molecule at a time. Nonetheless, chemical bonds are relatively strong intermolecular interactions compared to van der Waals interactions which means that CO₂ chemisorption is more effective at higher temperatures since CO₂ adsorptive molecules at higher temperatures have higher kinetic energies and can be more

easily attracted to the adsorbent surface through chemical bonds. The strong nature of these intermolecular interactions also means that CO₂ chemisorption is not entirely a reversible process at lower or higher temperatures because CO₂ adsorbate molecules require higher amounts of energy to overcome the chemical bonds keeping them adsorbed on the adsorbent surface and promote CO₂ desorption. Even when high amounts of energy are supplied, the chemical bonds during CO₂ chemisorption are not all typically surpassed meaning that some CO₂ adsorbate molecules remain adsorbed on the adsorbent surface following CO₂ desorption which makes CO₂ chemisorption not entirely a reversible process [3][6][7][15][23]. Based on the differences between these adsorption mechanisms, CO₂ physisorption is favored over CO₂ chemisorption for CO₂ adsorption in the absence of other adsorptive molecules and at low temperatures since van der Waals interactions are mostly nonspecific and may interact with other adsorptive molecules that are present. These intermolecular interactions are also weak and need less energy for CO₂ desorption so that the adsorbent can be reused. Likewise, CO₂ chemisorption is preferred over CO₂ physisorption for CO₂ adsorption in the presence of other adsorptive molecules and at high temperatures since chemical bonds are specific and can only interact with specific adsorptive molecules that are present. These intermolecular interactions are also strong and require more energy for CO₂ desorption so that the adsorbent can be reused [3][6][7][22][23]. However, under suitable adsorption conditions, CO₂ physisorption and chemisorption can occur sequentially or simultaneously since the adsorbent surface usually contains many different surface atoms, ions, and functional groups that can develop van der Waals interactions and chemical bonds with CO₂ adsorbate molecules. As such, CO₂ physisorption and chemisorption must both be considered when studying CO₂ adsorption since both adsorption mechanisms may be involved in adsorbing CO₂ in the process of interest [3][6][7][15].

1.4 CO₂ Adsorption in Mixtures

In terms of CO₂ adsorption in gas mixtures, the physisorption of CO₂ adsorbates onto an adsorbent or porous solid surface is achieved by making use of these intermolecular interactions through two types of separation strategies, namely size exclusion- and affinity-based separation. Size exclusion-based separation relies on differences in the molecular sizes of CO₂ molecules and the other gaseous molecules contained in gas mixtures. These discrepancies allow for the synthesis of porous solids with specific pore sizes that can selectively grant passage to CO₂ molecules while simultaneously excluding N₂, H₂O, O₂, CH₄, and CO molecules which simply pass through the porous solids with the rest of the gas mixture. Each of these molecules are attracted at different degrees to porous solid surfaces because of the development of differing extents of van der Waals interactions between these molecules and porous solid surfaces. Yet, only molecules less than a certain molecular size can pass through the pores of porous solids and be preferentially adsorbed onto their surfaces. Nevertheless, the application of size exclusion-based separation for separating CO₂ from gas mixtures is complicated by the small differences in the molecular sizes of CO₂ and N₂ with their respective kinetic diameters or molecular sizes being 3.30 and 3.64 Å [6]. As a result, this small size difference largely prevents the use of porous solids that are only capable of size exclusion-based separation for separating CO₂ from gas mixtures like flue gas since the synthesis of porous solids with the narrow pore size needed to preferentially adsorb CO₂ over N₂ is extremely difficult to perform regularly and on an industrial scale with low costs. To overcome this complication, porous solids that can separate CO₂ from gas mixtures by performing affinity-based separation are developed. Affinity-based separation depends on differences in physical properties like multipole moment and polarizability of CO₂ molecules and the other gaseous molecules

contained in gas mixtures. These physical characteristics govern the strength of the van der Waals interactions that are developed when CO₂, N₂, H₂O_v, O₂, CH₄, and CO molecules interact with porous solid surfaces. For example, CO₂ has a higher quadrupole moment and polarizability compared to those of N₂ with their quadrupole moments being 13.4×10^{-4} and 4.7×10^{-4} C·m² and polarizabilities being 26.3×10^{-25} and 17.6×10^{-25} cm³, respectively [6]. Consequently, these distinctions are used to construct porous solids with quadrupole moments and polarizabilities that are compatible with those of CO₂ to generate stronger van der Waals interactions between CO₂ molecules and porous solid surfaces relative to those developed between N₂ molecules and porous solid surfaces. The stronger interactions between CO₂ molecules and porous solid surfaces can then be used to selectively attract and adsorb CO₂ molecules onto porous solid surfaces over N₂ molecules. In addition, the tailoring of porous solids needed to bestow them with appropriate physical features for affinity-based separation is accomplished by manipulating the amount and type of charged moieties present on porous solid surfaces [6]. As such, porous solids that are capable of effectively separating CO₂ from gas mixtures through physisorption must be engineered with suitable physical characteristics to take advantage of both size exclusion- and affinity-based separation techniques to prevent the uptake of other gaseous molecules.

Conversely, the chemisorption of CO₂ adsorbates onto a porous solid surface depends on the creation of chemical bonds. The generation of these chemical bonds for separating CO₂ from gas mixtures relies on differences between the chemical characteristics of CO₂ molecules and the other gaseous molecules contained in the gas mixture. These disparities allow for the creation of porous solids with specific functional groups on their surfaces that are capable of selectively forming chemical bonds with CO₂ molecules while allowing N₂, H₂O_v, O₂, CH₄, and CO molecules to pass through the porous solids unaffected. However, chemical bonds between CO₂ molecules and surface functional groups or functionalities on porous solids are much stronger interactions than the intermolecular interactions developed in physisorption which indicates that a higher amount of energy is needed to break apart these bonds to regenerate porous solids during chemisorption. Consequently, surface functionalities on porous solids must be carefully selected and controlled so that the intermolecular interactions that occur between CO₂ molecules and porous solids do not result in the adsorption process having a high energy consumption. In terms of separating CO₂ from gas mixtures such as flue gas, CO₂ exhibits an acidic nature whereas N₂ does not which can be used to stimulate reactions between CO₂ adsorbates and porous solids to establish chemical bonds between them [3][6]. These bonds are selectively formed by conferring a basic quality to porous solids which along with the acidic character of CO₂ molecules allows for acid-base reactions to occur. This intricate engineering of porous solids to provide them with a basic nature is conducted by introducing certain metals and metal oxides (MO) and specific nitrogen (N), oxygen (O), sulfur (S), and fluorine (F) functionalities onto porous solid surfaces. As a result, these surface functionalities serve as active basic sites where acid-base reactions can occur as long as the sites remain available for such reactions following their attachment to porous solid surfaces [3][6][22]. Yet, since most porous solids adsorb CO₂ through both physisorption and chemisorption, the modification of porous solid surfaces must be performed diligently so that the added surface functionalities do not attach to and fill pores in porous solids. Pore filling results in pore blockages and reductions to the amount of available active sites for CO₂ adsorption which effectively diminishes the ability of porous solids to separate CO₂ from gas mixtures by physisorption and chemisorption [3][22]. Therefore, porous solids that can successfully separate CO₂ from gas mixtures like flue gas through chemisorption must be incorporated with suitable

surface functionalities to provide porous solids with ample basic character in a manner that does not curtail their porous structures.

1.5 CO₂ Adsorbent Characteristics and Properties

1.5.1 CO₂ Adsorption Capacity, Selectivity, and Kinetics

To facilitate CO₂ adsorption in gas mixtures, different kinds of adsorption systems such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA) systems are used to accommodate porous solids with differing physicochemical characteristics. PSA systems are a cost-competitive technology for separating CO₂ from gas mixtures like flue gas even when compared to a low-cost technology like amine or wet scrubbing systems [3]. However, the success of separating CO₂ from gas mixtures largely depends on the physicochemical characteristics of porous solids used in these systems which can vary significantly depending on the precursor or feedstock and production process used. Despite such concerns, many porous solids are characterized as having distinct physicochemical characteristics, high surface areas, controllable porosities, easily manipulatable surfaces, high chemical and thermal stabilities, and hydrophobic qualities [4]. As a result, porous solids with these traits require much simpler adjustments to their characteristics in response to changes in gas mixture properties such as pressure, temperature, flow rate, composition, and humidity which can occur across fossil fuel combustion processes and other industrial processes even at the same plant. This beneficial feature of porous solids has resulted in adsorption-based post-combustion carbon capture systems being more dynamic technologies relative to their counterparts. Regardless, porous solids have multiple adsorption characteristics, namely adsorption capacity, selectivity, kinetics, heat of adsorption, regenerability, stability, cyclability or durability, and cost, that must be optimized for each anticipated carbon capture scenario to overcome various adsorption challenges. Of these different characteristics, the key adsorption characteristics that must be improved immediately to produce porous solids suitable for separating CO₂ from gas mixtures are adsorption capacity and selectivity since porous solids must be able to separate as much CO₂ from gas mixtures as possible while maintaining high purity [6].

In terms of CO₂ adsorption, CO₂ adsorption capacity is defined as the amount of CO₂ adsorbed per unit mass of the porous solid used. By optimizing this characteristic, porous solids are capable of processing higher quantities of gas mixtures at a time using lower amounts of porous solids since more CO₂ can be contained within their porous structures per unit mass. Accordingly, the CO₂ adsorption capacity of porous solids can be changed by altering their physicochemical characteristics like specific surface area, total pore volume, average pore size, amount of surface functionalities, surface basicity, aromaticity, polarity, and hydrophobicity [6][7]. CO₂ desorption capacity is depicted as the amount of CO₂ desorbed per unit mass of the porous solid used. This characteristic is equally important in separating CO₂ from gas mixtures since porous solids must be capable of releasing most if not all adsorbed CO₂ following adsorption. Yet, CO₂ desorption is adversely affected by strong intermolecular interactions between CO₂ adsorbates and porous solids as well as process changes in pressure and temperature which result in a lower CO₂ desorption capacity and more CO₂ being retained within the porous structures of porous solids. In turn, CO₂ retention causes the CO₂ adsorption capacity of porous solids to decrease across multiple adsorption and desorption cycles because of the lower amounts of pores and active sites available for CO₂ adsorption. Therefore, CO₂ working capacity is specified as the difference between the CO₂ adsorption and desorption capacities of porous solids and accounts for the interactions between CO₂ adsorption and desorption [6][24]. CO₂ adsorption selectivity is described as the ratio

of the proportion of CO₂ adsorbed compared to the bulk CO₂ in a gas mixture to the proportion of other gases adsorbed relative to the bulk other gases in a gas mixture. Improving this characteristic of porous solids enhances the quantity of CO₂ adsorbed from gas mixtures compared to that of other gases present in gas mixtures since, in many cases, the complex set of intermolecular interactions between CO₂ and other gases in gas mixtures and porous solids results in competitive adsorption between CO₂ and other gases onto porous solids. CO₂ adsorption selectivity also relies on many of the same physicochemical characteristics of porous solids as CO₂ adsorption capacity with the main contributing characteristic being the amount of surface functionalities [6][24]. Aside from these important characteristics, CO₂ adsorption kinetics are crucial characteristics to optimize for porous solids since these characteristics dictate whether equilibrium or dynamic separation should be conducted to separate CO₂ from gas mixtures. For example, equilibrium separation benefits from faster CO₂ adsorption kinetics since porous solids with faster CO₂ adsorption kinetics that are used in adsorption systems such as PSA systems can reach saturation or their equilibrium CO₂ adsorption capacity within a PSA cycle and, as such, process gas mixtures more rapidly. In contrast, dynamic separation is used to separate CO₂ from gas mixtures by modifying porous solids to have suitable CO₂ adsorption kinetics to take advantage of disparities in the diffusivities of CO₂ and other gases in gas mixtures [6].

1.5.2 Heat of Adsorption, Regenerability, Stability, Cyclability, and Cost

As for the remaining adsorption characteristics, heat of adsorption is a measure of the strength of intermolecular interactions between CO₂ molecules and porous solids and can be used to differentiate whether these intermolecular interactions are predominantly physical or chemical in nature. Porous solids with a high heat of adsorption adsorb higher amounts of CO₂ because of strong intermolecular interactions that are developed between CO₂ molecules and porous solids. However, changing the heat of adsorption also affects the regenerability of porous solids among other characteristics with a higher heat of adsorption resulting in a lower regenerability [6]. Regenerability is the ratio of the CO₂ working capacity to the CO₂ adsorption capacity of porous solids and provides an indication of how effectively porous solids can maintain the same CO₂ adsorption capacity across multiple adsorption and desorption cycles. As more CO₂ is retained on porous solids across subsequent cycles, the CO₂ working capacity of porous solids can decrease which, in turn, causes regenerability to decrease. The relationship between heat of adsorption and regenerability is attributed to CO₂ adsorption being an exothermic process whereas CO₂ desorption is an endothermic process [6][24]. As a result, porous solids with a high heat of adsorption have high amounts of heat stored in their bulk phase as CO₂ is adsorbed which releases energy in the form of heat that is then stored since porous solids have a low thermal conductivity. The high temperatures within the bulk phase of porous solids that result from this phenomenon decrease the CO₂ working capacity of porous solids by increasing the kinetic energy of local CO₂ molecules which results in less CO₂ molecules encountering available active sites on porous solids and being adsorbed. Similarly, as CO₂ is desorbed from porous solids with a low heat of adsorption, the removal of heat present in the bulk phase of porous solids results in low temperatures in porous solids which cause CO₂ adsorbates to remain adsorbed on porous solids. This CO₂ retention occurs because less thermal energy is available for CO₂ adsorbates to overcome the intermolecular interactions that initially caused them to be adsorbed on porous solids [6]. Concerning stability, porous solids used for separating CO₂ from gas mixtures must be designed to not readily deteriorate after interacting with CO₂, H₂O_v, or other gases present in gas mixtures or degrade because of changes in temperature that arise during CO₂ adsorption. Resistance to these conditions

is commonly achieved by imparting porous solids with high chemical and thermal stabilities that are tailored to the specific gas mixture composition and adsorption process conditions of interest. In terms of cyclability or durability, porous solids must be physically tough enough to maintain their porous structures over multiple adsorption and desorption cycles since repeated exposure to high pressure during CO₂ adsorption can result in the collapse of such structures. The cost of porous solids used for separating CO₂ from gas mixtures must also be optimized so that the use of porous solids in industrial processes is practical from an economic standpoint [6].

1.6 Types of Porous Solids

1.6.1 Silica-Based Porous Solids

Because of the wide array of porous solid characteristics that must be carefully adjusted to effectively separate CO₂ from gas mixtures, many different types of porous solids have been synthesized and studied over the last few decades to produce porous solids with optimized characteristics for CO₂ adsorption. Disparate kinds of porous solids that have been successfully developed and researched include activated carbons (AC), carbon molecular sieves, graphene oxides (GO), mesoporous and microporous silicas, MOs, metal-organic frameworks (MOF), zeolites, and zeolitic imidazolate frameworks (ZIF) [3][4][6][7][12][22]. These various sorts of porous solids can be grouped into categories based on the feedstock used in their production with these categories involving silica-based, metal-based, and carbon-based porous solids. Regarding silica-based porous solids, silica gels have been used as commercial adsorbents since World War I and commonly have specific surface areas ranging from 200-800 m²/g [25]. The CO₂ adsorption capacity of these kinds of porous solids is typically improved by grafting amines onto the walls of pores within silicas through surface functionalization which increase chemical intermolecular interactions between CO₂ molecules and silicas like those developed with alkanolamine solvents in wet scrubbing systems. However, the surface functionalization of silica-based porous solids with amines does not improve their CO₂ adsorption capacity enough to justify the resulting increase in their production cost to make them competitive with other porous solids [25]. Aside from silica gels, zeolites also exhibit promising results as silica-based porous solids for separating CO₂ from gas mixtures but are very hydrophilic. This characteristic of zeolites has mostly prevented their application in CO₂ adsorption since some gas mixtures such as flue gas contain a significant amount of H₂O_v which inhibits CO₂ adsorption once H₂O_v is adsorbed onto zeolite surfaces. Furthermore, zeolites have a low CO₂ adsorption selectivity at high temperatures and high regeneration costs since temperatures of about 200°C must be applied to regenerate their porous structures which are factors that have limited the use of zeolites for CO₂ adsorption [3][25].

1.6.2 Metal-Based Porous Solids

Conversely, metal-based porous solids are used for CO₂ adsorption since metals and MOs that exhibit basic characteristics can develop chemical bonds with CO₂ molecules through acid-base reactions. Yet, metals and MOs that are used for CO₂ adsorption have low specific surface areas and total pore volumes and mechanically decompose and sinter during CO₂ adsorption at high temperatures which limit their effectiveness in separating CO₂ from gas mixtures [25]. To alleviate these issues, metals and MOs can be incorporated with organic molecules into ordered structures commonly referred to as MOFs. MOFs are considered a subclass of coordination polymers and described as inorganic-organic hybrid crystalline materials containing metal ions or clusters coordinated with organic ligands to form three-dimensional porous structures. Moreover,

more than 20,000 different MOFs have been synthesized to date with specific surface areas ranging from 1,000-10,000 m²/g and pore sizes varying from a few angstroms to 50 nm [25][26][27]. These porous solids have higher CO₂ adsorption capacities compared to those of metals and MOs under similar CO₂ adsorption conditions which is attributed to MOFs exhibiting higher localized charge densities, specific surface areas, and total pore volumes than conventional metals and MOs. Such beneficial characteristics are induced by the coordinated bonding that occurs between MOs and organic ligands which results in MOFs having highly porous surfaces and high stabilities relative to their constituents [3][25]. Additionally, MOFs are highly customizable in terms of the strength of their intermolecular interactions with CO₂ molecules since there are vast assortments of metals, MOs, and organic ligands that can be used to synthesize MOFs. For instance, different metals and MOs have disparate CO₂ adsorption capacities under uniform CO₂ adsorption conditions which suggests that intermolecular interactions between metals and MOs and CO₂ molecules have separate strengths [22]. Similarly, different organic ligands have varied lengths and contain disparate functional groups which provide MOFs with another method for adjusting the strength of their intermolecular interactions with CO₂ molecules. For example, the pore sizes of MOFs can be modified by selecting organic ligands with longer or shorter lengths which affect CO₂ physisorption onto MOFs while the inclusion of organic ligands with basic functional groups add to CO₂ chemisorption onto MOFs along with contributions from metal clusters [6][25].

Regardless of these advantages, MOFs also have detrimental qualities that outweigh their benefits related to separating CO₂ from gas mixtures. MOFs have high production costs associated with the specific organic ligands and solvents needed during synthesis. In terms of the structures of MOFs, the coordinating bonds between metal clusters and organic ligands that comprise MOFs have high susceptibilities towards being compromised by H₂O_v resulting in structural failure. The poor water (H₂O) resistance and chemical stabilities of MOFs is attributed to H₂O_v molecules forming covalent bonds with metal ions at metal-ligand linkages which slowly deteriorates the crystalline structures of MOFs [3][4][6][26][27]. Accordingly, MOFs adsorb high quantities of H₂O_v when H₂O_v is present which can be retained even after attempting desorption because of strong chemical bonds formed between H₂O_v molecules and MOFs resulting in permanent decreases to the CO₂ adsorption capacities of MOFs like those of zeolites. The thermal stabilities of MOFs are also lower than those of most other porous solids such as ACs and zeolites because MOFs rely on organic ligands to develop their porous structures. Many of these organic molecules decompose within the temperature range of 300-600°C which raises concerns related to the use of MOFs for separating CO₂ from gas mixtures like flue gas since flue gas may be at temperatures within this range upon reaching post-combustion carbon capture systems. Such concerns are reinforced by the realization that the degradation of organic ligands destroys the porous structures of MOFs rendering them ineffective for further CO₂ adsorption [3][6][26]. Furthermore, MOFs have low CO₂ adsorption capacities at low pressures which further restrict the incorporation of MOFs into post-combustion carbon capture systems. This disadvantageous characteristic of MOFs is linked to MOFs adsorbing CO₂ mainly through CO₂ physisorption which, as previously mentioned, depends on the development of van der Waals interactions.

Nevertheless, many MOFs are excellent porous solids because they are composed entirely of ordered micropores which each contribute to the generation of van der Waals interactions between CO₂ molecules and MOFs. However, van der Waals interactions are relatively weak intermolecular interactions that rely on pressure to help facilitate CO₂ adsorption which results in MOFs having poor CO₂ adsorption capacities in environments with low pressures [26][28]. In addition, MOFs that contain exclusively micropores have limited CO₂ diffusion and transport

kinetics. This finding is related to the knowledge that mesopores enhance CO₂ diffusion and transport kinetics whereas micropores improve CO₂ adsorption capacity [26]. As such, MOFs that contain both mesopores and micropores outperform microporous MOFs in separating CO₂ from gas mixtures. Other weaknesses of MOFs that limit their use for CO₂ adsorption include susceptibility towards slowly degrading at ambient conditions, low light stability, low electrical conductivity, and poor mechanical strength [26][27]. Because of these different shortcomings, different types of MOFs have been developed with specific metal ions, organic ligands, and coordination arrangements or topographies to improve the characteristics of these porous solids. ZIFs are a subclass of MOFs containing transition metal ions that are coordinated with imidazolate (C₃H₃N₂⁻) anions as organic ligands to form porous structures composed of tetrahedral complexes akin to the topologies of zeolites [29][30]. Moreover, the architectural similarities between ZIFs and zeolites is associated with the coordination angle of the metal-imidazolate-metal (M-C₃H₃N₂⁻-M) complex in ZIFs being 145° which is analogous to the silicon-oxygen-silicon (Si-O-Si) complex coordination angle in silicas and zeolites. These similar complex coordination angles also impart ZIFs with enhanced chemical and thermal stabilities compared to those of other MOFs which more closely resemble those of zeolites. Yet, like zeolites, ZIFs suffer from structural instability and difficulty in separating CO₂ from gas mixtures that contain H₂O_v which diminishes their usefulness for separating CO₂ from gas mixtures [3][29][30].

1.6.3 Carbon-Based Porous Solids

1.6.3.1 Description and Production of Carbon-Based Porous Solids

Of the different types of porous solids, carbon-based porous solids are the most commonly employed kind of porous solids in industrial processes to date. Typical applications of carbon-based porous solids or porous carbons over the past few centuries have included drug delivery, fuel storage, gas separation, groundwater remediation, pollutant removal, toxin treatment, and water filtration with ACs being the most traditionally used porous carbons in these areas [6][7]. In terms of gas separation such as separating CO₂ from gas mixtures, carbon-based porous solids are gaining increasing attention over silica- and metal-based porous solids because of the many advantageous characteristics that porous carbons have for separating CO₂ from gas mixtures. For example, porous carbons have high specific surface areas, easily customized porous structures, high thermal stabilities, high chemical stabilities in the presence of H₂O_v because of their largely nonpolar or weakly polar natures and preferential adsorption of nonpolar and weakly polar molecules, adequate chemical stabilities when exposed to both acidic and alkaline environments, broad range of operating conditions in terms of pressures and temperatures, low regeneration energy requirements, high availabilities because of the widespread accessibility of carbonaceous materials or carbons, and low production costs. Moreover, the International Union of Pure and Applied Chemistry (IUPAC) has developed a pore size classification system to compare the pore sizes of different porous carbons since many of their beneficial characteristics are tied to the wide distributions of pore sizes that constitute the porous structures of porous carbons. This categorical system differentiates between pores as macropores (>50 nm), mesopores (<50 nm and >2 nm), and micropores (<2 nm) [3][6][12]. However, despite the existence of newer varieties of porous carbons that have been synthesized with more precise control over their specific surface areas, pore structures, and surface functionalities, ACs are still regarded as being very promising porous carbons for separating CO₂ from gas mixtures. ACs are described as carbons that have been processed to contain high volumes of mesopores and micropores which impart high specific

surface areas, porosities, physical and chemical stabilities, and surface reactivities to the carbon (C) structures of these porous carbons. For instance, ACs have specific surface areas varying from 300-4,000 m²/g with those used for liquid phase applications having pore sizes typically close to or greater than 30 Å and those used for gas phase applications having pore sizes usually ranging from 10-25 Å. Furthermore, the existence of high volumes of mesopores and micropores throughout the porous structures of ACs is linked to these porous solids being highly active since many of the C atoms within their C structures can interact with other atoms or molecules through different chemical reactions or even through adsorption which results in these carbons being referred to as ACs and classified as porous carbons [19][31].

In terms of their production, ACs are synthesized through both natural and synthetic means from a diverse assortment of carbons. The different materials used to produce ACs include coals (anthracite, bituminous, and lignite coals), industrial by-products (petroleum cokes or residues and polymers), and lignocellulosic biomasses (coconut shells, fruit nuts, olive stones, peat, saw dust, and wood) with anthracite and bituminous coals being the main materials used [19][25][31]. Such precursors or feedstocks are typically converted into ACs through manufacturing processes involving three steps: preparation, carbonization, and activation. During the preparation stage, the feedstock undergoes mechanical conversion such as size reduction and densification to prepare the material for further processing in consecutive stages. These mechanical processes significantly alter the form of particles that comprise the feedstock and improve the uniformity of these particles which, in turn, impact the changes that the material experiences during carbonization and activation. Size reduction techniques like chipping, grinding, and milling are used to modify the particle shape and size of the feedstock used to make AC. By reducing the particle size of the feedstock, the heat flow through the bulk material during subsequent processing stages is enhanced which improves the quality and quantity of AC that are produced [19][32]. In addition, certain fractions of the particle shape and size distribution of the feedstock are commonly removed following the size reduction process through a separation method such as sieving to augment the uniformity of the mechanically processed material before the feedstock enters the next processing stage. Once size reduction and separation are performed, densification techniques such as pelletization are conducted in some instances to change the particle density among other characteristics of the sieved, mechanically processed feedstock used to produce AC. Pelletized feedstock has increased particle density and uniformity which improve heat transfer through this densified material during carbonization and activation and enhance the flowability of this sieved, mechanically processed material throughout the manufacturing process [19][32].

In the carbonization stage, the sieved, mechanically processed material undergoes thermochemical conversion like pyrolysis or more specifically carbonization at temperatures ranging from 400-500°C in an atmosphere or environment composed of inert gases like N₂ to produce char. The carbonization of the sieved, mechanically processed material results in the removal of moisture and volatile matter that composes this material which generates disordered, non-volatile C residues with new pores in their non-volatile C structures in addition to the pores inherently present in the particles of the feedstock [19][25]. Yet, regardless of the development of new pores from the release of moisture and volatile matter, the char created through carbonization still lacks the porous structures needed for this material to have the specific surface area and porosity needed to effectively separate CO₂ from gas mixtures. As a result, the non-porous char is processed further in the activation stage to improve these physicochemical characteristics and produce porous carbon in the form of AC [19][25][33]. For the activation stage, the non-porous char experiences activation such as physical or chemical activation at temperatures ranging from

500-1,000°C with an appropriate activating agent to transform this C residue into AC with increased specific surface area and porosity. Physical activation is defined as the activation of non-porous char through thermochemical conversion such as gasification at temperatures commonly ranging from 800-1,000°C with a physical activating agent in the form of a mild oxidizing gas like steam, CO₂, air, or a mixture of these gases [19][25][31][33]. The physical activation of non-porous char following carbonization occurs through extensive reactions between the physical activating agent or mild oxidizing gas and the non-porous char particles at high temperatures which create new volatile matter from the fixed carbon in this material as the physical activating agent diffuses into the C layers of the char particles and oxidizes the non-volatile constituents of the non-porous char. The newly formed volatile matter then undergoes decomposition and evaporation reactions leaving behind new pores or vacancies in the non-volatile C structure of this material as the evaporated compounds in the form of gases diffuse back through the C layers and out of the char particles. Such reactions enhance the specific surface area and porosity of the non-porous char resulting in the production of AC by widening existing pores and increasing mesoporosity, generating new pores and increasing microporosity, and decomposing tars produced during the carbonization stage [5][19][25][33].

Chemical activation is described as the activation of non-porous char through thermochemical conversion at temperatures usually ranging from 500-900°C with a chemical activating agent in the form of an inorganic compound such as an acid, alkali, or oxidant. Typical acids used for chemical activation include hydrochloric acid (HCl), nitric acid (HNO₃), phosphoric acid (H₃PO₄), sulfuric acid (H₂SO₄), and zinc chloride (ZnCl₂) whereas common alkalis involve potassium hydroxide (KOH) and sodium hydroxide (NaOH). Additionally, oxidants regularly used for chemical activation encompass hydrogen peroxide (H₂O₂) and potassium permanganate (KMnO₄), yet the most frequently used chemical activating agents for chemical activation are KOH, ZnCl₂, and H₃PO₄ [19][25][31][33]. The chemical activation of non-porous char following carbonization occurs through different reactions between the chemical activating agent and the non-porous char particles at moderate to high temperatures which dehydrate and oxidize the fixed carbon in this material as the chemical activating agent permeates into the C layers of the char particles and generate new volatile matter. Like physical activation, the newly produced volatile matter then experiences decomposition and evaporation reactions which create gases that diffuse back through the C layers and out of the char particles. The non-volatile C structure of the char particles then undergoes rearrangement reactions which form new pores in addition to those created by the departure of the gases generated from the previous reactions. Accordingly, these different reactions amplify the specific surface area and porosity of the non-porous char thereby generating AC. However, the chemical activating agent used for chemical activation of the non-porous char must be removed from the char particles which is commonly accomplished by washing this material with an acid, base, or water depending on the chemical activating agent used to neutralize and separate out the inorganic compound [5][19][25][33]. Furthermore, by altering the procedures used in the preparation stage and the temperatures, heating rates, holding times, and amounts of activating agent used during the carbonization and activation stages, a myriad of different types of ACs classified according to their particle shape and size can be produced with specific surface areas, porosities, and pore size distributions geared towards certain applications.

1.6.3.2 Types and Structure of Carbon-Based Porous Solids

Regarding the various types of ACs that are manufactured, two principal classes of ACs are used to categorize ACs produced through processes similar to the three-stage procedure

previously detailed based on particle shape and size, namely granulated activated carbons (GAC) and powdered activated carbons (PAC). GACs are described as having granular forms and are classified as ACs with particle sizes that are predominantly greater than an 80-mesh sieve (0.177 mm) or those with an average particle size higher than 0.177 mm. Therefore, GACs have relatively coarse or large particle sizes and small surface areas compared to other types of ACs and are primarily produced through AC manufacturing processes involving physical activation. This type of AC is mainly used for gas and vapor adsorption processes since the characteristics of GACs allow for the rapid diffusion of gases and vapors through the bulk phase of GACs. In addition, this class of AC has a higher rate of regeneration relative to other types of AC which gives GACs an advantage in being applied to industrial operations [19][33][34]. On the other hand, PACs are noted as having powder forms and are categorized as ACs with particle sizes principally less than an 80-mesh sieve (0.177 mm) and, more specifically, those with an average particle size lower than 45 μm . As a result, PACs have fine or small particle sizes and large surface areas relative to other kinds of AC like GACs and are chiefly created through AC manufacturing processes involving chemical activation. Moreover, this variety of AC is principally used for aqueous and gas adsorption processes because the characteristics of PACs enhance their ability to adsorb rapidly diffusing adsorbates such as gases and vapors [19][33][34]. Nevertheless, ACs have disordered structures in terms of their porosities despite the existence of distinct types of ACs like GACs and PACs that are produced with precise control over many of their physicochemical characteristics including their porosities. Conversely, other kinds of porous carbons such as soft- and hard-templated mesoporous carbons have ordered structures regarding their porosities since the templated mesopores developed in their C structures are carefully arranged into ordered arrays so that their porosities have relatively similar geometries. Despite these structural differences, all porous carbons including ACs have complex structural and surface features at the nanometer scale which govern the physicochemical characteristics of porous carbons [6].

Carbons have structures that continually decrease in terms of their degree of order from carbons with the most ordered C structures aside from diamond such as single-crystal hexagonal graphite to carbons with more disordered C structures containing pores of varying sizes like porous carbons and even those with disordered C structures and inaccessible pores such as glassy carbons. In graphite, the ordered C structure is depicted as being composed of layers of hexagonally arranged C atoms referred to as graphene or graphene layers that are stacked in a displaced configuration from one graphene layer to the next which alternates in an ABABAB sequence [35]. Moreover, the bonding between C atoms in each graphene layer has a trigonal planar molecular geometry with conjugated sp^2 -hybrid σ -bonds or alternating carbon-carbon single (C-C) and carbon-carbon double (C=C) bonds at bond angles of 120° that form the conjugated planar or aromatic hexagonal rings which constitute graphene and result in distances of 0.142 nm between bonded C atoms as well as delocalized π -bonds within each layer. Each graphene layer has two unique structural regions including the basal plane which constitutes the two-dimensional conjugated sp^2 C atoms and the edge plane which encompasses the defective ring of C atoms on the edge of each plane with dangling bonds or bonded with mixed moieties. The different graphene layers are also separated by interlayer distances of 0.335 nm which are longer than the lengths of 0.142 nm related to the C=C bonds within each layer. Such distances between graphene layers indicate that there is no chemical bonding between these layers and that the different graphene layers in graphite are attracted to one another through van der Waals interactions [35][36]. Other highly-ordered carbons include polycrystalline graphites with well-ordered stacking of their graphene sheets and pyrolytic carbons, yet carbons can be created that are progressively more and

more disordered with graphene layers that begin to forsake their alternating stacking arrangement, become more defective and smaller in size, and lose their graphene nature as in the case of glassy carbons. As a result, carbons that share similar characteristics with graphite are considered as being graphitic even if they do not have a single-crystal hexagonal C structure like graphite. These carbons which are called graphitizable, anisotropic carbons become graphitic upon being heated to temperatures higher than 2,000°C and have graphene layers that exhibit ample long-range parallelism, planarity, and stacking. Alternatively, some carbons do not share many similarities with graphite even after being heated to temperatures higher than 2,000°C. Such carbons also have graphene layers formed from various short-range non-parallel, non-planar structural units. Consequently, these carbons are non-graphitic and referred to as non-graphitizable, isotropic carbons with porous carbons being common examples of such carbons [35].

As previously discussed, porous carbons such as ACs are commonly produced through the carbonization of different carbons. During carbonization, the C structures of these diverse materials are transformed through a series of reactions involving the condensation of polynuclear aromatic compounds, cleavage of side-chain groups, and development of cross-linking reactions into non-graphitic C structures. These non-graphitic C structures of the C residues generated from carbonization are further changed through activation into three-dimensional networks of C atoms contained in defective graphene sheet segments nanometers in length, similar to polycyclic aromatic compounds of varying complexity, cross-linked by aliphatic bridging groups or C atoms with sp^3 -hybrid σ -bonds and incorporated with heteroatoms both inside of the network and on the edges of the various layer planes. In addition, the erratic bonding between the separate flawed polycyclic clusters of C atoms and the aliphatic bridging groups results in the creation of pores or spaces within the network of C atoms that give rise to the porosity of porous carbons like ACs. The distorted graphene sheet segments in these carbons also have different sizes and varying degrees of graphitic character or graphitization because of the creation of holes or pores, development of linear C atoms or dangling bonds, presence of heteroatoms like hydrogen (H) and O and functional groups such as hydroxyl (R-OH) and carbonyl (C=O) groups, and non-planar configurations [19][35]. The different layer planes composed of one, two, three, or even four defective graphene sheets are estimated to have sizes of approximately 5 nm wide with interlayer spacings commonly ranging anywhere from 0.34-0.8 nm. Because of these various attributes of the C structures of porous carbons, such carbons are often modeled as small, warped graphene sheets combined together to create particles of porous carbons with tiny gaps between these different sheets serving as the pores needed to conduct CO₂ adsorption. Furthermore, researchers that performed simulations using such models of porous carbons discovered that the center-to-center distances between two horizontally and vertically adjacent six-member rings in a graphene sheet are 2.46 and 4.26 Å, respectively [6][19]. Due to these different structural and surface characteristics such as the extensive development of mesopores, micropores, and sub-micropores, porous carbons such as ACs mainly perform CO₂ adsorption through CO₂ physisorption or the generation of van der Waals interactions between CO₂ molecules and porous carbon particles. This reliance on weak intermolecular interactions to facilitate CO₂ adsorption also explains why porous carbons are more easily regenerated compared to other porous solids since the heat of adsorption related to such intermolecular interactions is much less than that associated with chemical bonds created through CO₂ chemisorption [19].

1.6.3.3 Surface Chemistry of Carbon-Based Porous Solids

However, aside from the contributions of pore structures to the CO₂ adsorptive capabilities of porous carbons, the surface chemistries of porous carbons like ACs also impact CO₂ adsorption using such porous solids. For instance, the distorted graphene sheet segments that form the assorted layer planes of AC particles contain delocalized π -bonds that are comprised of delocalized electrons which can freely move throughout the basal plane of each graphene sheet as previously mentioned. Such delocalized electrons affect the surface chemistries of ACs by providing the surfaces of such porous carbons with basic character or inherent basicity which promotes the adsorption of acidic gases such as CO₂ through CO₂ chemisorption or the development of chemical reactions like acid-base reactions [6][19]. Aside from this feature of ACs, their surface chemistries are also influenced by the presence of heteroatoms attached to the surfaces of ACs in both the aromatic C rings of the basal plane and the unsaturated C atoms or dangling bonds of the edge plane of each graphene layer. Consequently, such heteroatoms commonly reside within sundry functional groups typically contained in aromatic compounds and react with different reagents in similar manners. Moreover, among the different heteroatoms that are found in porous carbons, O atoms are the most frequently observed heteroatoms in porous carbons like ACs aside from H atoms which is attributed to the feedstocks and activating agents used to synthesize the porous carbons [6]. For example, almost all natural and synthetic feedstocks used to produce porous carbons are comprised of molecules containing O atoms which are incorporated into the structures of porous carbons in the form of various O functionalities during carbonization. In addition, most of the activating agents used in physical or chemical activation consist of molecules containing O atoms which are similarly introduced into the structures of porous carbons in the shape of different O functionalities throughout activation. As a result, O functionalities are identified on the particle surfaces of countless porous carbons in the form of surface functionalities and significantly influence some of the different aspects of the surface chemistries of these particles such as their hydrophilicity/hydrophobicity and acidity/basicity [6].

In terms of hydrophilicity/hydrophobicity, the surfaces of pristine carbons or the most ordered carbons like graphite are hydrophobic since their particle surfaces exhibit largely nonpolar natures because of the nonpolar aromatic C rings that primarily constitute their structures. The overwhelming presence of these nonpolar compounds on the surfaces of pure carbons cause such carbons to have limited interactions with H₂O due to their incompatible polarities, thereby resulting in pristine carbons being hydrophobic. Conversely, the surfaces of porous carbons such as ACs are not entirely hydrophobic since ACs adsorb H₂O_v in amounts comparable to those of other porous solids. The adsorption of H₂O_v on porous carbons is explained by their surfaces portraying both nonpolar and slightly polar behaviors because of the presence of both nonpolar aromatic C rings and different polar O surface functionalities with the latter constituents being capable of adsorbing H₂O_v molecules through chemisorption or the development of chemical bonds like hydrogen bonds. As such, the CO₂ adsorption capacities of porous carbons such as ACs are diminished at low vapor pressures because of the restricted development of van der Waals interactions that ensues following the adsorption of H₂O_v [6][19]. Such decreased CO₂ adsorption in the presence of H₂O_v is associated with the smallest adsorption of such molecules onto the surfaces of ACs resulting in the generation of adsorbate-adsorbate interactions between adsorbed H₂O_v molecules which form clusters of such adsorbed molecules that eventually lead to detrimental phenomena such as pore filling and capillary condensation within porous structures of porous carbons. These effects reduce the available porosities of porous carbons like ACs and their abilities to conduct CO₂ physisorption which rely on the availability of these extensive porous structures.

Despite such relationships with H_2O_v , ACs are still used in various applications involving humid environments since nonpolar and weakly polar compounds produce stronger intermolecular interactions with porous carbon surfaces resulting in such compounds being preferentially adsorbed during competitive adsorption [6][19]. Moreover, since adsorbed H_2O_v molecules are held by chemical bonds with various O surface functionalities, attempts at regenerating porous carbons like ACs to remove H_2O_v are predominantly ineffective because of the high heat of adsorption of these hydrogen bonds. These differences in the hydrophilicity/hydrophobicity of ordered and porous carbons indicate that the hydrophobic essence of porous carbons like ACs can be modified by the inclusion of O surface functionalities with the addition of polar O surface functionalities shifting the polarity of AC particle surfaces from being relatively nonpolar to slightly polar. By carefully altering their surface polarity in this fashion, porous carbons incorporated with certain O surface functionalities can interact more regularly with H_2O_v which suggests that their surfaces have increased hydrophilicity compared to the surfaces of their counterparts without such O surface functionalities [6][19].

As for acidity/basicity, the surfaces of pure carbons like graphite are basic because of the existence of delocalized π -bonds throughout the different graphene layers that comprise the particle surfaces of graphite. The delocalized electrons that are contained in such bonds provide inherent basicity to pristine carbon particle surfaces. Comparably, porous carbon surfaces also contain delocalized π -bonds because porous carbon surfaces are comprised of segments of distorted graphene sheets. However, porous carbon surfaces are not entirely basic since some porous carbons exhibit acidic behaviors. Such inconsistencies in the surface chemistries of porous carbons is related to the existence of both acidic and basic O surface functionalities which impart their acidity or basicity to the surfaces of these carbons. In terms of acidic O surface functionalities, a variety of different acidic surface compounds and functional groups capable of being formed from or attached to aromatic C rings are discovered in ACs including lactol, lactone, and phenol compounds and hydroxyl and carboxyl ($\text{R}-\text{C}(=\text{O})-\text{OH}$) groups. These acidic O surface functionalities are created from the oxidation of porous carbons during both physical and chemical activation with O_2 or oxidants at elevated temperatures [6][19]. Regarding basic O surface functionalities, an array of distinct basic surface compounds and functional groups able to be generated from or connected to aromatic C rings are observed in ACs such as quinone, pyrone, and chromene compounds and ketone ($\text{R}-\text{C}(=\text{O})-\text{R}'$) groups. Such basic O surface functionalities are produced from the degassing of porous carbons at extreme temperatures in an inert atmosphere followed by oxidation at ambient or room temperatures during both physical and chemical activation. Moreover, the presence of these basic O surface functionalities more significantly impacts the basic nature of porous carbon particle surfaces than delocalized π -bonds since the latter have weaker basicity compared to such surface functionalities [6][19]. These differences between ordered and porous carbons in terms of acidity/basicity suggest that the basic character of porous carbons such as ACs can be altered by the introduction of O surface functionalities with the inclusion of basic surface functionalities enhancing the basicity of AC particle surfaces. Through the controlled adjustment of their surface basicity, porous carbons containing specific O surface functionalities have more basic surfaces which indicates that their surfaces have increased basicity relative to porous carbons without such O surface functionalities or those with acidic O surface functionalities. Aside from O functionalities, other heteroatoms like N, S, and F atoms can also be integrated into the structures of porous carbons like ACs to establish diverse matrices of surface functionalities. These N, S, and F functionalities transform the surface chemistries of ACs

similar to the changes caused by the insertion of O functionalities along with additional attribute modifications unique to the specific surface functionalities that are involved [3][6][19].

1.6.3.4 Advantages and Surface Functionalization of Carbon-Based Porous Solids

Concerning the preference for using ACs to separate CO₂ from gas mixtures over other porous solids, ACs effectively separate CO₂ from gas mixtures without requiring the removal of H₂O_v, have high CO₂ adsorption capacities at ambient pressures, and are easily regenerated which are not readily available traits of most other porous solids [3][6]. These beneficial characteristics of ACs for CO₂ adsorption are an important difference which elevates ACs compared to other porous solids. Furthermore, disparities in the production of ACs and other porous solids allow ACs to be more cost-effectively manufactured relative to other porous solids and result in ACs being preferred for numerous applications. However, the CO₂ adsorption capacities of ACs decrease with increasing temperatures similar to those of other porous carbons despite porous carbons largely having suitable CO₂ adsorption capacities at ambient temperatures and low CO₂ concentrations. Moreover, the application of ACs in separating CO₂ from gas mixtures is limited since ACs have low CO₂ adsorption selectivity which decreases the effectiveness of separating CO₂ from gas mixtures using these porous carbons. The low CO₂ adsorption selectivity of ACs is attributed to difficulties associated with properly generating and managing the pore sizes in porous carbons needed for CO₂ adsorption during their production, especially the sizes of sub-micropores like super-micropores which are ideal for adsorbing CO₂ [3][6]. Such drawbacks are typically overcome by adjusting the surface chemistries of ACs through the incorporation of different surface functionalities to transfer the mechanism of CO₂ adsorption onto these porous carbons from CO₂ physisorption to CO₂ chemisorption. This introduction of surface functionalities or surface functionalization is predominantly successful for overcoming decreased CO₂ adsorption capacities at high temperatures since CO₂ physisorption diminishes with increasing temperatures whereas CO₂ chemisorption is relatively stable under similar conditions. Additionally, the resistance of CO₂ chemisorption to increasing temperatures remains intact so long as the heat sustained by functionalized ACs remains below the heat of adsorption connected to the different chemical bonds developed through CO₂ chemisorption. Functionalized ACs also have increased CO₂ adsorption selectivity since the chemical bonds created between CO₂ molecules and different surface functionalities through CO₂ chemisorption are stronger adsorbate-adsorbent interactions compared to the weak van der Waals interactions generated during CO₂ physisorption. As a result, ACs and many other porous carbons more efficiently separate CO₂ from gas mixtures through affinity-based adsorption over size exclusion-based adsorption after surface functionalities have been incorporated onto their particle surfaces [3][6].

Regardless of these improvements, the surface functionalization of ACs results in these porous carbons having increased production costs which diminish the cost advantage that unfunctionalized ACs have over most other porous carbons used for separating CO₂ from gas mixtures. These increased production costs along with the non-renewable natures and relatively expensive procurement costs of the feedstocks traditionally used to synthesize ACs including coals and industrial by-products have caused many researchers to shift towards developing porous carbons from renewable and low-cost carbons like lignocellulosic biomasses [4][7][12][25][31]. Such preferable feedstocks normally include agricultural and forestry residues (crop remnants and wood wastes), bioenergy crops (alfalfa, eucalyptus, hybrid poplar, loblolly pine, miscanthus, sorghum, sweetgum, switchgrass, and willow), and solid wastes (animal manures, food scraps, municipal solid wastes, and sewage sludges) that are considered either abundantly available or as

waste biomasses and enhance the viability of large-scale porous carbon production. Furthermore, this increased feasibility of generating porous carbons using lignocellulosic biomasses is attributed to the increased availability and renewability of these feedstocks as well as reduced waste management costs of the industrial processes supplying these waste biomasses. To produce porous carbons suitable for separating CO₂ from gas mixtures, these feedstocks are typically transformed through thermochemical conversion into non-porous chars referred to as biochars which then undergo activation to generate porous carbons in a manner that has many similarities with the fabrication of ACs. However, biochar has unique structural and physicochemical characteristics that are derived from the properties of the lignocellulosic biomass serving as the feedstock, the type of thermochemical conversion process applied, and the process conditions used to change the feedstock into biochar and other thermochemical products. Therefore, the complexity and diversity of biochar provides new challenges and opportunities in the search for novel porous carbons that can be used for separating CO₂ from gas mixtures like flue gas [4][7][12][25][31].

1.7 Conclusions

The emission of CO₂ from fossil fuel combustion and other important industrial processes is a dire issue that must be addressed to mitigate the detrimental effects of global warming. Among the different CCS technologies that can be used to alleviate climate change, adsorption-based CCS systems have many beneficial attributes that elevate these systems above others. However, the selection of suitable porous solids to use in such systems is key to taking advantage of the physicochemical characteristics of different porous solids for CO₂ adsorption. Porous carbons represent a broad assortment of disparate carbon-based porous solids but share several important disadvantages regarding CO₂ adsorption such as low CO₂ adsorption capacities with increasing temperature and low CO₂ adsorption selectivity. These limitations can be overcome by creating different surface functionalities on porous carbon surfaces through surface functionalization which result in CO₂ chemisorption being favored over CO₂ physisorption under certain conditions. Nevertheless, porous carbons often have lower production costs compared to those of other porous solids which gives porous carbons an edge in terms of large-scale CCS processes. ACs have been traditionally used over other porous carbons for centuries across many separate applications including CO₂ adsorption. Yet, because most ACs are nonrenewable, lignocellulosic biomasses are being explored as potential feedstocks to create non-porous char from in the form of biochar that can serve as a starting point for the development of renewable and sustainable porous carbons.

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Chapter 2. The Effect of Lignocellulosic Biomass Type on Biochar Physicochemical Characteristics for CO₂ Adsorption

Abstract

Biochars have been reported to have different carbon dioxide (CO₂) adsorption performances largely connected to deviations in their physicochemical characteristics that affect CO₂ adsorption. These discrepancies have been linked to different types of lignocellulosic biomass and pyrolysis conditions creating biochars with varied physicochemical characteristics. This study aimed to ascertain the effect of lignocellulosic biomass type using hybrid poplar, loblolly pine, and switchgrass on the physicochemical characteristics of biochar that have been noted to affect CO₂ adsorption. Pyrolysis experiments were conducted by pyrolyzing these lignocellulosic biomasses through intermediate pyrolysis using a semi-pilot scale auger pyrolysis system at 500°C to create biochars. Physicochemical characteristics of biomasses and biochars including specific surface area, total pore volume, pore size distribution, and alkalinity were measured or obtained using standard or published methods. CO₂ adsorption and desorption experiments were performed in a CO₂ adsorption system at 35°C using 5 vol. % CO₂ balanced with nitrogen gas (N₂) flowing at 50 mL/min. Carbon (C) content increased in biochars compared to biomasses from 51.77-53.18 to 70.86-78.57 wt. %, dry, ash-free basis (dafb) indicating the creation of pores in biochars. Aromaticity ranged from 63.51-74.18% in biochars revealing that biochars contained mostly aromatic C atoms in their graphitic C crystallites which served as pores in biochars. However, specific surface area and total pore volume varied from 0.95-1.38 m²/g and 3.38-5.00 mm³/g in biochars signaling that biochar pores were blocked during pyrolysis. As a result, all biochars had low CO₂ adsorption capacities ranging from 0.17-0.18 mmol/g. These results indicated that biochar CO₂ adsorption capacity was not affected by lignocellulosic biomass type. Given the similar CO₂ adsorption performance of these biochars, loblolly pine biochar was speculated as being the most appropriate biochar to use for CO₂ adsorption among the biochars investigated because of the wider availability of loblolly pine compared to hybrid poplar and switchgrass.

2.1 Introduction

There is growing interest around the world related to finding alternative energy sources to fossil fuels. This search is inspired by the knowledge that fossil fuels are finite, non-renewable natural resources which are anticipated to be depleted in the next few centuries. The combustion of fossil fuels also releases high amounts of CO₂ into the atmosphere that significantly contribute to global warming [1][2]. To avoid these issues, several renewable and sustainable fuels are being explored as alternatives to fossil fuels with lignocellulosic biomass being one of the most promising alternatives for displacing crude petroleum-based fuels in the transportation sector. Lignocellulosic biomass can be transformed into an assortment of renewable fuels, otherwise known as biofuels, through either biochemical or thermochemical conversion pathways which each encompass a variety of separate conversion processes. However, in many cases, thermochemical conversion is preferred over biochemical conversion since thermochemical conversion converts whole biomass into different value-added products, occurs at much faster rates, and is more biomass agnostic [3][4][5]. This type of conversion is a broad category that includes multiple conversion processes with gasification and pyrolysis being the principal processes studied for thermochemically changing biomass into value-added products. Pyrolysis is favored over gasification in some situations because pyrolysis generates mostly liquid biofuels at low pressures close to atmospheric pressure and low temperatures which are easy to store and transport while gasification produces mainly gaseous biofuels at high pressures and temperatures which are difficult to store and transport [4][5][6][7][8]. Gasification also requires a gasification or oxidizing agent like air, CO₂, oxygen gas (O₂), or steam to facilitate the partial oxidation of

biomass that occurs during this process. Yet, the chemical reactions that occur during gasification are endothermic which means that additional heat must be supplied throughout the process to maintain the specific temperature needed to create the desired products [8]. As a result, pyrolysis is thermodynamically favored over gasification because pyrolysis does not require extra heat like that needed in gasification to produce the desired products.

Pyrolysis is the thermal decomposition of lignocellulosic biomass in the absence of O₂ at temperatures ranging from 400-1200°C and produces solids, liquids, and gases which are commonly referred to as biochar, bio-oil, and non-condensable gases, respectively. Pyrolysis can occur through three distinct regimes including fast, intermediate, and slow pyrolysis. These regimes differ in terms of temperature, heating rate, and vapor residence time. These differences in process conditions also mean that each regime creates biochar, bio-oil, and non-condensable gases in different proportions and qualities [4][5][9][10][11]. Fast pyrolysis has a high temperature of 850-1250°C, high heating rate of 10-200°C/s, and short vapor residence time of 1-10 s which increase primary devolatilization reactions on biomass and decrease secondary cracking reactions on volatiles released through devolatilization during pyrolysis. Consequently, this form of pyrolysis produces a high amount of bio-oil and low amounts of biochar and non-condensable gases with yields of about 60-75, 15-25, and 10-20 wt. %, respectively, since increased cleavage and devolatilization of biomass constituents enhance bio-oil creation and decreased cracking of volatile compounds reduces biochar and non-condensable gas synthesis [4][5][6][11][12][13]. Slow pyrolysis has a low temperature of 400-500°C, low heating rate of 0.1-1°C/s, and long vapor residence time of 5-30 min which decrease primary devolatilization reactions on biomass and increase secondary cracking reactions on volatiles released through devolatilization during pyrolysis. Therefore, this kind of pyrolysis creates high amounts of biochar and non-condensable gases and a low amount of bio-oil with yields close to 25-40, 20-30, and 35-50 wt. %, respectively, because decreased cleavage and devolatilization of biomass constituents diminish bio-oil formation and increased cracking of volatile compounds aids biochar and non-condensable gas production [4][5][6][11][12][13]. Intermediate pyrolysis represents a compromise between fast and slow pyrolysis since this pyrolysis regime has a moderate temperature of 500-650°C, moderate heating rate of 1-10°C/s, and moderate vapor residence time of 5-17 min which increase primary devolatilization reactions on biomass and secondary cracking reactions on volatiles released through devolatilization during pyrolysis. Accordingly, this type of pyrolysis generates amounts of bio-oil, non-condensable gases, and biochar in between those produced by fast and slow pyrolysis with yields of nearly 40-60, 20-30, and 15-25 wt. %, respectively [4][5][6][11][12][13]. Based on these distinguishing features, different pyrolysis regimes are used to thermochemically transform biomass when certain pyrolysis products are desired with fast or intermediate pyrolysis being chosen to create bio-oil and slow pyrolysis being selected to produce biochar.

Bio-oil is a crude fuel like crude oil or petroleum that typically does not have the physicochemical characteristics necessary to be directly used as a liquid fuel without being refined. For instance, bio-oil has a high moisture content, high oxygen content, high acidity, low stability, high viscosity, and low heating value which are poor fuel properties that negatively impact the fuel performance of bio-oil and originate from the chemical composition of bio-oil [4][5][11]. Many of the different organic compounds that constitute bio-oil are oxygenated compounds including acids, alcohols, aldehydes, esters, ethers, furans, ketones, phenols, and sugars which are highly acidic and reactive and have low heating values. To improve the quality of bio-oil as a fuel, refining processes such as catalytic upgrading and hydroprocessing are used to increase cracking reactions on high molecular weight hydrocarbons and hydrodeoxygenation reactions on unsaturated and

oxygenated compounds in bio-oil during refining. Such processes result in the creation of a refined fuel that has suitable physicochemical characteristics to be used as a liquid fuel [4][5][11]. Conversely, biochar and pyrolytic gas are used for an assortment of other applications. However, biochar is still largely considered to be a low-value product or waste in many biofuel production processes despite the vast number of uses for biochar including improving soil productivity, sequestering carbon in the soil, removing harmful environmental pollutants from the air and water, and separating specific gases from gas mixtures, among others [9][10]. Concerning the use of biochar in gas separation, many researchers are using biochar to develop adsorbents or porous solids that are carbon-based often referred to as porous carbons to separate CO₂ from a gas mixture known as flue gas through adsorption. This interest stems from the knowledge that biochar has an increased surface area and porosity compared to those of biomass because of the devolatilization of biomass that occurs as volatile matter is evolved from the biomass carbon structure during pyrolysis. Like other carbonaceous materials or carbons, biochar has a high thermal stability, mostly hydrophobic surface, and adequate water resistance or chemical stability which are important physicochemical characteristics for a porous solid to have to effectively separate CO₂ from flue gas since this gas mixture is usually produced at high temperatures and contains a high amount of water vapor (H₂O_v) [9][10][14][15].

Nevertheless, the CO₂ adsorption capability of biochar varies with differences in biochar physicochemical characteristics. Physical characteristics of biochar like specific surface area, total pore volume, and average pore size affect the development of van der Waals interactions between the biochar surface and CO₂ molecules which controls the physical adsorption or physisorption of CO₂. Chemical characteristics of biochar such as alkalinity, aromaticity, polarity, hydrophobicity, and inorganics content impact the formation of chemical bonds between basic ions or functional groups on the biochar surface and acidic CO₂ molecules which influences the chemical adsorption or chemisorption of CO₂ [9][14][15][16][17][18]. Furthermore, under similar thermochemical conversion conditions, differences in biochar physicochemical characteristics have been related to differences in the biomass type used for biochar production. For example, different types of lignocellulosic biomass including hardwoods, softwoods, and grasses have varying physical structures and chemical compositions that dictate the physicochemical characteristics of their resulting biochars [19][20]. As a result, our study aims to ascertain the effect of lignocellulosic biomass type on physicochemical characteristics of biochar, such as specific surface area, total pore volume, average pore size, and alkalinity, that are known to influence CO₂ adsorption.

2.2 Materials and Methodology

2.2.1 Materials and Biomass Preparation

Industrial grade liquid nitrogen, ultra high purity (UHP) grade N₂, and a 5 vol. % CO₂ balanced with N₂ mixture were purchased from Airgas Inc. Glass jars (~950 mL volume) were purchased from BASCO. 2-Propanol or isopropanol (suitable for high-performance liquid chromatography (HPLC), 99.9%), hydrochloric acid (HCl) solution (2 M), sodium hydroxide (NaOH) solution (0.5 M), phenolphthalein solution (0.5 wt. % in ethanol:water (1:1)), and a molecular sieve adsorbent (0.425-0.600 mm particle size, 5 Å pore size) were purchased from Sigma-Aldrich. In terms of biomass, hybrid poplar and loblolly pine trees were sourced from the University of Tennessee (UT) Forest Resources Research and Education Center's Cumberland Forest Unit in Oliver Springs, TN. The hybrid poplar and loblolly pine trees were approximately 20-25 and 10 years old, respectively. The trees were felled and delimbed before being cut into

logs. Logs were only taken from the trunks of the trees to minimize heterogeneity between the different biomasses. Limbs and leaves on the logs were removed and the logs were then debarked using a draw knife before being dried in a large kiln at 48°C for 10 days to lower the moisture content of the logs. Afterwards, the logs were chipped in a chipper and placed back in the kiln at 48°C for another 10 days. In contrast, Alamo switchgrass was chopped and harvested from a farm outside of Vonore, TN, dried, and stored by Genera Energy, Inc. before being provided for our study. Therefore, the Alamo switchgrass was not dried. The dried hybrid poplar and loblolly pine chips and switchgrass straws were ground in a hammermill crusher and subsequently sieved to a particle size of <1 mm using an automatic sieve shaker. The sieved fraction of each hammermilled biomass with a particle size of >1 mm was then re-milled in a Wiley knife mill to a particle size of <1 mm. Following milling, each hammermilled and knifemilled biomass was sieved again using an automatic sieve shaker and the sieved fraction with particle sizes between 0.18 and 1 mm was collected for pyrolysis. Before pyrolysis, the sieved fraction of each biomass was poured into buckets at specific increments and uniformly mixed so that the middle and top of each bucket formed representative sections of each biomass per bucket. Small amounts of biomass were then taken from each of these sections, mixed to obtain a representative sample, divided by an automatic sample divider into 3 subsamples, and stored for characterization.

2.2.2 Biomass Characterization

Each biomass was characterized according to the following analyses and measurements on either a wet (wb), dry (db), or dafb where appropriate. Chemical analysis encompassing cellulose, hemicellulose, lignin, extractives, and ash contents (wt. %, db) was completed by following NREL/TP-510-42620, NREL/TP-510-42622, NREL/TP-510-42621, NREL/TP-510-42619, and NREL/TP-510-42618 [21][22][23][24][25]. Proximate analysis including moisture, ash, volatile matter, and fixed carbon contents (wt. %, wb or db) was performed according to ASTM E871-82, ASTM E1534-93, ASTM E872-82, and ASTM E870-82, respectively [26][27][28][29]. Ultimate analysis involving C, hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) contents (wt. %, dafb) was conducted by knifemilling about 2 mg of each biomass to a particle size of <0.425 mm, analyzing each knifemilled biomass using an Elementar vario MICRO cube elemental analyzer, and calculating O content by difference. Atomic ratios including H/C, O/C, and (O+N+S)/C were calculated after ultimate analysis and used as indications of aromaticity, hydrophilicity and carbonization, and polarity, respectively [30][31]. A van Krevelen diagram was created using H/C and O/C following ultimate analysis. Higher heating value (HHV) (kJ/g, db) was measured by pressing approximately 0.63-0.65 g of each knifemilled biomass into a pellet using a 13 mm die set and hydraulic press, loading 2 pellets in the decomposition vessel of an IKA C 6000 isoperibol oxygen bomb calorimeter, and analyzing each pelleted biomass in the isoperibol 22°C measuring mode with benzoic acid as a standard. Bulk density (ρ_b) (g/cm³) was measured using about 15-30 g of each biomass according to ASTM E873-82 using the following formula [32]:

$$\text{F2.1: } \rho_b = \frac{Mass_{Biomass}}{Volume_{Biomass}} \quad (1)$$

where $Mass_{Biomass}$ is the mass of biomass (g) and $Volume_{Biomass}$ is the volume of biomass (cm³). Particle density (ρ_p) (g/cm³) was measured by loading close to 0.5-0.8 g of each biomass into a Quantachrome ULTRAPYC 1200e automatic gas pycnometer and analyzing each biomass using helium gas (He) [33]. Bulk porosity (ϕ) (vol. %) was calculated using bulk and particle densities using the following formula [33]:

$$\text{F2.2: } \varphi = (1 - \frac{\rho_b}{\rho_p}) \times 100 \quad (2)$$

Particle size distribution was measured by pouring nearly 0.6-0.9 g of each biomass through a Microtrac PARTAN 3D particle size and shape analyzer.

Inorganics analysis including aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), nickel (Ni), phosphorus (P), S, silicon (Si), zinc (Zn), and total inorganics contents (mg/kg, db) was performed by acid digesting each biomass and analyzing the biomass digestate using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Acid digestion was accomplished by mixing about 0.35 g of each knifemilled biomass with 8 mL of 70 vol. % nitric acid (HNO₃) solution, 0.2 mL of 51 vol. % hydrofluoric acid (HF) solution, and 3 mL of hydrogen peroxide (H₂O₂) solution. The mixture was then heated to about 180-210°C for 100 min in an Anton Paar Multiwave 3000 microwave reaction system before being cooled and heated again using these same conditions to ensure that the biomass was completely digested. After acid digestion, the biomass digestate was neutralized by mixing the cooled solution with 1 mL of 4 vol. % boric acid (H₃BO₃) solution, diluted with deionized (DI) water to 50 mL, filtered using 0.2 µm filter paper, and analyzed using a PerkinElmer Optima 7300 DV ICP-OES spectrometer [34]. pH was measured by mixing roughly 10 g of each biomass with 200 mL of DI water, stirring the mixture for 24 h on an automatic shaker table, and placing a Fisherbrand accumet AB15 Basic pH/mV/°C meter in the supernatant of the stirred mixture [34][35][36]. Thermal analysis including thermogravimetric (TGA) and derivative thermogravimetric analysis (DTG) was conducted by loading approximately 5-7 mg of each knifemilled biomass into a crucible, heating the loaded crucible from 25-750°C at 5°C/min under N₂ flowing at 20 mL/min in a PerkinElmer Pyris 1 TGA thermogravimetric analyzer, and holding the loaded crucible at 750°C for 5 min. Mass loss thermographs were obtained for TGA and derivative mass loss thermographs were calculated and smoothed using a standard algorithm for DTG [37]. Fourier-transform infrared (FTIR) spectroscopy was carried out by analyzing approximately 1 g of each knifemilled biomass using a PerkinElmer Spectrum One FTIR spectrometer equipped with a universal attenuated total reflection (ATR) attachment. FTIR spectra were collected by accumulating 8 scans in absorbance mode from 4000-600 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and scan speed of 0.2 cm/s.

X-ray diffraction (XRD) was performed by putting about 0.1 g of each knifemilled biomass into a powder sample holder and analyzing each knifemilled biomass using a Malvern Panalytical Empyrean x-ray diffractometer equipped with a PIXcel^{3D} Medipix3 1x1 detector and Ni β filter. X-ray diffractograms were obtained at 45 kV and 40 mA from 5-100° 2θ using Cu Kα radiation at a scan speed of approximately 13 s per 0.09° 2θ step. After collection, x-ray diffractograms were processed through baseline subtraction and peak deconvolution using HighScore Plus 5.1. The deconvoluted peaks at close to 14, 16, 21, 22, and 35° 2θ were assigned to the cellulose crystalline phase, while the deconvoluted peak at roughly 17° 2θ was identified as the cellulose amorphous phase. The deconvoluted peaks were fit using a pseudo-voigt function. Cellulose crystallinity index ($CI_{Cellulose}$) (%) was computed using the following formula [38][39][40]:

$$\text{F2.3: } CI_{Cellulose} = \frac{A_{Crystalline}}{A_{Amorphous} + A_{Crystalline}} \times 100 \quad (3)$$

where $A_{Crystalline}$ is the area of the cellulose crystalline peaks and $A_{Amorphous}$ is the area of the amorphous peak. Cellulose crystallite size ($L_{c,Cellulose}$) (Å) was determined from the 22° 2θ peak using the following formula based on the Scherrer equation [39][40]:

$$F2.4: L_{c,Cellulose} = \frac{K_s \lambda}{\beta_{22} \cos \theta_{22}} \quad (4)$$

where K_s is the crystallite shape factor (1.00 for cellulose), λ is the wavelength of the incident beam (Å), β_{22} is the full width at half maximum (FWHM) of the 22° 2θ peak (° 2θ), and θ_{22} is the position of the 22° 2θ peak (° 2θ). Textural analysis encompassing specific surface area (SSA) (m²/g), total pore volume (V_T) (mm³/g), and pore width distribution was carried out by loading an estimated 1 g of each biomass into a sample cell, outgassing the loaded cell at 80°C for 24 h, and analyzing each biomass through N₂ physisorption at -196°C for nearly 3 h using a Quantachrome autosorb iQ-MP/XR surface area analyzer. N₂ adsorption isotherms were created and used to calculate SSA through the multi-point Brunauer-Emmett-Teller (BET) method and V_T from the volume of N₂ adsorbed at a relative pressure (P/P_0) of 0.99 according to the following formulas, respectively [41][42][43][44]:

$$F2.5: SSA = \frac{Q_M N_A A_{Cross,N_2}}{M_{N_2} Mass_{Biomass}} \quad (5)$$

$$F2.6: V_T = \frac{P_{Sat,0.99} V_{N_2,0.99} V_{M,N_2}}{RT} \quad (6)$$

where Q_M is the N₂ monolayer capacity (g), N_A is Avogadro's number (mol⁻¹), A_{Cross,N_2} is the cross-sectional area of N₂ (Å²), M_{N_2} is the molar mass of N₂ (g/mol), $P_{Sat,0.99}$ is the saturated vapor pressure of N₂ at 0.99 P/P_0 (Torr), $V_{N_2,0.99}$ is the volume of N₂ adsorbed at 0.99 P/P_0 (cm³/g), V_{M,N_2} is the molar volume of N₂ (m³/mol), R is the universal gas constant (Torr·L/mol·K), and T is the adsorption temperature (K). Pore width distribution was computationally determined by applying a non-local density-functional theory (NLDF) equilibrium model for N₂ physisorption at -196°C on carbon assuming slit-shaped pore geometry to the N₂ adsorption isotherms using Quantachrome ASiQwin 5.0. Pore width was analyzed using pore width distributions with pores with widths from 20-500 Å being classified as mesopores and pores with widths of <20 Å being distinguished as micropores [41][42][43][44]. Each of these analyses and measurements were performed in triplicates per sample per type of biomass.

2.2.3 Pyrolysis

Each biomass was pyrolyzed using a semi-pilot scale auger pyrolysis system designed and manufactured by Proton Power, Inc. The pyrolysis system was composed of a feeding system, semi-cylindrical auger pyrolysis reactor, particle separator, set of bio-oil condensers, and biochar collector as shown in Figure 2.1. A more detailed description of the pyrolysis system used in our study has been previously provided by other authors [34][35][45]. For each pyrolysis experiment, roughly 9 kg of each prepared biomass was divided into 3.5-4.5 kg portions and placed in buckets as previously described. Small amounts of biomass from each representative section in each bucket were then collected, mixed to obtain a sample, and used to determine the moisture content of the biomass used in each experiment by performing proximate analysis on each sample using the method previously detailed. At the beginning of each experiment, a bucket of portioned biomass

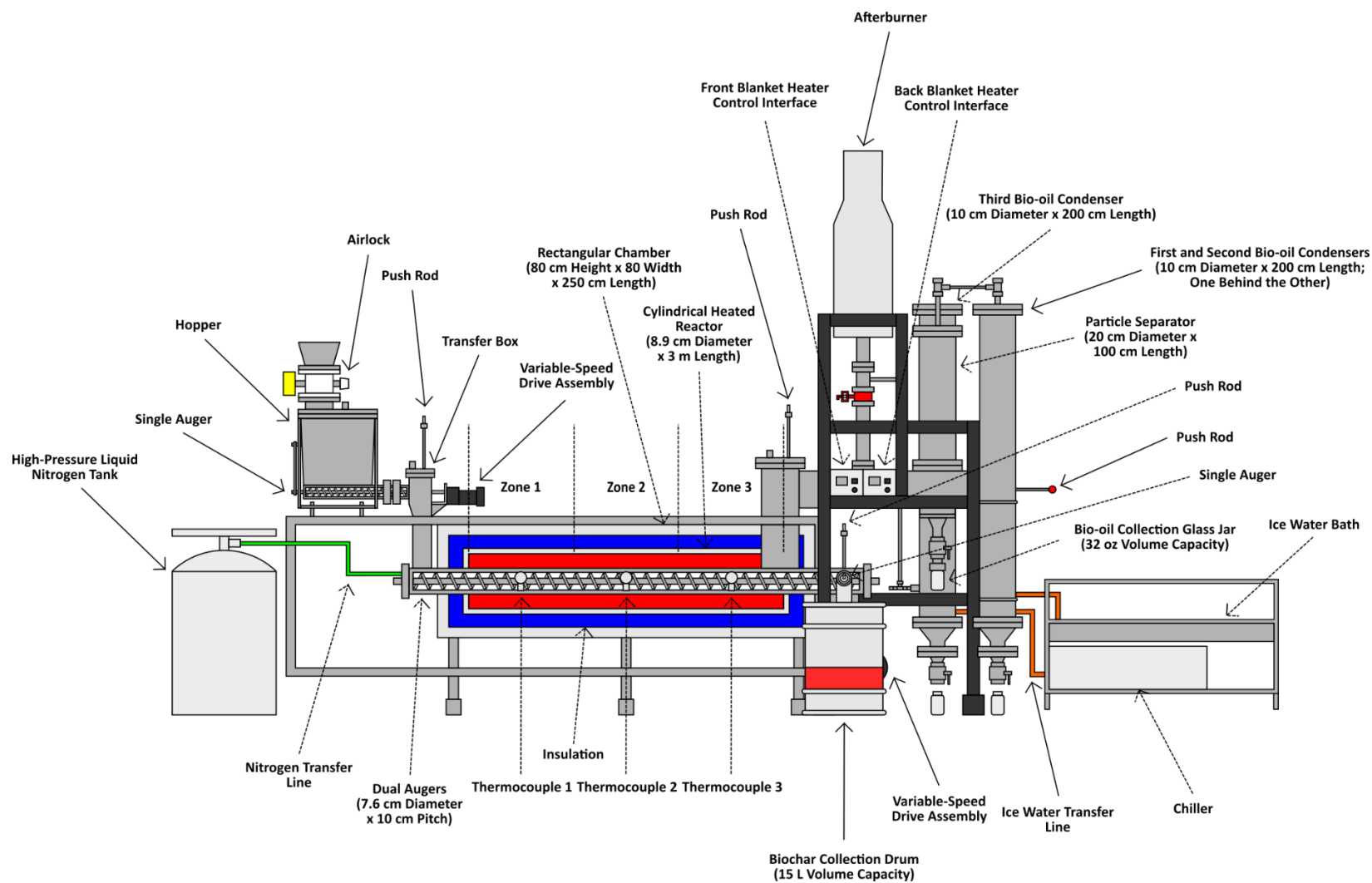


Figure 2.1. Semi-pilot scale auger pyrolysis system used to create hybrid poplar, loblolly pine, and switchgrass biochars.

was fed into the feedstock hopper. Ice was added to the circulating water-cooling system and the temperature of the system was set to 5°C. The front and back blanket heaters were set to heat to 350 and 250°C, respectively. Glass jars were connected to the closed valves at the bottoms of the particle separator and each of the bio-oil condensers to collect bio-oil. Afterwards, the pyrolysis reactor was heated to 500°C at 350°C/h under N₂ flowing at 10 L/min. While the reactor was being heated, the internal augers in the pyrolysis reactor were turned on and set to rotate at 40 revolutions per minute (rpm) and then the internal auger in the biochar collector was turned on. Once the temperatures of the pyrolysis reactor and blanket heaters reached their setpoints and equilibrated, the single auger in the feeding system was turned on and set to rotate at 8 rpm which marked the beginning of the experiment. Both auger speeds together resulted in a feeding rate of about 3.1 kg/h which corresponded to a residence time in the pyrolysis reactor of approximately 13 min. After a bucket of portioned biomass had been pyrolyzed, the next bucket of portioned biomass was fed into the feedstock hopper. The pyrolysis reactor was then closely monitored until the prepared biomass had been pyrolyzed which signified the end of the experiment. The timestamp that each 3.5-4.5 kg portion of prepared biomass was fed into the feedstock hopper was recorded to confirm that the feeding rate was kept at close to 3.1 kg/h.

During the experiment, extra ice was added to the circulating water-cooling system when needed to maintain the temperature of the water between 2-6°C. Following the experiment, the pyrolysis reactor and biochar collector were continuously purged with N₂ for 2-4 h and biochar produced during the experiment was left inside the biochar collection drum for 24 h to cool before being retrieved. Once the temperature of the pyrolysis reactor was at nearly 200°C, the blanket heaters, pyrolysis reactor and biochar collector internal augers, and N₂ flow were turned off. The valves at the bottoms of the particle separator and each of the bio-oil condensers were then opened to let bio-oil pour into the attached glass jars. Filled glass jars were labeled according to which bio-oil condenser each glass jar was removed from, weighed, and stored in a walk-in freezer. After being cooled, biochar was removed from the biochar collection drum, weighed, and stored in a plastic bag. To open blocked pores in the biochar and remove any bio-oil that had potentially condensed on the biochar during pyrolysis, the biochar was washed with isopropanol. Roughly 100 g of biochar were stirred in a mixture of 100 mL of isopropanol and 400 mL of DI water on a heated stir plate at 70°C and 300 rpm for 70 min. Halfway through washing, the isopropanol/DI water mixture was replaced with a fresh mixture. The washed biochar was then filtered using 5 µm filter paper, dried at 25°C for 24 h to let the isopropanol evaporate, and dried at 105°C for 24 h to remove any remaining moisture. Once the biochar was dry, TGA was performed on a sample of the biochar to ensure that bio-oil was not present by making sure that mass losses from 100-200°C associated with bio-oil were either absent from the mass loss thermograph or negligible. The biochar was then sieved in an automatic sieve shaker to break apart any conglomerated particles that were formed during washing before being weighed again and stored in a plastic bag. A small amount of biochar was taken from the bag as a sample, divided by an automatic sample divider into 3 subsamples, and stored for characterization. Biochar yield ($Yield_{Biochar}$) (wt. %, db) was then calculated using the following formula:

$$F2.7: Yield_{Biochar} = \frac{Mass_{Biochar}}{Mass_{Biomass}} \times 100 \quad (7)$$

where $Mass_{Biochar}$ is the mass of biochar (g). Triplicate experiments were performed using each biomass resulting in 3 samples of biomass and biochar each with 3 subsamples being obtained for characterization. Accordingly, characterization was completed on 9 subsamples for each biomass

and biochar resulting in 9 measurements per characterization technique per biomass and biochar unless otherwise stated. Before the experiments for each type of biomass were conducted, the pyrolysis system was cleaned and then conditioned by pyrolyzing the sieved fraction of each biomass with particle sizes <0.18 mm to minimize cross-contamination.

2.2.4 Biochar Characterization

Each biochar was characterized according to the following analyses and measurements on either a db or dafb where appropriate. Proximate analysis including moisture, ash, volatile matter, and fixed carbon contents (wt. %, db) was performed based on ASTM D1762-84 [46]. Ultimate analysis involving C, H, O, N, and S contents (wt. %, dafb), atomic ratios encompassing H/C, O/C, and (O+N+S)/C, HHV (kJ/g, db), ρ_b (g/cm³), ρ_p (g/cm³), ϕ (vol. %), and particle size distribution were conducted or measured following the same procedures previously discussed for biomass characterization. Inorganics analysis encompassing Al, Ca, Cu, Fe, K, Mg, Mn, Ni, P, S, Si, Zn, and total inorganics contents (mg/kg, db) was carried out by implementing the same procedure previously introduced for biomass characterization except that only roughly 0.1-0.3 g of each biochar was acid digested and 3 mL of 35 vol. % HCl solution was also mixed with each biochar during acid digestion. pH was measured following the same procedure previously noted for biomass characterization. Alkalinity (mmol H⁺/g) was measured by mixing about 1 g of each biochar with 50 mL of 0.05 M HCl solution, shaking the mixture on an automatic shaker table for 72 h, and filtering the mixture using 0.2 μ m filter paper. Two drops or 10 μ L of phenolphthalein indicator were poured into the extracts and the extracts were stirred. The extracts were then titrated to a pH of approximately 7 using 0.05 M NaOH solution and the amount of HCl titrated was calculated. Similarly, 50 mL of 0.05 M HCl solution were titrated to a pH of close to 7 using 0.05 M NaOH solution and the amount of HCl titrated was determined as a blank. The difference in the amounts of HCl titrated for the extracts and blank was recorded as the alkalinity of each biochar [36]. Water contact angle ($^\circ$) was measured to assess hydrophobicity by pouring nearly 1 g of each biochar onto a glass microscope slide covered in double-sided adhesive tape, knocking off excess biochar, smoothing the layer of adhered biochar with a clean slide, dropping eight 10 μ L DI water droplets onto the smoothed biochar layer at a speed of 405.1 μ L/min using a microsyringe, and measuring the contact angle between each droplet and the smoothed biochar layer at the three-phase contact line using a KRÜSS EasyDrop Standard contact angle goniometer and DSA1. The water contact angles measured for each slide were averaged to obtain the water contact angle for each biochar [47][48][49]. Thermal analysis including TGA and DTG and FTIR spectroscopy were performed using the same procedure previously mentioned for biomass characterization.

XRD was conducted following the same procedure previously discussed for biomass characterization except that different peaks were deconvoluted using HighScore Plus 5.1. The deconvoluted peaks at approximately 18, 23, 43, and 79 $^\circ$ 2 θ were assigned to the graphite crystalline phase and fit using a pseudo-voigt function. Aliphatic interchain spacing (d_γ) (Å) was calculated according to Bragg's law using the following formula [50][51]:

$$\text{F2.8: } d_\gamma = \frac{\lambda}{2 \sin \theta_\gamma} \quad (8)$$

where θ_γ is the position of the 18 $^\circ$ 2 θ peak or γ band ($^\circ$ 2 θ). Aromatic interlayer spacing (d_{002}) (Å) was computed based on Bragg's law using the following formula [50][51][52][53][54]:

$$\text{F2.9: } d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \quad (9)$$

where θ_{002} is the position of the $23^\circ 2\theta$ peak or (002) band ($^\circ 2\theta$). Aromatic stacking diameter (L_c) (Å), aromatic sheet diameter (L_a) (Å), and number of stacked aromatic sheets (N_a) were found using the following formulas based on the Scherrer equation, respectively [50][51][52][53][54]:

$$\text{F2.10: } L_c = \frac{0.89\lambda}{\beta_{002} \cos \theta_{002}} \quad (10)$$

$$\text{F2.11: } L_a = \frac{1.84\lambda}{\beta_{100} \cos \theta_{100}} \quad (11)$$

$$\text{F2.12: } N_a = \frac{L_c}{d_{002}} \quad (12)$$

where β_{002} is the FWHM of the (002) band ($^\circ 2\theta$), β_{100} is the FWHM of the $43^\circ 2\theta$ peak or (100) band ($^\circ 2\theta$), and θ_{100} is the position of the (100) band ($^\circ 2\theta$). Aromaticity (f_a) (%) was calculated using the following formula [50][51][53]:

$$\text{F2.13: } f_a = \frac{A_{Aromatic}}{A_{Aliphatic} + A_{Aromatic}} \times 100 \quad (13)$$

where $A_{Aromatic}$ is the area of the (002) band and $A_{Aliphatic}$ is the area of the γ band. Textural analysis involving SSA (m^2/g), V_T (mm^3/g), and pore size distribution was carried out following the same procedure previously detailed for biomass characterization. Each of these analyses and measurements were performed in triplicates per sample per type of biochar.

2.2.5 CO₂ Adsorption

CO₂ adsorption using each biochar was accomplished with a CO₂ adsorption system composed of a stainless-steel adsorption column, Lindberg 70-SV tube furnace, Digi-Sense TC9500 advanced multiparameter temperature controller, OMEGA type K thermocouple sensor, and a Thermo Scientific TRACE 1310 gas chromatograph (GC) as shown in Figure 2.2. For each adsorption experiment, about 1 g of each biochar was loaded into the adsorption column in between pieces of glass wool. The loaded adsorption column was then outgassed at 100°C under N₂ flowing at 150 mL/min for 24 h. After outgassing, the loaded adsorption column was cooled and 5 vol. % CO₂ balanced with N₂ was passed through a line bypassing the adsorption system at 25°C and 50 mL/min to the GC. Five gas chromatograms were collected and used to determine the inlet CO₂ concentration ($C_{CO_2,In}$) (vol. %). N₂ was then passed through the adsorption system at 150 mL/min to remove CO₂ from the adsorption system prior to the experiment. Once CO₂ had been removed, the loaded adsorption column was heated to 35°C and 5 vol. % CO₂ balanced with N₂ was passed through the loaded adsorption column at 50 mL/min which denoted the beginning of the experiment [44][55]. The outlet CO₂ concentration ($C_{CO_2,out}$) (vol. %) was monitored by the GC close to every 4 min. When $C_{CO_2,out}$ was nearly equal to $C_{CO_2,In}$, the biochar in the adsorption column was saturated which marked the end of adsorption. CO₂ concentration ratio (C_{CO_2}) was calculated using the following formula [44][56]:

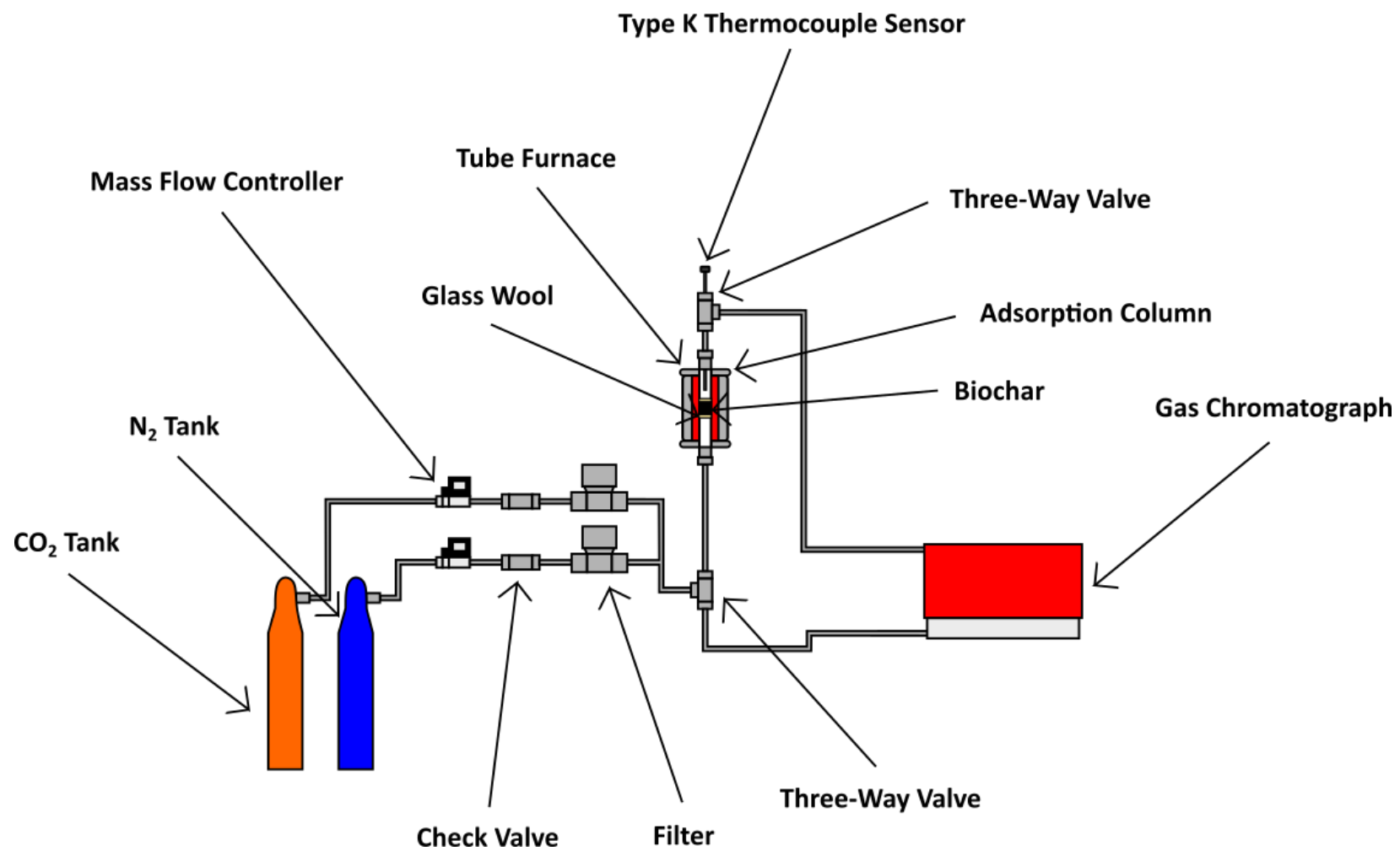


Figure 2.2. CO₂ adsorption system used to adsorb CO₂ onto and desorb CO₂ from biochar.

$$\text{F2.14: } C_{CO_2} = \frac{C_{CO_2,Out}}{C_{CO_2,In}} \quad (14)$$

CO₂ breakthrough curves were obtained by plotting C_{CO_2} versus adsorption time (t_A) (s). Adsorbed CO₂ concentration ratio ($C_{CO_2,A}$) was computed using the following formula:

$$\text{F2.15: } C_{CO_2,A} = 1 - \frac{C_{CO_2,Out}}{C_{CO_2,In}} \quad (15)$$

CO₂ adsorption volume ($V_{CO_2,A}$) (mL) and CO₂ adsorption capacity ($Q_{CO_2,A}$) (mmol/g) were determined using the following formulas, respectively [56][57]:

$$\text{F2.16: } V_{CO_2,A} = \int_0^{t_A} F_A C_{CO_2,A} dC_{CO_2,A} \quad (16)$$

$$\text{F2.17: } Q_{CO_2,A} = \frac{P_A V_{CO_2,A}}{m_B RT} \quad (17)$$

where F_A is the flow rate of 5 vol. % CO₂ balanced with N₂ (mL/min), P_A is the pressure during adsorption (atm), m_B is the mass of the biochar in the adsorption column (g), and R is the universal gas constant (atm·L/mol·K).

Following adsorption, N₂ was passed through a line bypassing the adsorption column at 150 mL/min to remove CO₂ from the adsorption system before continuing the experiment. Once CO₂ had been removed, the loaded adsorption column was heated to 35°C and N₂ was passed through the loaded adsorption column at 50 mL/min which indicated the beginning of desorption. $C_{CO_2,Out}$ was monitored by the GC roughly every 4 min. When $C_{CO_2,Out}$ was about 0, the biochar in the adsorption column was regenerated which signified the end of the experiment. Desorbed CO₂ concentration ratio ($C_{CO_2,D}$) was calculated using the following formula:

$$\text{F2.18: } C_{CO_2,D} = C_{CO_2} \quad (18)$$

CO₂ desorption volume ($V_{CO_2,D}$) (mL) and CO₂ desorption capacity ($Q_{CO_2,D}$) (mmol/g) were computed using the following formulas, respectively:

$$\text{F2.19: } V_{CO_2,D} = \int_0^{t_D} F_D C_{CO_2,D} dC_{CO_2,D} \quad (19)$$

$$\text{F2.20: } Q_{CO_2,D} = \frac{P_D V_{CO_2,D}}{m_B RT} \quad (20)$$

where F_D is the flow rate of N₂ (mL/min), P_D is the pressure during desorption (atm), and t_D is the desorption time (s). CO₂ working capacity (ΔQ_{CO_2}) (mmol/g) and regenerability (R_A) (%) were determined using the following formulas, respectively [57]:

$$\text{F2.21: } \Delta Q_{CO_2} = Q_{CO_2,A} - Q_{CO_2,D} \quad (21)$$

$$F2.22: R_A = 100 - \left(\frac{\Delta Q_{CO_2}}{Q_{CO_2,A}} \times 100 \right) \quad (22)$$

After being cooled, spent biochar was removed from the adsorption column and stored in a plastic bag. Singlet experiments were performed using each biochar. An experiment using a molecular sieve adsorbent was conducted as a standard. Differences in biomass and biochar characterization and CO₂ adsorption data were assessed through significance testing by performing analysis of variance (ANOVA) using Microsoft Excel.

2.3 Results and Discussion

2.3.1 Chemical Analysis, Biochar Yield, and Proximate Analysis

Chemical analysis of hybrid poplar, loblolly pine, and switchgrass biomasses are displayed in Table 2.1. Hemicellulose and ash contents were higher ($p < 0.05$) in switchgrass than hybrid poplar and loblolly pine differing from 29.89 and 1.25 to 18.34-18.38 and 0.19-0.47 wt. %, db, while lignin content was higher ($p < 0.05$) in hybrid poplar and loblolly pine than switchgrass varying from 23.71-31.11 to 21.03 wt. %, db, respectively. Additionally, the variations in lignin content between the wood biomasses portrayed the differences noted between hardwood and softwood biomasses with softwood biomasses having higher lignin contents than hardwood biomasses [19][35]. Accordingly, chemical analysis indicated that there were differences in chemical composition between biomasses as expected. Biochar yield and proximate analysis of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are depicted in Table 2.2. Biochar yield ranged from 16.04-24.58 wt. %, db with loblolly pine biochar having the highest yield and hybrid poplar biochar having the lowest yield. These biochar yields were lower than those reported in other studies that produced biochars through pyrolysis at 500°C using similar biomasses and pyrolysis conditions [35][58][59][60][61][62]. However, such differences were attributed to discrepancies in biomass preparation and the use of isopropanol to wash the biochars which altered biochar formation and resulted in biochar loss, respectively. Volatile matter content decreased ($p < 0.05$) in biochars compared to biomasses from 79.65-82.02 to 29.14-43.59 wt. %, db, whereas ash and fixed carbon contents increased ($p < 0.05$) in biochars relative to biomasses from 0.19-1.25 and 10.95-13.89 to 1.73-3.12 and 50.46-66.43 wt. %, db, respectively. These alterations indicated that volatile matter or labile C was removed from biomasses through devolatilization which included dehydration of hydroxyl (R-OH) groups, thermal degradation of biomass constituents such as cellulose, hemicellulose, and lignin, and evolution of volatiles as carbon monoxide (CO), CO₂, methane (CH₄), H₂O, and hydrogen gas (H₂). Because of these changes, inorganics and stable C were concentrated in biochars as ash and fixed carbon, respectively [35][60][61][62][63]. As a result, proximate analysis denoted that biomasses were devolatilized during pyrolysis which should have created pores in biochars that could adsorb CO₂.

2.3.2 Ultimate Analysis and HHV

Ultimate analysis, atomic ratios, and HHV of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are exhibited in Table 2.3. H and O contents decreased ($p < 0.05$) in biochars compared to biomasses from 7.06-7.17 and 39.44-40.96 to 4.19-4.84 and 16.93-23.27 wt. % dafb, respectively, while C content increased ($p < 0.05$) in biochars relative to biomasses from 51.77-53.18 to 70.86-78.57 wt. % dafb. These changes revealed that R-OH groups were dehydrated and volatile matter, which is largely composed of C, H, and O, was devolatilized through dehydrogenation and deoxygenation. Moreover, these devolatilization reactions occurred through cleavage of weak O bonds like those found in ether (R-O-R') groups between alkyl

Table 2.1. Chemical analysis of hybrid poplar, loblolly pine, and switchgrass biomasses.

	Biomass				
	Chemical Analysis (wt. %, db)				
	Cellulose	Hemicellulose	Lignin	Extractives	Ash
Hybrid Poplar	42.71 (1.04)	18.38 (0.75)	23.71 (0.23)	7.01 (1.00)	0.47 (0.04)
Loblolly Pine	36.89 (0.50)	18.34 (0.35)	31.11 (0.27)	5.32 (0.57)	0.19 (0.02)
Switchgrass ¹	37.33 (1.23)	29.89 (1.08)	21.03 (0.25)	5.31 (0.45)	1.25 (0.06)

Values in table are averages with standard deviations in parentheses. ¹Values are based on averages of 18 rather than 9 measurements.

Table 2.2. Biochar yield and proximate analysis of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

Biomass					
	Biochar	Proximate Analysis			
	Yield	Moisture	Ash	Volatile Matter	Fixed Carbon
	(wt. %, db)	(wt. %, wb)	(wt. %, db)	(wt. %, db)	(wt. %, db)
Hybrid Poplar	NA	6.56 (0.12)	0.47 (0.04)	82.02 (0.36)	10.95 (0.29)
Loblolly Pine	NA	6.27 (0.15)	0.19 (0.02)	79.65 (0.20)	13.89 (0.22)
Switchgrass	NA	7.76 (0.30)	1.25 (0.06)	79.82 (0.59)	11.17 (0.46)
Biochar					
Hybrid Poplar	16.04 (3.25)	2.70 (0.32)	1.73 (0.39)	29.14 (1.62)	66.43 (1.92)
Loblolly Pine	24.58 (1.14)	2.72 (0.28)	0.59 (0.21)	38.66 (5.25)	58.04 (4.98)
Switchgrass	19.47 (6.14)	2.82 (0.14)	3.12 (0.75)	43.59 (3.72)	50.46 (2.92)

Values in table are averages with standard deviations in parentheses. NA stands for not applicable.

Table 2.3. Ultimate analysis, atomic ratios, and HHV of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

Biomass					
	Ultimate Analysis (wt. %, dafb)				
	C	H	N	S	O
Hybrid Poplar	51.77 (0.22)	7.06 (0.07)	0.09 (0.03)	0.13 (0.05)	40.96 (0.28)
Loblolly Pine	53.18 (0.18)	7.17 (0.11)	0.10 (0.04)	0.12 (0.04)	39.44 (0.21)
Switchgrass	51.80 (0.19)	7.07 (0.12)	0.20 (0.03)	0.17 (0.05)	40.76 (0.21)
Biochar					
Hybrid Poplar	78.57 (1.45)	4.19 (0.28)	0.24 (0.08)	0.06 (0.03)	16.93 (1.56)
Loblolly Pine	74.52 (1.95)	4.70 (0.39)	0.32 (0.28)	0.02 (0.02)	20.44 (1.74)
Switchgrass	70.86 (2.16)	4.84 (0.20)	0.97 (0.79)	0.06 (0.03)	23.27 (2.67)
Biomass					
	Atomic Ratios			HHV	
	H/C	O/C	(O+N+S)/C	(kJ/g, db)	
Hybrid Poplar	1.62 (0.02)	0.59 (0.01)	0.60 (0.01)	20.96 (0.05)	
Loblolly Pine	1.60 (0.03)	0.56 (0.00)	0.56 (0.00)	21.80 (0.07)	
Switchgrass	1.62 (0.03)	0.59 (0.01)	0.60 (0.01)	20.96 (0.07)	
Biochar					
Hybrid Poplar	0.63 (0.04)	0.16 (0.02)	0.17 (0.02)	29.86 (0.54)	
Loblolly Pine	0.75 (0.08)	0.21 (0.02)	0.21 (0.02)	29.01 (0.64)	
Switchgrass	0.81 (0.05)	0.25 (0.04)	0.26 (0.03)	26.91 (0.43)	

Values in table are averages with standard deviations in parentheses.

(R-C_nH_{2n+1}) and aryl (R-Ar) groups (R-O-Ar) in biomass constituents which caused C to be concentrated in biochars [35][61][63]. N content increased ($p<0.05$) in hybrid poplar and switchgrass biochars compared to their biomasses from 0.09-0.20 to 0.24-0.97 wt. %, dafb, whereas S content decreased ($p<0.05$) in biochars relative to biomasses from 0.12-0.17 to 0.02-0.06 wt. %, dafb. These transitions signaled that N was concentrated in hybrid poplar and switchgrass biochars while S was evolved from biomasses through desulfurization. Other studies showed that N was evolved from biomass through pyrolysis using similar biomasses and pyrolysis conditions [61][64]. As such, ultimate analysis demonstrated that biomasses were dehydrated, dehydrogenated, and deoxygenated through pyrolysis. This analysis also signaled that biomasses were not denitrogenated but were desulfurized during pyrolysis. H/C, O/C, and (O+N+S)/C decreased ($p<0.05$) in biochars compared to biomasses from 1.60-1.62 to 0.63-0.81, 0.56-0.59 to 0.16-0.25, and 0.56-0.60 to 0.17-0.26, respectively. These alterations denoted that biomass C structures were carbonized during pyrolysis and became more aromatic and stable and less hydrophilic and polar as biochar C structures [30][31]. The decreases in H/C through pyrolysis evidenced that aliphatic chains were cleaved through cracking, alicyclic rings were formed from cyclization, aromatic rings were generated by aromatization, and π -conjugated ring systems or aromatic ring clusters were produced through aromatic condensation causing biochars to have more aromatic C structures than those of biomasses. The decreases in O/C during pyrolysis showed that O heteroatoms and functional groups were removed by deoxygenation and devolatilization resulting in biochars having more stable and less hydrophilic C structures than those of biomasses. The decreases in (O+N+S)/C through pyrolysis signified that O and S heteroatoms and functional groups were removed by deoxygenation, desulfurization, and devolatilization giving biochars less polar C structures than those of biomasses [30][31][35][60][61][62][63]. Consequently, atomic ratios signified that biomasses were aromatized, carbonized, and depolarized through pyrolysis.

HHV increased ($p<0.05$) in biochars compared to biomasses from 20.96-21.80 to 26.91-29.86 kJ/g, db. These changes implied that heteroatoms such as O were removed from biomasses through pyrolysis since higher C contents are associated with higher HHVs which caused C to be concentrated in biochars [62][64]. Therefore, HHV conveyed that biomasses were carbonized and obtained higher energy contents during pyrolysis. A van Krevelen diagram of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars is illustrated in Figure 2.3. van Krevelen diagrams are used to determine degrees of aromatization and carbonization of biomasses and biochars based on H/C and O/C atomic ratios obtained through ultimate analysis. Transitions on van Krevelen diagrams can also be used to illustrate reactions associated with aromatization and carbonization like dehydration, deoxygenation including decarboxylation and decarbonylation, dehydrogenation, and demethylation [35][63][64]. H/C and O/C decreased ($p<0.05$) in biochars relative to biomasses which were represented by the shifting of biochars down and left of biomasses on the van Krevelen diagram. These movements on the van Krevelen diagram signaled that biomasses were aromatized, dehydrated, decarboxylated, decarbonylated, and dehydrogenated during pyrolysis. Such transitions agreed with those shown in other studies for biochars produced through pyrolysis at 500°C. Dehydration, decarboxylation, and decarbonylation are the dominant reactions that occur at pyrolysis temperatures from 300-600°C and cause H₂O_v, CO₂, and CO to be released as volatiles, respectively, whereas dehydrogenation, and demethylation are the principal reactions that occur at pyrolysis temperatures from 600-800°C and result in H₂ and CH₄ being released as volatiles, respectively [35][63]. Furthermore, a H/C of ≤ 0.1 as represented by the dashed line on the van Krevelen diagram is indicative of a graphitic C structure revealing that a C structure is highly crystalline or ordered and contains regularly stacked C layers or sheets

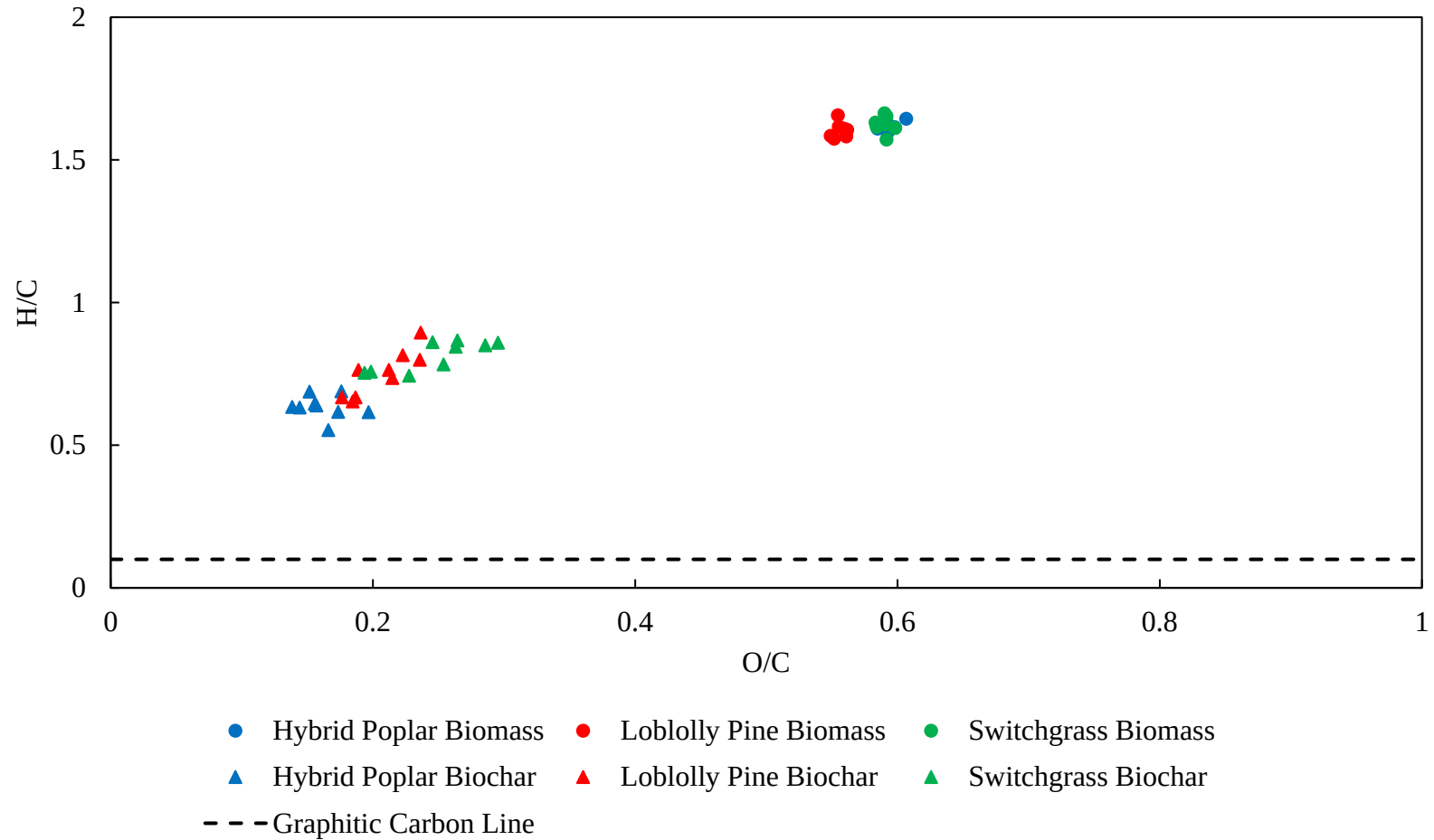


Figure 2.3. van Krevelen diagram of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

composed of aromatic ring clusters. Based on this relationship, biochars had largely amorphous or non-graphitic C structures because H/C atomic ratios of biochars were well above 0.1 although some local graphitic C structures may have been present in biochars [58]. Accordingly, the van Krevelen diagram denoted that biomasses were aromatized and carbonized through pyrolysis and that biochars had amorphous C structures. Overall, ultimate analysis and HHV revealed that biomasses were carbonized during pyrolysis creating amorphous C structures which should have contained pores that could adsorb CO₂.

2.3.3 Bulk and Particle Densities, Bulk Porosity, and Particle Size Distribution

Bulk and particle densities and bulk porosity of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are presented in Table 2.4. Bulk density decreased ($p < 0.05$) in switchgrass biochar compared to its biomass from 0.18 to 0.14 g/cm³, whereas particle density decreased ($p < 0.05$) in biochars compared to biomasses from 1.45-1.84 to 1.26-1.42 g/cm³. Bulk porosity decreased ($p < 0.05$) in hybrid poplar and loblolly pine biochars relative to their biomasses from 86.70-92.60 to 85.24-90.05 vol. %. These changes denoted that softening and melting of biomasses and confinement of volatiles as bio-oil condensates in biochar pores collapsed or blocked pores in hybrid poplar and loblolly pine biochars but left pores in switchgrass biochar largely open or unaffected through pyrolysis [33][65][66][67]. During devolatilization, biomasses were softened and melted or plasticized through cleavage of weak O bonds in biomass constituents and formation of a plastic layer known as a metaplast which consists of liquid volatiles created through devolatilization of volatile matter on biomass particle surfaces. Biomass particles were deformed by particle expansion, metaplast formation, and particle contraction as volatile matter was transformed into liquid volatiles, transported through biomass particles, and evolved from biomass particle surfaces as gaseous volatiles through evaporation. Biomasses were then repolymerized to form biochars [68][69][70]. Because of devolatilization, existing biomass pores were enlarged and new biomass pores were developed which should have resulted in increases in particle density and bulk porosity in biochars. Other studies highlighted that particle density and bulk porosity increased in biochar during pyrolysis because of these changes [33][67][70].

However, such discrepancies were attributed to biomass pores being collapsed by softening and melting of biomasses and partially blocked by entrapment of bio-oil condensates. Hybrid poplar and loblolly pine biomasses were melted because biomass constituents, such as lignin, experienced bridge-breaking to a significant extent before cross-linking could occur which caused plastic deformation of these biomasses and metaplast formation resulting in pore collapse [68][71]. Conversely, switchgrass biomass was melted to a lesser extent because switchgrass biomass contained a lower lignin content (21.03 wt. %, db) and higher ash content (1.25 wt. %, db) than those of hybrid poplar (23.71 and 0.47 wt. %, db) and loblolly pine biomasses (31.11 and 0.19 wt. %, db), respectively. The lower amount of lignin in switchgrass biomass diminished bridge-breaking and cross-linking which mitigated metaplast formation in switchgrass biomass. Moreover, the higher amount of ash in switchgrass biomass resulted in inorganics like Ca and K catalyzing cross-linking in switchgrass biomass which inhibited plasticization and prevented pore collapse [68]. Therefore, these differences in melting between biomasses explained the variations in the changes to bulk and particle densities and bulk porosity of biomasses and biochars. Apart from pore collapse because of melting, pyrolysis products may have become trapped in biochar pores and partially blocked biochar pores which impacted the changes to bulk and particle densities and bulk porosity of biomasses through pyrolysis [67]. As a result, bulk and particle densities and bulk porosity conveyed that biomasses were devolatilized and that biochar pores were collapsed

Table 2.4. Bulk and particle densities and bulk porosity of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

Biomass			
	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Bulk Porosity (vol. %)
Hybrid Poplar	0.13 (0.00)	1.84 (0.18)	92.60 (0.63)
Loblolly Pine	0.21 (0.01)	1.58 (0.08)	86.70 (0.86)
Switchgrass	0.18 (0.01)	1.45 (0.06)	87.25 (0.74)
Biochar			
Hybrid Poplar	0.14 (0.01)	1.42 (0.10)	90.05 (1.26)
Loblolly Pine	0.20 (0.02)	1.35 (0.07)	85.24 (1.86)
Switchgrass	0.14 (0.01)	1.26 (0.04)	89.01 (0.73)

Values in table are averages with standard deviations in parentheses.

or blocked during pyrolysis which should reduce CO₂ adsorption onto biochars.

Particle size distributions of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are illustrated in Figure 2.4. Particle size decreased in biochars compared to biomasses with 27.18-37.24 and 0.83-1.62 vol. % of biomass particles having particle sizes evenly distributed around 594.3-768.8 and 126.8 μm and 9.08-23.79 and 11.93-22.82 vol. % of biochar particles having particle sizes evenly distributed close to 594.3-768.8 and 126.8 μm , respectively. These alterations indicated that devolatilization of biomasses caused biomass particles to contract and deteriorate through pyrolysis. Plasticization of biomass particles resulted in particle contraction as previously discussed which caused biomass particle size to decrease as volatiles were released from biomasses. Expansion and contraction of biomass particles also caused their tensile strength to decrease which resulted in biomass particles being more fragile and susceptible to being broken apart by abrasion [58][72]. As such, biomass particle size was further decreased because of friction developed between biomass particles as biomass particles moved through the pyrolysis system during pyrolysis. Because of this shrinkage and deterioration, particle size distribution shifted from most biomass particles having particle sizes between 500.0-1000.0 μm to large portions of biochar particles having particle sizes ranging from both 35.0-165.0 and 500.0-1000.0 μm . Other than these changes, 10.23 vol. % of hybrid poplar biomass had particle sizes evenly distributed near 2153.0 μm which did not occur for loblolly pine and switchgrass biomasses. This behavior was attributed to hybrid poplar biomass being statically charged and tending to form conglomerates. Some conglomeration was also observed in hybrid poplar biochar but to a lesser extent with 4.85 vol. % of hybrid poplar biochar having particle sizes evenly distributed around 1664.0 μm . As such, particle size distribution demonstrated that biomass particles were contracted and weakened during pyrolysis which may influence CO₂ adsorption onto biochar particles.

2.3.4 Inorganics Analysis, pH, Alkalinity, and Water Contact Angle

Inorganics analysis of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars is revealed in Table 2.5. Al, Ca, Cu, Fe, K, Mg, Mn, Ni, P, S, Si, and Zn contents increased ($p < 0.05$) in biochars compared to biomasses except for Si content of loblolly pine biochar. Similarly, total inorganics content increased ($p < 0.05$) in biochars relative to biomasses from 2913.07-8204.35 to 10979.44-22221.30 mg/kg, db. These changes signified that many inorganics present in biomasses were concentrated because of the removal of volatile matter from biomasses [34][60]. Switchgrass biomass had the highest total inorganics content which was largely related to the high Si content of switchgrass biomass. Consequently, switchgrass biochar had the highest total inorganics content as well. However, the distribution of inorganics in biomasses was modified during pyrolysis because certain inorganics were concentrated in greater amounts in particular biomasses. Apart from C, H, O, and N, Ca, K, Mg, P, and S are macronutrients, while boron (B), chlorine (Cl), Cu, Fe, Mn, molybdenum (Mo), and Zn are micronutrients since these elements are essential nutrients that are accumulated in plants in high and low amounts, respectively, for plant growth and completion of the plant life cycle [73][74][75]. Switchgrass biomass had the highest amounts of macro- and micronutrients since Ca, Cu, Mg, P, and S contents were highest in switchgrass biomass while K and Zn and Fe and Mn contents were highest in hybrid poplar and loblolly pine biomasses, respectively. Yet, after pyrolysis, hybrid poplar biochar had the highest amounts of macro- and micronutrients because Ca, Cu, K, P, and Zn contents were highest in hybrid poplar biochar whereas Fe and Mn and Mg and S contents were highest in loblolly pine and switchgrass biochars, respectively. This transformation in the distribution of inorganics following pyrolysis was associated with hybrid poplar biomass losing more volatile matter during devolatilization than

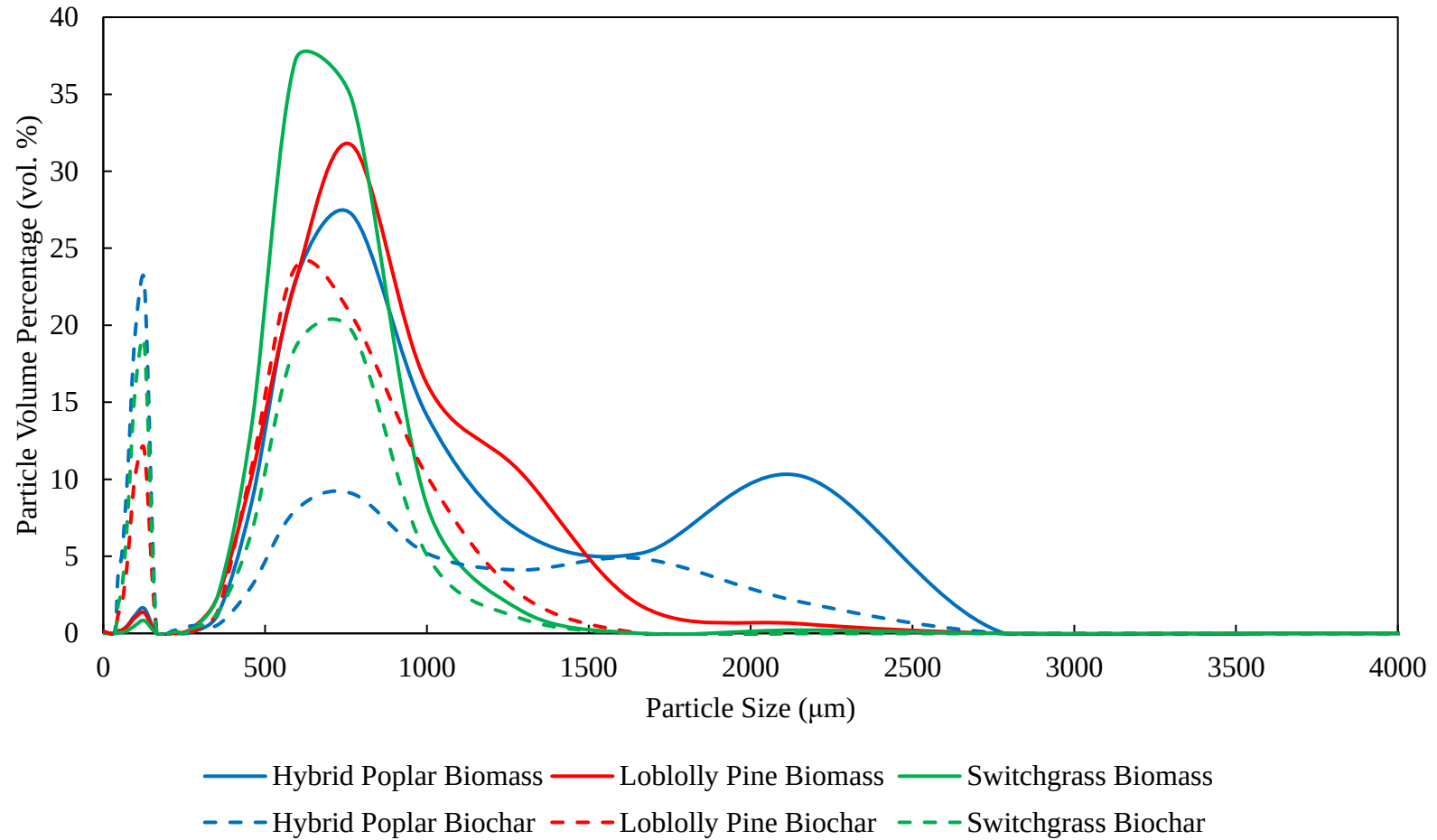


Figure 2.4. Particle size distributions of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

Table 2.5. Inorganics analysis of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

Table 2.5: Inorganics analysis of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.					
Biomass					
	Inorganics Analysis (mg/kg, db)				
	Al	Ca	Cu	Fe	K
Hybrid Poplar	15.34 (18.42)	1181.49 (31.18)	0.56 (0.43)	34.04 (18.27)	957.72 (34.39)
Loblolly Pine	31.69 (17.09)	712.47 (28.59)	1.07 (0.86)	92.19 (30.52)	572.29 (39.54)
Switchgrass	14.15 (6.55)	1492.72 (297.10)	1.53 (2.92)	78.91 (16.19)	533.52 (28.11)
Biochar					
Hybrid Poplar	46.32 (26.37)	5504.74 (723.83)	44.02 (19.86)	2924.23 (558.85)	3896.72 (619.06)
Loblolly Pine	77.95 (39.16)	2392.83 (580.90)	16.06 (5.62)	3305.49 (901.86)	1527.61 (632.98)
Switchgrass	76.51 (47.15)	3647.56 (1047.18)	20.82 (10.70)	3135.37 (1904.41)	801.30 (268.57)
Biomass					
	Mg	Mn	Ni	P	S
Hybrid Poplar	192.13 (4.57)	10.14 (0.62)	42.39 (12.73)	160.84 (11.76)	94.88 (5.00)
Loblolly Pine	202.97 (8.75)	92.48 (2.20)	43.51 (10.69)	65.97 (14.65)	70.92 (4.51)
Switchgrass	835.97 (86.26)	63.79 (11.39)	168.28 (25.81)	236.30 (40.28)	292.62 (37.18)
Biochar					
Hybrid Poplar	1009.02 (111.53)	66.21 (7.85)	94.01 (25.83)	682.02 (70.99)	175.67 (13.86)
Loblolly Pine	663.63 (165.54)	307.41 (71.37)	60.84 (11.27)	234.25 (64.44)	89.71 (15.00)
Switchgrass	1555.08 (564.55)	146.29 (54.93)	94.27 (37.01)	543.08 (169.91)	386.42 (99.23)
Biomass					
	Si	Zn	Total Inorganics		
Hybrid Poplar	936.15 (327.15)	9.33 (0.68)	3634.96 (366.19)		
Loblolly Pine	1021.22 (371.66)	6.64 (0.69)	2913.07 (443.52)		
Switchgrass	4477.81 (897.89)	8.74 (1.68)	8204.35 (1391.10)		
Biochar					
Hybrid Poplar	2086.07 (539.49)	62.13 (16.42)	15909.14 (1973.93)		
Loblolly Pine	2509.61 (2540.87)	28.29 (17.42)	10979.44 (3234.14)		
Switchgrass	12330.26 (5832.14)	27.42 (12.57)	22221.30 (9131.80)		

Values in table are averages with standard deviations in parentheses.

that lost by loblolly pine and switchgrass biomasses which resulted in specific inorganics being more heavily concentrated in hybrid poplar biochar. Consequently, inorganics analysis signaled that inorganics were concentrated in biochars through pyrolysis.

pH, alkalinity, and water contact angle of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are shown in Table 2.6. pH decreased ($p < 0.05$) in biochars compared to biomasses from 4.78-5.63 to 4.00-4.42. This change demonstrated that acidic functional groups were imparted to biomasses and basic functional groups were removed from biomasses because of bio-oil condensation on biochars and isopropanol washing of biochars which caused biochars to be more acidic [34]. Prior to washing the biochars with isopropanol, small clumps of biochar particles were found in some biochars which indicated that bio-oil had condensed on biochars and caused some biochar particles to form agglomerates. This finding was reinforced by the pH of unwashed loblolly pine biochar which was measured to be 2.74. Such a low pH signaled that biochar contamination had occurred during pyrolysis since the pyrolysis of biomass at 500°C should have created biochar that was basic. Other studies showcased that pH increased in biomass through pyrolysis because of the removal of volatile matter from biomass which contains acidic functional groups and the concentration of inorganics in biochar which are basic [34][35][36][61]. Therefore, this result supported that bio-oil had condensed on loblolly pine biochar as well as the other biochars since bio-oil is acidic. Based on this realization, our biochars were washed with isopropanol to remove bio-oil from biochar particles and break apart any agglomerates. Elimination of bio-oil from the biochars was confirmed by the absence of mass losses from 100-200°C linked to the thermal decomposition of bio-oil in the mass loss thermographs of washed biochars. However, by washing the biochars, portions of the inorganics in biochars were removed since some of the inorganics that were more loosely attached to biochars were soluble in the DI water and isopropanol used to dissolve bio-oil. This removal of inorganics caused acidic functional groups in the volatile matter remaining in biochars to have a greater impact on pH than these functional groups otherwise would have had if some of the inorganics had not been dissolved. Therefore, pH signified that biomasses were acidified through pyrolysis since dissolution of part of the inorganics in biochars resulted in biochars being more acidic than biomasses despite acidic functional groups being removed from biomasses through devolatilization of volatile matter and separated from biochars through dissolution of condensed bio-oil.

Alkalinity ranged from 0.14-0.26 mmol H⁺/g with switchgrass biochar having the highest alkalinity and loblolly pine biochar having the lowest alkalinity ($p < 0.05$). These alkalinities were lower than those reported in another study that made biochars through pyrolysis at 500°C using similar biomasses [36]. Such disparities were attributed to isopropanol washing of the biochars which removed some of the inorganics that functioned as alkalis from biochars. Alkalinity is divided into several different categories depending on the nature or type of the alkali contributing to alkalinity. For biochar alkalinity, these classifications include organic and inorganic alkalinities which can be further divided into structural organic and other organic and carbonate and other inorganic alkalinities, respectively [36]. Each of these separate alkalinity groupings contribute to biochar total alkalinity but the distribution of these different kinds of alkalinities differs according to the type of biochar being examined. For example, in this other study, the alkalinity of hardwood biochar pyrolyzed at 500°C was higher than those of red oak and corn stover biochars and chiefly connected to inorganic alkalinity, specifically carbonate alkalinity, whereas the alkalinity of red oak biochar pyrolyzed at 500°C was lower than that of corn stover biochar and was largely linked to organic and inorganic alkalinities, specifically structural organic and carbonate alkalinities. In contrast, the alkalinity of corn stover biochar pyrolyzed at 500°C was only slightly lower than that

Table 2.6. pH, alkalinity, and water contact angle of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

Biomass			
	pH	Alkalinity (mmol H ⁺ /g)	Water Contact Angle (°)
Hybrid Poplar	5.18 (0.06)	NA	NA
Loblolly Pine	4.78 (0.08)	NA	NA
Switchgrass	5.63 (0.12)	NA	NA
Biochar			
Hybrid Poplar	4.42 (0.09)	0.20 (0.04)	117.40 (6.48)
Loblolly Pine	4.01 (0.11)	0.14 (0.03)	116.06 (6.85)
Switchgrass	4.00 (0.17)	0.26 (0.03)	116.15 (6.62)

Values in table are averages with standard deviations in parentheses. NA stands for not applicable.

of hardwood biochar and was mainly related to inorganic alkalinity involving carbonate and other inorganic alkalinities [36]. Such differences indicated that certain types of alkalis had greater impacts on the total alkalinities of specific biochars over others. However, each of the different types of alkalinities were prominent in the biochars that were studied and total alkalinity was found to be mostly influenced by the presence of base cations with higher amounts of base cations in biochar causing biochar to have a higher total alkalinity [36]. As a result, our biochars had lower amounts of alkalis than the biochars analyzed in this other study because some of the inorganics in biochars were removed during isopropanol washing which decreased the amount of other inorganic alkalis in biochars and therefore decreased the alkalinities of biochars. This result was also indicated by the similar relationships observed between the total inorganics contents and alkalinities of biochars with switchgrass biochar having the highest total inorganics content and alkalinity and loblolly pine biochar having the lowest total inorganics content and alkalinity. The similarity between these trends suggested that other inorganic alkali had a significant influence on the alkalinities of biochars. Accordingly, alkalinity denoted that biochars contained alkalis.

Water contact angle ranged from 116.06-117.40° but was not different between biochars ($p>0.05$). Water contact angle is used as an indication of hydrophobicity in biochars with water contact angles $>90^\circ$ denoting that biochar is hydrophobic and water contact angles $\leq 90^\circ$ indicating that biochar is hydrophilic [47][49]. This distinction signified that biochars were hydrophobic based on the water contact angles of biochars. Other studies reported that biochar hydrophobicity was associated with biochar functional groups with the presence of higher amounts of $R-C_nH_{2n+1}$ groups increasing hydrophobicity and higher amounts of O functional groups such as R-OH and carboxyl ($R-C(=O)-OH$) groups increasing hydrophilicity. The increased biochar hydrophilicity connected to O functional groups was ascribed to the presence of such functional groups increasing biochar polarity which allowed these functional groups to interact with H_2O molecules near biochar surfaces [47][76][77]. Additionally, the impact of polarity on biochar hydrophobicity explained why higher amounts of $R-C_nH_{2n+1}$ groups increased biochar hydrophobicity since the presence of these functional groups decreased biochar polarity which prevented these functional groups from interacting with H_2O molecules. These studies also highlighted that biochar hydrophobicity was associated with biochar ash content, surface area, and pore volume with higher biochar ash content, surface area, and pore volume decreasing biochar hydrophobicity [47]. Higher biochar ash content indicated that more hydrophilic inorganics were present in biochar which increased biochar hydrophilicity. Higher biochar surface area and pore volume revealed that more pores were present in biochar which increased the development of capillary forces between biochar surfaces and H_2O molecules and, as a result, increased biochar hydrophilicity [47]. As such, water contact angle conveyed that biochars had high amounts of $R-C_nH_{2n+1}$ groups, low amounts of R-OH and $R-C(=O)-OH$ groups, and low ash contents, surface areas, and pore volumes since biochars were hydrophobic. Overall, inorganics analysis, pH, and alkalinity implied that inorganics were concentrated in biochars through pyrolysis but that some inorganics were removed from biochars through isopropanol washing which should have removed basic functional groups that could adsorb CO_2 . Similarly, water contact angle supported that biochar pores were collapsed or blocked during pyrolysis which should diminish the amounts of pores that could adsorb CO_2 .

2.3.5 Thermal Analysis

Mass loss and derivative mass loss thermographs of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are presented in Figures 2.5 and 2.6, respectively. Mass losses decreased in biochars compared to biomasses from 7.35-7.98, 63.87-72.39, and 8.89-20.85 wt. %

over approximately 25-100, 200-400, and 400-750°C to 2.66-3.29, 11.44-22.94, and 17.24-31.94 wt. % over 25-100, 200-400, and 400-750°C, respectively. Derivative mass losses also decreased in biochars compared to biomasses from 0.18-0.23, 0.41-0.72, and 1.02-1.15 wt. %/°C at close to 42, 302, and 357°C to 0.06-0.07 and 0.16-0.28 wt. %/°C at nearly 35 and 343°C, respectively. These transitions denoted that volatile matter was removed from biomasses during pyrolysis which caused biochars to have lower mass losses and derivative mass losses with further heating and higher thermal stability. Mass losses and derivative mass loss maxima or peaks in certain temperature ranges are usually associated with the removal or thermal decomposition of specific biomass constituents including moisture, cellulose, hemicellulose, and lignin. For instance, mass losses from and peaks at <120°C are connected to the removal of moisture, whereas mass losses from and peaks that appear as shoulders at 150-360°C correspond to the decomposition of hemicellulose [37]. Mass losses from and peaks at 360-425°C are linked to the decomposition of cellulose and lignin, while mass losses from and peaks at >500°C are related to the decomposition of lignin. Low derivative mass losses that occur at high temperatures over wide temperature ranges are also associated with the decomposition of lignin because lignin is thermoplastic [37][78]. Consequently, the mass losses from 25-100°C and peaks at about 39.02-45.11°C for biomasses and 33.88-37.08°C for biochars conveyed that moisture was removed from biomasses and biochars with higher mass losses occurring in biomasses since biomasses had been dried at 48°C prior to being pyrolyzed whereas biochars had been dried at 105°C after being washed with DI water and isopropanol. The mass losses from 200-400 and 400-750°C, shoulders at approximately 282.06-322.28°C for biomasses, peaks at close to 352.02-363.56°C for biomasses, and peaks at nearly 335.77-352.23°C for biochars indicated that cellulose, hemicellulose, and lignin were decomposed and removed from biomasses and that volatile compounds derived from cellulose, hemicellulose, and lignin remained in biochars with higher mass losses occurring in biomasses because only some of the cellulose, hemicellulose, and lignin present in biomasses was transformed and retained as volatile compounds in biochars following pyrolysis.

Furthermore, the mass loss from 200-400°C of loblolly pine biomass was lower than those of hybrid poplar and switchgrass biomasses since hybrid poplar and switchgrass biomasses had higher cellulose and hemicellulose contents than those of loblolly pine biomass and cellulose and hemicellulose had mostly decomposed by 400°C. Yet, the higher peak of switchgrass biochar between 335.77-352.23°C compared to that of loblolly pine biochar in this temperature range signaled that more volatile compounds derived from biomass constituents remained in switchgrass biochar than loblolly pine biochar. The lack of a peak in this temperature range for hybrid poplar biochar signified that few volatile compounds derived from biomass constituents were retained in hybrid poplar biochar. Moreover, the mass loss from 400-750°C of switchgrass biomass was lower than those of hybrid poplar and loblolly pine biomasses because hybrid poplar and loblolly pine biomasses had higher lignin contents (23.71 and 31.11 wt. %, db) than that of switchgrass biomass (21.03 wt. %, db), respectively, and lignin continued to decompose up to 750°C [37]. The mass loss from 400-750°C of loblolly pine biochar was also higher than that of hybrid poplar biochar because hybrid poplar biomass had a lower lignin content (23.71 wt. %, db) than that of loblolly pine biomass (31.11 wt. %, db) and more volatile compounds derived from lignin remained in loblolly pine biochar and continued to decompose up to 750°C. Based on these differences in mass loss among biochars, hybrid poplar biochar had a higher thermal stability than those of loblolly pine and switchgrass biochars. Therefore, thermal analysis demonstrated that biochars became more thermally stable after pyrolysis but still contained some volatile matter that may have blocked biochar pores because of incomplete devolatilization which supported previous findings.

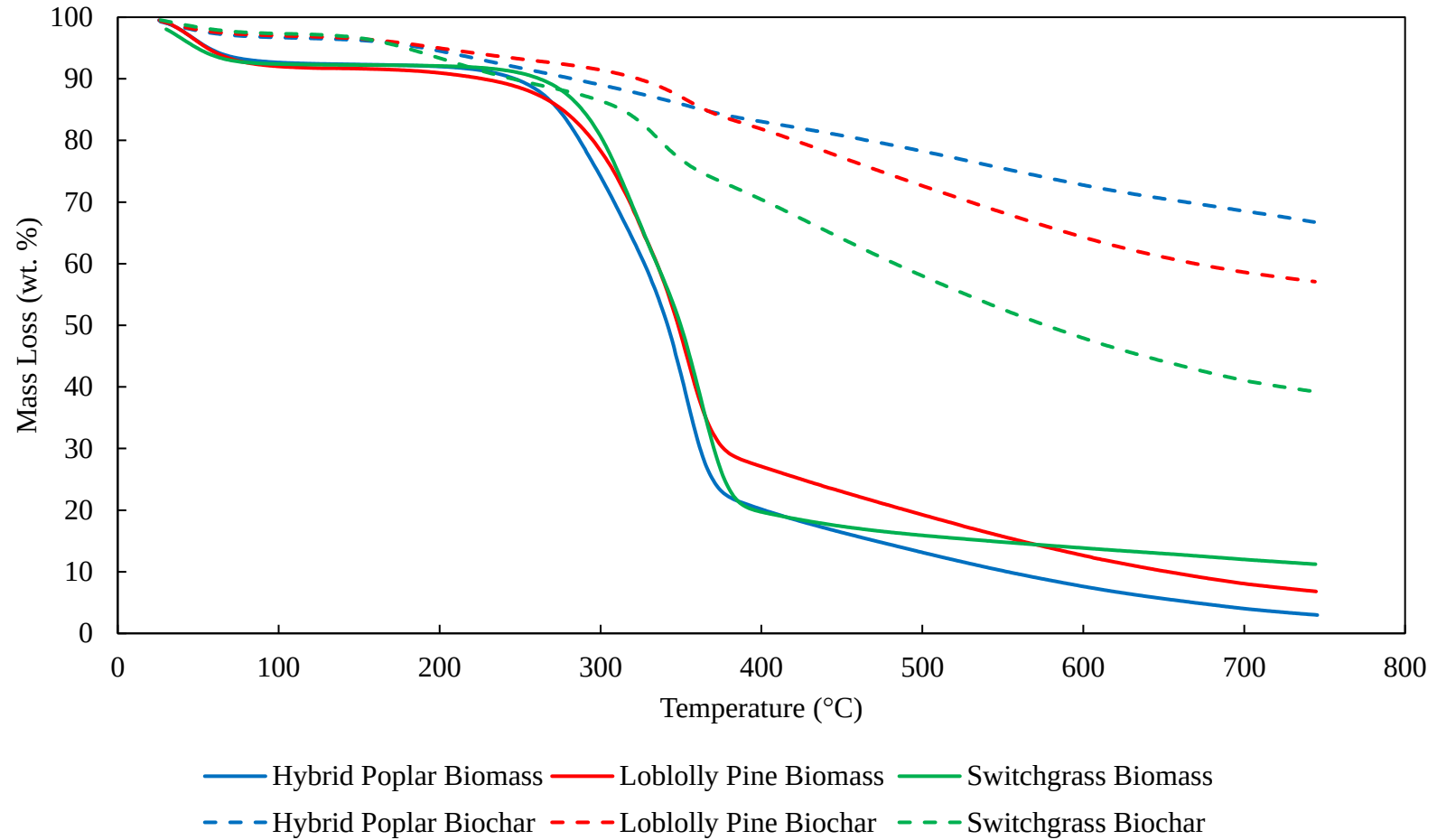


Figure 2.5. Mass loss thermographs of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

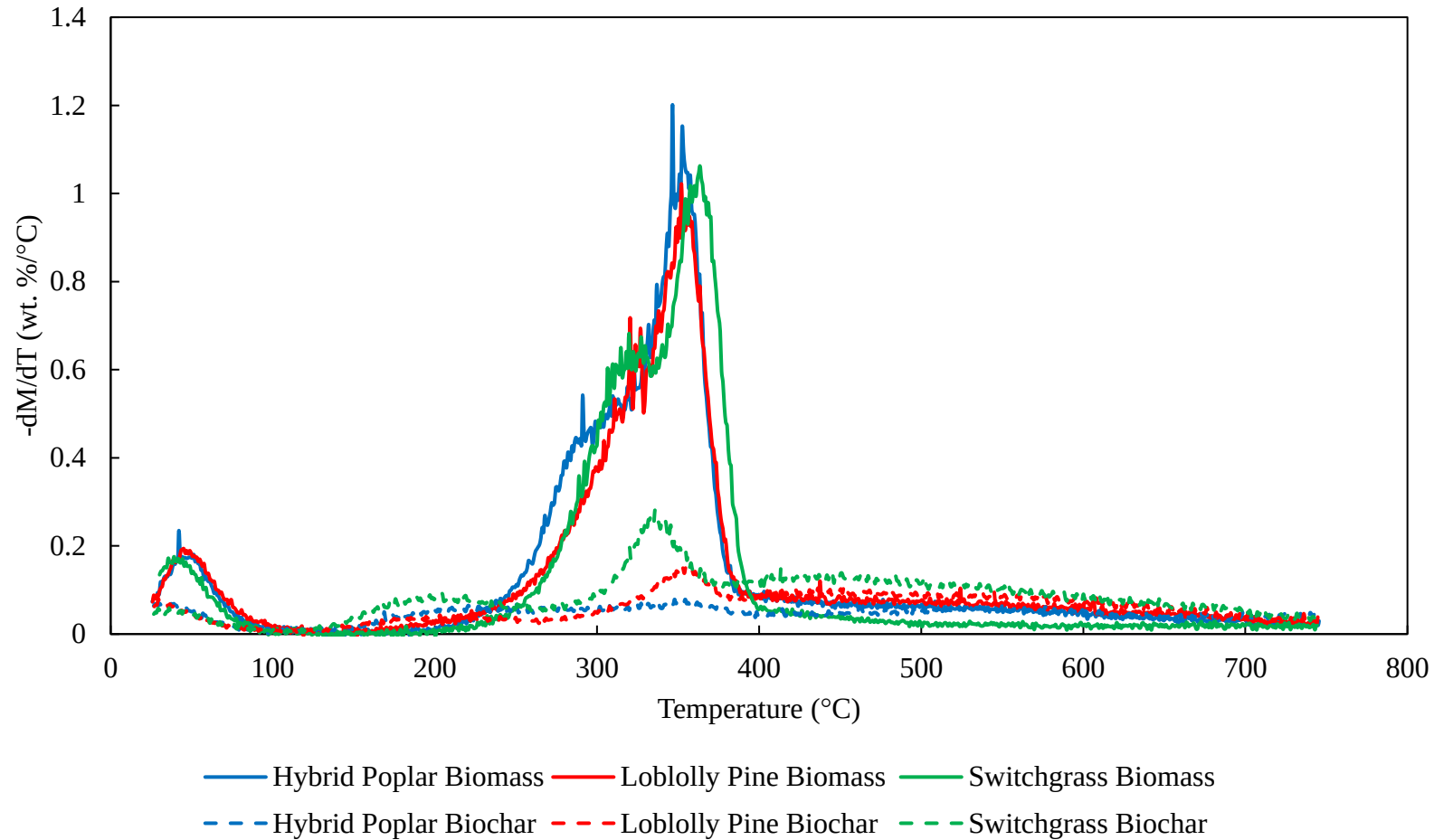


Figure 2.6. Derivative mass loss thermographs of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

2.3.6 Fourier-Transform Infrared Spectroscopy

FTIR spectra of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are depicted in Figures 2.7 and 2.8. R-OH group stretching peak absorbances from about 3349-3326 cm^{-1} decreased in biochars compared to biomasses except for switchgrass biochar which conveyed that carboxylic acids, phenols, or H_2O were removed from hybrid poplar and loblolly pine biochars. Aliphatic and aromatic methyl (R-CH_3) and aliphatic methylene ($\text{R-C(-H}_2\text{)-R'}$) group stretching peak absorbances from approximately 2925-2850 cm^{-1} decreased in biochars relative to biomasses except for switchgrass biochar which demonstrated that aliphatic compounds and unconjugated rings associated with cellulose and lignin were removed from hybrid poplar and loblolly pine biochars [34][35][60][63][65][78][79]. Carbon-oxygen double (C=O) bond stretching peak absorbances shifted from approximately 1733-1729 cm^{-1} in biomasses to 1697-1694 cm^{-1} in biochars because of the biomasses being pyrolyzed. C=O bond stretching peak absorbances from about 1733-1694 cm^{-1} remained relatively constant between biomasses and biochars which denoted that carboxylic acids, esters, ketones, or quinones were still present in biochars. Carbon-carbon double (C=C) bond stretching peak absorbances from close to 1597-1501 cm^{-1} increased in biochars compared to biomasses which indicated that conjugated or aromatic rings and aromatic ring clusters were formed in biochars [34][35][60][65][79]. Carbon-hydrogen (C-H) bond bending peak absorbances from roughly 1461-1417 and 1371-1365 cm^{-1} decreased in biochars relative to biomasses which revealed that cellulose and lignin and hemicellulose were removed from biochars, respectively.

C-H bond stretching, carbon-oxygen single (C-O) bond stretching, R-O-R' group stretching, R-OH group stretching, and C-O bond stretching peak absorbances from about 1315-1314, 1238-1222, 1157-1154, 1107-1101, and 1055-1024 cm^{-1} , respectively, also decreased in biochars compared to biomasses which reinforced that cellulose, hemicellulose, and lignin were removed from biochars. C-H bond wagging peak absorbances appeared from approximately 866-744 cm^{-1} which signaled that aromatic rings were produced in biochars [34][35][60]. These alterations signified that biochars still contained some volatile matter which caused biochars to still have some characteristic peaks of cellulose, hemicellulose, and lignin. However, these changes also conveyed that aromatic rings were created through cyclization and aromatization in biochars which resulted in biochars having characteristic peaks of aromatic C=C and C-H bonds. Among biochars, hybrid poplar and loblolly pine biochars had the fewest characteristic peaks of cellulose, hemicellulose, and lignin which illustrated that hybrid poplar and loblolly pine biochars retained the lowest amounts of volatile compounds derived from cellulose, hemicellulose, and lignin after pyrolysis compared to switchgrass biochar. Based on these findings, peaks associated with aliphatic and labile structures like biomass constituents encompassing cellulose, hemicellulose, and lignin in biomass spectra either decreased in absorbance or disappeared entirely from biochar spectra whereas peaks connected to aromatic and stable structures increased in absorbance or appeared in biochar spectra. Accordingly, FTIR spectroscopy indicated that biomasses were deoxygenated and aromatized through pyrolysis but that some volatile matter still resided in biochars which supported the results previously discussed.

2.3.7 X-Ray Diffraction

XRD diffractograms of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are displayed in Figures 2.9 and 2.10. Biomass constituents including cellulose, hemicellulose, and lignin have different structures with cellulose being ordered or crystalline and hemicellulose and lignin being disordered or amorphous. Concerning biomass diffractograms,

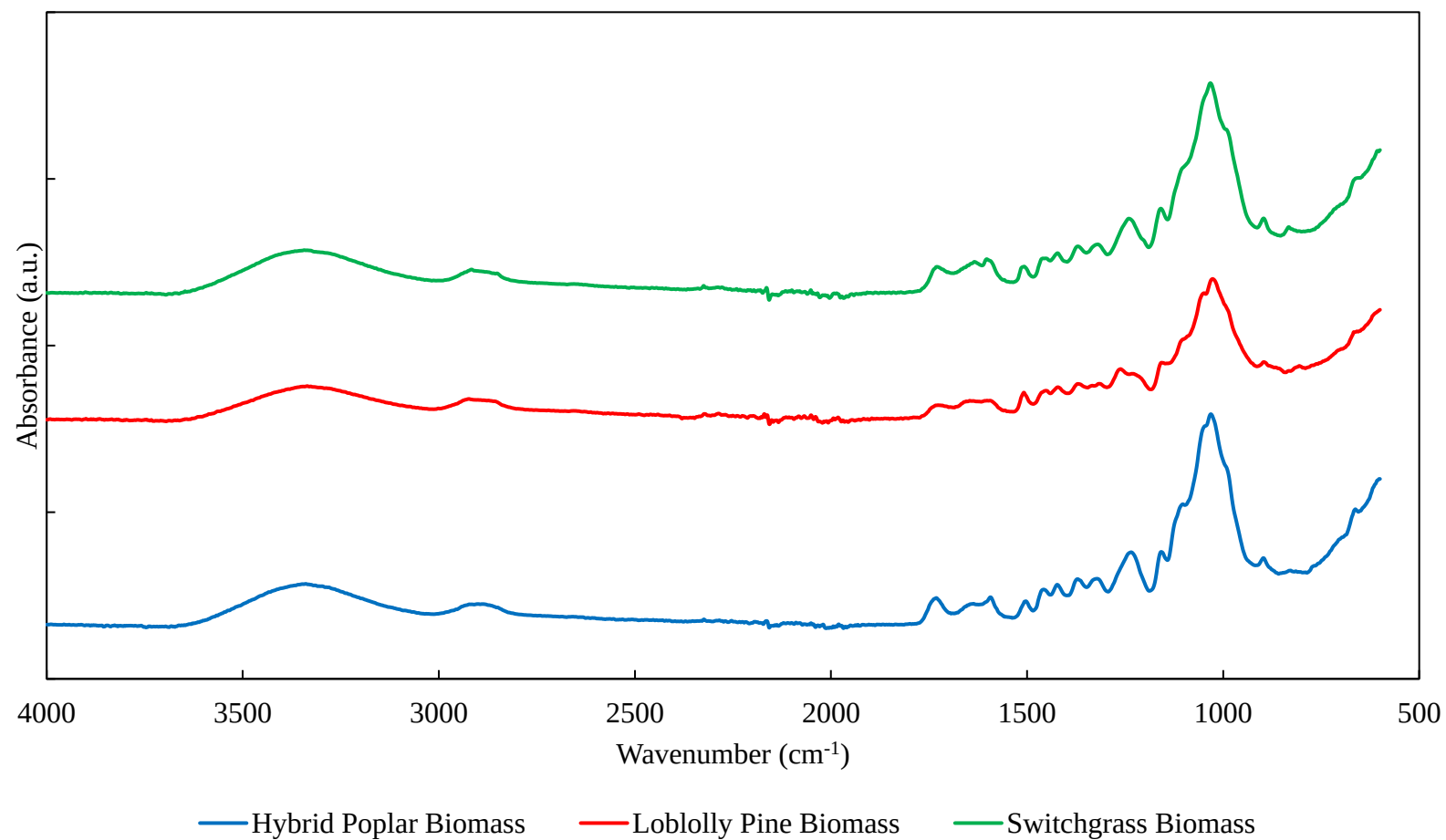


Figure 2.7. FTIR spectra of hybrid poplar, loblolly pine, and switchgrass biomasses.

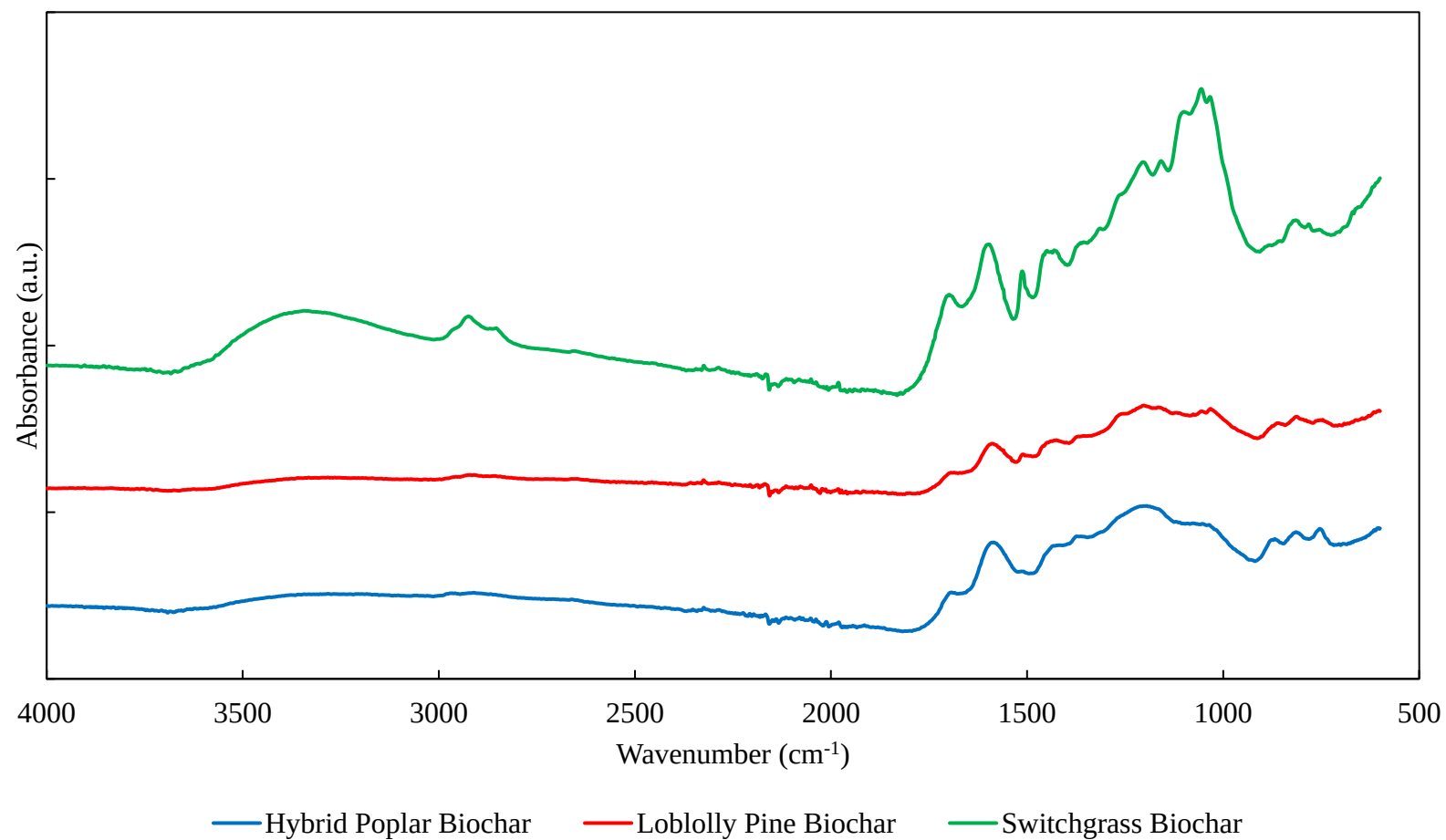


Figure 2.8. FTIR spectra of hybrid poplar, loblolly pine, and switchgrass biochars.

peaks at 14, 16, 21, 22, and 35° 2 θ were assigned to the cellulose crystalline phase and peaks at 17° 2 θ were assigned to the cellulose amorphous phase. Reflections at 14, 16, 21, 22 and 35° 2 θ were indexed with the (1 $\bar{1}$ 0), (110), (102), (200), and (004) crystallographic planes of cellulose I, respectively [38][39][40][80]. The cellulose crystallographic planes and amorphous cellulose peak faintly differed between biomasses with the (1 $\bar{1}$ 0), (110), (102), (200), and (004) planes ranging from 14.46-15.01, 16.09-16.43, 20.93-21.29, 22.17-22.42, and 34.70-35.11° 2 θ and the amorphous cellulose peak varying from 16.51-17.65° 2 θ , respectively. Cellulose crystalline and amorphous peak broadenings and intensities slightly differed between biomasses as well which denoted that biomasses had vaguely disparate cellulose structures. Cellulose crystallinity index demonstrates the amount of crystalline cellulose contained in biomass which denotes the rigidity of the cellulose structure in biomass with an increased cellulose crystallinity index indicating an increased cellulose structure rigidity. Cellulose crystallite size indicates the size of cellulose crystallites or crystalline cellulose regions contained in biomass with an increased cellulose crystallite size signaling an increased cellulose crystallinity index since the presence of larger cellulose crystallites signifies the presence of smaller amorphous cellulose regions [81]. Cellulose crystallinity index and crystallite size of hybrid poplar, loblolly pine, and switchgrass biomasses are illustrated in Table 2.7. Cellulose crystallinity index ranged from 57.30-59.68% but was not different between biomasses ($p>0.05$), while cellulose crystallite size varied from 30-34 Å with switchgrass biomass having the highest cellulose crystallite size and loblolly pine biomass having the lowest cellulose crystallite size ($p<0.05$). These findings signified that switchgrass biomass contained larger cellulose crystallites than hybrid poplar and loblolly pine biomasses. Nevertheless, the cellulose crystallite sizes of the biomasses agreed with the cellulose crystallite sizes of various biomasses of close to 30 Å reported in other studies [82][83][84].

Cellulose crystalline and amorphous peaks vanished from biochar diffractograms apart from some loblolly pine and switchgrass biochar diffractograms which still had cellulose peaks albeit at higher peak broadenings and lower peak intensities and were not portrayed in Figure 2.10. Regarding biochar diffractograms, peaks at 18, 23, 43, and 79° 2 θ were assigned to the graphitic C crystalline phase. Reflections at 18, 23, 43, and 79° 2 θ were indexed with the γ band and (002), (100), and (110) crystallographic planes of graphite, respectively [50][51][52][53][54][80][85]. The graphite crystallographic planes faintly differed between biochars with the γ band and (002), (100), and (110) planes ranging from 17.01-18.84, 22.55-23.58, 42.29-43.63, and 78.12-80.15° 2 θ , respectively. Graphitic C crystalline peak broadenings and intensities somewhat varied between biochars which demonstrated that biochars had slightly disparate graphitic C structures. Aliphatic interchain spacing, aromatic interlayer spacing, aromatic stacking diameter, aromatic sheet diameter, number of stacked aromatic sheets, and aromaticity of hybrid poplar, loblolly pine, and switchgrass biochars are shown in Table 2.8. Aliphatic interchain spacing or the distance between aliphatic side chains attached to aromatic ring clusters was 5 Å which implied that branching in the form of aliphatic side chains connected to aromatic sheets in biochars was minimal and likely only involved R-CH₃ and ethyl (R-C(H₂)-CH₃) groups [50][51]. This finding was supported by the volatile matter contents and H/C and O/C atomic ratios of biochars which indicated that biochars contained lower amounts of aliphatic C and heteroatoms than biomasses. Aromatic interlayer spacing or the distance between aromatic C sheets in graphitic C crystallites was 4 Å which revealed that biochars contained condensed and ordered aromatic sheet clusters since biochar C structures were less saturated and contained fewer heteroatoms than those of biomasses. This result was supported by the knowledge that the saturation of C structures and presence of heteroatoms in C structures cause aromatic sheets in aromatic sheet clusters to bend

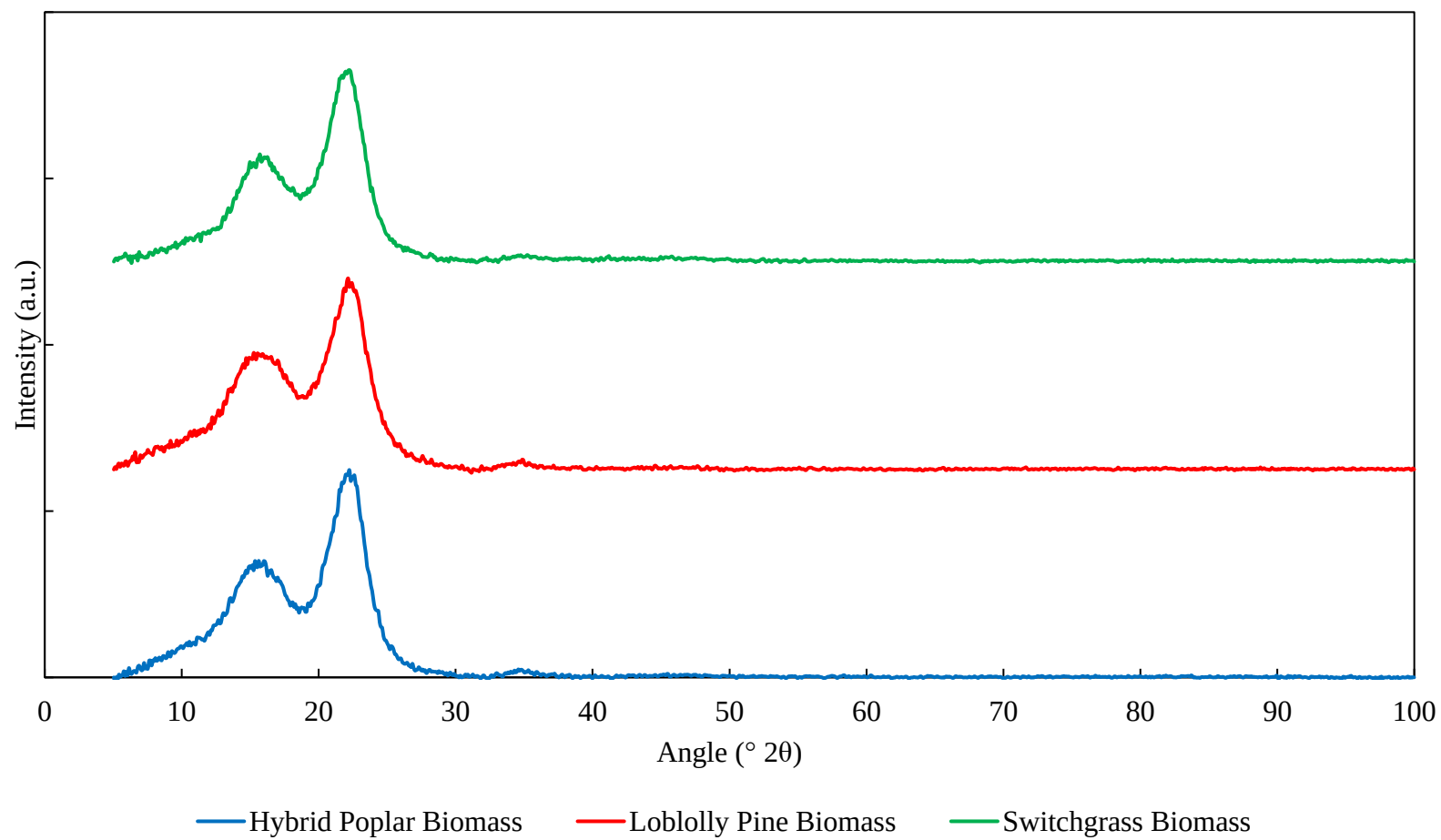


Figure 2.9. XRD diffractograms of hybrid poplar, loblolly pine, and switchgrass biomasses.

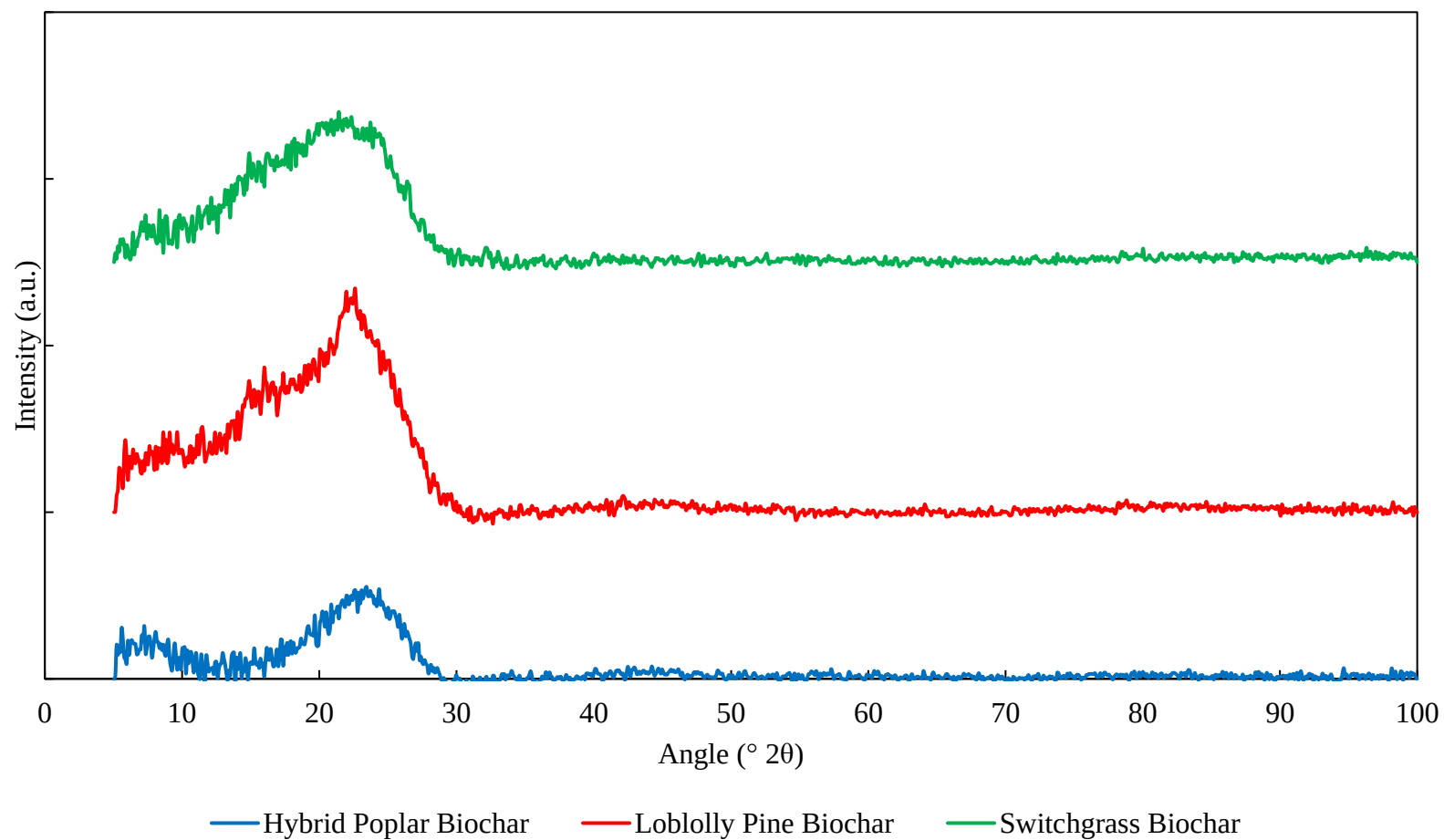


Figure 2.10. XRD diffractograms of hybrid poplar, loblolly pine, and switchgrass biochars.

Table 2.7. Cellulose crystallinity index and crystallite size of hybrid poplar, loblolly pine, and switchgrass biomasses.

Biomass		
	Cellulose Crystallinity Index (%)	Cellulose Crystallite Size (Å)
Hybrid Poplar	59.68 (4.21)	32 (1)
Loblolly Pine	57.30 (3.61)	30 (0)
Switchgrass	57.91 (1.20)	34 (2)

Values in table are averages with standard deviations in parentheses.

Table 2.8. Aliphatic interchain spacing, aromatic interlayer spacing, aromatic stacking diameter, aromatic sheet diameter, number of stacked aromatic sheets, and aromaticity of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar			
	Aliphatic Interchain Spacing (Å)	Aromatic Interlayer Spacing (Å)	Aromatic Stacking Diameter (Å)
Hybrid Poplar	5 (0)	4 (0)	14 (1)
Loblolly Pine	5 (0)	4 (0)	14 (0)
Switchgrass	5 (0)	4 (0)	13 (1)

Biochar			
	Aromatic Sheet Diameter (Å)	Number of Stacked Aromatic Sheets	Aromaticity (%)
Hybrid Poplar	18 (2)	4 (0)	63.51 (0.40)
Loblolly Pine	16 (2)	4 (0)	74.18 (3.63)
Switchgrass	16 (3)	3 (0)	71.64 (3.70)

Values in table are averages with standard deviations in parentheses.

or bulge which prevents aromatic sheets from being closely stacked [50][51][54].

Aromatic stacking diameter or the distance of aromatic sheet clusters or the height of graphitic C crystallites ranged from 13-14 Å which signaled that aromatic sheets were stacked together in aromatic sheet clusters creating tall graphitic C crystallites in biochars. Aromatic sheet diameter or the distance of aromatic sheets or the width of graphitic C crystallites varied from 16-18 Å which signified that aromatic sheets contained in aromatic sheet clusters were long and formed wide graphitic C crystallites in biochars [50][51][54][85][86][87]. Number of stacked aromatic sheets or the number of ordered aromatic sheets in an aromatic sheet cluster or graphitic C crystallite differed from 3-4 which exhibited that biochars contained multiple aromatic sheets stacked together in graphitic C crystallites since aromatic sheets in the tall graphitic C crystallites in biochars were organized close together. This finding expressed that biochar C structures were somewhat ordered because of the formation of these graphitic C crystallites [51][52]. Aromaticity or the fraction of ordered or aromatic C atoms in graphitic C crystallites fluctuated from 63.51-74.18% with loblolly pine biochar having the highest aromaticity and hybrid poplar biochar having the lowest aromaticity ($p < 0.05$). Such discrepancies implied that loblolly pine biochar contained more aromatic C atoms in graphitic C crystallites than those contained by hybrid poplar and switchgrass biochars [50][51][53]. However, this finding contrasted with the other structural results obtained for biochars since biochar C structures did not display any other differences. This contradiction was attributed to the difficulty associated with deconvoluting the γ band and (002) plane. Based on these findings, peaks associated with the cellulose crystalline and amorphous phases in biomass diffractograms either widened and decreased in intensity or disappeared entirely from biochar diffractograms, whereas peaks connected to the graphitic C crystalline phase which were missing in biomass diffractograms appeared in biochar diffractograms. As a result, XRD revealed that biomasses became disordered as crystalline C structures in biomasses were thermally decomposed during pyrolysis, while biochars were largely amorphous but contained some graphitic C structures. Such crystallites should provide pores in biochars that could adsorb CO₂ because CO₂ can diffuse through the aromatic interlayer spacings of these crystallites.

2.3.8 Textural Analysis

Textural analysis of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars is illustrated in Table 2.9. Specific surface area decreased ($p < 0.05$) in hybrid poplar and switchgrass biochars compared to their biomasses from 2.08 and 1.21 to 1.38 and 0.95 m²/g, respectively, whereas total pore volume decreased ($p < 0.05$) in hybrid poplar biochar relative to its biomass from 6.94 to 5.00 mm³/g. These changes revealed that the porosity of hybrid poplar biomass was reduced and those of loblolly pine and switchgrass biomasses did not change ($p > 0.05$) despite large amounts of volatile matter being evolved from biomasses through pyrolysis which caused biochars to have low porosities. Other studies have related the lack of extensive pore growth and production during pyrolysis to softening and melting of biomass constituents and entrapment of bio-oil condensates in biochars which can effectively block biochar pores [65][66][67]. These findings supported the results previously noted. Pore width distributions of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars are shown in Figure 2.11. Pore width increased in biochars compared to biomasses with most of the pore volumes of biomasses being associated with pores with widths of about 28 Å and the pore volumes of biochars being split between pores with widths fluctuating from approximately 18-32 and 48-68 Å. These alterations exhibited that mesopores were expanded and micropores were formed in biochars because volatile matter was evolved from biomasses which caused existing pores to grow and new pores to be generated.

Table 2.9. Textural analysis of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

Biomass		
	Textural Analysis	
	Specific Surface Area (m ² /g)	Total Pore Volume (mm ³ /g)
Hybrid Poplar	2.08 (0.53)	6.94 (1.97)
Loblolly Pine	1.11 (0.15)	3.88 (1.01)
Switchgrass	1.21 (0.20)	5.37 (1.39)
Biochar		
Hybrid Poplar	1.38 (0.46)	5.00 (1.35)
Loblolly Pine	1.06 (0.28)	3.38 (1.22)
Switchgrass	0.95 (0.22)	4.54 (0.84)

Values in table are averages with standard deviations in parentheses.

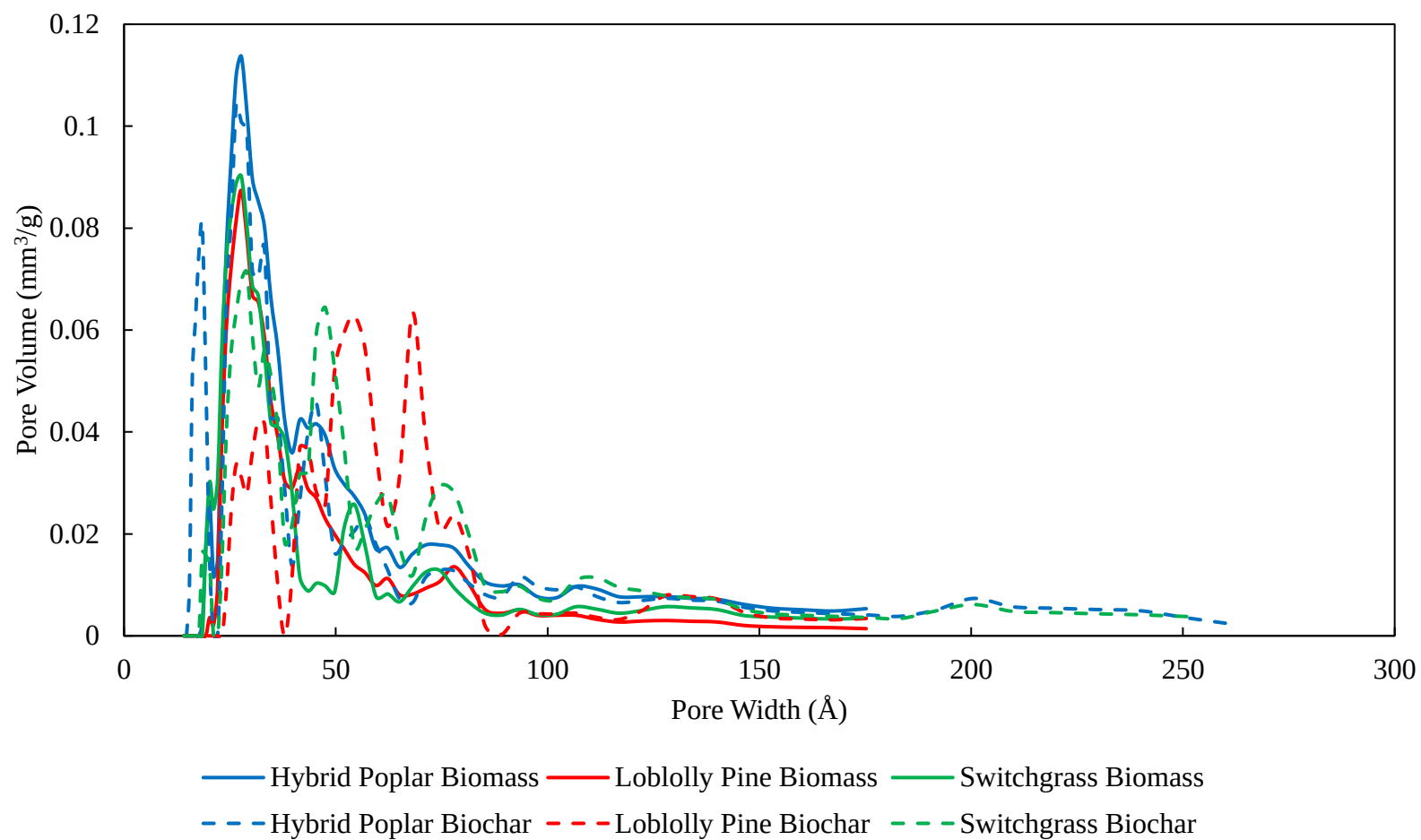


Figure 2.11. Pore width distributions of hybrid poplar, loblolly pine, and switchgrass biomasses and biochars.

However, pore size distribution differed between biochars with hybrid poplar biochar maintaining smaller mesopores with widths close to 28 Å and forming micropores with widths of nearly 18 Å, whereas loblolly pine and switchgrass biochars retained some smaller mesopores with widths of roughly 28 Å and developed larger mesopores with widths ranging from about 48-68 Å. As such, textural analysis indicated that biochar pores were collapsed or blocked during pyrolysis which should limit CO₂ adsorption onto biochars but that existing biomass pores were enlarged and new pores were formed in biochars.

2.3.9 CO₂ Adsorption

CO₂ breakthrough curves of hybrid poplar, loblolly pine, and switchgrass biochars are depicted in Figure 2.12. Breakthrough curves are used to illustrate the saturation of an adsorbent bed in an adsorption column from the column inlet to outlet as an adsorbate such as CO₂ is gradually adsorbed over time until the bed is completely saturated. Breakthrough denotes the point during adsorption when the portion of the bed closest to the column inlet becomes saturated which causes the region of the bed where mass transfer of CO₂ into the bed is occurring to move down the bed and the concentration of CO₂ at the column outlet to increase as the bed nears total saturation [44]. The breakthroughs of biochars as shown by the straight line in Figure 2.12 demonstrated that biochars had very fast breakthroughs with biochars beginning to be saturated by around 15 s. This finding implied that the inlet sections of biochar beds took short times to become saturated which was attributed to biochars having low specific surface areas and total pore volumes. Consequently, the CO₂ breakthrough curves demonstrated that biochars adsorbed low amounts of CO₂. CO₂ adsorption, desorption, and working capacities and regenerability of hybrid poplar, loblolly pine, and switchgrass biochars are represented in Table 2.10. CO₂ adsorption, desorption, and working capacities and regenerability ranged from 0.17-0.18 mmol/g, 0.12-0.14 mmol/g, 0.04-0.05 mmol/g, and 71.45-77.55%, respectively. These results revealed that biochars adsorbed low amounts of CO₂ which supported that biochars had low specific surface areas, total pore volumes, and amounts of basic functional groups since these biochar physicochemical characteristics influence CO₂ adsorption mechanisms. Such findings also signaled that some of the CO₂ that was adsorbed onto biochars was not removed through desorption which indicated that either mass transfer limitations or the formation of strong intermolecular interactions between biochar surfaces and CO₂ molecules prevented complete desorption. Therefore, CO₂ adsorption, desorption, and working capacities and regenerability indicated that biochars adsorbed low amounts of CO₂ and that some adsorbed CO₂ was retained on biochars following desorption.

2.4 Conclusions

The effect of lignocellulosic biomass selection on the physicochemical characteristics of biochar that are known to control CO₂ adsorption was explored using hybrid poplar, loblolly pine, and switchgrass pyrolyzed through intermediate pyrolysis at 500°C. Most physicochemical characteristics of hybrid poplar, loblolly pine, and switchgrass biochars produced under these conditions differed ($p < 0.05$) based on biomass type. However, such differences did not impact CO₂ adsorption onto biochars since all biochars adsorbed low amounts of CO₂ because of their low specific surface areas, total pore volumes, and alkalinities which are characteristics that are known to govern CO₂ adsorption. Consequently, loblolly pine may be the better lignocellulosic biomass to create biochar from for CO₂ adsorption compared to hybrid poplar and switchgrass since loblolly pine is more widely available than these other lignocellulosic biomasses. Future research should increase the pyrolysis temperature and heating rate used to form biochars since

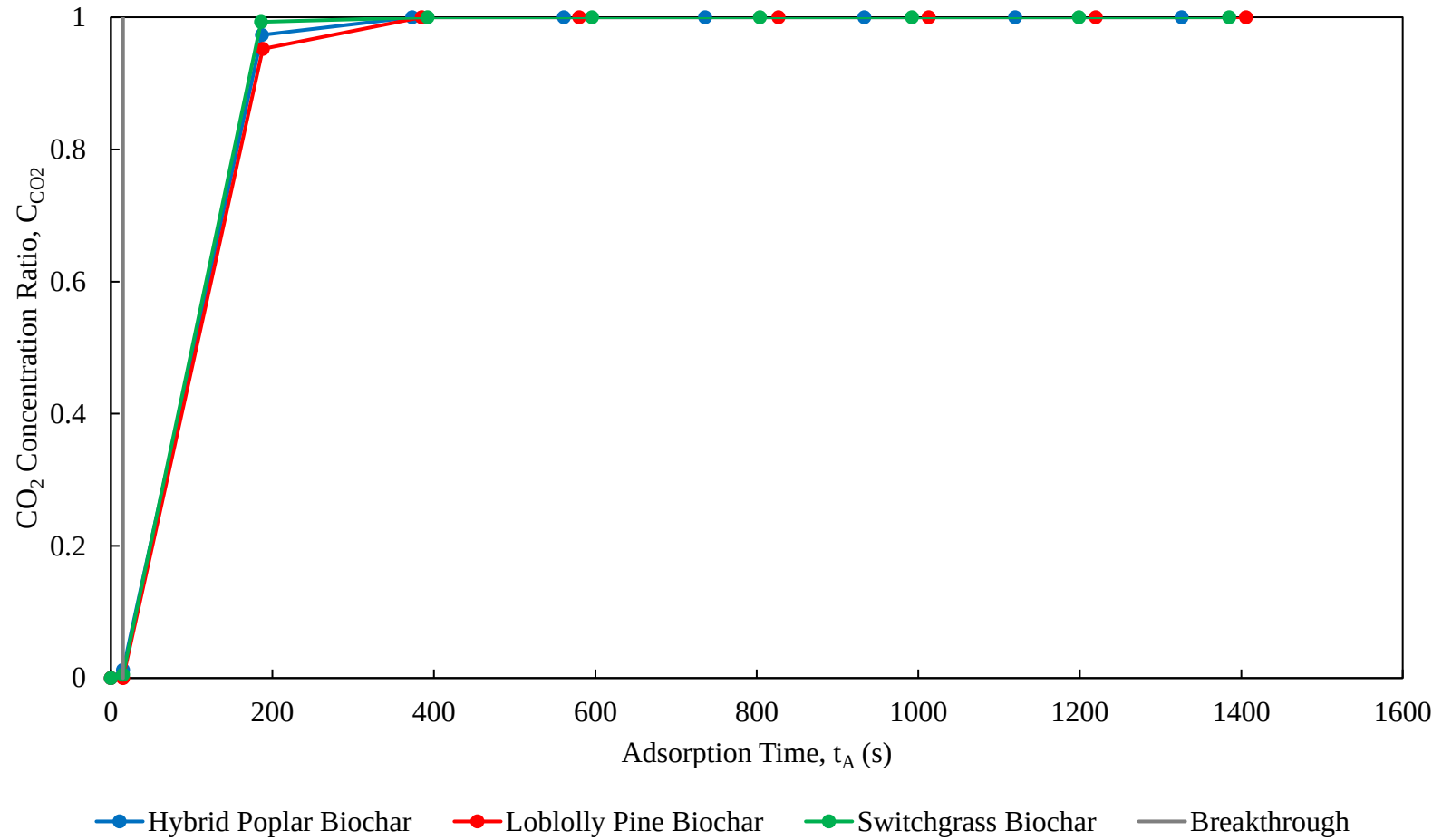


Figure 2.12. CO₂ breakthrough curves of hybrid poplar, loblolly pine, and switchgrass biochars.

Table 2.10. CO₂ adsorption, desorption, and working capacities and regenerability of hybrid poplar, loblolly pine, and switchgrass biochars.

	Biochar			
	CO ₂ Adsorption Capacity (mmol/g)	CO ₂ Desorption Capacity (mmol/g)	CO ₂ Working Capacity (mmol/g)	Regenerability (%)
Hybrid Poplar	0.17	0.14	0.04	77.55
Loblolly Pine	0.18	0.14	0.05	73.51
Switchgrass	0.17	0.12	0.05	71.45

these changes are anticipated to improve the CO₂ adsorption performance of biochars. Such conditions are expected to overcome the possible heat and mass transfer limitations that caused pore blockages to form during pyrolysis.

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Appendices

Appendix A. Biomass Characterization

Table 2.11. Chemical analyses of hybrid poplar, loblolly pine, and switchgrass biomasses.

Biomass									
	Sample	Subsample	Chemical Analysis (wt. %, db)						
			Cellulose	Hemicellulose	Lignin	Extractives	Ash	Acetyl	Mass Closure
Hybrid Poplar	1	1	43.69	19.23	23.92	7.23	0.48	5.28	99.83
		2	43.53	18.99	23.66	7.16	0.54	4.94	98.82
		3	43.23	18.91	23.83	7.31	0.52	5.57	99.36
	2	1	43.42	18.79	23.81	6.10	0.46	5.42	97.99
		2	43.07	18.71	23.68	7.16	0.48	5.84	98.94
		3	41.89	18.19	23.92	6.30	0.42	5.40	96.13
	3	1	42.91	18.02	23.24	6.14	0.46	5.73	96.49
		2	42.22	17.67	23.44	6.39	0.44	5.88	96.03
		3	40.43	16.91	23.86	9.32	0.43	6.63	97.59
Loblolly Pine	1	1	37.58	18.94	31.15	5.84	0.18	2.49	96.19
		2	36.53	18.14	31.20	5.70	0.17	2.14	93.89
		3	36.97	18.41	30.83	6.17	0.19	2.14	94.72
	2	1	37.33	18.69	31.42	5.51	0.19	2.45	95.59
		2	37.16	18.39	30.94	5.17	0.23	2.47	94.36
		3	36.07	17.78	30.70	5.48	0.21	2.25	92.50
	3	1	36.62	18.24	31.32	4.84	0.15	2.15	93.32
		2	37.29	18.46	31.50	4.52	0.21	2.21	94.19
		3	36.41	18.00	30.96	4.64	0.20	2.20	92.41
Switchgrass	1	1	34.55	24.92	21.52	5.59	1.21	5.38	93.17
		2	33.74	24.62	21.76	5.40	1.17	5.60	92.29
		3	33.55	24.54	21.54	5.50	1.19	5.58	91.89
		4	36.32	28.86	20.89	5.50	NM	3.72	95.29
		5	38.51	30.69	20.84	5.50	NM	4.29	99.82
		6	37.79	30.44	21.45	5.98	NM	3.99	99.66

(Table 2.11. Continued)

Biomass									
	Sample	Subsample	Chemical Analysis (wt. %, db)						
			Cellulose	Hemicellulose	Lignin	Extractives	Ash	Acetyl	Mass Closure
Switchgrass	2	1	33.12	23.62	21.45	5.16	1.23	5.13	89.71
		2	32.63	23.85	21.63	4.57	1.26	5.33	89.27
		3	32.16	23.43	21.43	5.79	1.22	5.03	89.07
		4	35.11	28.14	20.83	5.17	NM	3.62	92.87
		5	37.58	29.80	21.15	5.17	NM	3.83	97.53
		6	38.69	31.01	21.43	5.79	NM	3.95	100.87
	3	1	32.16	23.18	21.71	4.57	1.38	5.33	88.33
		2	33.17	23.96	21.95	4.81	1.30	5.22	90.42
		3	33.26	24.14	21.64	6.06	1.25	5.17	91.54
		4	36.47	29.39	20.86	5.15	NM	3.57	95.44
		5	36.87	29.25	20.92	5.15	NM	3.78	95.97
		6	38.67	31.40	20.89	4.41	NM	3.89	99.27

NM stands for not measured.

Table 2.12. Proximate analyses of hybrid poplar, loblolly pine, and switchgrass biomasses.

Biomass						
	Sample	Subsample	Proximate Analysis			
			Moisture (wt. %, wb)	Ash (wt. %, db)	Volatile Matter (wt. %, db)	Fixed Carbon (wt. %, db)
Hybrid Poplar	1	1	6.55	0.48	81.97	11.00
		2	6.50	0.54	82.11	10.85
		3	6.51	0.52	81.66	11.31
	2	1	6.33	0.46	82.72	10.49
		2	6.63	0.48	81.45	11.45
		3	6.51	0.42	82.21	10.87
	3	1	6.71	0.46	81.94	10.89
		2	6.66	0.44	82.20	10.70
		3	6.68	0.43	81.91	10.98
Loblolly Pine	1	1	6.60	0.18	79.46	13.76
		2	6.29	0.17	79.75	13.78
		3	6.37	0.19	79.72	13.72
	2	1	6.29	0.19	79.98	13.55
		2	6.10	0.23	79.74	13.94
		3	6.19	0.21	79.41	14.19
	3	1	6.08	0.15	79.64	14.13
		2	6.27	0.21	79.38	14.14
		3	6.28	0.20	79.75	13.77
Switchgrass	1	1	7.58	1.21	80.22	10.99
		2	7.49	1.17	80.18	11.15
		3	7.50	1.19	80.59	10.73
	2	1	7.70	1.23	79.46	11.61
		2	7.54	1.26	80.21	10.98
		3	7.59	1.22	79.65	11.54

(Table 2.12. Continued)

Biomass						
Sample		Subsample	Proximate Analysis			
			Moisture (wt. %, wb)	Ash (wt. %, db)	Volatile Matter (wt. %, db)	Fixed Carbon (wt. %, db)
Switchgrass	3	1	8.17	1.38	79.25	11.20
		2	8.08	1.30	78.72	11.90
		3	8.19	1.25	80.14	10.42

Table 2.13. Ultimate analyses of hybrid poplar, loblolly pine, and switchgrass biomasses.

		Biomass					
	Sample	Subsample	Ultimate Analysis (wt. %, dafb)				
			C	H	N	S	O
Hybrid Poplar	1	1	51.68	7.02	0.09	0.05	41.16
		2	51.63	7.00	0.10	0.13	41.14
		3	52.05	7.05	0.13	0.21	40.56
	2	1	51.78	7.10	0.13	0.15	40.84
		2	51.94	7.12	0.12	0.17	40.65
		3	51.31	7.10	0.05	0.07	41.47
	3	1	51.86	6.95	0.09	0.17	40.93
		2	51.74	7.02	0.08	0.09	41.07
		3	51.88	7.16	0.06	0.10	40.80
Loblolly Pine	1	1	60.09	8.29	0.10	0.08	31.45
		2	53.02	7.16	0.05	0.11	39.67
		3	53.42	7.07	0.12	0.13	39.27
	2	1	53.17	7.23	0.09	0.18	39.33
		2	53.03	7.15	0.07	0.09	39.66
		3	53.00	7.05	0.14	0.19	39.61
	3	1	53.16	7.40	0.10	0.07	39.27
		2	53.12	7.19	0.04	0.09	39.55
		3	53.49	7.13	0.17	0.09	39.13
Switchgrass	1	1	51.77	7.24	0.19	0.11	40.70
		2	51.68	7.19	0.21	0.19	40.73
		3	51.80	6.85	0.26	0.26	40.83
	2	1	51.81	7.07	0.20	0.20	40.73
		2	51.58	6.99	0.19	0.13	41.11
		3	51.54	6.99	0.22	0.20	41.05

(Table 2.13. Continued)

Biomass							
Sample	Subsample	Ultimate Analysis (wt. %, dafb)					
		C	H	N	S	O	
Switchgrass	3	1	52.08	7.14	0.19	0.13	40.47
		2	51.85	7.10	0.23	0.18	40.64
		3	52.11	7.08	0.17	0.10	40.55

Table 2.14. Atomic ratios and HHVs of hybrid poplar, loblolly pine, and switchgrass biomasses.

Biomass						
	Sample	Subsample	Atomic Ratios			HHV (kJ/g, db)
			H/C	O/C	(O+N+S)/C	
Hybrid Poplar	1	1	1.61	0.60	0.60	20.95
		2	1.61	0.60	0.60	20.91
		3	1.61	0.58	0.59	20.89
	2	1	1.63	0.59	0.60	20.93
		2	1.63	0.59	0.59	20.98
		3	1.64	0.61	0.61	20.94
	3	1	1.59	0.59	0.60	21.04
		2	1.61	0.60	0.60	21.00
		3	1.64	0.59	0.59	20.95
Loblolly Pine	1	1	1.64	0.39	0.39	21.94
		2	1.61	0.56	0.56	21.83
		3	1.57	0.55	0.55	21.86
	2	1	1.62	0.56	0.56	21.83
		2	1.60	0.56	0.56	21.78
		3	1.58	0.56	0.56	21.79
	3	1	1.67	0.55	0.56	21.71
		2	1.61	0.56	0.56	21.73
		3	1.58	0.55	0.55	21.72
Switchgrass	1	1	1.66	0.59	0.59	20.92
		2	1.65	0.59	0.60	20.94
		3	1.57	0.59	0.60	20.91
	2	1	1.62	0.59	0.59	20.92
		2	1.61	0.60	0.60	20.88
		3	1.61	0.60	0.60	20.91

(Table 2.14. Continued)

Biomass						
Sample		Subsample	Atomic Ratios			HHV (kJ/g, db)
			H/C	O/C	(O+N+S)/C	
Switchgrass	3	1	1.63	0.58	0.59	21.05
		2	1.63	0.59	0.59	21.04
		3	1.62	0.58	0.59	21.08

Table 2.15. Bulk and particle densities and bulk porosities of hybrid poplar, loblolly pine, and switchgrass biomasses.

Biomass					
	Sample	Subsample	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Bulk Porosity (vol. %)
Hybrid Poplar	1	1	0.13	1.60	91.92
		2	0.14	1.71	92.06
		3	0.13	2.16	93.78
	2	1	0.14	1.88	92.52
		2	0.13	1.74	92.46
		3	0.13	2.04	93.38
	3	1	0.14	1.74	92.20
		2	0.14	1.74	92.20
		3	0.14	1.92	92.87
Loblolly Pine	1	1	0.20	1.51	86.82
		2	0.20	1.52	87.10
		3	0.20	1.62	87.95
	2	1	0.21	1.61	87.06
		2	0.22	1.65	86.54
		3	0.22	1.54	85.91
	3	1	0.22	1.67	87.03
		2	0.21	1.64	87.02
		3	0.22	1.44	84.91
Switchgrass	1	1	0.19	1.42	86.43
		2	0.19	1.36	85.95
		3	0.19	1.49	87.12
	2	1	0.19	1.47	87.33
		2	0.18	1.57	88.37
		3	0.18	1.42	87.23

(Table 2.15. Continued)

Biomass					
	Sample	Subsample	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Bulk Porosity (vol. %)
Switchgrass	3	1	0.18	1.49	88.06
		2	0.18	1.41	87.41
		3	0.18	1.39	87.36

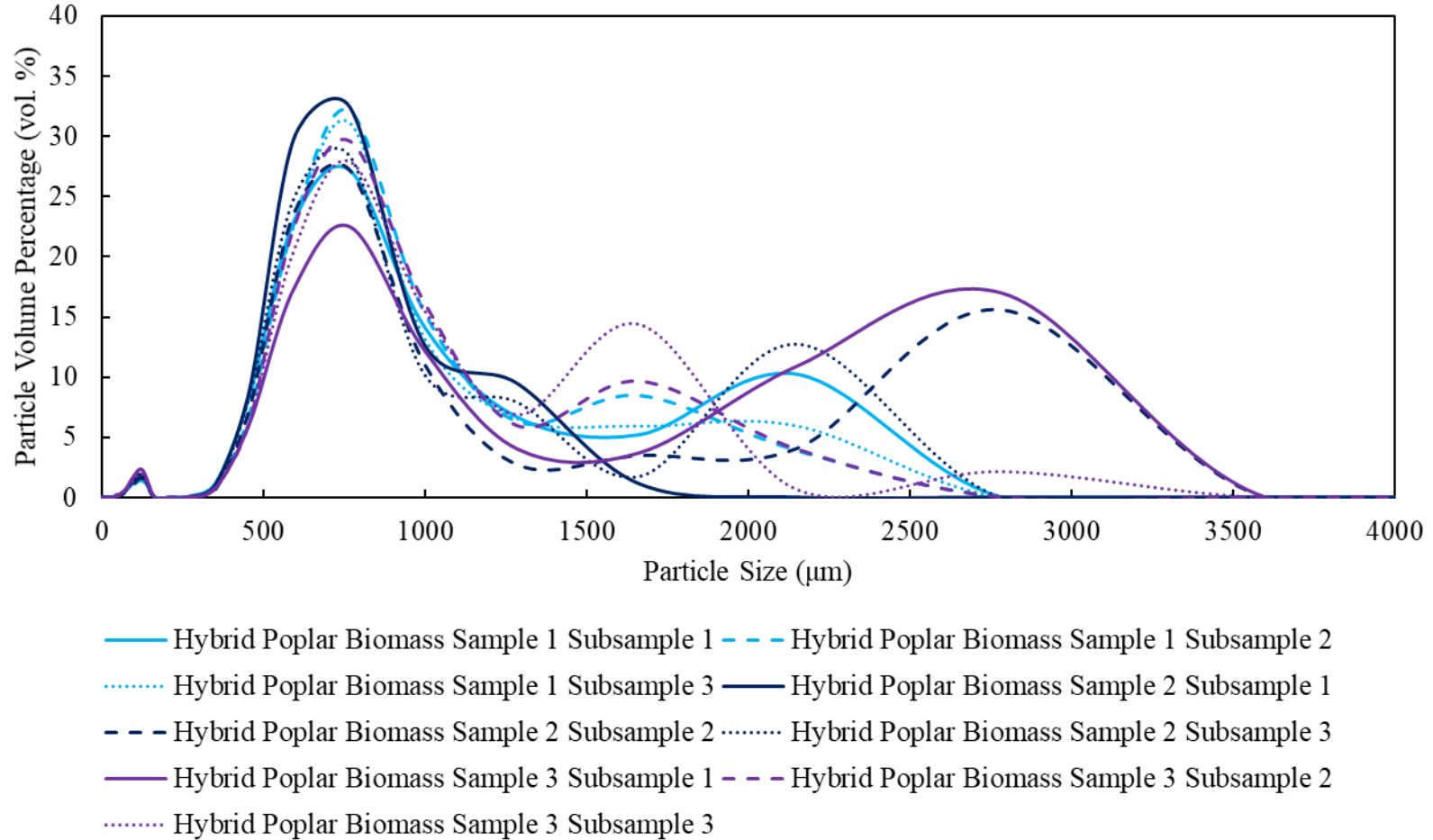


Figure 2.13. Particle size distributions of hybrid poplar biomass.

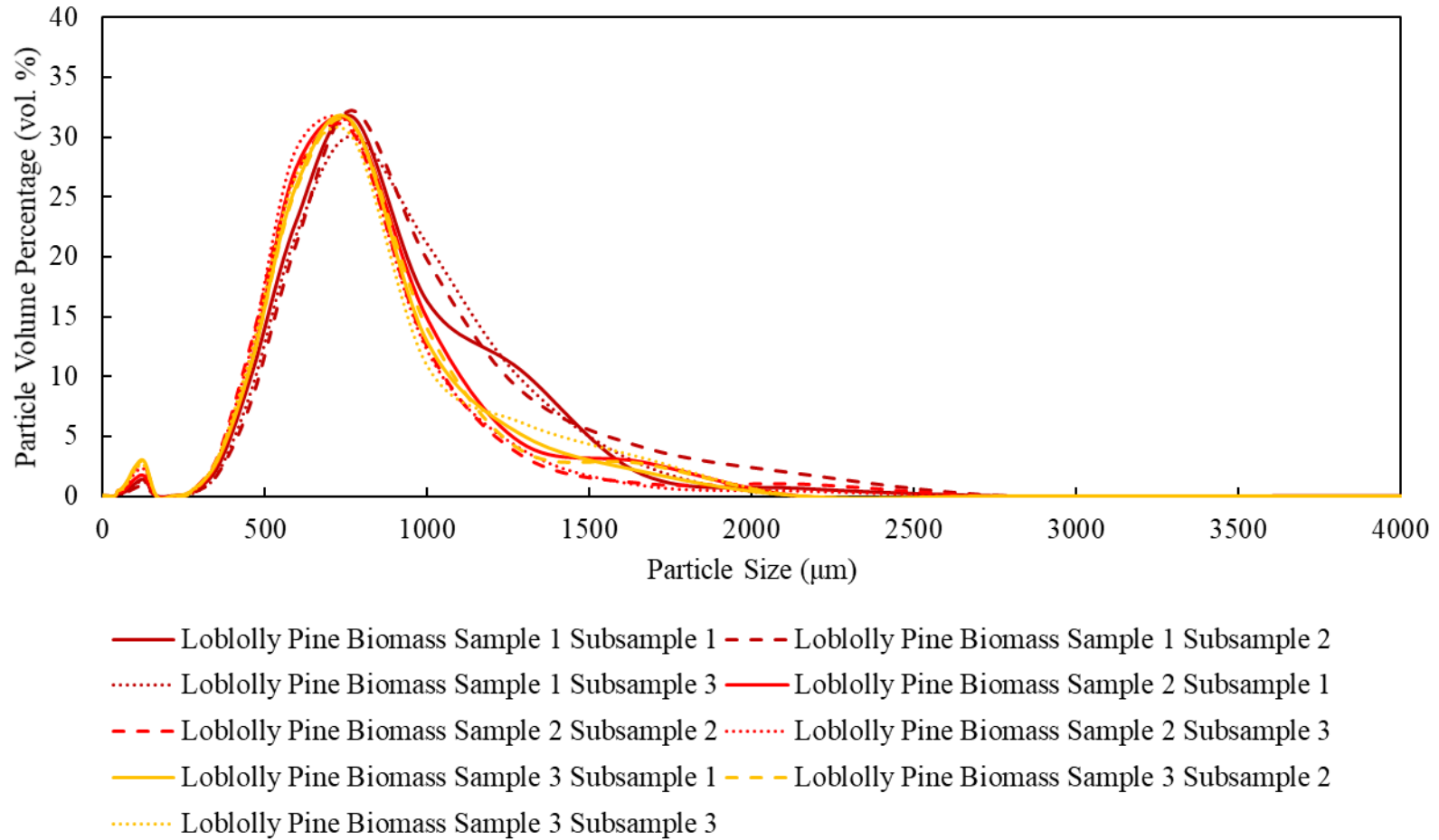


Figure 2.14. Particle size distributions of loblolly pine biomass.

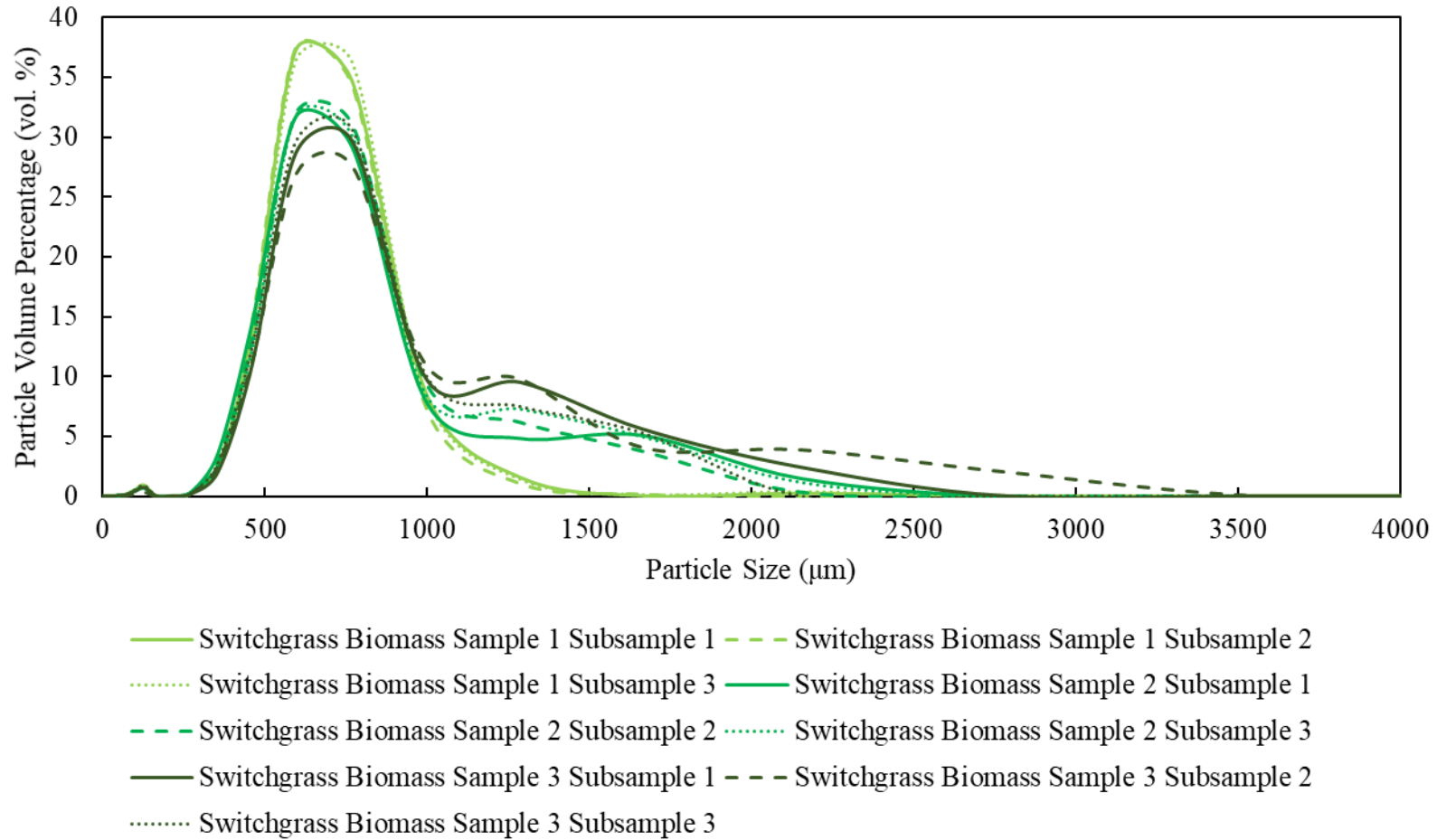


Figure 2.15. Particle size distributions of switchgrass biomass.

Table 2.16. Inorganics analyses of hybrid poplar, loblolly pine, and switchgrass biomasses.

		Biomass							
	Sample	Subsample	Inorganics Analysis (mg/kg, db)						
			Al	Ca	Cu	Fe	K	Mg	
Hybrid Poplar	1	1	61.64	1130.81	0.26	11.78	912.16	184.01	9.28
		2	15.09	1198.27	1.28	40.50	931.14	188.77	9.88
		3	7.49	1230.78	0.45	77.53	1001.31	197.58	10.90
	2	1	9.19	1168.30	0.54	27.45	958.53	193.52	9.94
		2	6.79	1147.40	0.10	25.80	952.09	186.95	10.13
		3	8.02	1163.69	0.09	26.38	925.96	194.00	9.79
	3	1	3.30	1196.87	0.76	27.09	1004.91	196.97	9.85
		2	3.47	1201.61	ND	38.17	992.69	193.43	10.13
		3	23.08	1195.67	1.01	31.66	940.72	193.93	11.34
Loblolly Pine	1	1	34.77	742.31	1.70	110.00	582.87	205.98	95.03
		2	46.49	729.22	2.36	124.47	545.60	206.08	95.03
		3	31.84	764.34	1.10	98.04	585.73	214.55	95.81
	2	1	15.52	714.79	0.32	50.26	639.85	212.10	91.07
		2	17.32	684.36	ND	91.42	580.61	199.20	91.59
		3	23.02	683.31	ND	88.99	518.40	189.41	90.72
	3	1	68.27	695.89	0.91	71.96	577.84	203.17	92.14
		2	16.67	712.98	ND	53.54	602.41	206.23	90.98
		3	31.28	685.01	0.06	141.03	517.31	190.03	89.96
Switchgrass	1	1	8.54	1103.12	0.36	63.74	558.68	721.97	49.69
		2	17.53	1628.93	0.58	95.77	503.31	820.88	60.71
		3	15.04	1221.25	0.56	71.39	515.49	779.13	57.69
	2	1	9.32	1121.51	0.25	58.63	499.09	725.15	49.11
		2	24.01	1630.95	1.25	89.91	519.17	895.85	71.67
		3	4.54	1346.44	0.27	63.02	554.37	805.18	56.72

(Table 2.16. Continued)

Biomass									
Sample	Subsample	Inorganics Analysis (mg/kg, db)							
		Al	Ca	Cu	Fe	K	Mg	Mn	
Switchgrass	3	1	22.71	1823.53	9.26	105.43	528.70	923.40	77.64
		2	15.04	1708.71	0.85	84.89	538.58	891.58	76.33
		3	10.65	1850.07	0.44	77.38	584.28	960.56	74.59
Sample	Subsample	Inorganics Analysis (mg/kg, db)							
		Ni	P	S	Si	Zn	Total Inorganics		
Hybrid Poplar	1	1	30.10	150.56	93.47	719.47	9.02	3312.56	
		2	37.85	164.25	87.82	863.66	9.50	3548.00	
		3	46.88	172.93	99.32	1102.00	10.17	3957.35	
	2	1	51.14	168.95	99.02	1285.35	8.94	3980.88	
		2	55.25	145.50	88.34	1268.13	8.75	3895.24	
		3	20.05	153.53	100.91	254.44	8.82	2865.66	
	3	1	35.25	180.75	99.08	768.41	9.14	3532.39	
		2	45.20	159.76	91.09	1014.96	8.96	3759.46	
		3	59.83	151.30	94.91	1148.95	10.70	3863.11	
Loblolly Pine	1	1	48.15	79.69	78.39	1210.64	7.81	3197.36	
		2	49.38	59.51	67.97	1182.03	7.25	3115.39	
		3	51.05	72.24	77.17	1274.30	7.21	3273.38	
	2	1	50.31	89.07	69.71	1305.96	6.23	3245.19	
		2	49.25	64.31	69.72	1211.05	5.97	3064.79	
		3	18.07	39.27	63.95	135.37	6.16	1856.67	
	3	1	35.79	62.28	68.87	781.09	6.99	2665.20	
		2	42.34	72.97	72.53	948.90	6.18	2825.72	
		3	47.28	54.36	69.99	1141.65	5.93	2973.89	

(Table 2.16. Continued)

Biomass								
Sample	Subsample	Inorganics Analysis (mg/kg, db)						
		Ni	P	S	Si	Zn	Total Inorganics	
Switchgrass	1	1	154.63	194.14	242.97	4007.68	7.79	7113.31
		2	179.22	213.51	292.06	4821.87	8.30	8642.66
		3	133.94	191.17	269.99	3070.01	7.62	6333.27
	2	1	130.73	205.11	247.41	3305.85	7.20	6359.35
		2	179.19	252.44	319.84	4790.68	9.47	8784.43
		3	153.12	235.36	268.93	4184.05	7.57	7679.56
	3	1	196.90	269.62	337.13	5253.22	12.62	9560.18
		2	194.88	251.05	315.43	5166.24	9.68	9253.25
		3	191.93	314.28	339.86	5700.71	8.41	10113.16

ND stands for not detected.

Table 2.17. pH of hybrid poplar, loblolly pine, and switchgrass biomasses.

Biomass			
	Sample	Subsample	pH
Hybrid Poplar	1	1	5.19
		2	5.15
		3	5.16
	2	1	5.15
		2	5.10
		3	5.13
	3	1	5.29
		2	5.24
		3	5.19
Loblolly Pine	1	1	4.87
		2	4.92
		3	4.82
	2	1	4.71
		2	4.72
		3	4.68
	3	1	4.75
		2	4.76
		3	4.77
Switchgrass	1	1	5.76
		2	5.75
		3	5.72
	2	1	5.58
		2	5.40
		3	5.59

(Table 2.17. Continued)

Biomass			
	Sample	Subsample	pH
Switchgrass	3	1	5.70
		2	5.60
		3	5.53

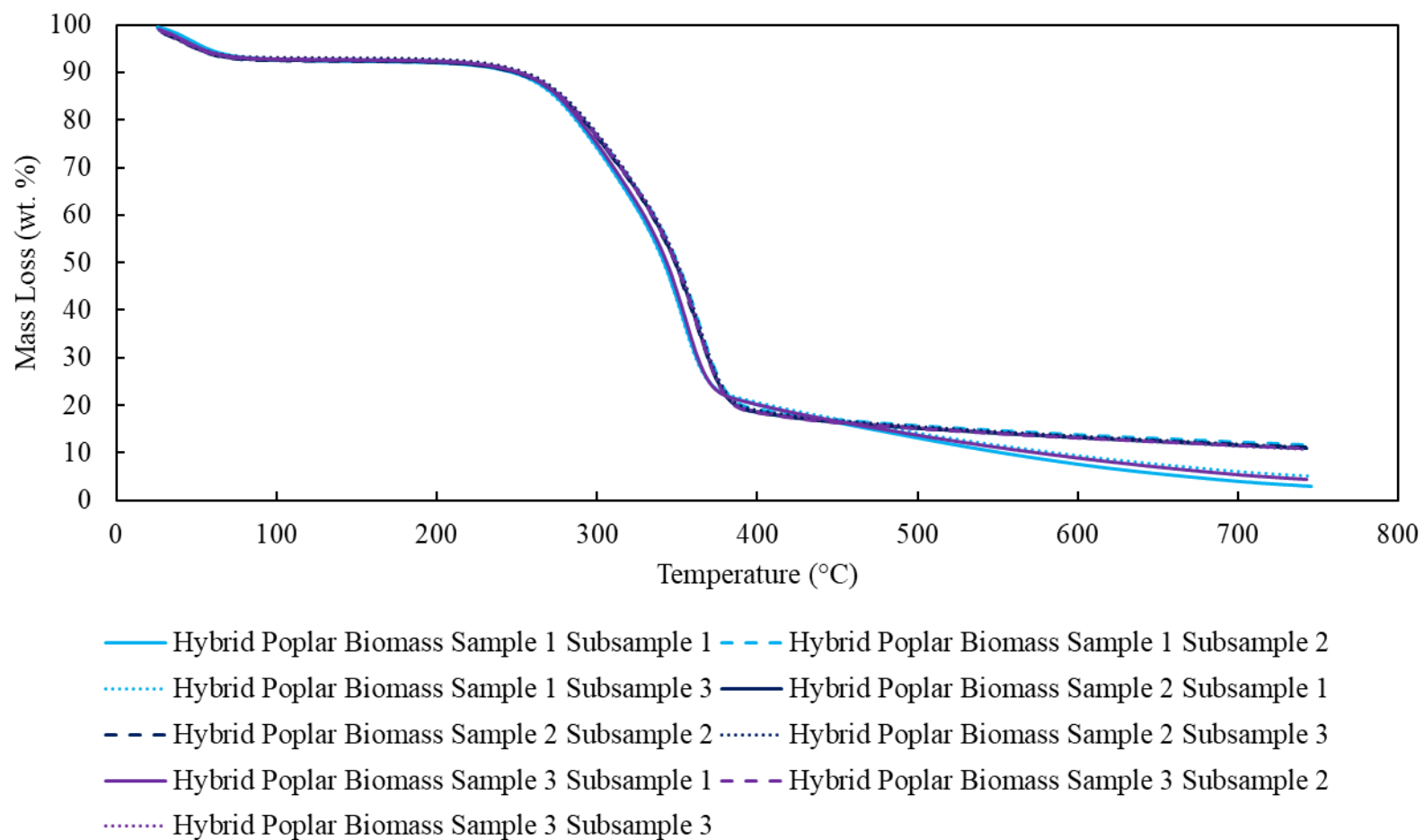


Figure 2.16. Mass loss thermographs of hybrid poplar biomass.

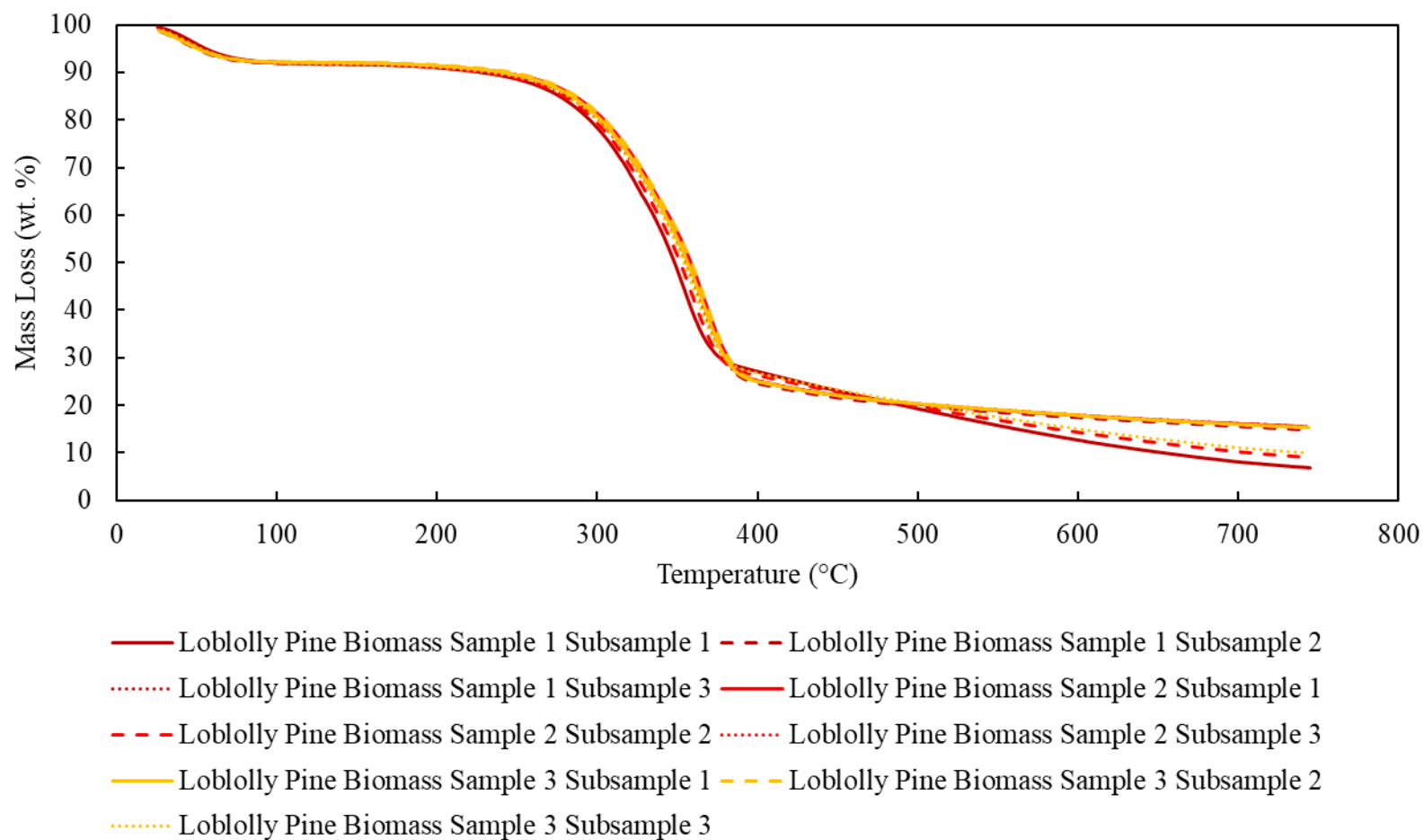


Figure 2.17. Mass loss thermographs of loblolly pine biomass.

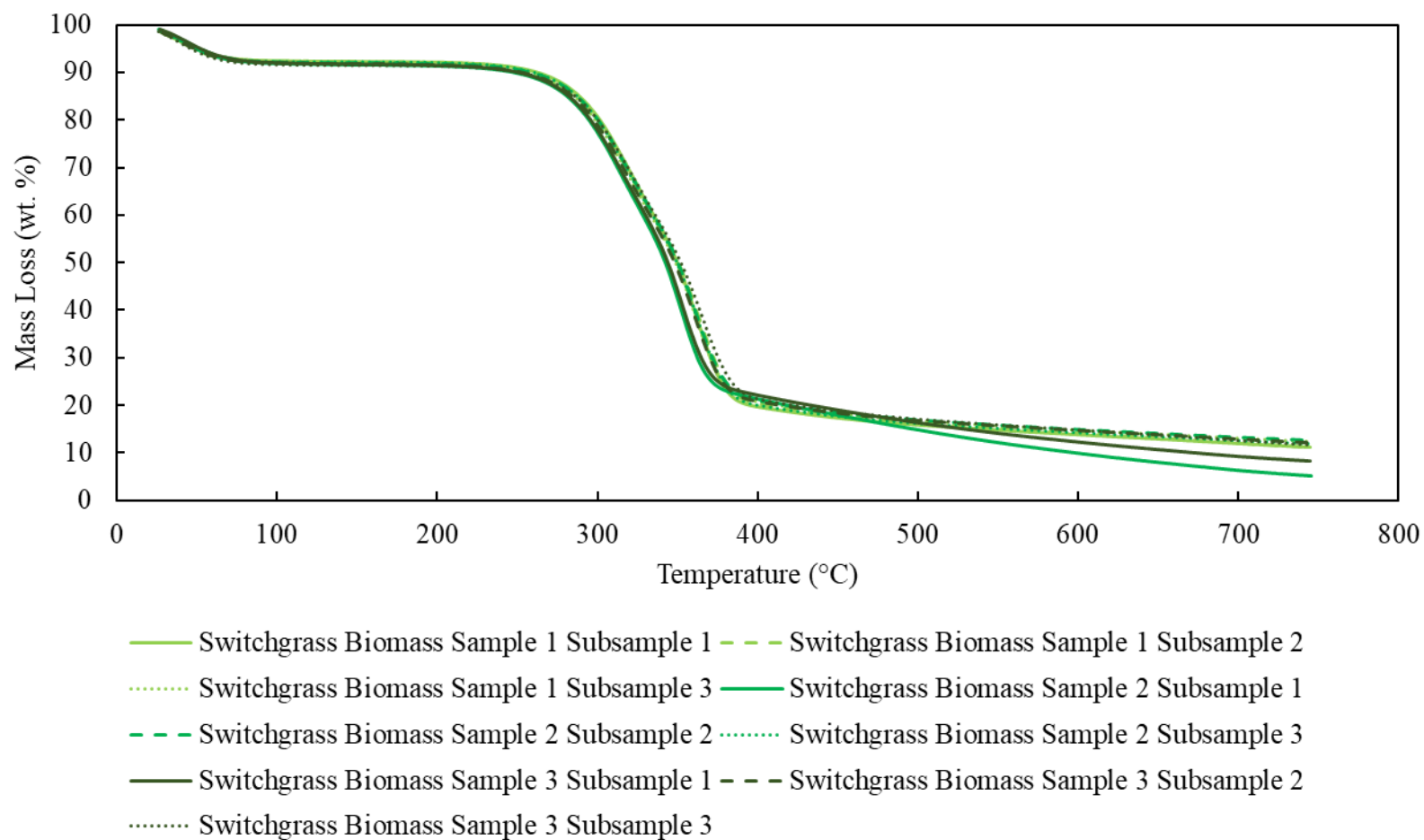


Figure 2.18. Mass loss thermographs of switchgrass biomass.

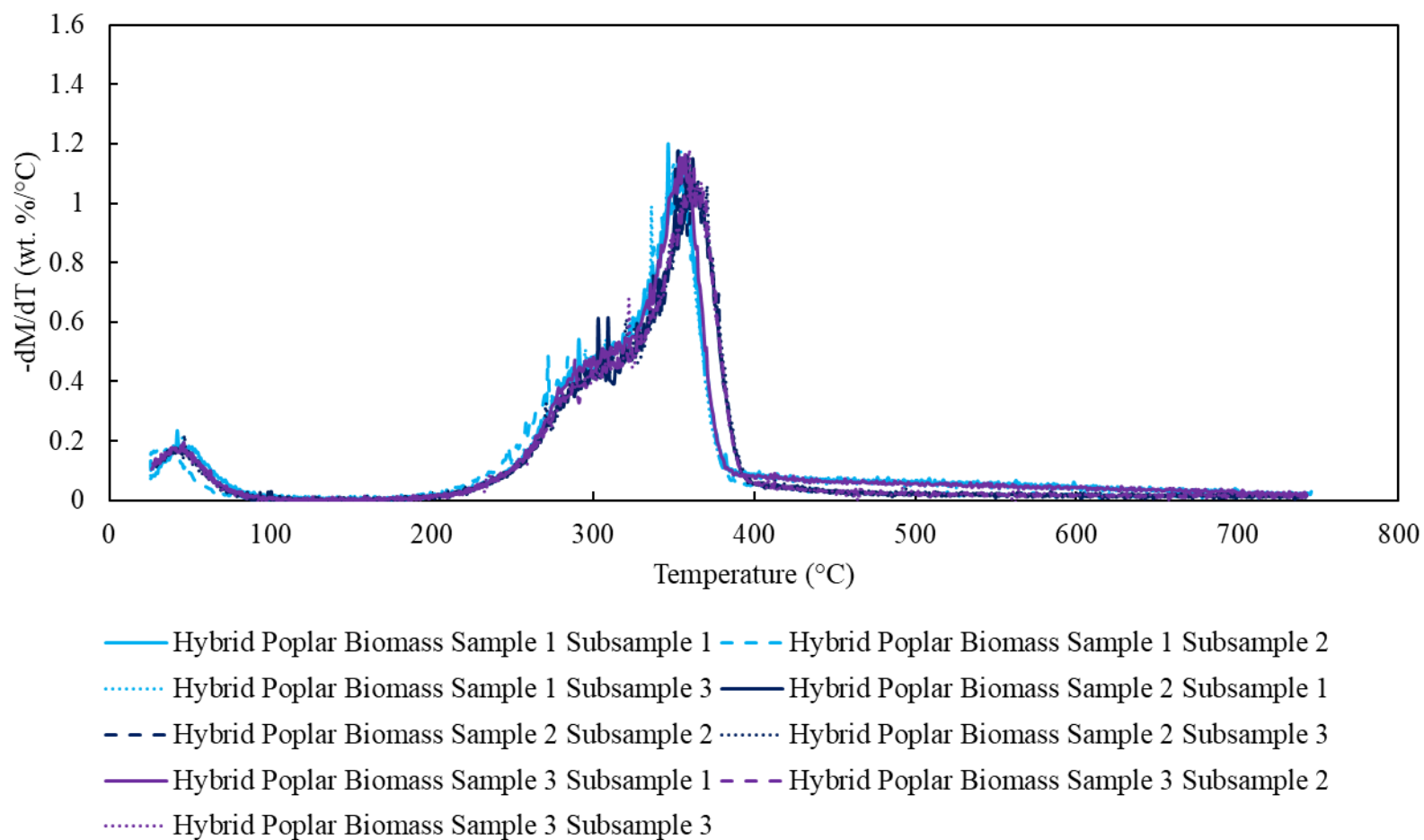


Figure 2.19. Derivative mass loss thermographs of hybrid poplar biomass.

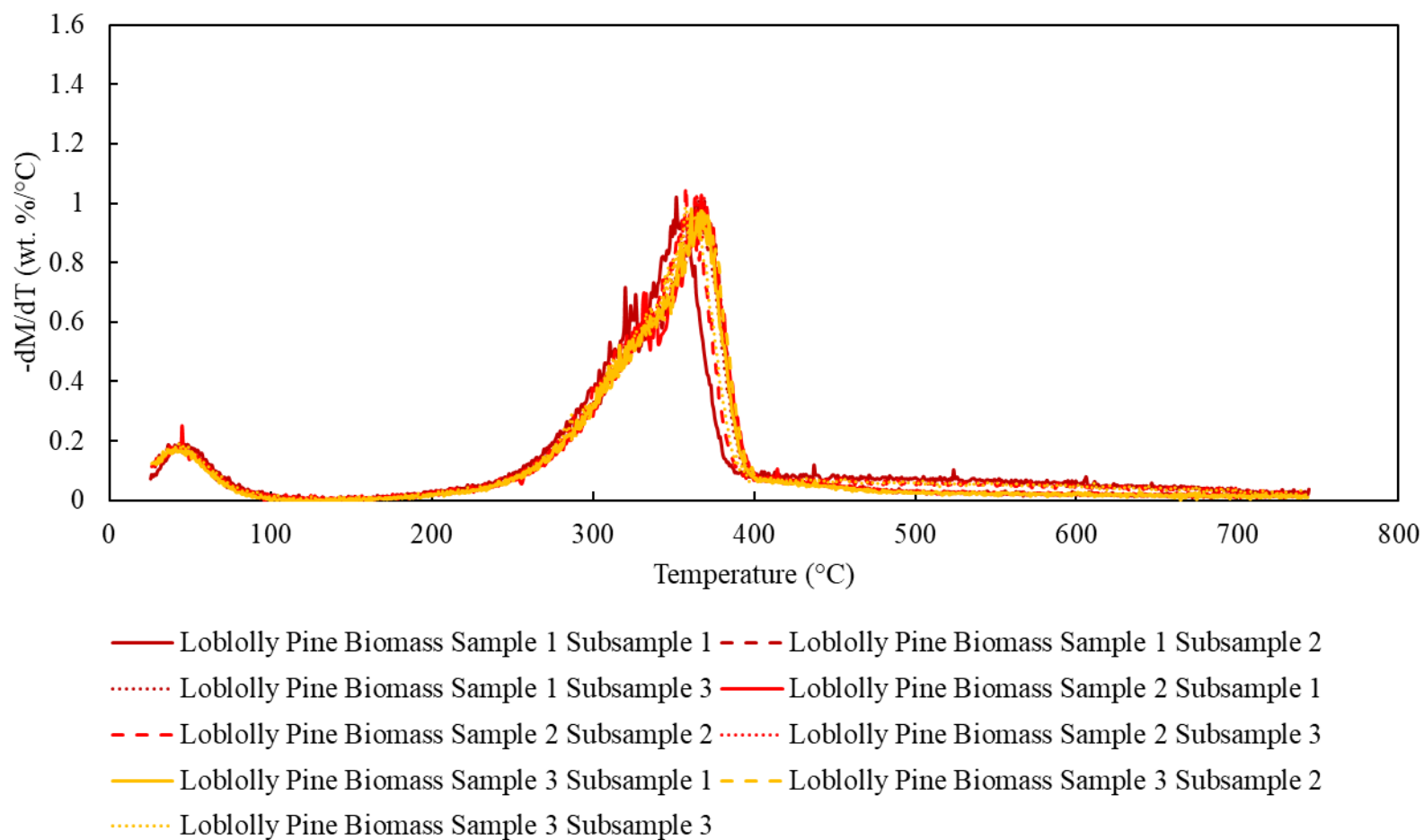


Figure 2.20. Derivative mass loss thermographs of loblolly pine biomass.

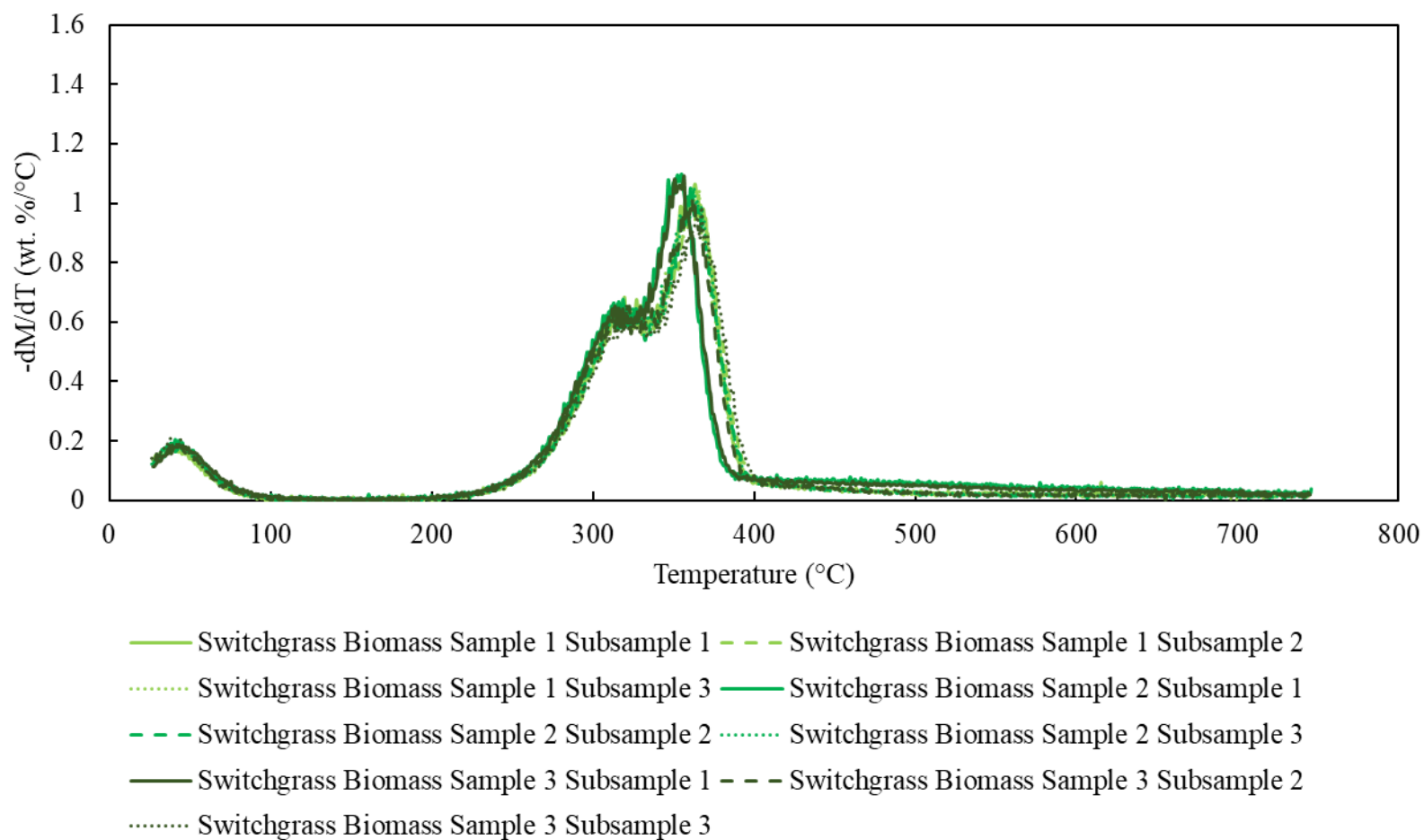


Figure 2.21. Derivative mass loss thermographs of switchgrass biomass.

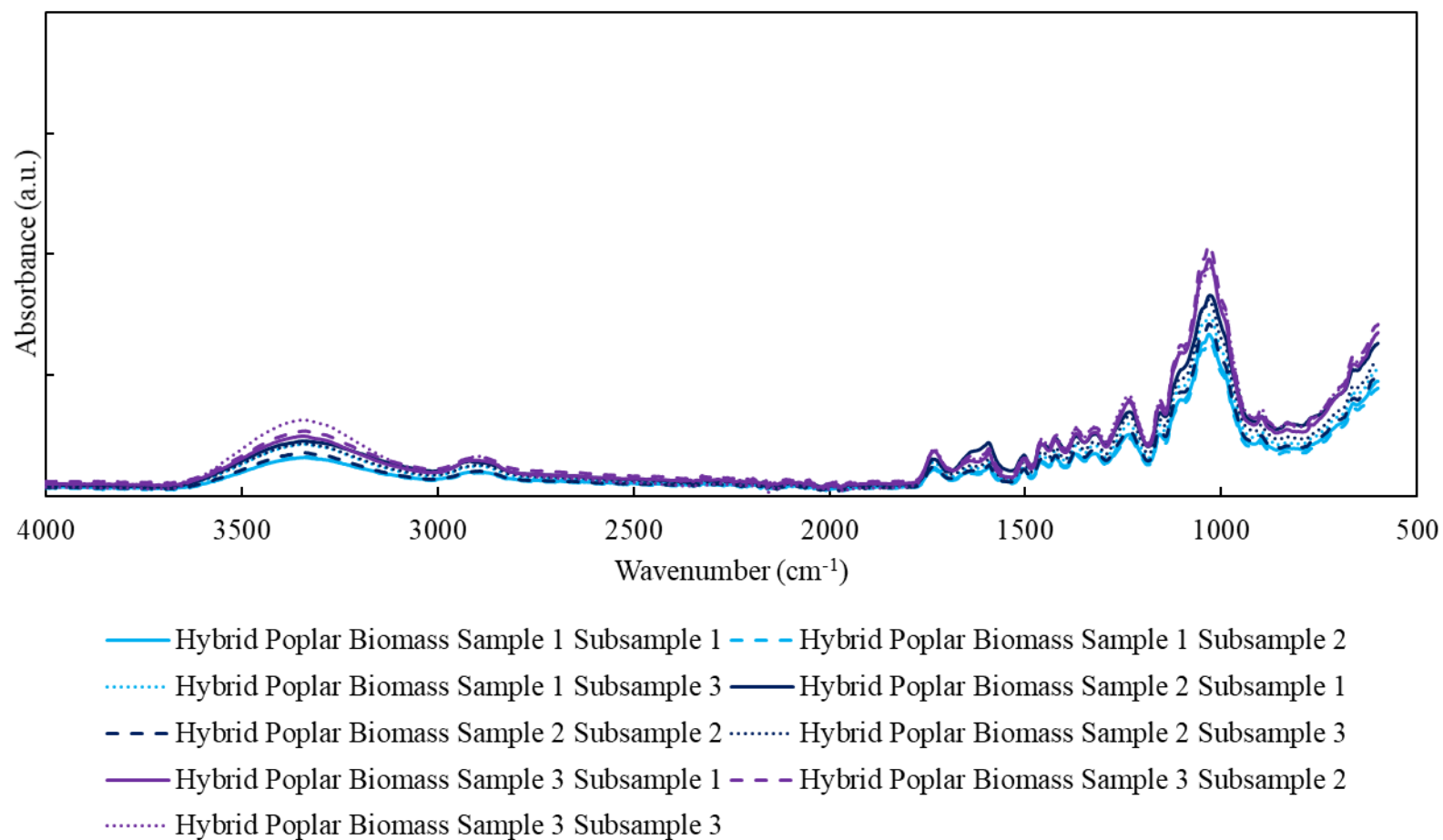


Figure 2.22. FTIR spectra of hybrid poplar biomass.

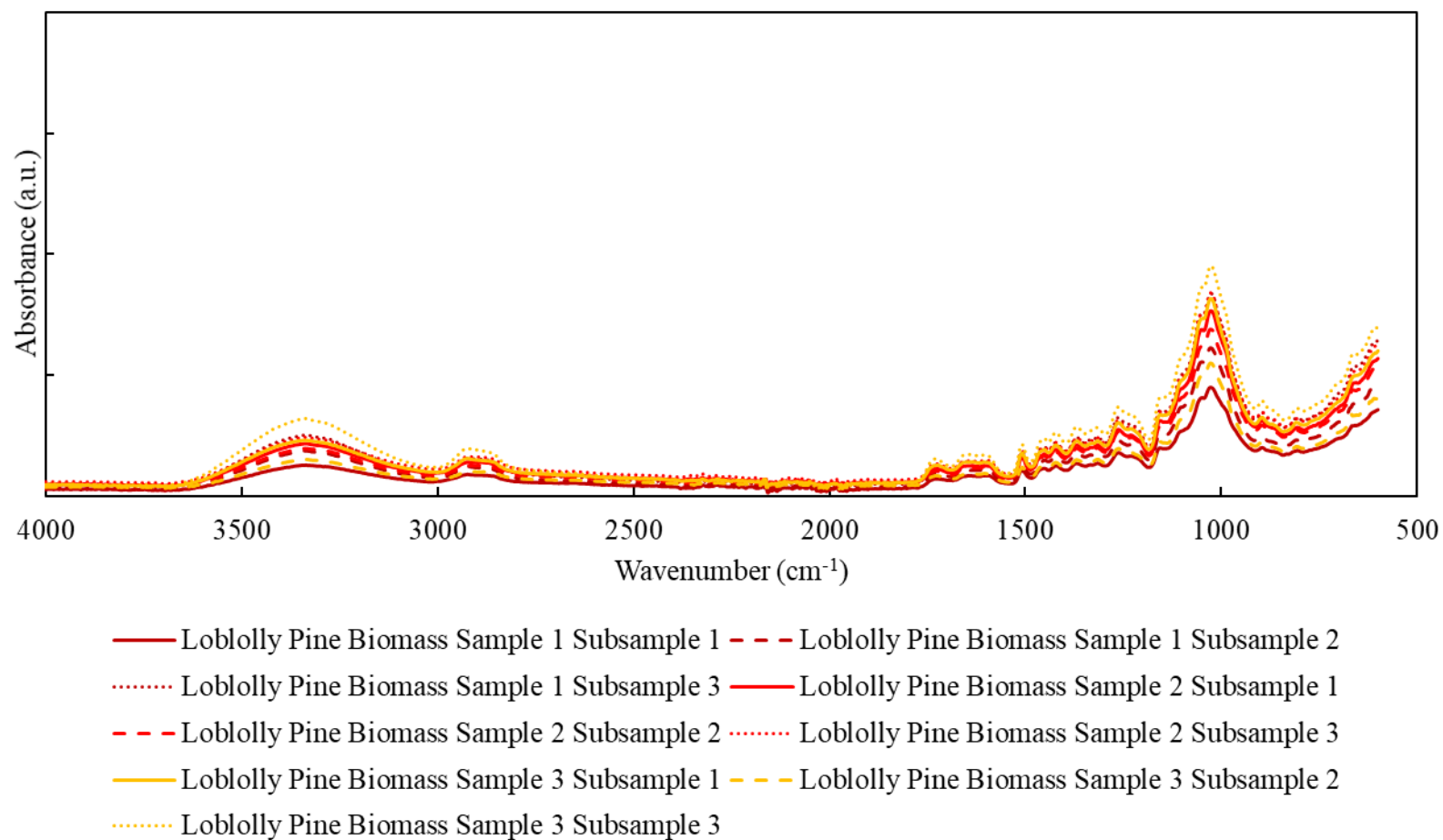


Figure 2.23. FTIR spectra of loblolly pine biomass.

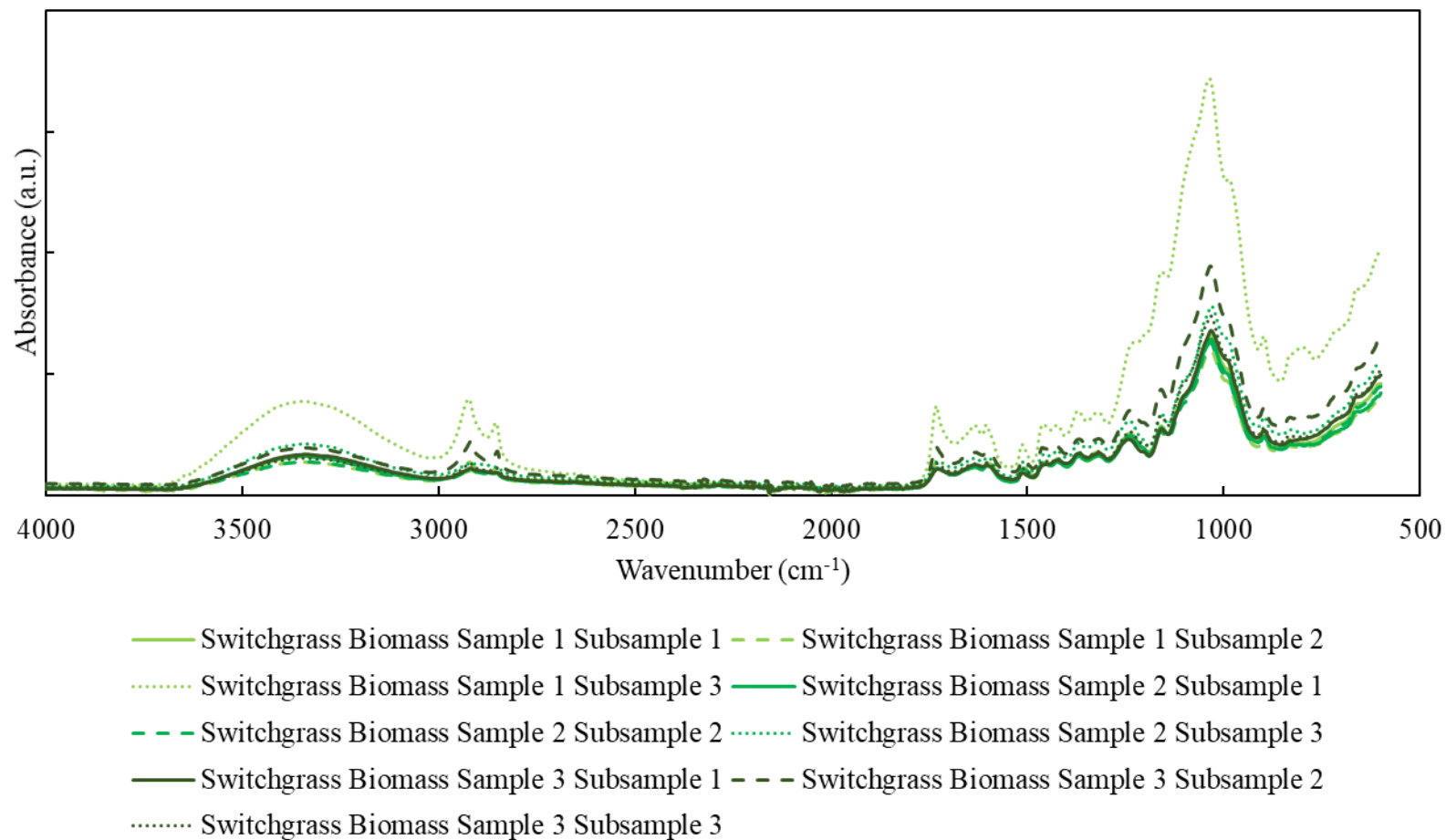


Figure 2.24. FTIR spectra of switchgrass biomass.

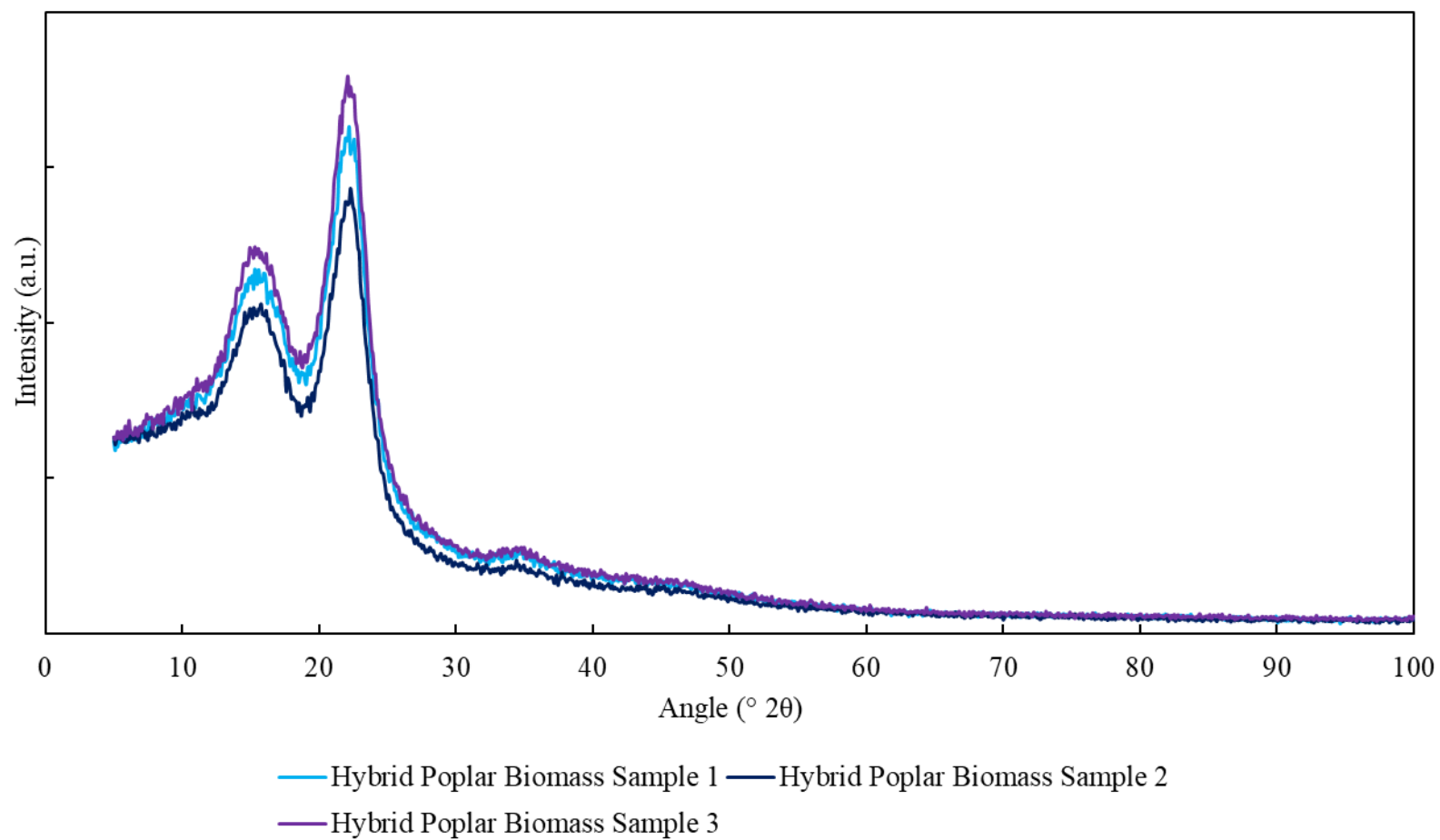


Figure 2.25. XRD diffractograms of hybrid poplar biomass.

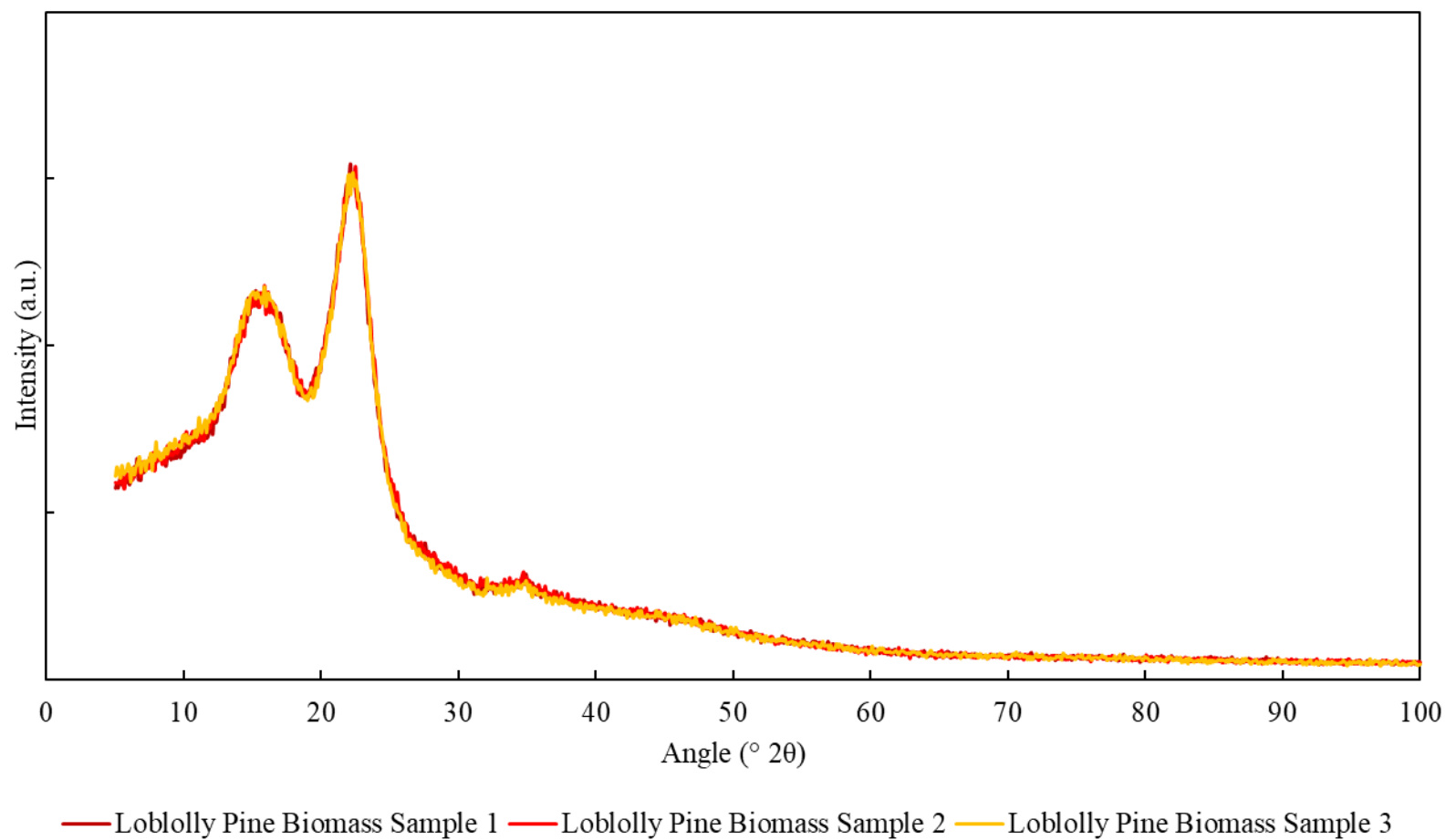


Figure 2.26. XRD diffractograms of loblolly pine biomass.

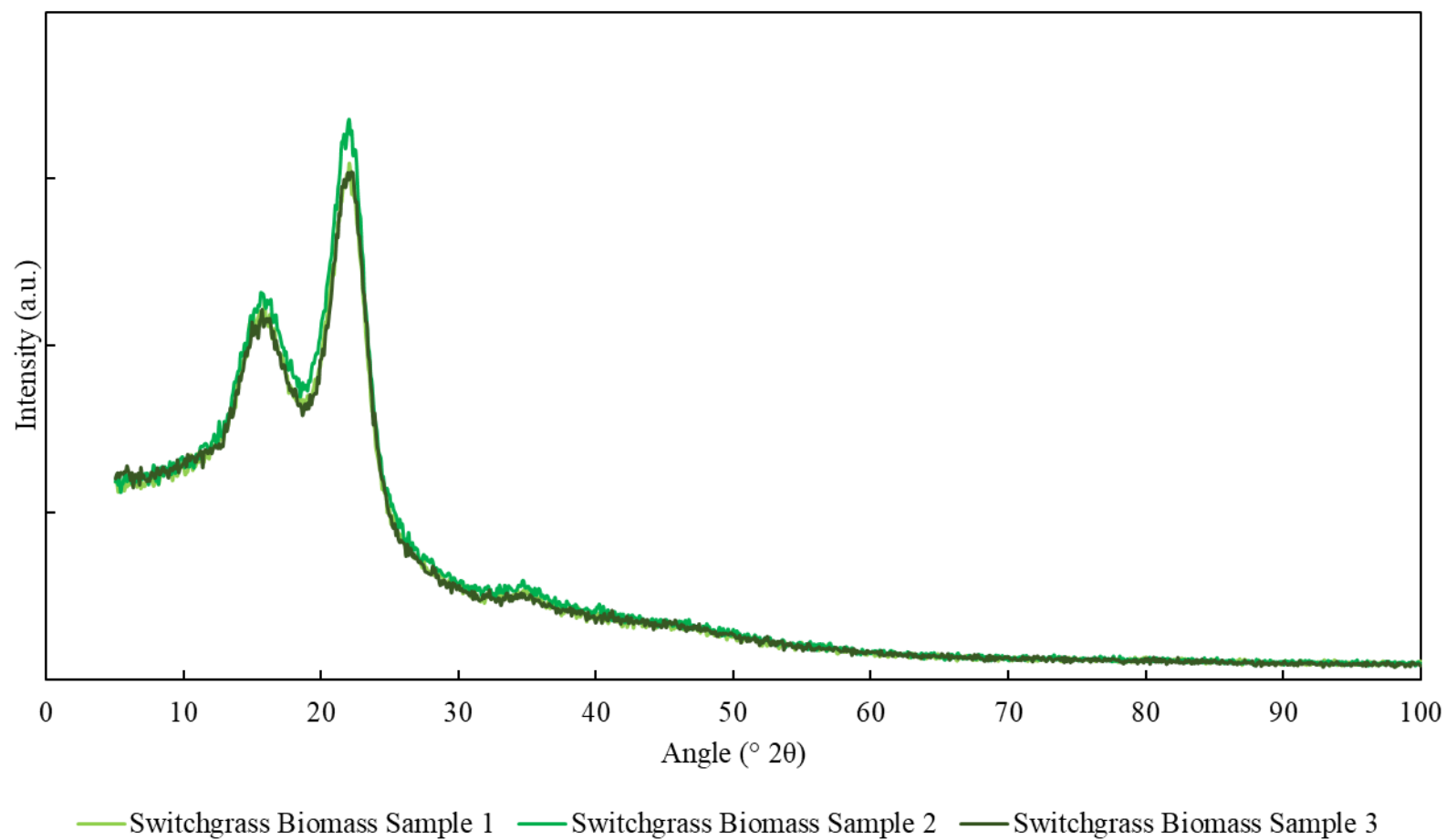


Figure 2.27. XRD diffractograms of switchgrass biomass.

Table 2.18. Cellulose crystallinity indexes and crystallite sizes of hybrid poplar, loblolly pine, and switchgrass biomasses.

Biomass			
	Sample	Cellulose Crystallinity Index (%)	Cellulose Crystallinity Size (Å)
Hybrid Poplar	1	54.81	32
	2	62.15	31
	3	62.08	33
Loblolly Pine	1	60.89	31
	2	53.68	30
	3	57.34	30
Switchgrass	1	59.13	34
	2	57.88	35
	3	56.74	32

Table 2.19. Textural analyses of hybrid poplar, loblolly pine, and switchgrass biomasses.

Biomass				
	Sample	Subsample	Textural Analysis	
			Specific Surface Area (m ² /g)	Total Pore Volume (mm ³ /g)
Hybrid Poplar	1	1	1.57	6.55
		2	1.50	6.46
		3	1.52	6.95
	2	1	1.95	4.45
		2	2.03	5.13
		3	2.33	9.78
	3	1	3.09	9.57
		2	2.18	5.03
		3	2.59	8.57
Loblolly Pine	1	1	1.32	1.84
		2	1.16	3.59
		3	1.23	4.27
	2	1	1.15	4.11
		2	0.99	4.57
		3	0.97	4.57
	3	1	1.02	3.10
		2	1.28	3.57
		3	0.90	5.29
Switchgrass	1	1	1.08	5.00
		2	1.25	4.60
		3	1.22	3.82
	2	1	1.52	8.05
		2	1.33	5.93
		3	1.28	4.67

(Table 2.19. Continued)

Biomass				
	Sample	Subsample	Textural Analysis	
			Specific Surface Area (m ² /g)	Total Pore Volume (mm ³ /g)
Switchgrass	3	1	1.29	4.34
		2	1.11	4.88
		3	0.81	7.08

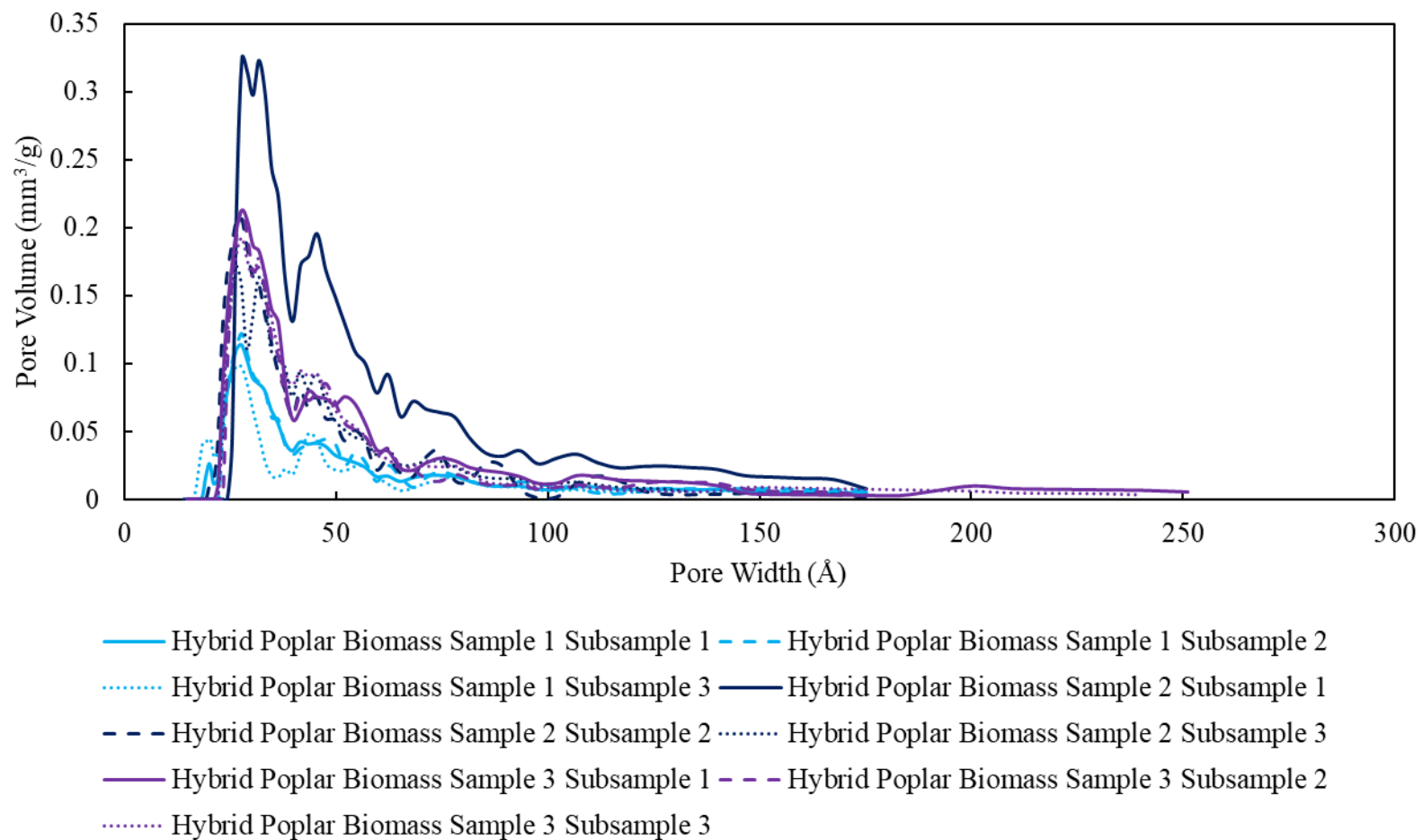


Figure 2.28. Pore width distributions of hybrid poplar biomass.

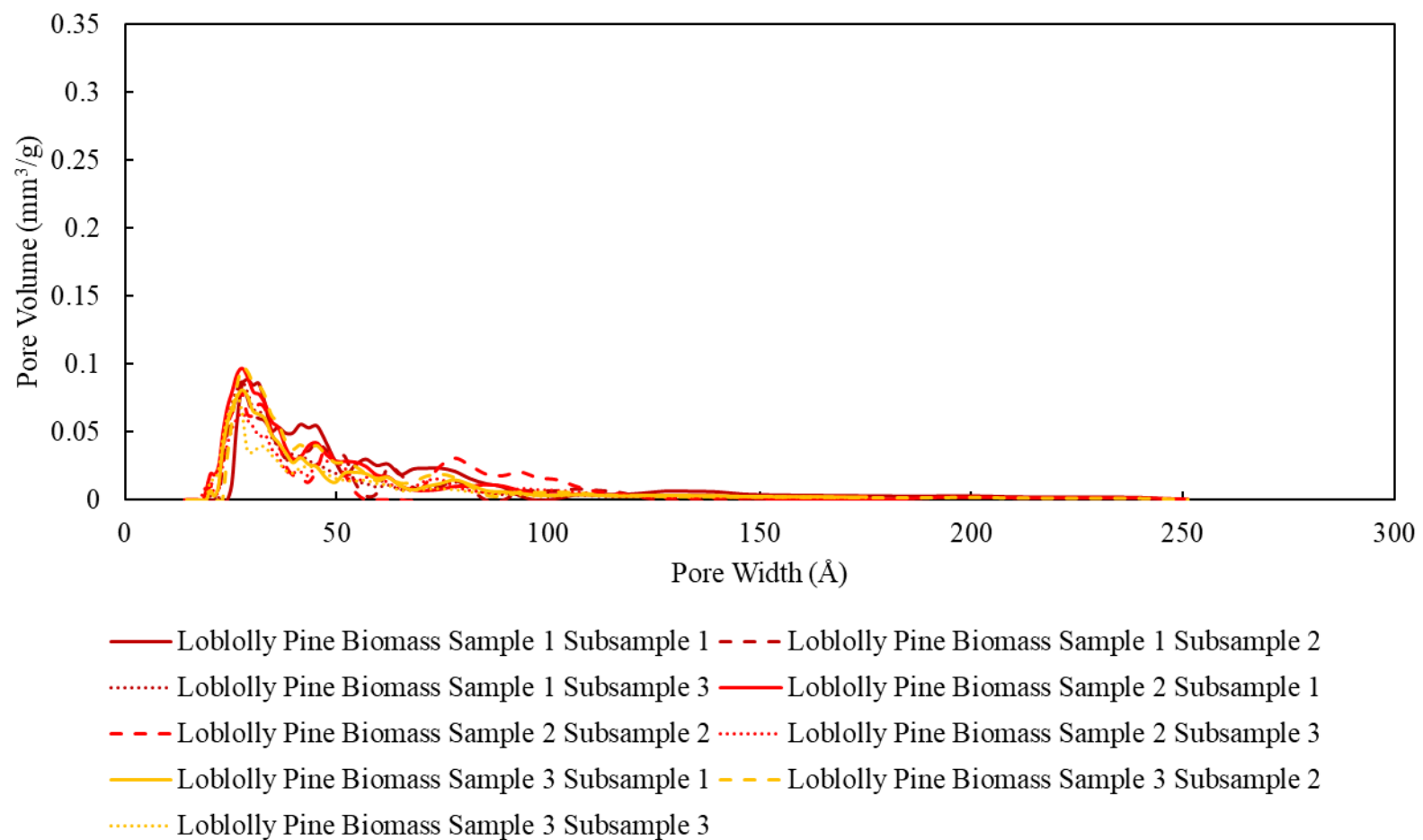


Figure 2.29. Pore width distributions of loblolly pine biomass.

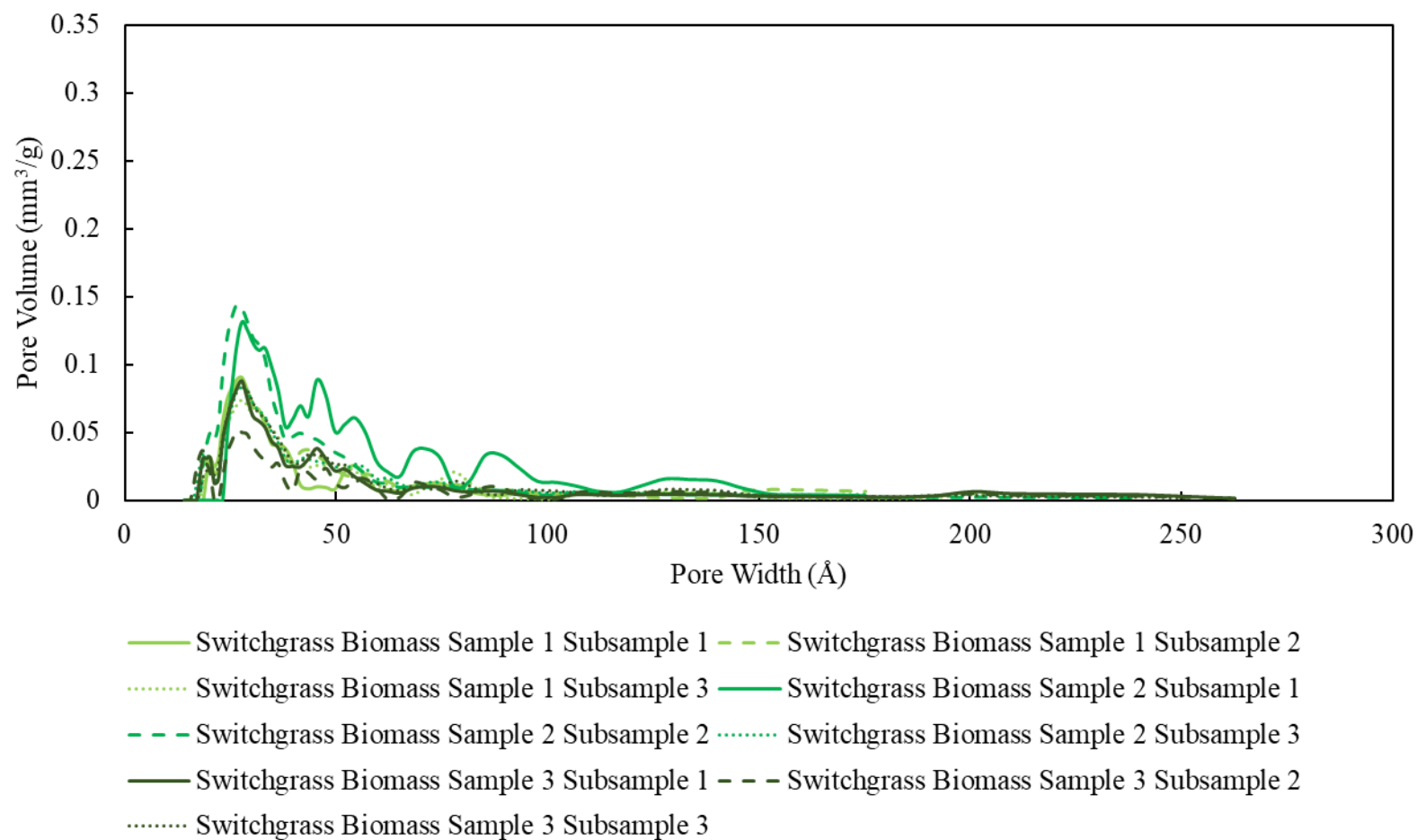


Figure 2.30. Pore width distributions of switchgrass biomass.

Appendix B. Pyrolysis

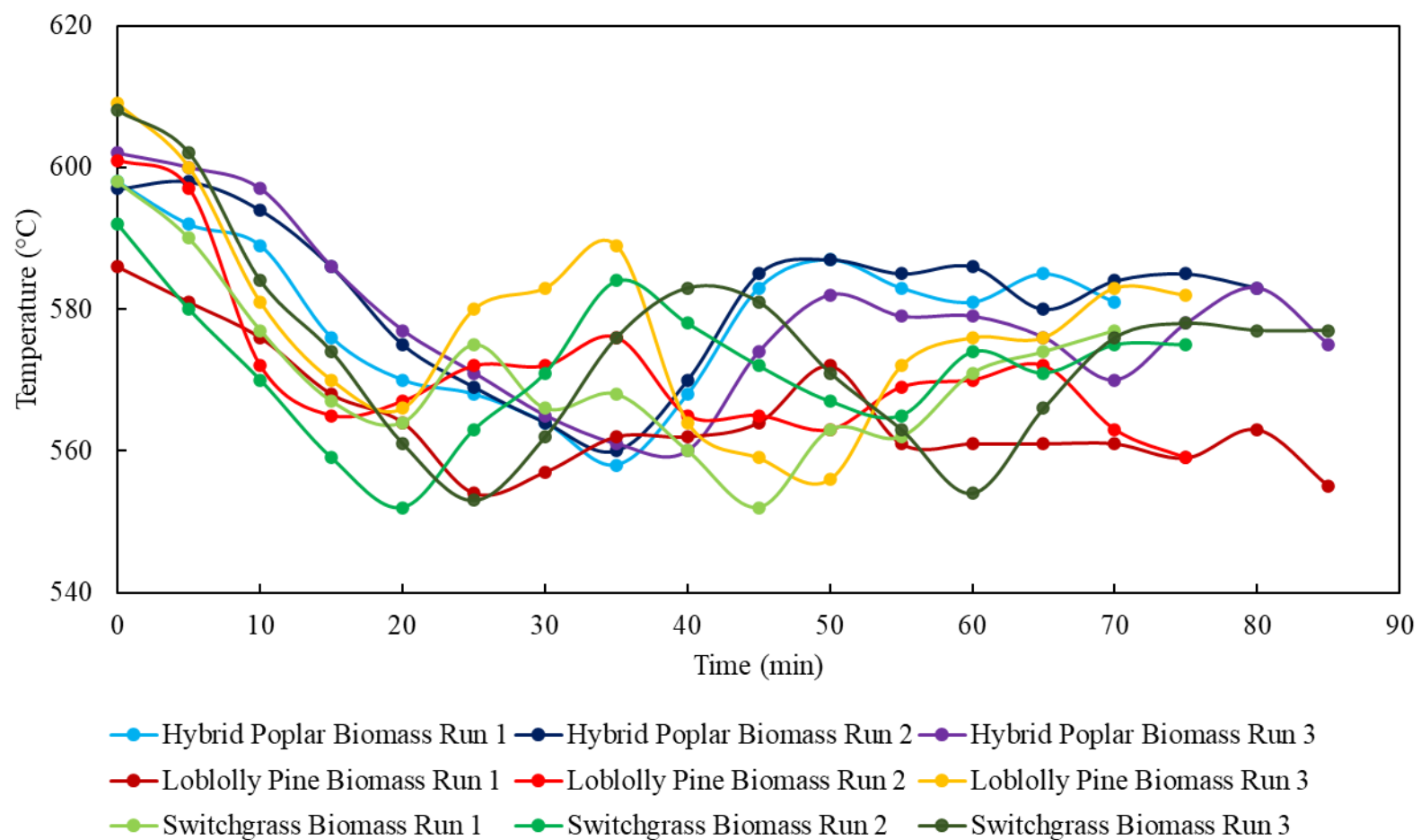


Figure 2.31. Pyrolysis reactor thermocouple temperatures of hybrid poplar, loblolly pine, and switchgrass biomass pyrolysis experiments.

Table 2.20. Biochar yields of hybrid poplar, loblolly pine, and switchgrass biomass pyrolysis experiments.

Biomass		
	Run	Biochar Yield (wt. %, db)
Hybrid Poplar	1	13.30
	2	15.18
	3	19.63
Loblolly Pine	1	24.08
	2	23.76
	3	25.88
Switchgrass	1	24.81
	2	12.76
	3	20.82

Appendix C. Biochar Characterization

Table 2.21. Proximate analyses of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar						
	Sample	Subsample	Proximate Analysis			
			Moisture (wt. %, wb)	Ash (wt. %, db)	Volatile Matter (wt. %, db)	Fixed Carbon (wt. %, db)
Hybrid Poplar	1	1	3.17	2.39	29.86	64.59
		2	3.10	2.06	29.32	65.52
		3	3.11	2.01	30.44	64.44
	2	1	2.52	1.33	26.98	69.18
		2	2.58	1.46	26.36	69.60
		3	2.56	1.88	28.01	67.56
	3	1	2.44	1.62	30.53	65.41
		2	2.43	1.17	30.08	66.31
		3	2.42	1.61	30.67	65.30
Loblolly Pine	1	1	3.10	0.61	32.08	64.21
		2	3.08	0.57	31.70	64.65
		3	3.04	0.44	33.23	63.29
	2	1	2.65	0.72	38.55	58.08
		2	2.54	0.82	40.34	56.30
		3	2.60	0.49	39.24	57.67
	3	1	2.47	0.71	43.33	53.50
		2	2.50	0.80	44.46	52.23
		3	2.45	0.14	45.01	52.41
Switchgrass	1	1	2.72	2.82	46.03	48.43
		2	2.79	3.04	43.93	50.24
		3	2.82	3.11	43.80	50.27
	2	1	2.64	2.26	46.38	48.71
		2	2.66	2.52	47.51	47.31
		3	2.98	2.27	47.57	47.18

(Table 2.21. Continued)

Biochar						
Sample	Subsample	Proximate Analysis				
		Moisture (wt. %, wb)	Ash (wt. %, db)	Volatile Matter (wt. %, db)	Fixed Carbon (wt. %, db)	
Switchgrass	3	1	2.84	4.11	39.54	53.52
		2	2.86	4.24	37.62	55.28
		3	3.09	3.75	39.94	53.23

Table 2.22. Ultimate analyses of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar							
	Sample	Subsample	Ultimate Analysis (wt. %, dafb)				
			C	H	N	S	O
Hybrid Poplar	1	1	77.71	4.03	0.24	0.06	17.96
		2	77.14	4.47	0.25	0.06	18.08
		3	75.92	3.93	0.19	0.08	19.88
	2	1	80.11	4.26	0.19	0.06	15.38
		2	78.61	3.66	0.19	0.15	17.39
		3	80.57	4.30	0.25	0.04	14.84
	3	1	79.13	4.58	0.26	0.05	15.98
		2	78.82	4.24	0.44	0.03	16.48
		3	79.08	4.29	0.18	0.06	16.38
Loblolly Pine	1	1	76.88	4.31	0.73	0.00	18.07
		2	76.50	4.29	0.12	0.04	19.04
		3	76.74	4.22	0.14	0.05	18.85
	2	1	75.43	4.84	0.73	0.01	18.98
		2	73.87	4.57	0.42	0.01	21.13
		3	74.16	4.76	0.07	0.03	20.97
	3	1	72.33	4.86	0.08	0.02	22.71
		2	72.90	5.00	0.48	0.00	21.62
		3	71.83	5.40	0.11	0.04	22.62
Switchgrass	1	1	70.05	4.98	0.35	0.07	24.55
		2	70.54	4.65	0.92	0.04	23.85
		3	70.35	5.10	1.51	0.03	23.01
	2	1	68.41	4.89	0.54	0.13	26.03
		2	69.89	5.10	0.32	0.08	24.62
		3	68.02	4.92	0.26	0.04	26.76

(Table 2.22. Continued)

Biochar							
	Sample	Subsample	Ultimate Analysis (wt. %, dafb)				
			C	H	N	S	O
Switchgrass	3	1	73.93	4.69	2.27	0.05	19.06
		2	73.68	4.69	2.11	0.04	19.47
		3	72.84	4.55	0.43	0.07	22.10

Table 2.23. Atomic ratios and HHVs of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar						
	Sample	Subsample	Atomic Ratios			HHV (kJ/g, db)
			H/C	O/C	(O+N+S)/C	
Hybrid Poplar	1	1	0.62	0.17	0.18	29.02
		2	0.69	0.18	0.18	29.19
		3	0.62	0.20	0.20	29.23
	2	1	0.63	0.14	0.15	30.18
		2	0.55	0.17	0.17	30.31
		3	0.63	0.14	0.14	30.20
	3	1	0.69	0.15	0.15	30.17
		2	0.64	0.16	0.16	30.38
		3	0.65	0.16	0.16	30.04
Loblolly Pine	1	1	0.67	0.18	0.18	30.01
		2	0.67	0.19	0.19	29.66
		3	0.65	0.18	0.19	29.59
	2	1	0.76	0.19	0.20	29.01
		2	0.74	0.21	0.22	28.93
		3	0.76	0.21	0.21	29.02
	3	1	0.80	0.24	0.24	28.25
		2	0.82	0.22	0.23	28.29
		3	0.89	0.24	0.24	28.37
Switchgrass	1	1	0.85	0.26	0.27	26.68
		2	0.78	0.25	0.27	26.75
		3	0.86	0.25	0.26	26.73
	2	1	0.85	0.29	0.29	26.54
		2	0.87	0.26	0.27	26.48
		3	0.86	0.30	0.30	26.56

(Table 2.23. Continued)

Biochar						
	Sample	Subsample	Atomic Ratios			HHV (kJ/g, db)
			H/C	O/C	(O+N+S)/C	
Switchgrass	3	1	0.75	0.19	0.22	27.41
		2	0.76	0.20	0.22	27.48
		3	0.74	0.23	0.23	27.52

Table 2.24. Bulk and particle densities and bulk porosities of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar					
	Sample	Subsample	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Bulk Porosity (vol. %)
Hybrid Poplar	1	1	0.13	1.49	91.30
		2	0.13	1.55	91.70
		3	0.13	1.60	91.69
	2	1	0.14	1.37	90.05
		2	0.14	1.38	89.80
		3	0.14	1.36	89.71
	3	1	0.15	1.37	88.95
		2	0.15	1.30	88.35
		3	0.15	1.34	88.90
Loblolly Pine	1	1	0.17	1.42	88.08
		2	0.18	1.35	86.95
		3	0.18	1.40	87.48
	2	1	0.21	1.24	83.23
		2	0.21	1.38	84.89
		3	0.21	1.23	82.89
	3	1	0.21	1.31	84.01
		2	0.21	1.41	84.97
		3	0.21	1.38	84.64
Switchgrass	1	1	0.14	1.29	88.89
		2	0.15	1.26	88.44
		3	0.15	1.24	88.02
	2	1	0.13	1.30	90.07
		2	0.13	1.29	89.87
		3	0.13	1.30	89.83

(Table 2.24. Continued)

Biochar					
Sample	Subsample	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Bulk Porosity (vol. %)	
Switchgrass	3	1	0.14	1.20	88.64
		2	0.14	1.24	88.73
		3	0.14	1.21	88.60

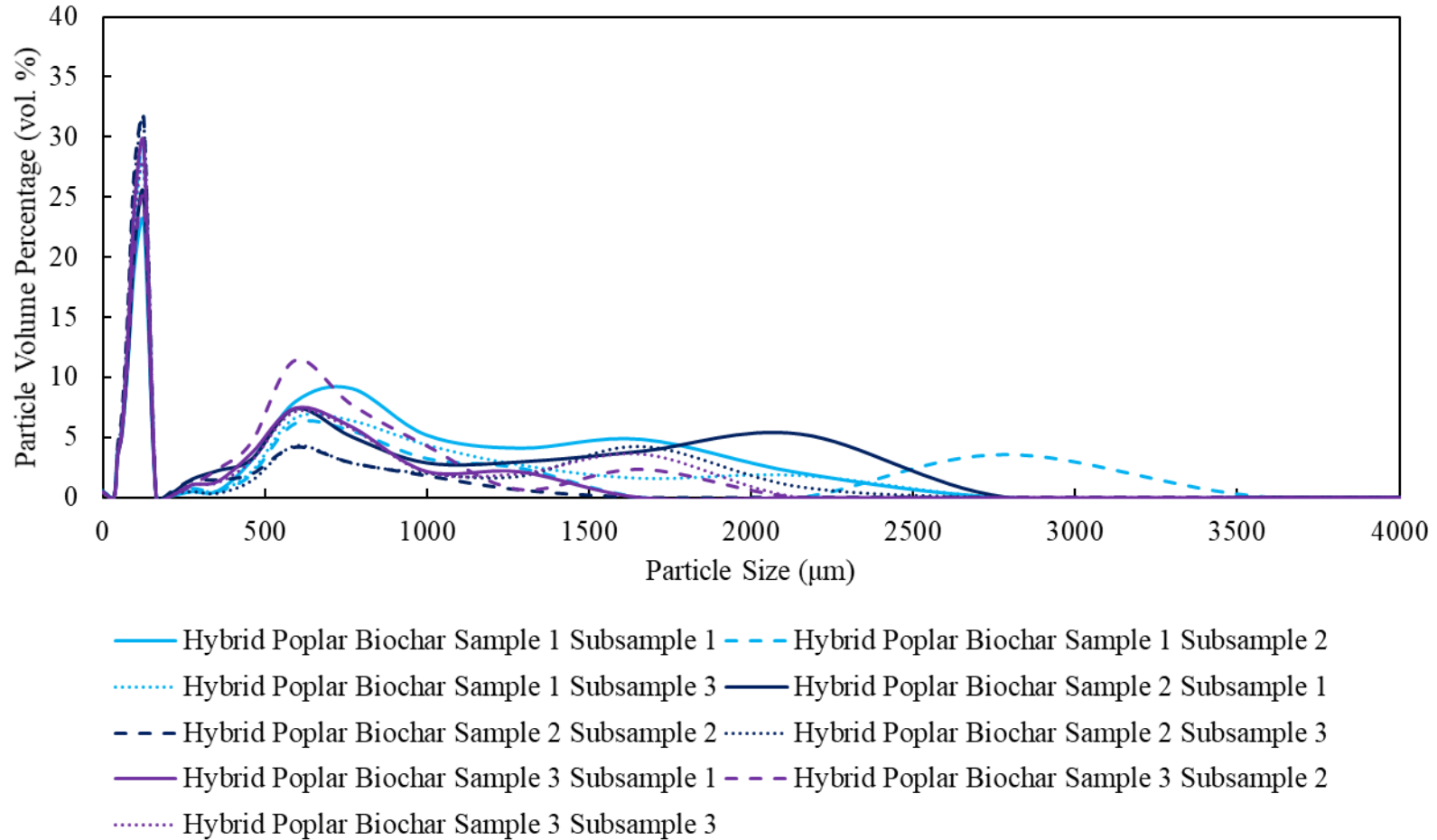


Figure 2.32. Particle size distributions of hybrid poplar biochar.

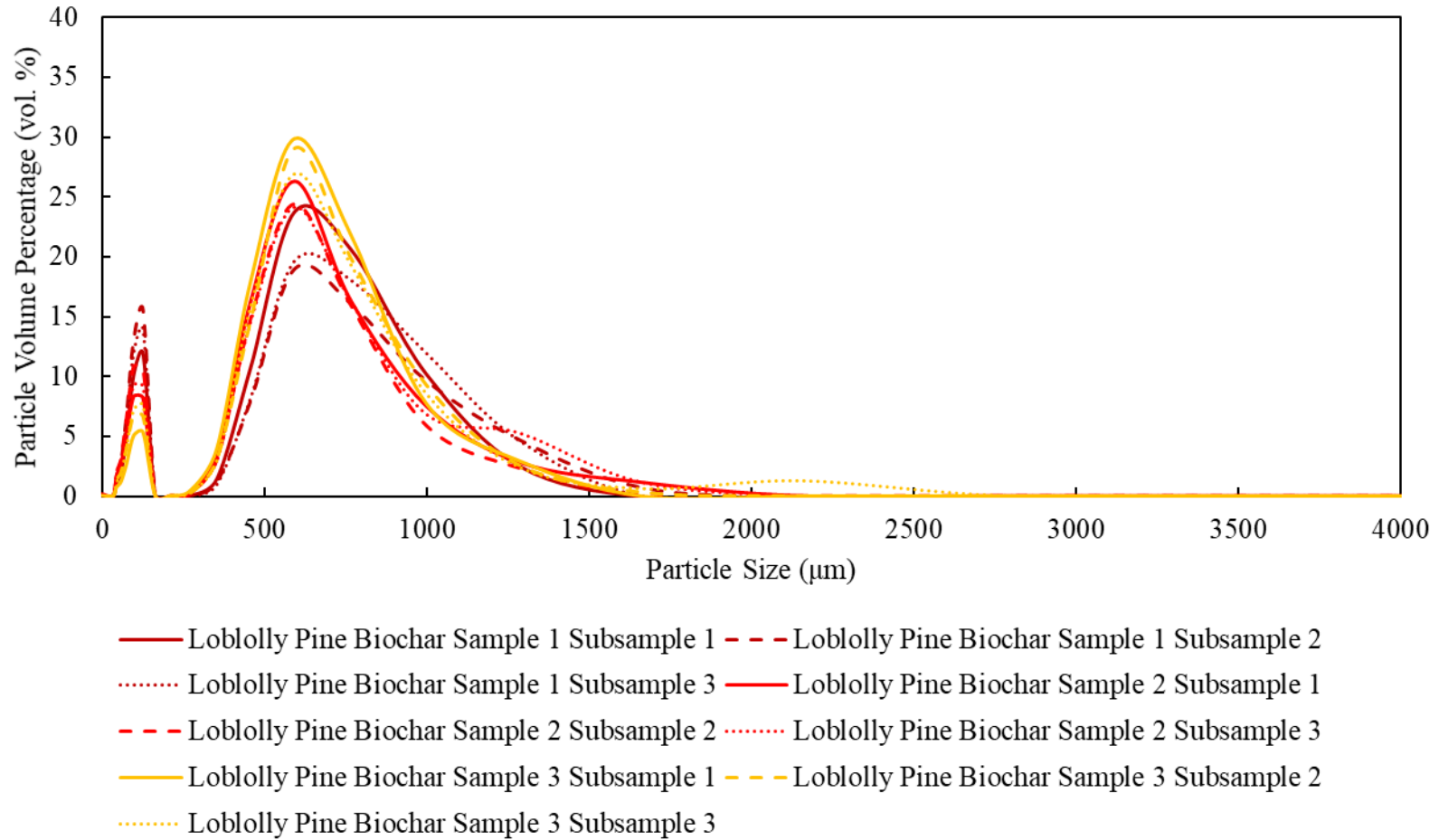


Figure 2.33. Particle size distributions of loblolly pine biochar.

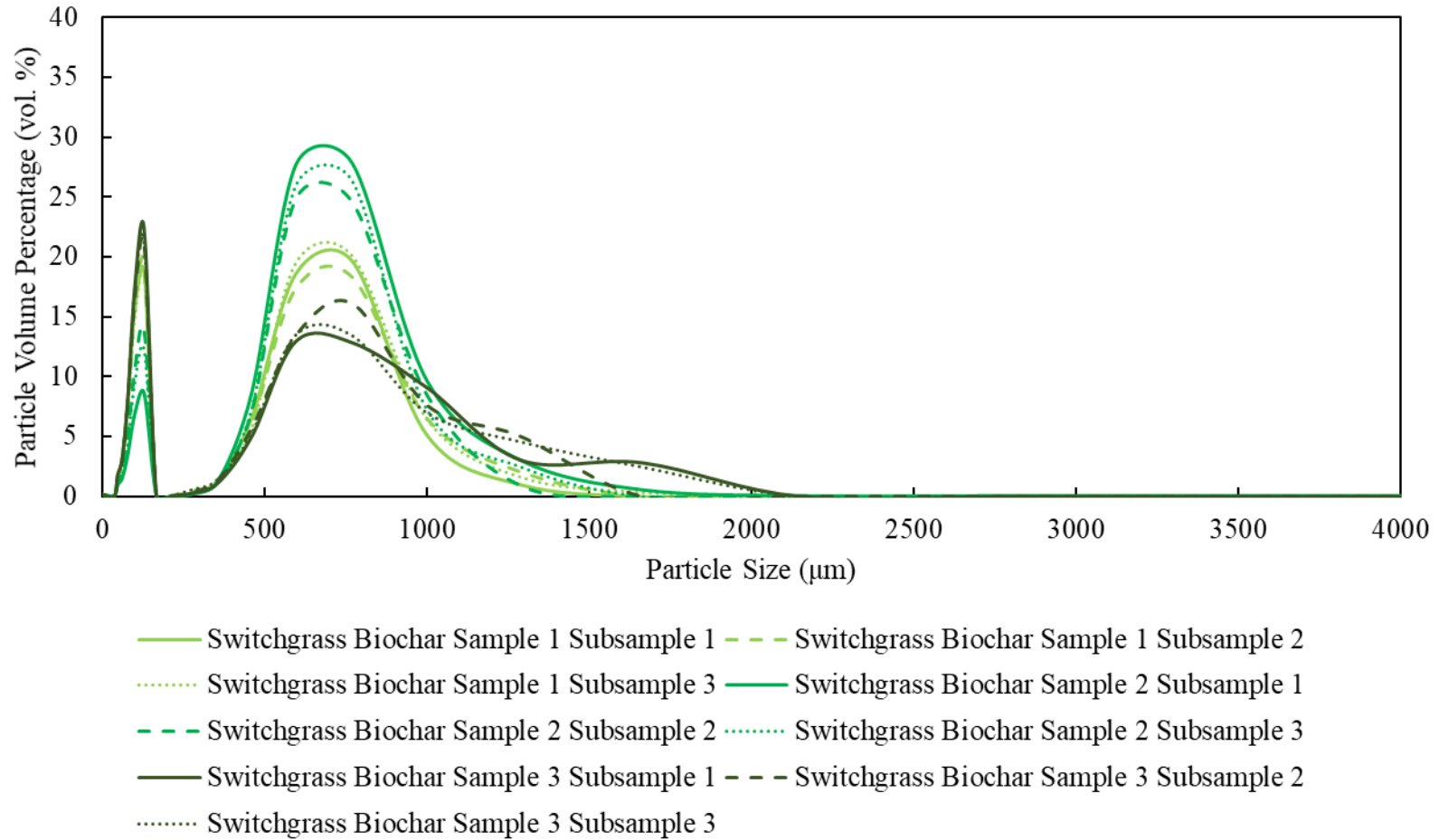


Figure 2.34. Particle size distributions of switchgrass biochar.

Table 2.25. Inorganics analyses of hybrid poplar, loblolly pine, and switchgrass biochars.

		Biochar							
	Sample	Subsample	Inorganics Analysis (mg/kg, db)						
			Al	Ca	Cu	Fe	K	Mg	
Hybrid Poplar	1	1	104.18	6890.98	78.95	3522.06	4866.05	1172.17	83.41
		2	44.02	6416.20	58.79	2739.01	4753.36	1150.73	70.49
		3	66.04	5751.37	65.17	2624.51	4197.71	968.29	67.50
	2	1	24.99	4921.10	18.03	1782.06	3688.74	915.57	54.43
		2	45.70	5420.67	25.88	2812.57	3940.87	1030.26	64.34
		3	52.10	5258.88	43.58	2757.74	3841.53	1106.92	62.37
	3	1	37.28	4955.26	34.97	3218.96	3240.67	915.58	62.21
		2	21.87	4759.78	31.17	3621.11	3130.01	864.12	66.75
		3	20.75	5168.39	39.66	3240.06	3411.56	957.53	64.39
Loblolly Pine	1	1	80.00	3022.60	22.09	2856.50	2270.08	836.73	371.57
		2	82.79	2886.99	14.72	2401.13	2217.17	824.29	377.88
		3	81.32	3325.36	22.47	2754.29	2527.58	917.15	422.44
	2	1	53.81	2302.97	13.43	4370.00	1262.33	624.23	296.40
		2	53.37	2401.50	13.11	4567.58	1360.37	659.95	310.84
		3	69.63	2254.53	20.13	4506.92	1262.94	639.90	294.51
	3	1	174.26	1835.50	21.46	2629.96	969.55	478.37	239.57
		2	37.86	1625.45	8.01	3064.38	882.79	438.82	210.63
		3	68.51	1880.60	9.17	2598.65	995.67	553.26	242.85
Switchgrass	1	1	196.75	3169.96	18.32	2720.07	844.72	1428.66	133.47
		2	55.33	2616.95	13.73	2046.16	704.48	1178.47	112.69
		3	71.16	3102.54	16.10	2394.88	801.27	1389.25	127.23
	2	1	54.37	3645.24	15.33	1411.64	570.39	1246.08	111.31
		2	33.83	2631.90	8.18	1034.48	429.56	901.86	82.13
		3	68.38	3195.19	13.82	2055.33	560.95	1156.07	112.74

(Table 2.25. Continued)

Biochar								
Sample	Subsample	Inorganics Analysis (mg/kg, db)						
		Al	Ca	Cu	Fe	K	Mg	Mn
Switchgrass	3	1	58.74	3913.68	26.74	4692.93	952.67	1857.26
		2	83.65	5811.47	37.82	6428.26	1263.40	2641.44
		3	66.42	4741.12	37.39	5434.61	1084.26	2196.61
Sample	Subsample	Inorganics Analysis (mg/kg, db)						
		Ni	P	S	Si	Zn	Total Inorganics	
Hybrid Poplar	1	1	111.41	795.40	197.69	2275.17	94.69	19396.76
		2	87.28	779.43	198.08	2537.51	79.09	18134.55
		3	96.14	701.26	172.81	2205.99	73.79	16289.31
	2	1	59.97	640.98	158.57	780.30	47.20	12450.96
		2	66.14	703.02	169.90	1759.76	50.92	15387.01
		3	83.86	684.06	169.39	2493.07	53.80	15923.25
	3	1	90.30	605.71	167.90	2323.45	52.95	15099.52
		2	147.32	599.40	166.07	2112.75	50.39	14971.32
		3	103.63	628.89	180.65	2286.66	56.33	15529.62
Loblolly Pine	1	1	77.85	310.99	107.91	9144.91	11.32	18801.57
		2	47.92	288.86	106.07	1353.86	33.31	10346.14
		3	63.11	338.29	97.53	2089.39	37.09	12337.72
	2	1	67.23	218.02	95.39	502.01	25.21	9613.01
		2	67.55	233.02	72.58	1540.14	22.42	11069.41
		3	71.49	210.95	100.37	1869.12	25.85	11115.40
	3	1	46.66	165.30	70.37	1987.07	68.66	8521.44
		2	49.20	165.59	72.28	1922.69	11.88	8323.98
		3	56.53	177.25	84.88	2177.31	18.86	8686.29

(Table 2.25. Continued)

Biochar								
Sample	Subsample	Inorganics Analysis (mg/kg, db)						
		Ni	P	S	Si	Zn	Total Inorganics	
Switchgrass	1	1	88.67	492.18	306.39	11951.68	23.21	20881.90
		2	82.05	413.72	273.72	10547.30	17.02	17647.88
		3	86.14	494.57	319.79	11633.66	23.71	19965.73
	2	1	54.26	470.38	433.78	558.11	46.65	8147.15
		2	37.62	358.50	314.45	10718.45	9.40	16201.86
		3	92.56	424.98	367.89	11094.87	17.33	18735.14
	3	1	128.27	627.27	410.78	14410.03	29.85	26655.77
		2	157.65	885.80	589.48	18861.70	42.58	36168.69
		3	121.22	720.32	461.49	21196.51	36.99	35587.61

Table 2.26. pH, alkalinities, and water contact angles of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar					
	Sample	Subsample	pH	Alkalinity (mmol H ⁺ /g)	Water Contact Angle (°)
Hybrid Poplar	1	1	4.55	0.22	112.00
		2	4.50	0.23	117.70
		3	4.54	0.28	114.60
	2	1	4.34	0.21	118.80
		2	4.33	0.21	116.60
		3	4.30	0.18	121.90
	3	1	4.41	0.17	116.60
		2	4.38	0.18	115.60
		3	4.40	0.13	122.80
Loblolly Pine	1	1	4.13	0.16	116.90
		2	4.17	0.19	120.60
		3	4.16	0.11	117.80
	2	1	3.91	0.12	116.00
		2	3.91	0.12	114.40
		3	3.95	0.10	116.40
	3	1	3.94	0.14	114.50
		2	3.95	0.18	112.30
		3	3.96	0.13	115.60
Switchgrass	1	1	3.89	0.25	120.50
		2	3.93	0.21	112.20
		3	3.94	0.25	119.50
	2	1	3.86	0.31	114.40
		2	3.84	0.27	118.80
		3	3.85	0.28	114.10

(Table 2.26. Continued)

Biochar					
	Sample	Subsample	pH	Alkalinity (mmol H ⁺ /g)	Water Contact Angle (°)
Switchgrass	3	1	4.25	0.30	118.60
		2	4.22	0.22	113.40
		3	4.20	0.27	113.80

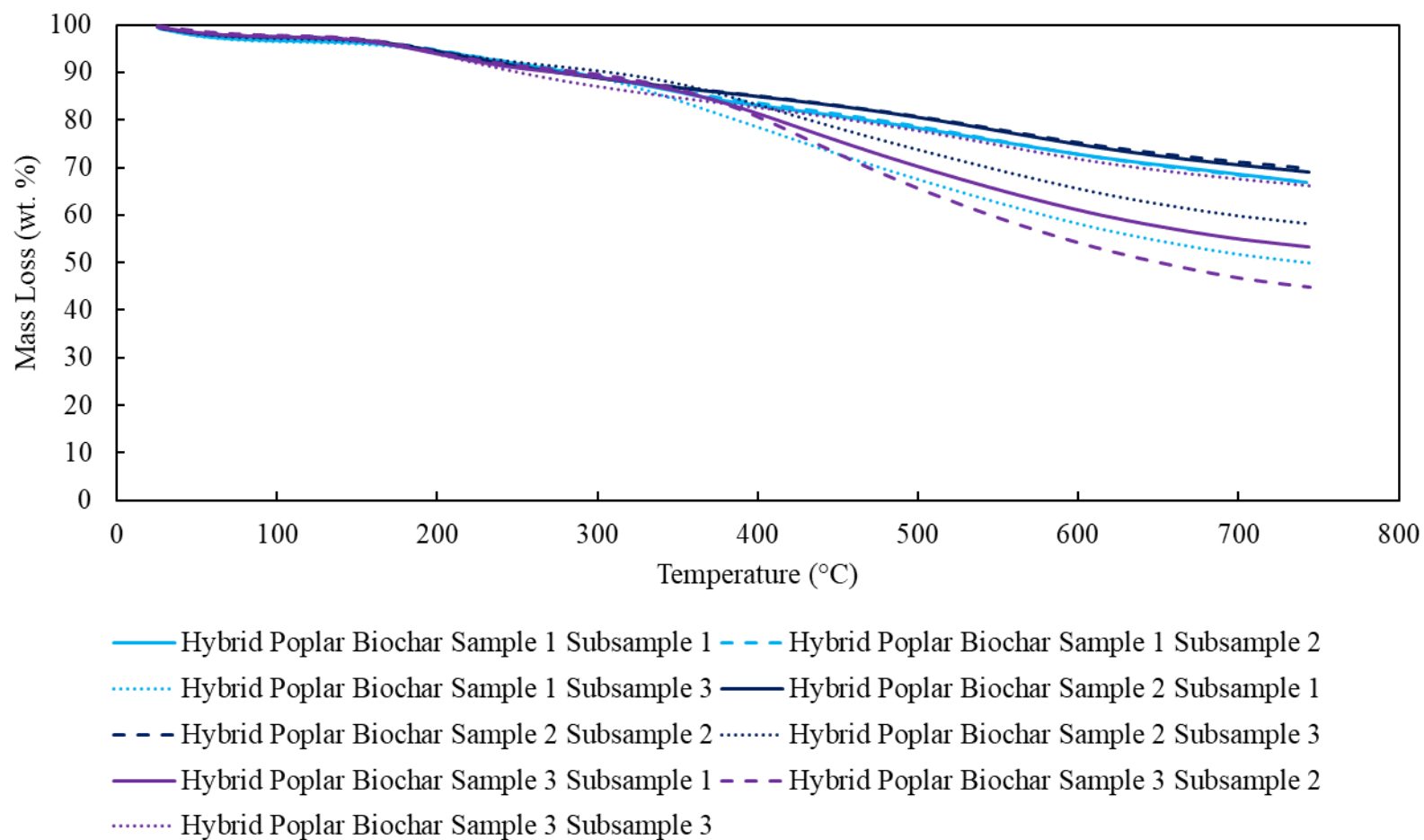


Figure 2.35. Mass loss thermographs of hybrid poplar biochar.

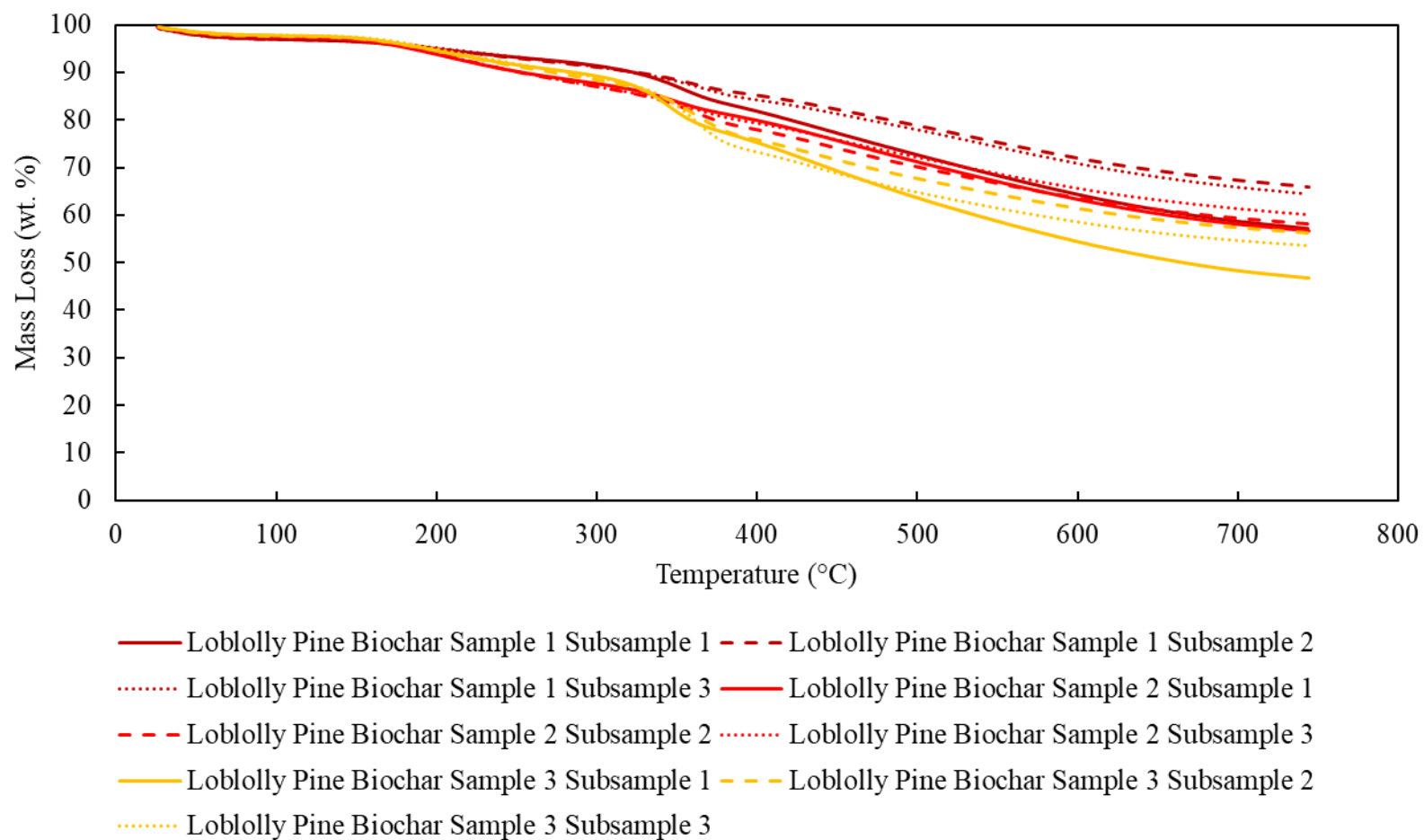


Figure 2.36. Mass loss thermographs of loblolly pine biochar.

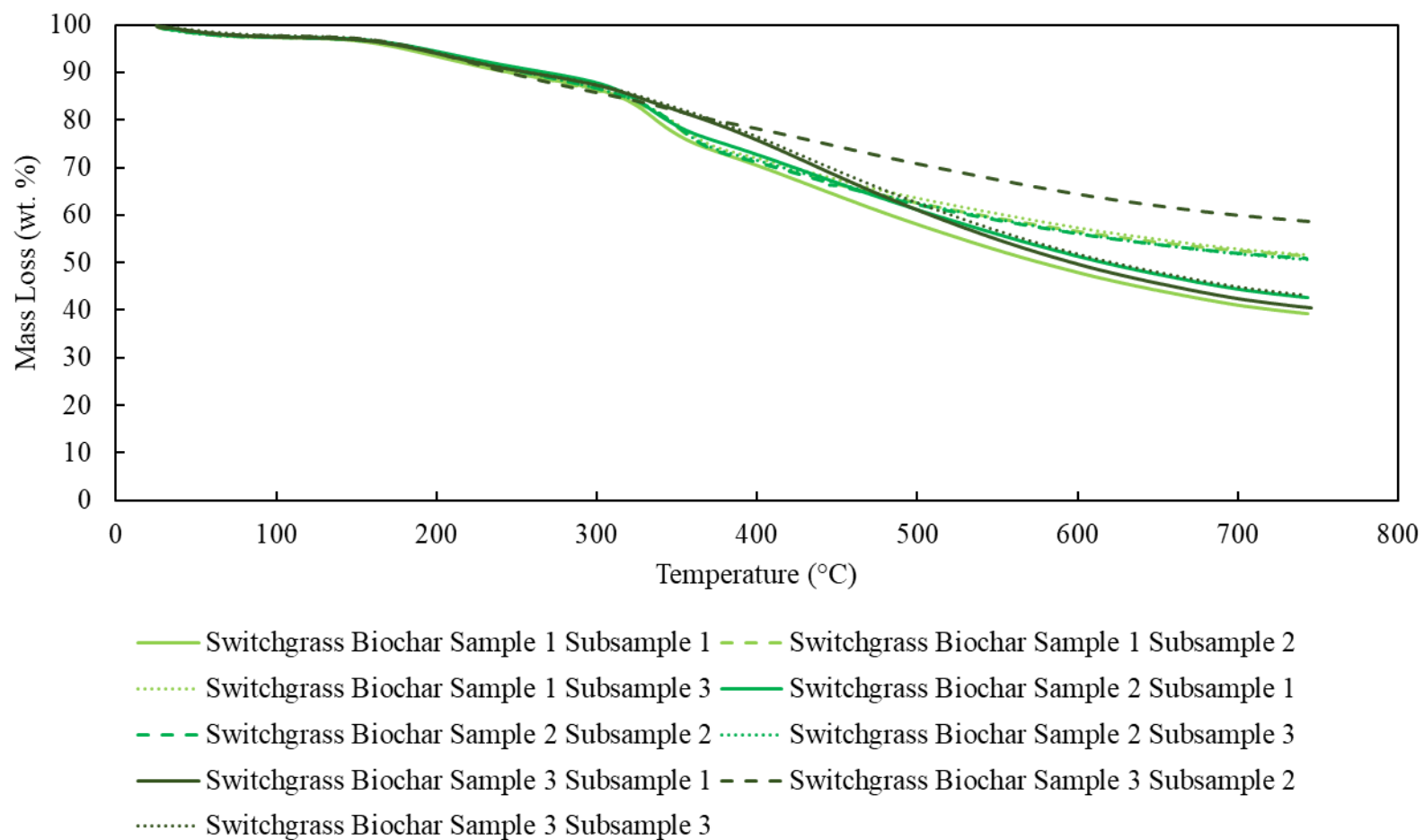


Figure 2.37. Mass loss thermographs of switchgrass biochar.

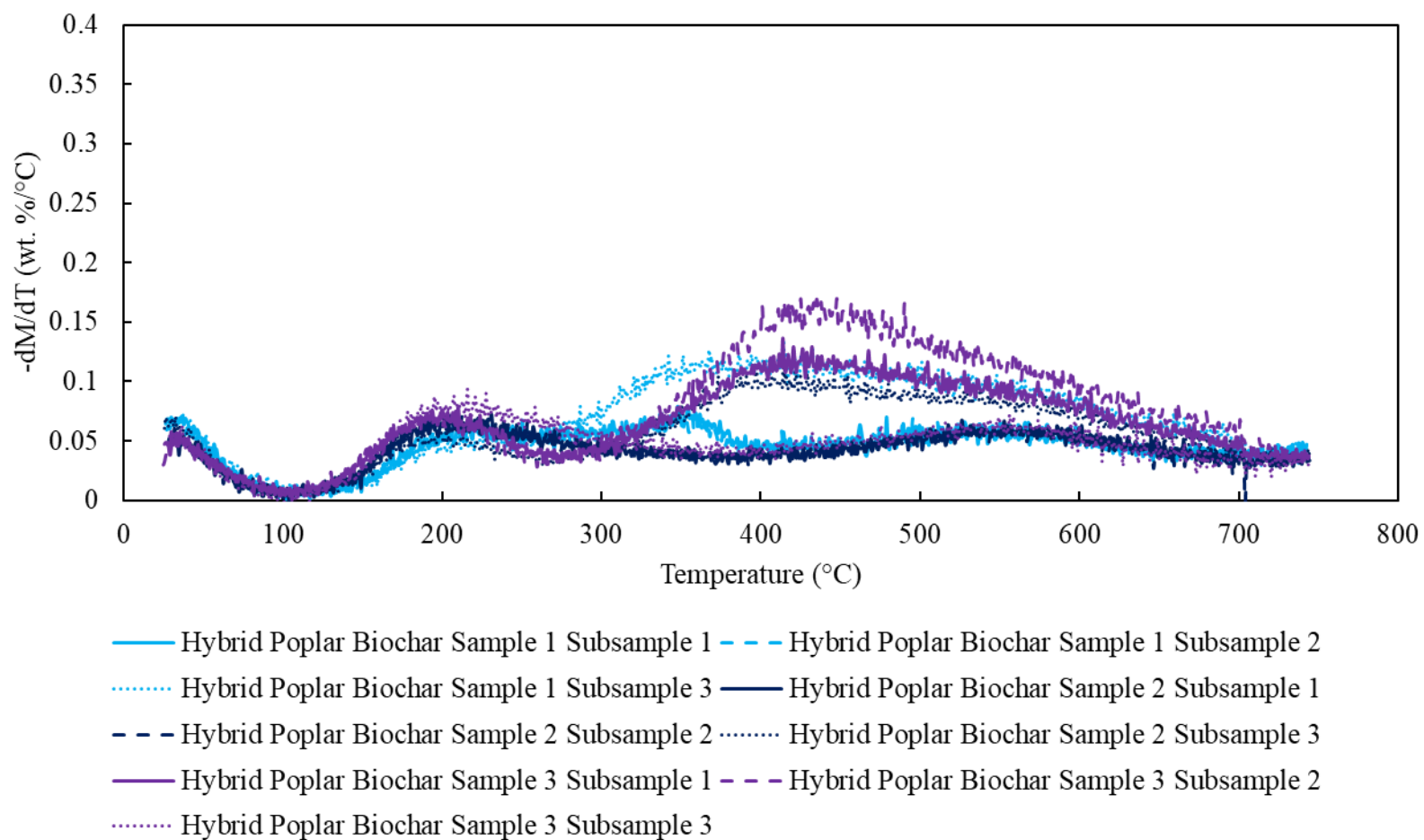


Figure 2.38. Derivative mass loss thermographs of hybrid poplar biochar.

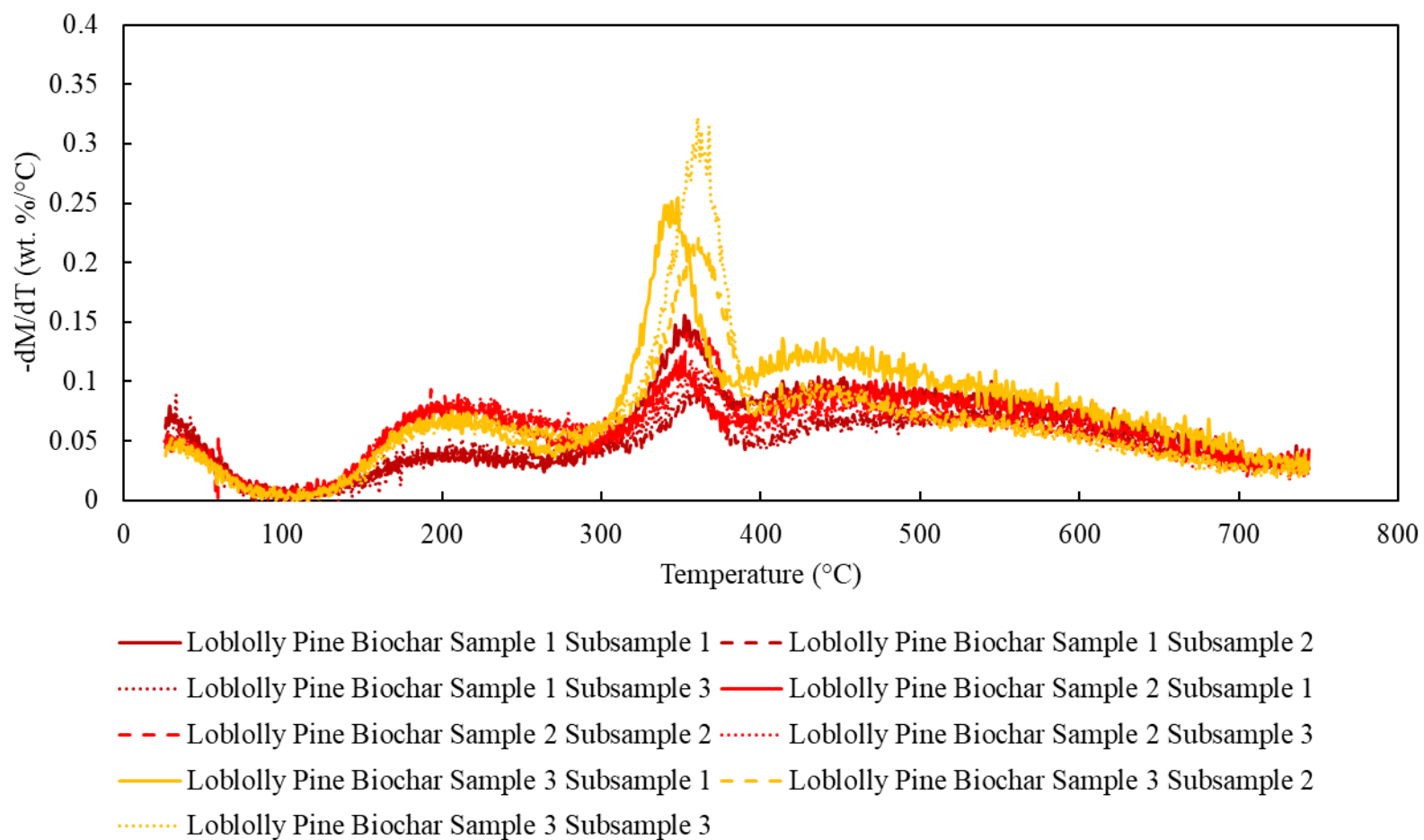


Figure 2.39. Derivative mass loss thermographs of loblolly pine biochar.

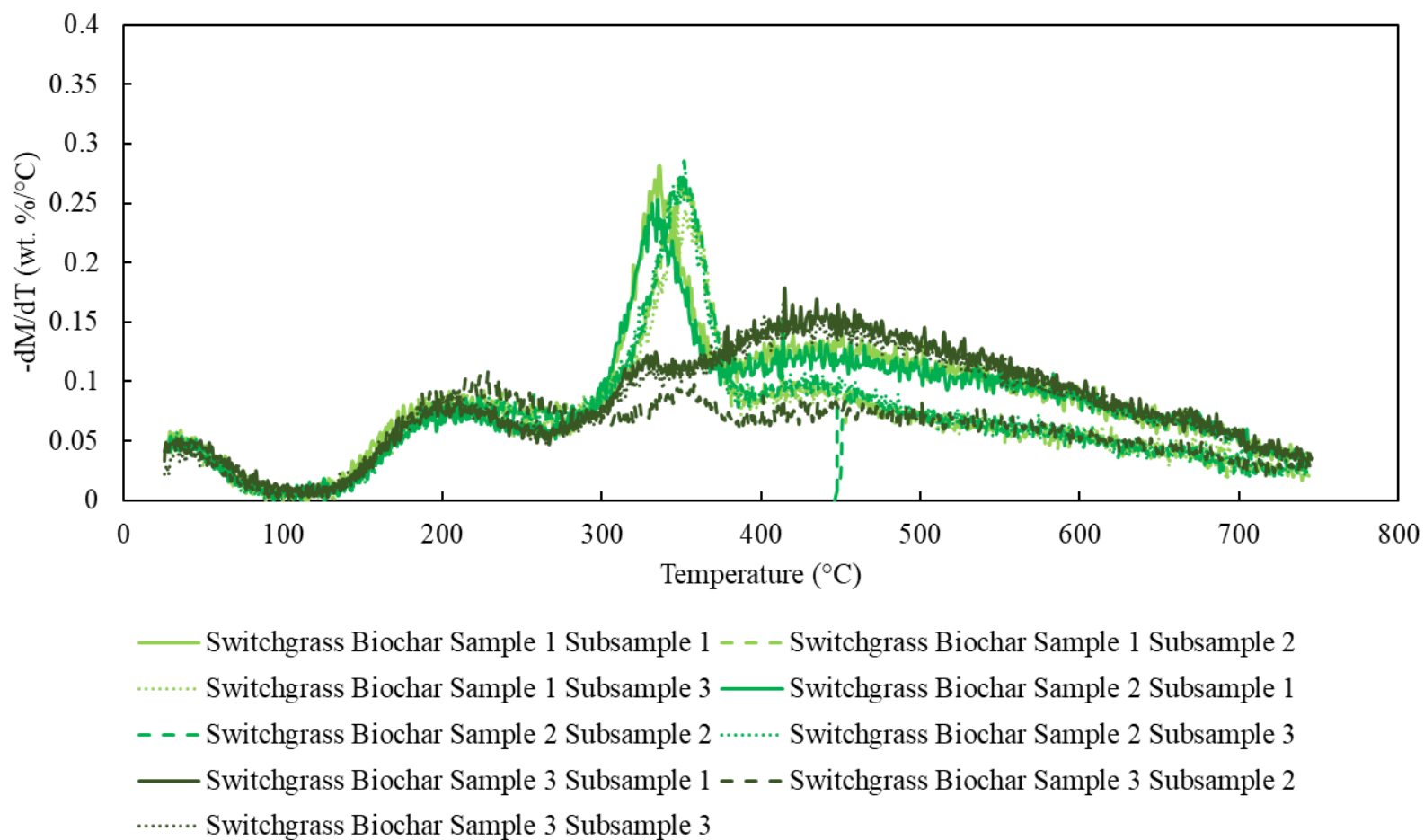


Figure 2.40. Derivative mass loss thermographs of switchgrass biochar.

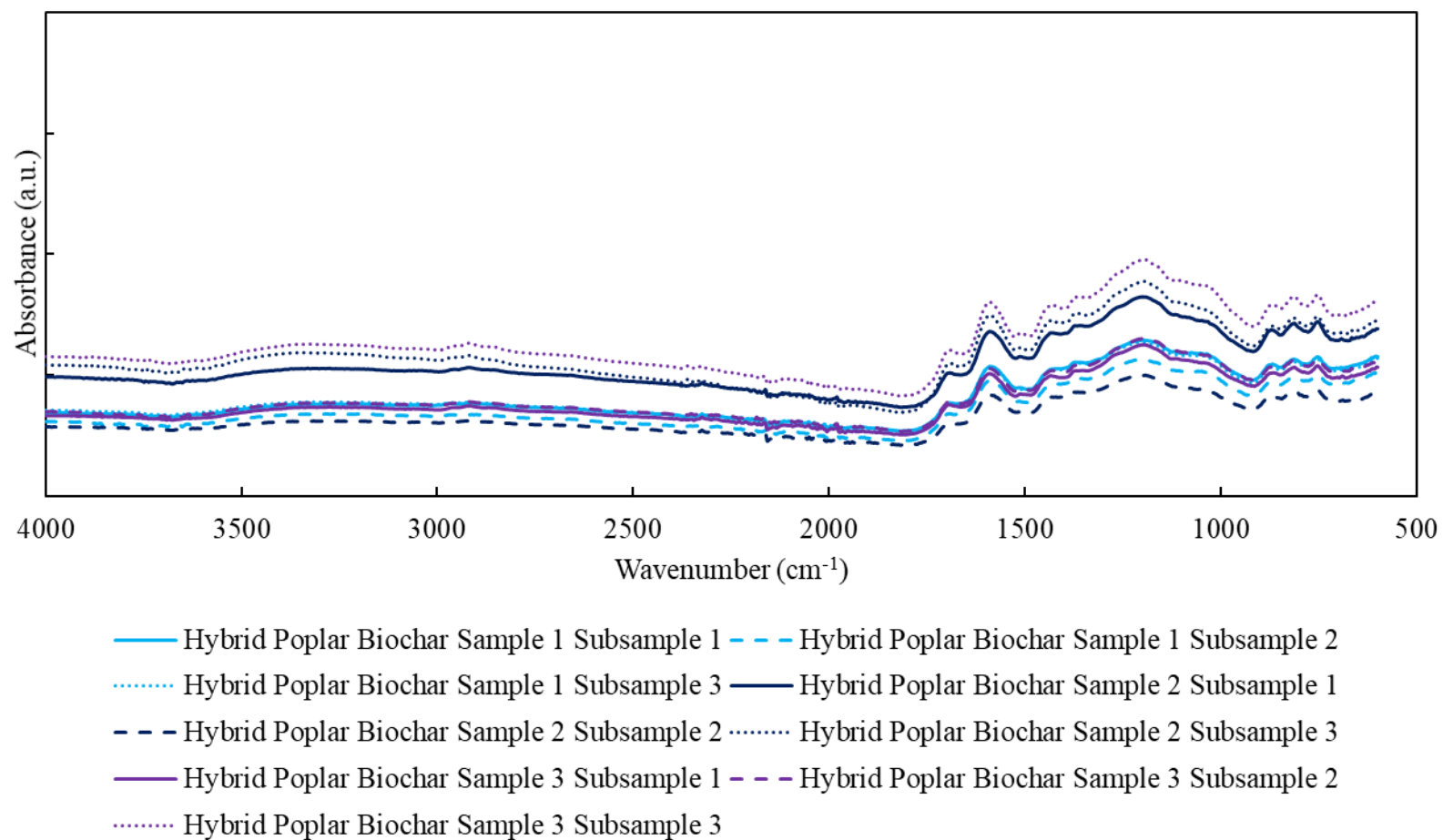


Figure 2.41. FTIR spectra of hybrid poplar biochar.

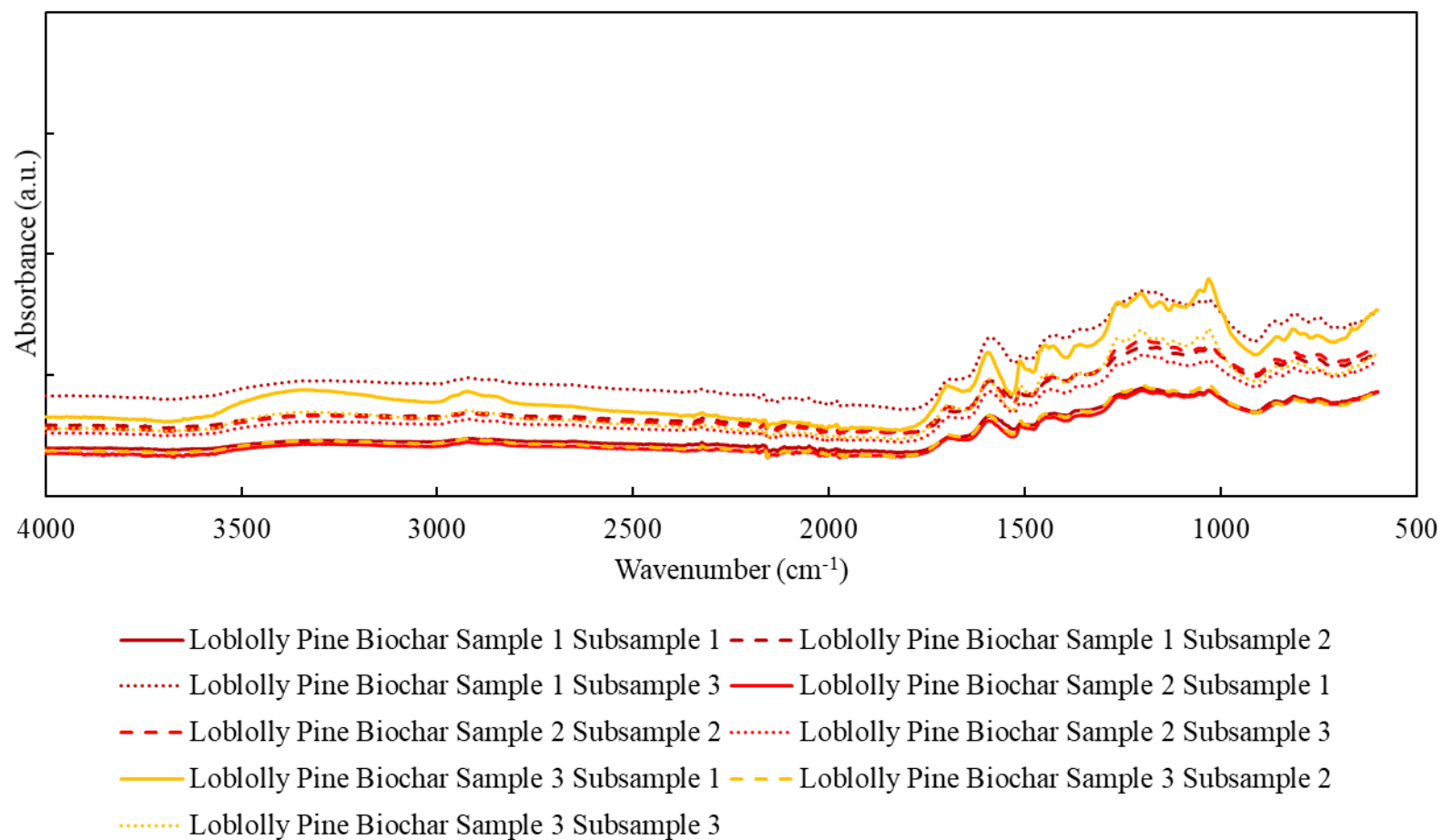


Figure 2.42. FTIR spectra of loblolly pine biochar.

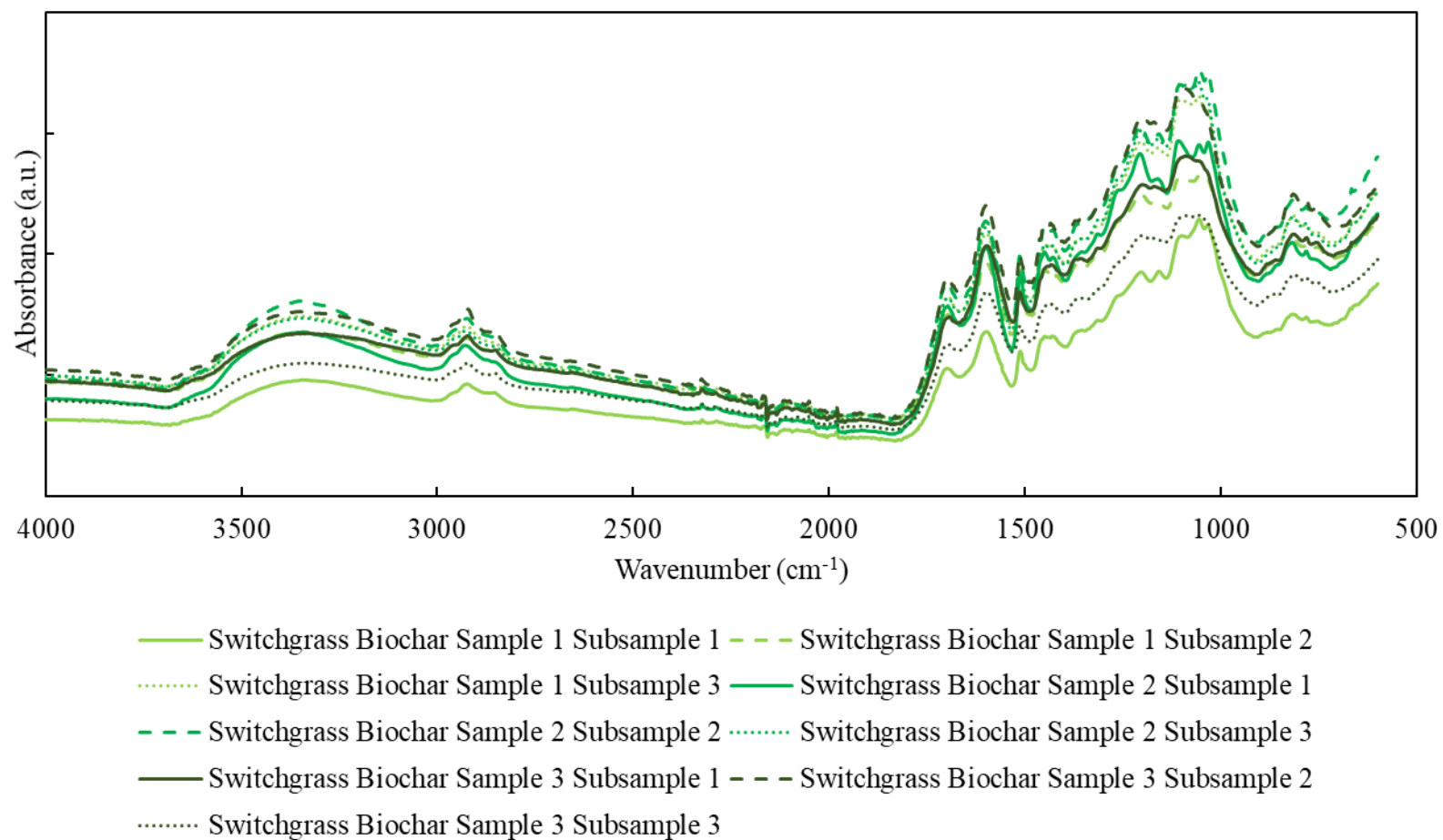


Figure 2.43. FTIR spectra of switchgrass biochar.

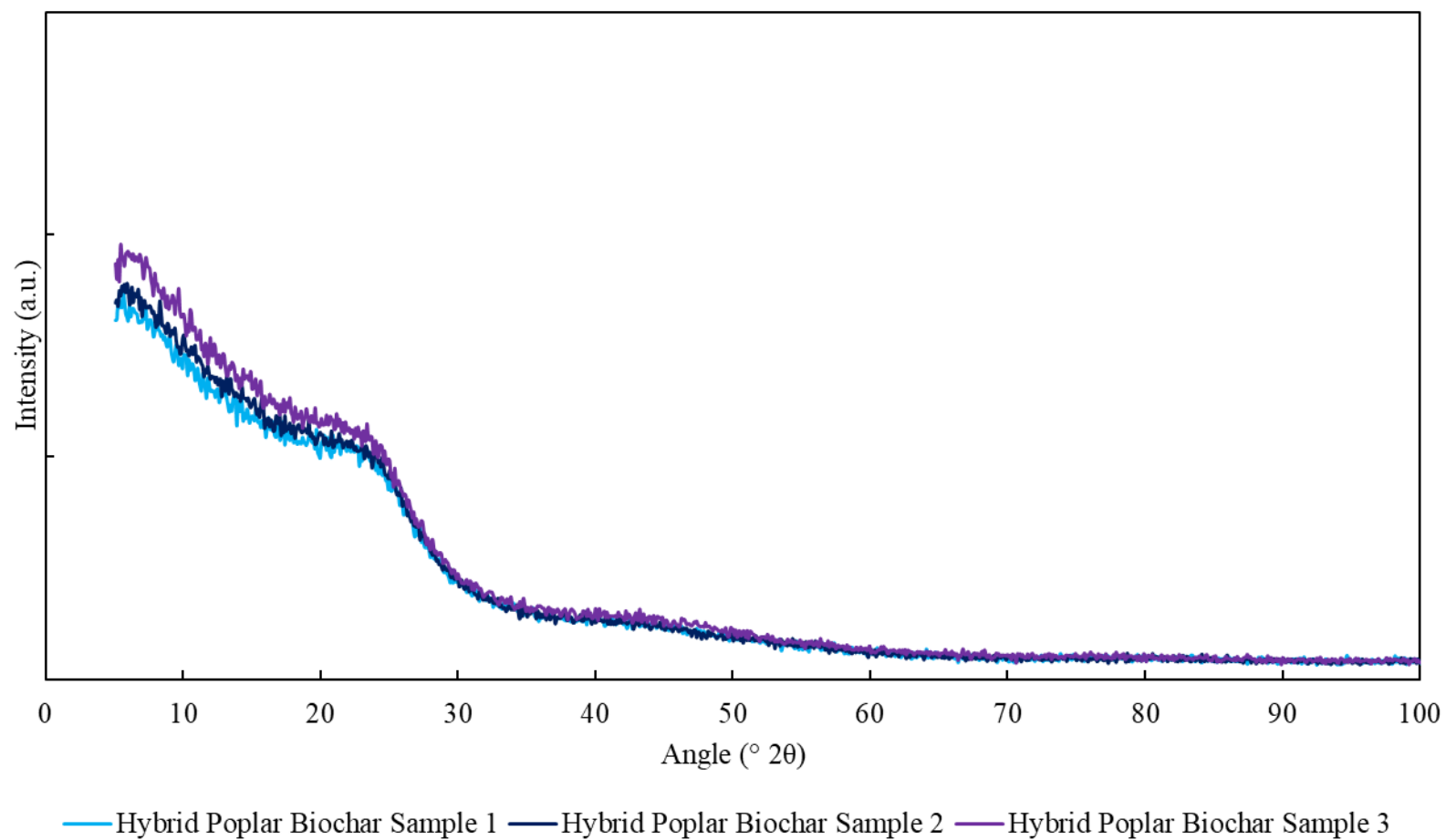


Figure 2.44. XRD diffractograms of hybrid poplar biochar.

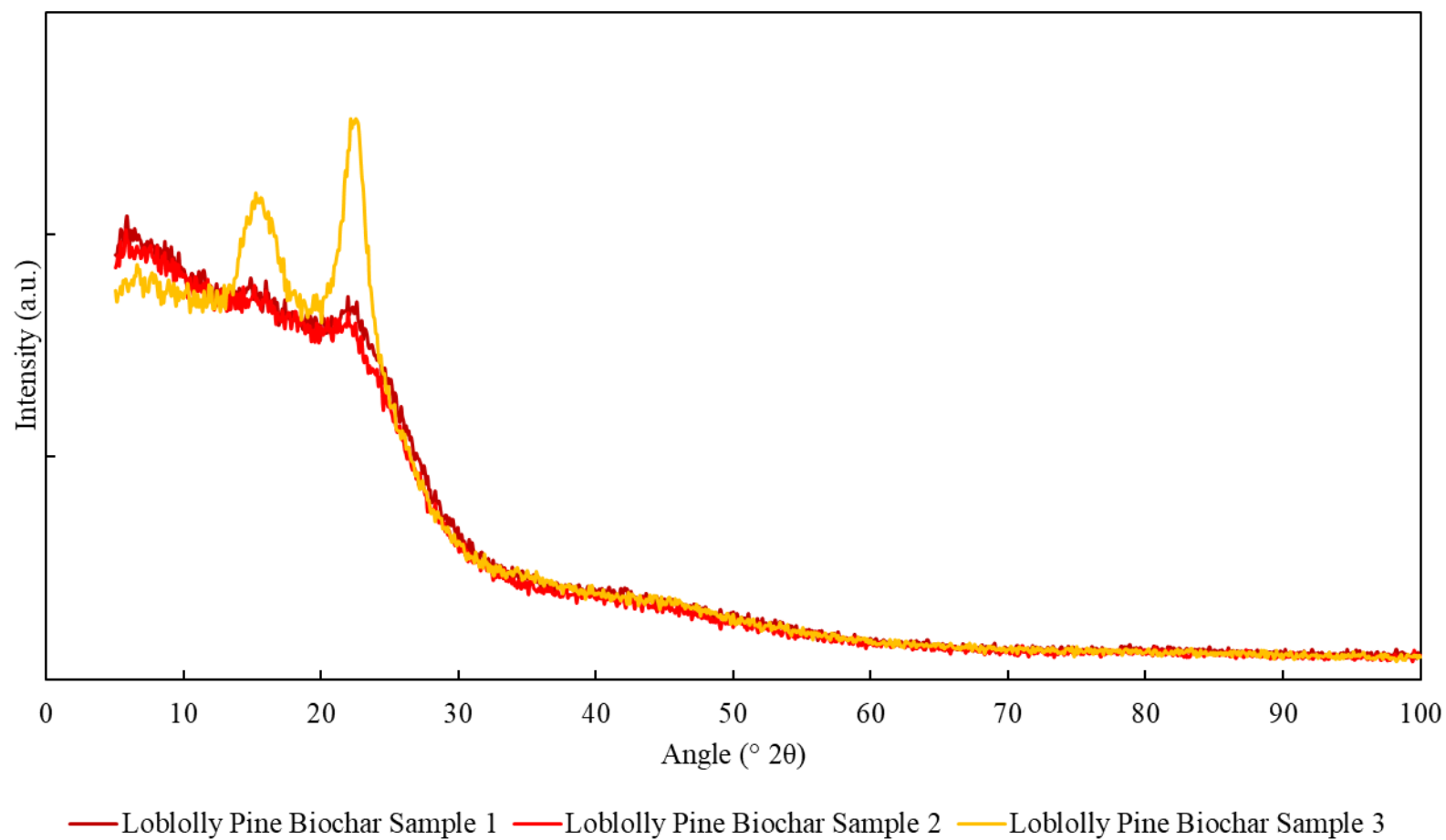


Figure 2.45. XRD diffractograms of loblolly pine biochar.

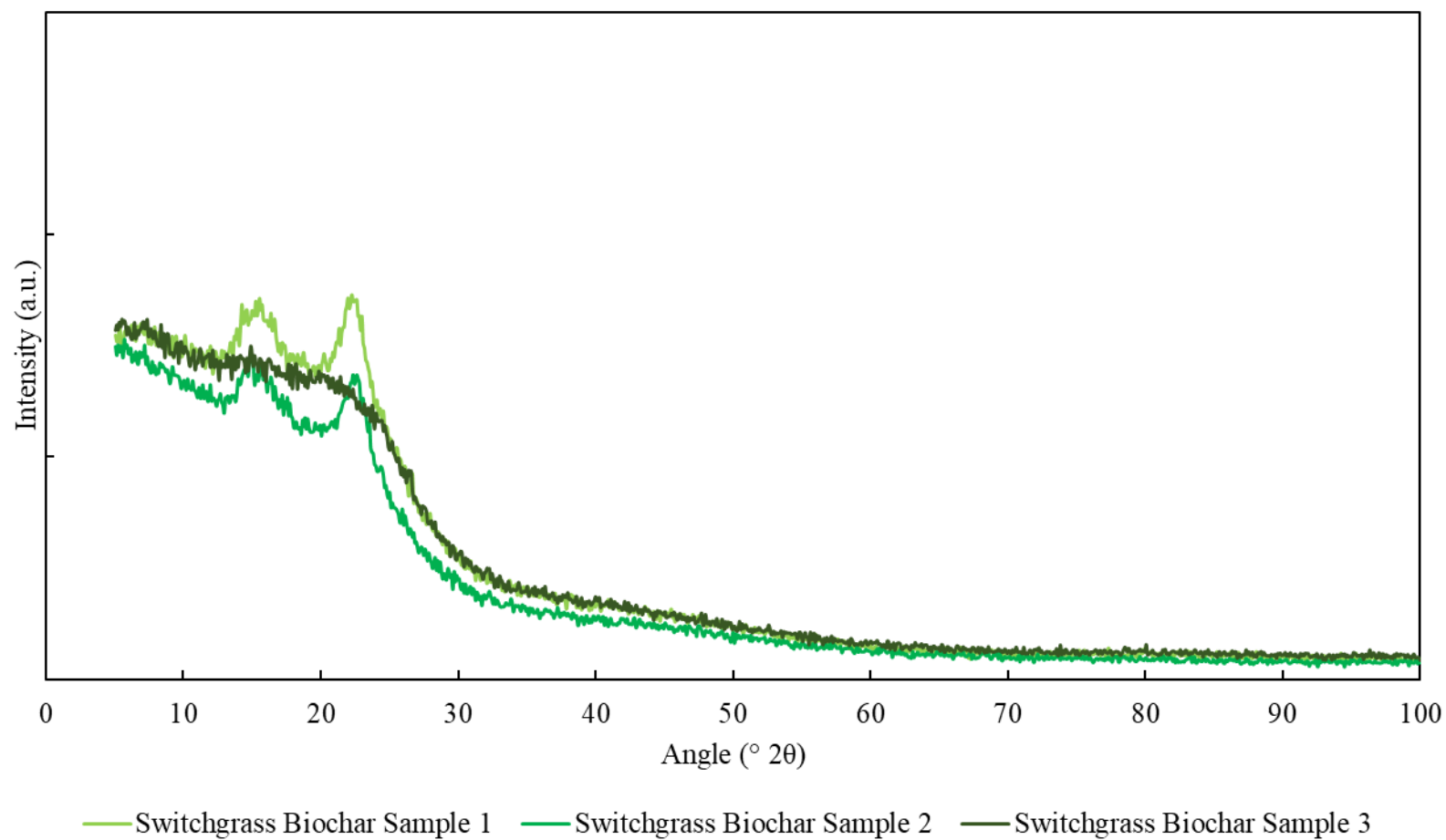


Figure 2.46. XRD of diffractograms of switchgrass biochar.

Table 2.27. Aliphatic interchain spacings, aromatic interlayer spacings, aromatic stacking diameters, aromatic sheet diameters, numbers of stacked aromatic sheets, and aromaticities of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar				
	Sample	Aliphatic Interchain Spacing (Å)	Aromatic Interlayer Spacing (Å)	Aromatic Stacking Diameter (Å)
Hybrid Poplar	1	5	4	14
	2	5	4	14
	3	5	4	13
Loblolly Pine	1	5	4	14
	2	5	4	14
	3	NM	NM	NM
Switchgrass	1	5	4	14
	2	5	4	14
	3	5	4	12
	Sample	Aromatic Sheet Diameter (Å)	Number of Stacked Aromatic Sheets	Aromaticity (%)
Hybrid Poplar	1	18	4	63.97
	2	16	4	63.23
	3	19	3	63.34
Loblolly Pine	1	18	4	76.75
	2	15	4	71.61
	3	NM	NM	NM
Switchgrass	1	14	4	69.27
	2	17	4	69.75
	3	19	3	75.90

NM stands for not measured.

Table 2.28. Textural analyses of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar				
	Sample	Subsample	Textural Analysis	
			Specific Surface Area (m ² /g)	Total Pore Volume (mm ³ /g)
Hybrid Poplar	1	1	1.49	6.08
		2	1.31	4.88
		3	1.65	6.71
	2	1	1.09	3.63
		2	2.08	4.30
		3	1.94	4.85
	3	1	0.84	3.69
		2	0.76	7.16
		3	1.24	3.71
Loblolly Pine	1	1	1.15	3.50
		2	1.56	3.54
		3	1.28	4.11
	2	1	1.25	5.47
		2	1.06	4.55
		3	0.75	1.75
	3	1	0.83	1.92
		2	0.88	2.69
		3	0.75	2.87
Switchgrass	1	1	0.87	5.50
		2	0.87	5.84
		3	1.07	3.67
	2	1	1.13	4.66
		2	1.34	4.60
		3	1.06	4.36

(Table 2.28. Continued)

Biochar				
	Sample	Subsample	Textural Analysis	
			Specific Surface Area (m ² /g)	Total Pore Volume (mm ³ /g)
Switchgrass	3	1	0.84	4.66
		2	0.85	4.52
		3	0.55	3.04

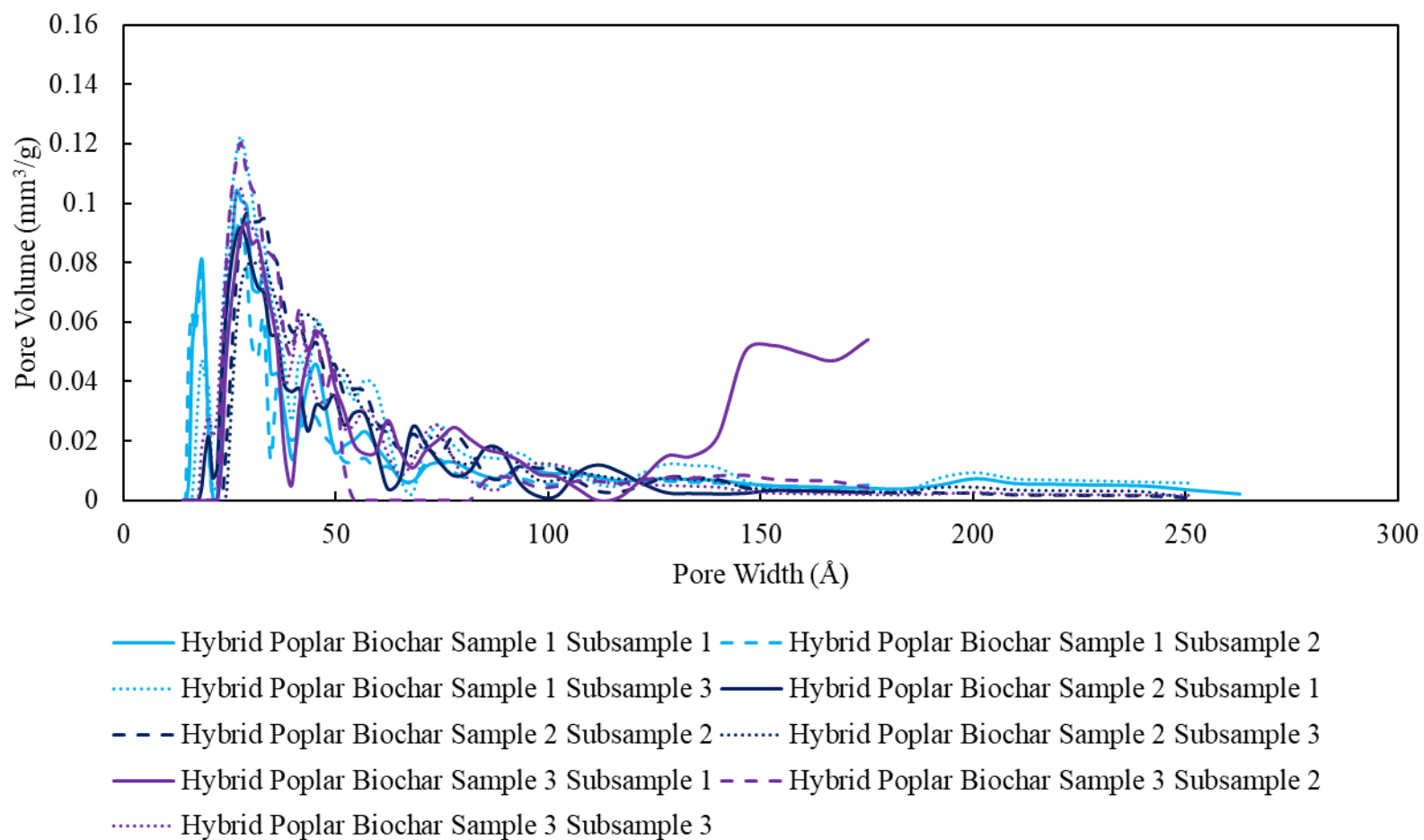


Figure 2.47. Pore width distributions of hybrid poplar biochar.

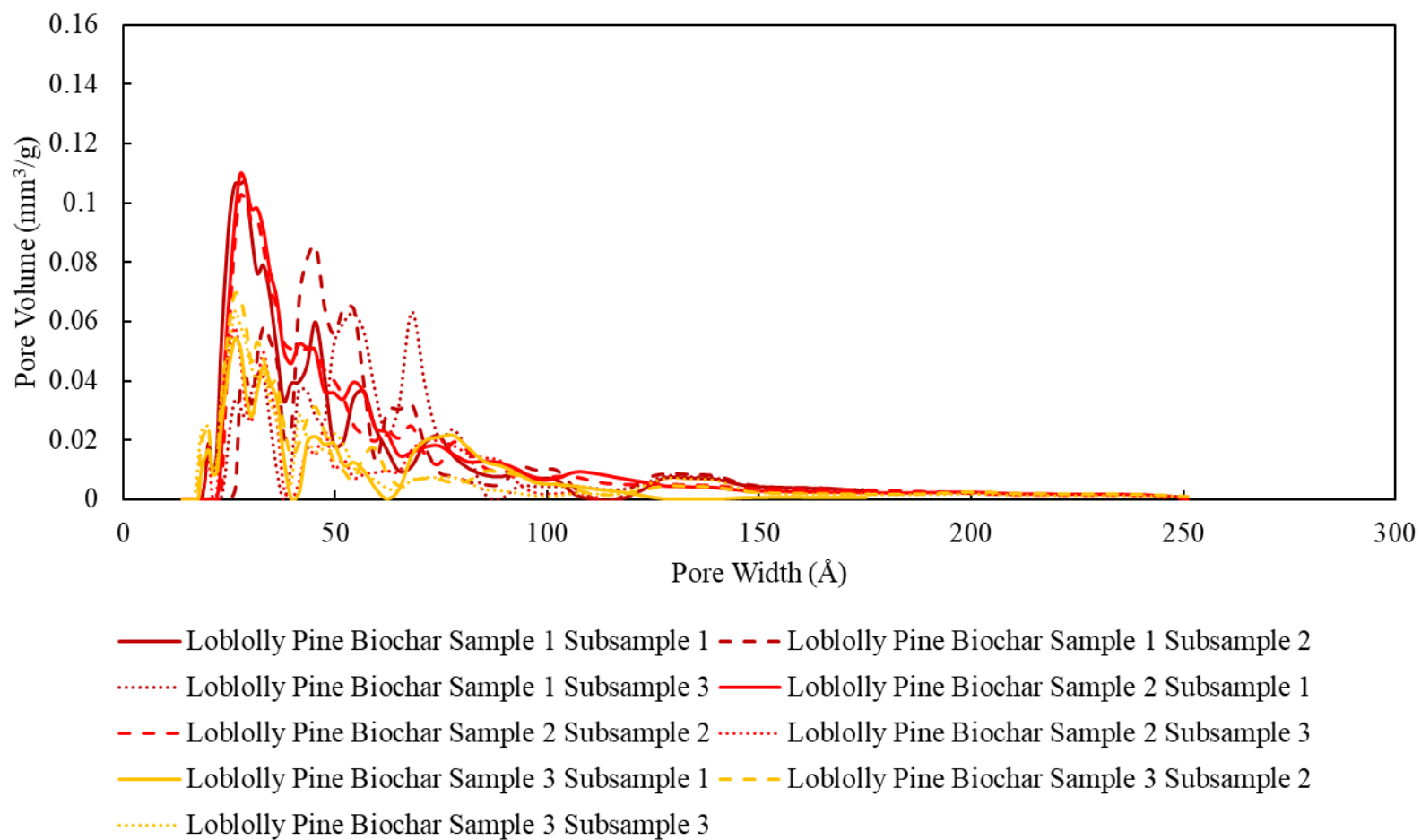


Figure 2.48. Pore width distributions of loblolly pine biochar.

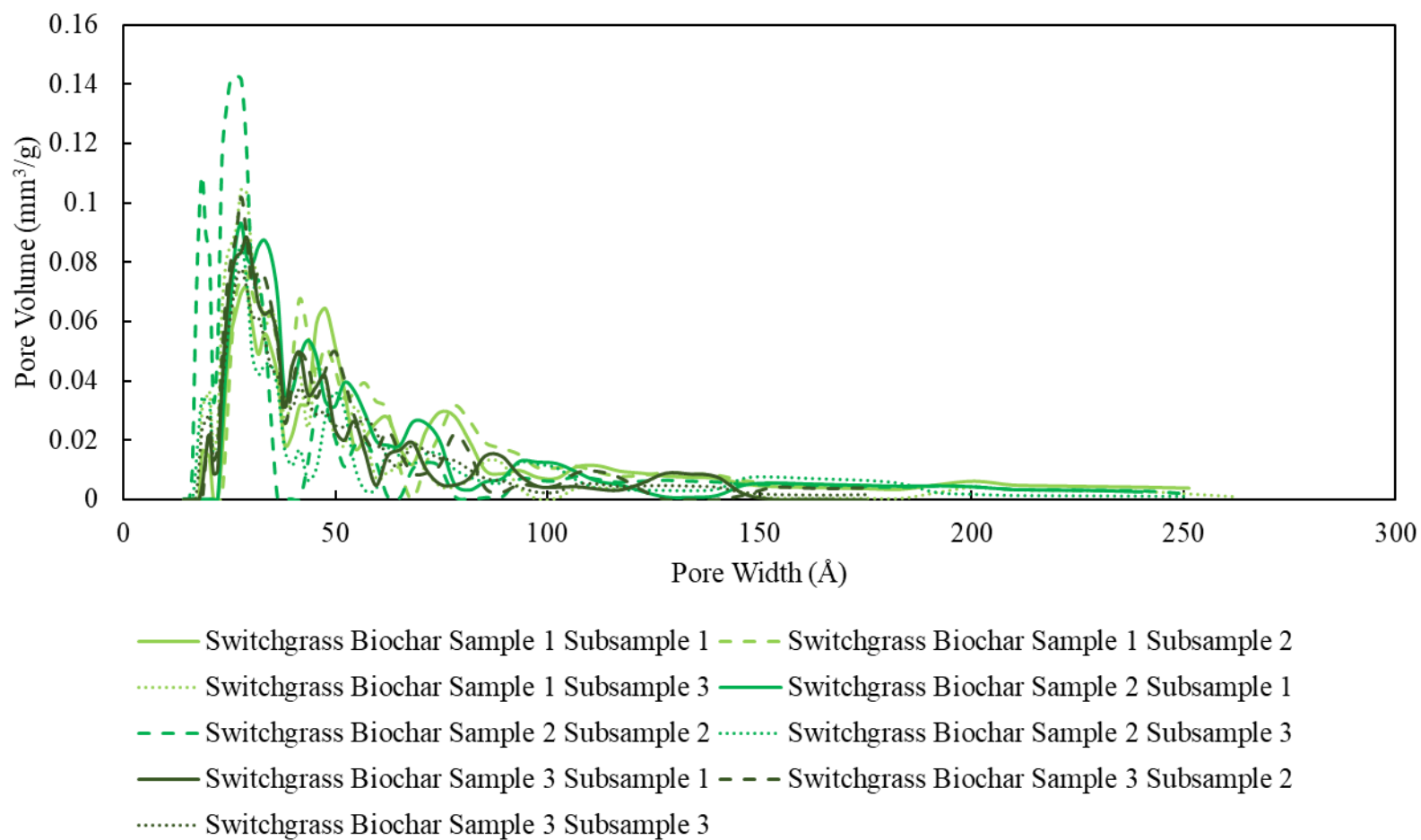


Figure 2.49. Pore width distributions of switchgrass biochar.

Appendix D. CO₂ Adsorption

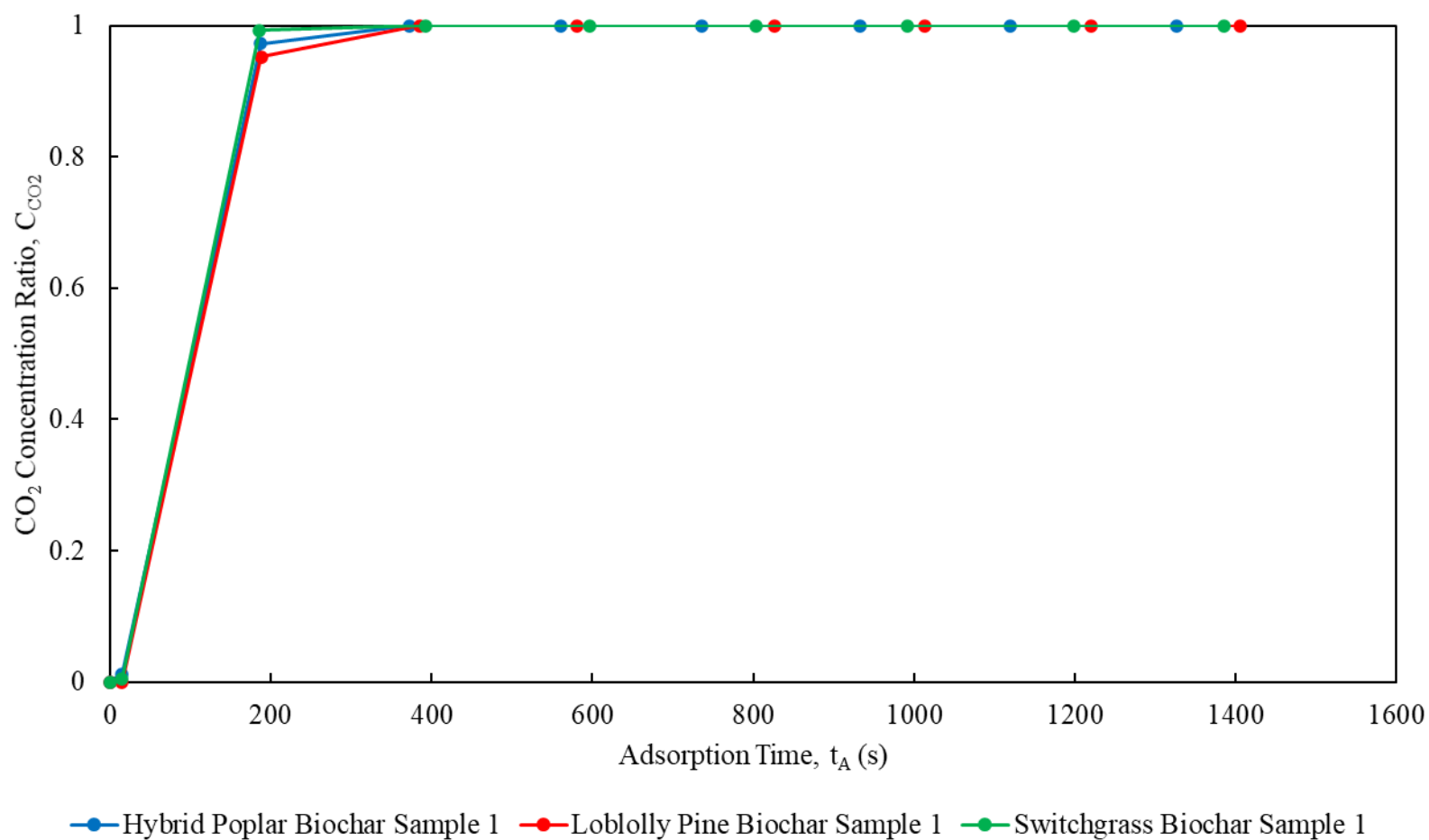


Figure 2.50. CO₂ breakthrough curves of hybrid poplar, loblolly pine, and switchgrass biochars.

Table 2.29. CO₂ adsorption, desorption, and working capacities and regenerabilities of hybrid poplar, loblolly pine, and switchgrass biochars.

Biochar						
	Sample	CO ₂ Adsorption Capacity (mmol/g)	CO ₂ Desorption Capacity (mmol/g)	CO ₂ Working Capacity (mmol/g)	Regenerability (%)	
	Hybrid Poplar	1	0.17	0.14	0.04	77.55
	Loblolly Pine	1	0.18	0.14	0.05	73.51
	Switchgrass	1	0.17	0.12	0.05	71.45

Chapter 3. The Impact of Activation on Biochar Physicochemical Characteristics and CO₂ Adsorption

Abstract

Biochar has been expressed as being a more sustainable porous carbon that can be used for carbon dioxide (CO₂) adsorption than activated carbon (AC). However, biochar must be activated with an activation agent like potassium hydroxide (KOH) to create activated biochar (AB) before biochar can compete with AC in adsorbing CO₂. This study intended to determine the impact of KOH activation on the physicochemical characteristics and CO₂ adsorption behavior of loblolly pine AB compared to those of loblolly pine biochar. KOH activation experiments were conducted by mixing loblolly pine biochar with KOH at a KOH/biochar mass ratio of 3 and carbonizing the dried mixture at 800°C for 2 h to create loblolly pine AB. Physicochemical characteristics of the loblolly pine biochar and AB involving carbon (C) content, alkalinity, and aromaticity were measured or retrieved using standard or published techniques. CO₂ adsorption and desorption experiments were performed in a CO₂ adsorption system at 35°C using 5 vol. % CO₂ balanced with nitrogen gas (N₂) flowing at 50 mL/min. C content increased in AB compared to biochar from 74.52 to 93.74 wt. %, dry, ash-free basis (dafb) indicating the formation of pores in AB. Aromaticity fluctuated from 74.18-81.19% but did not differ between biochar and AB showcasing that AB still contained mostly aromatic C atoms in its graphitic C crystallites which functioned as pores in AB. Consequently, CO₂ adsorption capacity increased in AB compared to biochar from 0.18 to 0.51 mmol/g representing a 183% improvement in CO₂ adsorption capacity. These results demonstrated that biochar CO₂ adsorption capacity was improved by KOH activation.

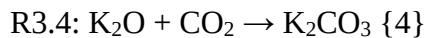
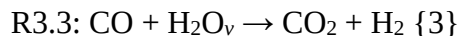
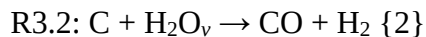
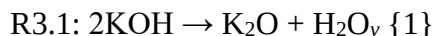
3.1 Introduction

AC is the foremost carbon-based porous solid or porous carbon used for CO₂ adsorption. However, biochar has been gaining momentum over AC in this application because biochar can be created from an assortment of renewable precursors and wastes while AC is formed from coal. Apart from being more sustainable, biochar generation involves much lower precursor or feedstock costs compared to those of AC production since the coal, lignite, peat, and polymers used to create AC are more expensive to source relative to the different biomasses and wastes used to produce biochar [1][2]. Additionally, AC is produced through a multi-step process that includes carbonization and activation. Coal is carbonized through thermal decomposition in the absence of oxygen gas (O₂) at temperatures ranging from 400-1000°C which generates carbonized char. This char is then activated through either physical or chemical activation using an activating agent at temperatures reaching from 500-1000°C which produces AC. The AC formed through activation has improved porosity and different surface chemistry compared to those of the carbonized char created during carbonization [3][4][5][6]. Conversely, biochar is produced through pyrolysis at temperatures varying from 300-700°C. As a result, the production costs of AC and biochar differ because of the higher temperatures needed during carbonization and the activating agent required for activation. However, while the production of biochar involves lower temperatures and is a simpler process, biochar has a low CO₂ adsorption capacity. This poor CO₂ adsorption behavior is mostly associated with biochar having a low porosity and amount of basic functional groups since CO₂ adsorption is dependent on surface area, pore volume, pore size, and alkalinity. Consequently, biochar activation has gained considerable attention as a means of developing environmentally friendly and sustainable porous carbons in the form of AB which has a high porosity and amount of basic functional groups comparable to those of AC [1][2][3][7][8].

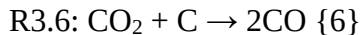
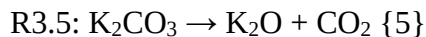
Concerning the kinds of activation, physical activation of biochar entails heating biochar at temperatures ranging from 800-1000°C in the presence of a mild oxidizing gas like steam, O₂, or CO₂ which enhances biochar surface area, pore volume, and pore size. In contrast, chemical

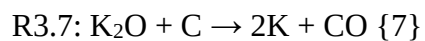
activation of biochar involves heating biochar at temperatures varying from 500-900°C in the presence of an inorganic compound such as an acid, alkali, or oxidant which magnifies biochar surface area, pore volume, and pore size. These improvements to biochar porosity through physical and chemical activation occur because the mild oxidizing agent and inorganic compound catalyze the oxidation of fixed carbon in biochar which transforms fixed carbon into volatile matter. The volatile matter then experiences devolatilization and is evolved from biochar which either enlarges existing biochar pores or creates new pores in biochar [1][2][3][4][5][8]. Yet, AB formed through chemical activation typically has a higher CO₂ adsorption capacity relative to that of AB generated through physical activation. This difference has been attributed to chemical activation developing a higher amount of narrow micropores in biochar than physical activation which has been conveyed to greatly influence CO₂ adsorption [3][7]. Furthermore, there is a wide array of inorganic compounds that have been demonstrated as being effective activating agents for chemical activation including hydrochloric acid (HCl), hydrogen peroxide (H₂O₂), phosphoric acid (H₃PO₄), KOH, sodium hydroxide (NaOH), and zinc chloride (ZnCl₂), among others. Out of these activating agents, KOH has become a popular chemical activating agent because biochar activated with KOH has been denoted to have a higher micropore volume and, hence, higher CO₂ adsorption capacity than those of biochar activated with other chemical activating agents [3][7][9].

The activation process of biochar with KOH occurs through a series of reactions that includes dehydration, water-gas, water-gas shift, and potassium carbonate (K₂CO₃) formation reactions. At 400°C, KOH is dehydrated through a dehydration reaction which creates potassium oxide (K₂O) and water vapor (H₂O_v). Fixed carbon in biochar is then oxidized by H₂O_v through a water-gas reaction which forms carbon monoxide (CO) and hydrogen gas (H₂). Afterwards, CO is oxidized by H₂O_v through a water-gas shift reaction which generates CO₂ and H₂. K₂O then reacts with CO₂ through a K₂CO₃ formation reaction which makes K₂CO₃. These reactions continue until KOH is depleted which occurs at 600°C. The separate reactions involved in KOH activation of biochar at temperatures below 700°C are depicted below [7][9]:



The activation process then continues through a few more reactions that involve decomposition and reduction reactions. At 700°C, K₂CO₃ is decomposed through a decomposition reaction which produces K₂O and CO₂. CO₂ is then reduced by fixed carbon in biochar through a reduction reaction which creates CO. Similarly, K₂O and K₂CO₃ are reduced by fixed carbon in biochar through reduction reactions which form potassium (K) and CO. These reactions continue until K₂CO₃ is exhausted which occurs at 800°C. The various reactions involved in KOH activation of biochar at temperatures above 700°C are displayed below [7][9]:





Based on these different reactions, the activation process is composed of three disparate reaction mechanisms, namely chemical activation, physical activation, and C lattice expansion. During chemical activation, separate K-containing compounds carve into the biochar C structure through redox reactions. These reactions form micropores in biochar which develop porosity in the relatively nonporous biochar C structure [7][9]. For physical activation, H_2O_v and CO_2 etch the biochar C structure through gasification and reduction reactions. These reactions enlarge existing micropores and generate new micropores in the biochar C structure which further enhance the porosity developed in the biochar C structure during chemical activation [7][9]. In C lattice expansion, K intercalates between layers of distorted graphene sheet segments that comprise the biochar C structure. This phenomenon increases the interlayer spacing between adjacent layers in the biochar C structure which expands the biochar C lattice. Such expansion further magnifies the porosity developed in the biochar C structure during physical activation. Moreover, even after intercalated K and other K-containing compounds are removed from AB by washing AB with HCl and water (H_2O), the biochar C lattice remains deformed and retains micropores produced through KOH activation [3][7][9]. Therefore, AB has a higher CO_2 adsorption capacity compared to that of biochar because of the extensive microporosity created in AB during KOH activation. The CO_2 adsorption capacities of porous carbons created through KOH activation like AB have also been indicated to increase as the KOH/nonporous carbon mass ratio increases from 2-4 [7]. However, at 900°C , porosity formed through KOH activation in porous carbons is destroyed because of the continued growth of existing micropores and production of new micropores which causes pores to coalesce into larger pores such as mesopores. This detrimental effect is called over-activation and diminishes the improvement to porous carbon surface area that arises during KOH activation as micropores are created [7]. Such differences in the physicochemical characteristics of porous carbons like AB at slightly different activation conditions convey that further understanding of how KOH activation influences porous carbon physicochemical characteristics is needed to take advantage of KOH activation for CO_2 adsorption. Accordingly, this study aims to determine the impact of KOH activation on the physicochemical characteristics and CO_2 adsorption behavior of loblolly pine AB compared to those of loblolly pine biochar.

3.2 Materials and Methodology

3.2.1 Materials and KOH Activation

Ultra high purity (UHP) grade N_2 and a 5 vol. % CO_2 balanced with N_2 mixture were purchased from Airgas Inc. KOH (powder, for synthesis), HCl solution (2 M), NaOH solution (0.5 M), phenolphthalein solution (0.5 wt. % in ethanol:water (1:1)), potassium bromide (KBr) (Fourier-transform infrared (FTIR) grade, $\geq 99\%$ trace metals basis), and a molecular sieve adsorbent (0.425-0.600 mm particle size, 5 Å pore size) were purchased from Sigma-Aldrich. In terms of biochar, loblolly pine biochar was created by pyrolyzing loblolly pine biomass through intermediate pyrolysis in a semi-pilot scale auger pyrolysis system at 500°C and 350°C/h under N_2 flowing at 10 L/min with a residence time of about 13 min. The biochar was sieved to particle sizes between 0.250 and 0.425 mm before KOH activation. For each KOH activation experiment,

approximately 10 g of loblolly pine biochar were mixed with KOH at a KOH/biochar mass ratio of 3 in a close to 7 M KOH solution with deionized (DI) water for 30 min on an automatic shaker table at 25°C and 120 revolutions per minute (rpm). The mixture was then filtered using 5 µm filter paper and dried at 105°C for 24 h. Afterwards, the dried mixture was loaded into a glass column in between pieces of quartz wool and the loaded column was heated to 800°C at nearly 25°C/min and held at 800°C for 2 h under N₂ flowing at 25 mL/min [10][11][12]. Following activation, the loaded column was cooled to 25°C and loblolly pine AB was removed from the glass column. To open blocked pores in the AB and remove K-containing compounds formed on the AB during activation, the AB was washed with a mixture of 100 mL of 0.1 M HCl and 500 mL of DI water twice and filtered using 5 µm filter paper. AB was then repeatedly washed with 500 mL of DI water until the filtrate pH was roughly 7 to neutralize the AB [10][11][12]. Then, the AB was dried at 105°C for 24 h, weighed, and stored in a plastic bag. A small amount of AB was taken from the bag as a sample and stored for characterization. AB yield ($Yield_{Activated\ Biochar}$) (wt. %, dry basis (db)) was calculated using the following formula:

$$F3.1: Yield_{Activated\ Biochar} = \frac{Mass_{Activated\ Biochar}}{Mass_{Biochar}} \times 100 \quad (1)$$

where $Mass_{Activated\ Biochar}$ is the mass of activated biochar (g) and $Mass_{Biochar}$ is the mass of biochar (g). Triplicate experiments were performed using loblolly pine biochar created across 3 pyrolysis experiments resulting in 3 samples of biochar each with 3 subsamples and 3 samples of AB being obtained for characterization. As such, characterization was completed on 9 subsamples of biochar and 3 samples of AB resulting in 9 measurements per characterization technique for biochar and 3 measurements per characterization technique for AB unless otherwise stated. Before each experiment was conducted, the glass column was replaced to minimize cross-contamination.

3.2.2 Biochar and AB Characterization

Loblolly pine biochar and AB were characterized according to the following analyses and measurements on either a wet (wb), db, or dafb where appropriate. Proximate analysis including moisture, ash, volatile matter, and fixed carbon contents (wt. %, db) was accomplished based on ASTM D1762-84 [13]. Ultimate analysis involving C, hydrogen (H), oxygen (O), and nitrogen (N) contents (wt. %, dafb) was conducted by analyzing about 2 mg of biochar using an Elementar vario MICRO cube elemental analyzer, having Hazen Research, Inc. analyze the AB, and calculating O content by difference. Atomic ratios encompassing H/C, O/C, and (O+N)/C were calculated after ultimate analysis and used as indications of aromaticity, hydrophilicity and carbonization, and polarity, respectively [14][15]. A van Krevelen diagram was developed using H/C and O/C following ultimate analysis. Bulk density (ρ_b) (g/cm³) was measured using about 12-26 g of each biochar or AB according to ASTM E873-82 using the following formula [16]:

$$F3.2: \rho_b = \frac{Mass_{Biochar}}{Volume_{Biochar}} \quad (2)$$

where $Mass_{Biochar}$ is the mass of biochar or AB (g) and $Volume_{Biochar}$ is the volume of biochar or AB (cm³). Particle density (ρ_p) (g/cm³) was measured by loading approximately 0.7-0.8 g of biochar or AB into a Quantachrome ULTRAPYC 1200e automatic gas pycnometer and analyzing biochar or AB using helium gas (He) [17]. Bulk porosity (ϕ) (vol. %) was calculated using bulk and particle densities using the following formula [17]:

$$\text{F3.3: } \varphi = (1 - \frac{\rho_b}{\rho_p}) \times 100 \quad (3)$$

Inorganics analysis including aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), K, magnesium (Mg), manganese (Mn), nickel (Ni), phosphorus (P), S, silicon (Si), zinc (Zn), and total inorganics contents (mg/kg, db) was performed by acid digesting biochar or AB and analyzing the biochar or AB digestate using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Acid digestion was accomplished by mixing about 0.1-0.3 g of biochar or AB with 8 mL of 70 vol. % nitric acid (HNO₃) solution, 0.2 mL of 51 vol. % hydrofluoric acid (HF) solution, 3 mL of H₂O₂ solution, and 3 mL of 35 vol. % HCl solution. The mixture was then heated to about 180-210°C for 100 min in an Anton Paar Multiwave 5000 microwave reaction system before being cooled and heated again using these same conditions to ensure that the biochar or AB was completely digested. After acid digestion, the biochar or AB digestate was neutralized by mixing the cooled solution with 1 mL of 4 vol. % boric acid (H₃BO₃) solution, diluted with DI water to 50 mL, filtered using 0.2 µm filter paper, and analyzed using a PerkinElmer Optima 7300 DV ICP-OES spectrometer [18]. Alkalinity (mmol H⁺/g) was measured by mixing about 1 g of biochar or AB with 50 mL of 0.05 M HCl solution, shaking the mixture on an automatic shaker table for 72 h, and filtering the mixture using 0.2 µm filter paper. Two drops or 10 µL of phenolphthalein indicator were poured into the extracts and the extracts were stirred. The extracts were then titrated to a pH of approximately 7 using 0.05 M NaOH solution and the amount of HCl titrated was calculated. Similarly, 50 mL of 0.05 M HCl solution were titrated to a pH of close to 7 using 0.05 M NaOH solution and the amount of HCl titrated was determined as a blank. The difference in the amounts of HCl titrated for the extracts and blank was recorded as the alkalinity of the biochar or AB [19]. Thermal analysis involving thermogravimetric (TGA) and derivative thermogravimetric analysis (DTG) was conducted by loading close to 5-7 mg of biochar or AB into a crucible, heating the loaded crucible from 25-750°C at 5°C/min under N₂ flowing at 20 mL/min in a PerkinElmer Pyris 1 TGA thermogravimetric analyzer, and holding the loaded crucible at 750°C for 5 min. Mass loss thermographs were obtained for TGA and derivative mass loss thermographs were calculated and smoothed using a standard algorithm for DTG [20]. FTIR spectroscopy was performed by grinding nearly 1 mg of biochar or AB using a mortar and pestle, mixing the ground biochar or AB with roughly 220-250 mg of KBr, pressing the mixture into a pellet using a 13 mm die set and hydraulic press, and analyzing each KBr-pelleted biochar or AB using a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with a KBr beamsplitter and deuterated triglycine sulfate (DTGS) detector. Pellets were also made using only KBr and analyzed as blanks. FTIR spectra were collected by accumulating 64 scans in transmission mode from 4000-600 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and converted from transmittance to absorbance for analysis.

XRD was accomplished by putting approximately 0.1 g of biochar or AB into a powder sample holder and analyzing the biochar or AB using a Malvern Panalytical Empyrean x-ray diffractometer equipped with a PIXcel^{3D} Medipix3 1x1 detector and Ni β filter. X-ray diffractograms were obtained at 45 kV and 40 mA from 5-100° 2θ using Cu Kα radiation at a scan speed of close to 13 s per 0.09° 2θ step. After collection, x-ray diffractograms were processed through baseline subtraction and peak deconvolution using HighScore Plus 5.1. The deconvoluted peaks at nearly 18, 23, 43, and 79° 2θ were assigned to the graphite crystalline phase and fit using a pseudo-voigt function. Aliphatic interchain spacing (*d_v*) (Å) was calculated according to Bragg's law using the following formula [21][22]:

$$\text{F3.4: } d_{\gamma} = \frac{\lambda}{2 \sin \theta_{\gamma}} \quad (4)$$

where λ is the wavelength of the incident beam (Å) and θ_{γ} is the position of the 18° 2 θ peak or γ band (° 2 θ). Aromatic interlayer spacing (d_{002}) (Å) was computed based on Bragg's law using the following formula [21][22][23][24][25]:

$$\text{F3.5: } d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \quad (5)$$

where θ_{002} is the position of the 23° 2 θ peak or (002) band (° 2 θ). Aromatic stacking diameter (L_c) (Å), aromatic sheet diameter (L_a) (Å), and number of stacked aromatic sheets (N_a) were found using the following formulas based on the Scherrer equation, respectively [21][22][23][24][25]:

$$\text{F3.6: } L_c = \frac{0.89\lambda}{\beta_{002} \cos \theta_{002}} \quad (6)$$

$$\text{F3.7: } L_a = \frac{1.84\lambda}{\beta_{100} \cos \theta_{100}} \quad (7)$$

$$\text{F3.8: } N_a = \frac{L_c}{d_{002}} \quad (8)$$

where β_{002} is the full width at half maximum (FWHM) of the (002) band (° 2 θ), β_{100} is the FWHM of the 43° 2 θ peak or (100) band (° 2 θ), and θ_{100} is the position of the (100) band (° 2 θ). Aromaticity (f_a) (%) was calculated using the following formula [21][22][24]:

$$\text{F3.9: } f_a = \frac{A_{\text{Aromatic}}}{A_{\text{Aliphatic}} + A_{\text{Aromatic}}} \times 100 \quad (9)$$

where A_{Aromatic} is the area of the (002) band and $A_{\text{Aliphatic}}$ is the area of the γ band. Each of these analyses and measurements were accomplished in triplicates per sample for biochar and in singlets per sample for AB.

3.2.3 CO₂ Adsorption

CO₂ adsorption using loblolly pine biochar and AB was conducted with a CO₂ adsorption system composed of a stainless-steel adsorption column, Lindberg 70-SV tube furnace, Digi-Sense TC9500 advanced multiparameter temperature controller, OMEGA type K thermocouple sensor, and a Thermo Scientific TRACE 1310 gas chromatograph (GC) as shown in Figure 3.1. For each adsorption experiment, about 1 g of biochar or AB was loaded into the adsorption column in between pieces of glass wool. The loaded adsorption column was then outgassed at 100°C under N₂ flowing at 150 mL/min for 24 h. After outgassing, the loaded adsorption column was cooled and 5 vol. % CO₂ balanced with N₂ was passed through a line bypassing the adsorption system at 25°C and 50 mL/min to the GC. Five gas chromatograms were collected and used to determine the inlet CO₂ concentration ($C_{\text{CO}_2, \text{In}}$) (vol. %). N₂ was then passed through the adsorption system at 150 mL/min to remove CO₂ from the adsorption system prior to the experiment. Once CO₂ had been removed, the loaded adsorption column was heated to 35°C and 5 vol. % CO₂ balanced with N₂ was passed through the loaded adsorption column at 50 mL/min which denoted the beginning

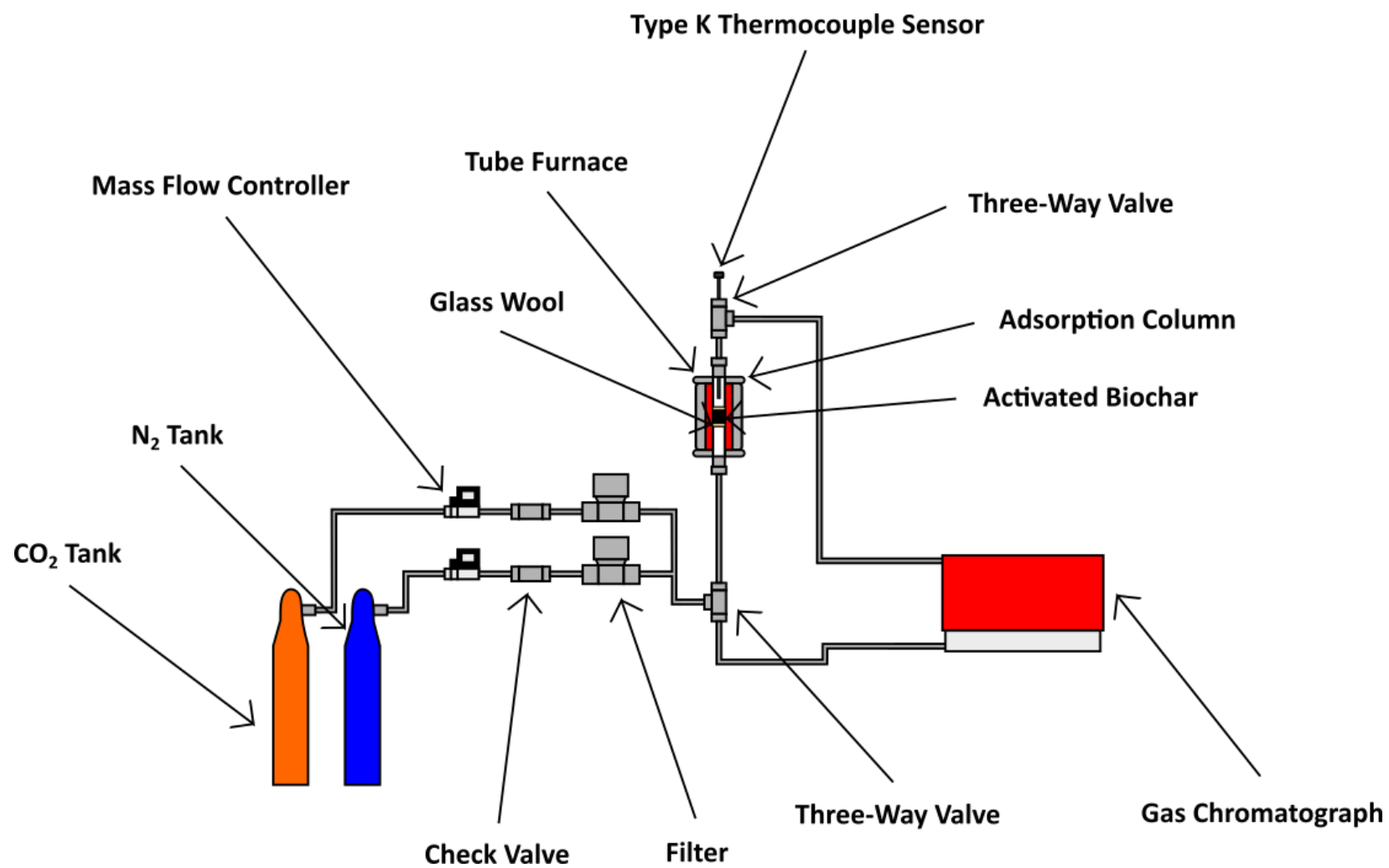


Figure 3.1. CO₂ adsorption system used to adsorb CO₂ onto and desorb CO₂ from loblolly pine biochar and activated biochar.

of the experiment [26][27]. The outlet CO₂ concentration ($C_{CO_2,out}$) (vol. %) was monitored by the GC close to every 4 min. When $C_{CO_2,out}$ was nearly equal to $C_{CO_2,in}$, the biochar or AB in the adsorption column was saturated which marked the end of adsorption. CO₂ concentration ratio (C_{CO_2}) was calculated using the following formula [26][28]:

$$F3.12: C_{CO_2} = \frac{C_{CO_2,out}}{C_{CO_2,in}} \quad (12)$$

CO₂ breakthrough curves were obtained by plotting C_{CO_2} versus adsorption time (t_A) (s). Adsorbed CO₂ concentration ratio ($C_{CO_2,A}$) was computed using the following formula:

$$F3.13: C_{CO_2,A} = 1 - \frac{C_{CO_2,out}}{C_{CO_2,in}} \quad (13)$$

CO₂ adsorption volume ($V_{CO_2,A}$) (mL) and CO₂ adsorption capacity ($Q_{CO_2,A}$) (mmol/g) were determined using the following formulas, respectively [28][29]:

$$F3.14: V_{CO_2,A} = \int_0^{t_A} F_A C_{CO_2,A} dC_{CO_2,A} \quad (14)$$

$$F3.15: Q_{CO_2,A} = \frac{P_A V_{CO_2,A}}{m_{AB} RT} \quad (15)$$

where F_A is the flow rate of 5 vol. % CO₂ balanced with N₂ (mL/min), P_A is the pressure during adsorption (atm), m_{AB} is the mass of the biochar or AB in the adsorption column (g), and R is the universal gas constant (atm·L/mol·K).

Following adsorption, N₂ was passed through a line bypassing the adsorption column at 150 mL/min to remove CO₂ from the adsorption system before continuing the experiment. Once CO₂ had been removed, the loaded adsorption column was heated to 35°C and N₂ was passed through the loaded adsorption column at 50 mL/min which indicated the beginning of desorption. $C_{CO_2,out}$ was monitored by the GC roughly every 4 min. When $C_{CO_2,out}$ was about 0, the biochar or AB in the adsorption column was regenerated which signified the end of the experiment. Desorbed CO₂ concentration ratio ($C_{CO_2,D}$) was calculated using the following formula:

$$F3.16: C_{CO_2,D} = C_{CO_2} \quad (16)$$

CO₂ desorption volume ($V_{CO_2,D}$) (mL) and CO₂ desorption capacity ($Q_{CO_2,D}$) (mmol/g) were computed using the following formulas, respectively:

$$F3.17: V_{CO_2,D} = \int_0^{t_D} F_D C_{CO_2,D} dC_{CO_2,D} \quad (17)$$

$$F3.18: Q_{CO_2,D} = \frac{P_D V_{CO_2,D}}{m_{AB} RT} \quad (18)$$

where F_D is the flow rate of N₂ (mL/min), P_D is the pressure during desorption (atm), and t_D is the desorption time (s). CO₂ working capacity (ΔQ_{CO_2}) (mmol/g) and regenerability (R_A) (%) were

determined using the following formulas, respectively [29]:

$$\text{F3.19: } \Delta Q_{CO_2} = Q_{CO_2,A} - Q_{CO_2,D} \quad (19)$$

$$\text{F3.20: } R_A = 100 - \left(\frac{\Delta Q_{CO_2}}{Q_{CO_2,A}} \times 100 \right) \quad (20)$$

After being cooled, spent biochar or AB was removed from the adsorption column and stored in a plastic bag. Singlet experiments were accomplished using loblolly pine biochar and triplicate experiments were conducted using loblolly pine AB. An experiment using a molecular sieve adsorbent was performed as a standard. Differences in biochar and AB characterization and CO₂ adsorption data were evaluated through significance testing by conducting analysis of variance (ANOVA) using Microsoft Excel.

3.3 Results and Discussion

3.3.1 AB Yield and Proximate Analysis

AB yield and proximate analysis of loblolly pine biomass, biochar, and AB are depicted in Table 3.1. AB yield was 46.96 wt. %, db and faintly differed across activation experiments due to some AB loss associated with the use of HCl to wash the AB. This AB yield was different than those reported in other studies that created AB using similar activation conditions [10][30]. However, such differences were attributed to variations in biomass type and preparation, pyrolysis conditions, KOH concentration, and activation heating rate which altered AB creation. Volatile matter content decreased ($p < 0.05$) in AB compared to biochar from 38.66 to 5.84 wt. %, db, whereas fixed carbon content increased ($p < 0.05$) in AB relative to biochar from 58.04 to 87.55 wt. %, db. These alterations denoted that volatile matter or labile C was removed from biochar through devolatilization which encompassed dehydration of hydroxyl (R-OH) groups, thermal degradation of volatile compounds derived from biomass constituents such as cellulose, hemicellulose, and lignin that remained in biochar following pyrolysis, and evolution of volatiles as CO, CO₂, methane (CH₄), H₂O_v, and H₂. These changes also exhibited that fixed carbon or stable C was removed from biochar through activation which included oxidation of stable C by H₂O_v, CO₂, K₂O, and K₂CO₃ and evolution of more volatiles as H₂O_v, CO, H₂, and CO₂. Because of these changes, stable C was concentrated in AB as fixed carbon [7][9][31][32][33][34][35]. Accordingly, proximate analysis conveyed that biochar was devolatilized and activated during activation which should have formed pores in AB that could adsorb CO₂.

3.3.2 Ultimate Analysis

Ultimate analysis and atomic ratios of loblolly pine biomass, biochar, and AB are shown in Table 3.2. H and O contents decreased ($p < 0.05$) in AB compared to biochar from 4.70 and 20.47 to 0.24 and 5.54 wt. %, dafb, respectively, while C content increased ($p < 0.05$) in AB relative to biochar from 74.52 to 93.74 wt. %, dafb. These transitions implied that R-OH groups were dehydrated, volatile matter, which is chiefly composed of C, H, and O, was devolatilized through dehydrogenation and deoxygenation, and fixed carbon, which is largely comprised of C and H, was volatilized through oxidation and then devolatilized through dehydrogenation and deoxygenation. Other studies demonstrated that O content increased and C content decreased in AB compared to biochar during activation [36][37]. Yet, these discrepancies were associated with the KOH/biochar mass ratio of 3 being too low and activation temperature of 800°C being too high

Table 3.1. Activated biochar yield and proximate analysis of loblolly pine biomass, biochar, and activated biochar.

Loblolly Pine					
	Activated Biochar Yield (wt. %, db)	Proximate Analysis			
		Moisture (wt. %, wb)	Ash (wt. %, db)	Volatile Matter (wt. %, db)	Fixed Carbon (wt. %, db)
Biomass	NA	6.27 (0.15)	0.19 (0.02)	79.65 (0.20)	13.89 (0.22)
Biochar	NA	2.72 (0.28)	0.59 (0.21)	38.66 (5.25)	58.04 (4.98)
Activated Biochar	46.96 (4.16)	5.50 (0.38)	1.11 (1.00)	5.84 (0.47)	87.55 (1.25)

Values in table are averages with standard deviations in parentheses. NA stands for not applicable.

Table 3.2. Ultimate analysis and atomic ratios of loblolly pine biomass, biochar, and activated biochar.

Loblolly Pine				
	Ultimate Analysis (wt. %, dafb)			
	C	H	N	O
Biomass	53.18 (0.18)	7.17 (0.11)	0.10 (0.04)	39.55 (0.22)
Biochar	74.52 (1.95)	4.70 (0.39)	0.32 (0.28)	20.47 (1.74)
Activated Biochar ¹	93.74 (0.73)	0.24 (0.33)	1.25 (0.11)	5.54 (0.00)

Loblolly Pine			
	Atomic Ratios		
	H/C	O/C	(O+N)/C
Biomass	1.60 (0.03)	0.56 (0.00)	0.56 (0.00)
Biochar	0.75 (0.08)	0.21 (0.02)	0.21 (0.02)
Activated Biochar ¹	0.03 (0.04)	0.04 (0.00)	0.06 (0.00)

Values in table are averages with standard deviations in parentheses. ¹Values are based on 2 measurements.

to facilitate oxygenation and excessive fixed carbon oxidation which resulted in O being removed and C being concentrated in AB. N content increased ($p < 0.05$) in AB relative to biochar from 0.32 to 1.25 wt. %, dafb. This change revealed that N was concentrated in AB instead of being evolved through denitrogenation. Other studies showed that N content decreased in AB compared to biochar during activation [10][11][30][36][37]. As such, ultimate analysis expressed that biochar was dehydrated, dehydrogenated, and deoxygenated through activation. This analysis also demonstrated that biochar was not denitrogenated during activation. H/C, O/C, and (O+N)/C decreased ($p < 0.05$) in AB compared to biochar from 0.75, 0.21, and 0.21 to 0.03, 0.04, and 0.06, respectively. These transitions denoted that the biochar C structure was carbonized through activation and became more aromatic and stable and less hydrophilic and polar as the AB C structure [14][15][37]. The decreases in H/C through activation conveyed that aliphatic chains were cleaved through cracking, alicyclic rings were created through cyclization, aromatic rings were formed through aromatization, and π -conjugated ring systems or aromatic ring clusters were generated through aromatic condensation causing AB to have a more aromatic C structure than that of biochar. The decreases in O/C and (O+N)/C during activation showcased that O heteroatoms and functional groups were removed through deoxygenation and devolatilization resulting in AB having a more stable, less hydrophilic, and less polar C structure than that of biochar [14][15][31][32][33][34][35]. As such, atomic ratios signaled that biochar was aromatized, carbonized, and depolarized through activation.

A van Krevelen diagram of loblolly pine biomass, biochar, and AB is exhibited in Figure 3.2. van Krevelen diagrams are used to ascertain degrees of aromatization and carbonization of biochar and AB based on H/C and O/C atomic ratios determined through ultimate analysis. Movements on van Krevelen diagrams can also be used to represent reactions associated with aromatization and carbonization including dehydration, deoxygenation involving decarboxylation and decarbonylation, dehydrogenation, and demethylation [31][35][38]. H/C and O/C decreased ($p < 0.05$) in AB relative to biochar which were shown by the shifting of AB down and left of biochar on the van Krevelen diagram. These transitions on the van Krevelen diagram implied that biochar was aromatized, dehydrated, decarboxylated, decarbonylated, dehydrogenated, and demethylated through activation. Dehydration, decarboxylation, and decarbonylation are the major reactions that occur at activation temperatures from 300-600°C and cause H_2O_v , CO_2 , and CO to be released as volatiles, respectively, while dehydrogenation and demethylation are the primary reactions that occur at activation temperatures from 600-800°C and result in H_2 and CH_4 being released as volatiles, respectively [31][35]. In addition, a H/C of ≤ 0.1 as shown by the dashed line on the van Krevelen diagram is indicative of a graphitic C structure signaling that a C structure is highly crystalline or ordered and contains consistently stacked C layers or sheets comprised of aromatic ring clusters. According to this relationship, AB had a crystalline or graphitic C structure because the H/C of AB was below 0.1 [39]. Consequently, the van Krevelen diagram expressed that biochar was aromatized and carbonized through activation and that AB had a crystalline C structure. Overall, ultimate analysis indicated that biochar was carbonized during activation forming crystalline C structures which should have contained pores that could adsorb CO_2 .

3.3.3 Bulk and Particle Densities and Bulk Porosity

Bulk and particle densities and bulk porosity of loblolly pine biomass, biochar, and AB are illustrated in Table 3.3. Particle density and bulk porosity increased ($p < 0.05$) in AB compared to biochar from 1.35 and 85.24 to 2.16 g/cm³ and 92.82 vol. %, respectively, whereas bulk density decreased ($p < 0.05$) in AB relative to biochar from 0.20 to 0.16 g/cm³. These changes conveyed

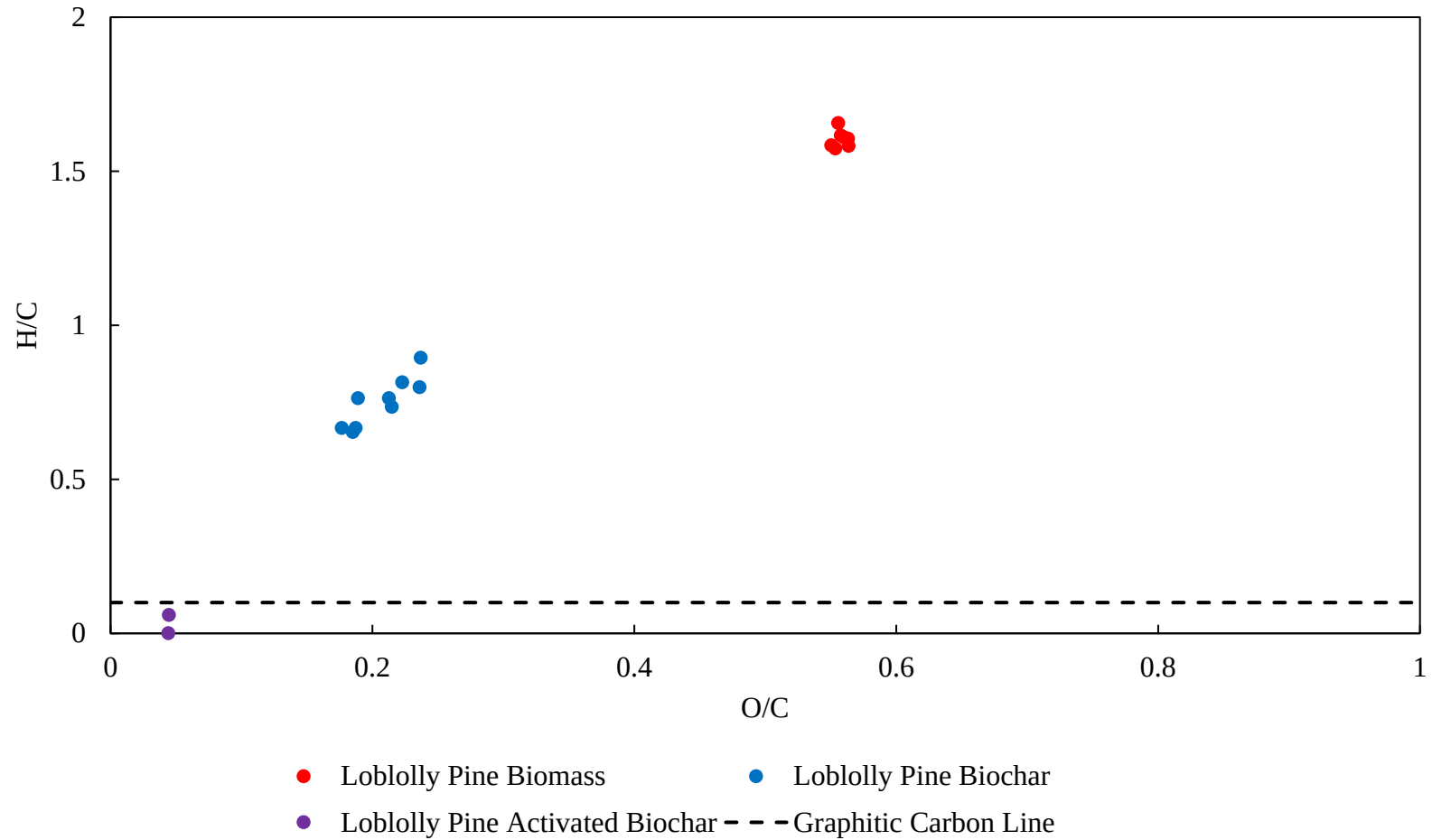


Figure 3.2. van Krevelen diagram of loblolly pine biomass, biochar, and activated biochar.

Table 3.3. Bulk and particle densities and bulk porosity of loblolly pine biomass, biochar, and activated biochar.

Loblolly Pine			
	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Bulk Porosity (vol. %)
Biomass	0.21 (0.01)	1.58 (0.08)	86.70 (0.86)
Biochar	0.20 (0.02)	1.35 (0.07)	85.24 (1.86)
Activated Biochar	0.16 (0.00)	2.16 (0.05)	92.82 (0.16)

Values in table are averages with standard deviations in parentheses.

that softening and melting of volatile compounds derived from biomass constituents that remained in biochar following pyrolysis and oxidized fixed carbon formed pores in biochar through activation. During oxidation and devolatilization, fixed carbon in biochar that was in contact with K-containing compounds and oxidizing gases like H_2O and CO_2 was oxidized through redox and gasification reactions causing fixed C to be transformed into volatile matter. Biochar particles were then deformed through particle expansion and contraction as volatile matter was converted into gaseous volatiles, moved through biochar particles, and evolved from biochar particle surfaces through evaporation. Biochar particles were also deformed by C lattice expansion as K intercalated into the biochar C structure and expanded the biochar C lattice [7][9][40]. Because of oxidation and devolatilization, existing biochar pores were enlarged and new biochar pores were formed which resulted in increases in particle density and bulk porosity in AB. Therefore, bulk and particle densities and bulk porosity signified that biochar was devolatilized and that AB pores were created during activation which should enhance CO_2 adsorption onto AB.

3.3.4 Inorganics Analysis and Alkalinity

Inorganics analysis of loblolly pine biomass, biochar, and AB is portrayed in Table 3.4. Cu, Fe, Ni, S, and Zn contents decreased ($p < 0.05$) in AB compared to biochar, whereas K content increased ($p < 0.05$) in AB relative to biochar from 1527.61 to 6396.96 mg/kg, db. These alterations denoted that some inorganics present in biochar were removed despite the amount of ash in biochar being unchanged. The most abundant inorganics in biochar and AB were Ca, Fe, K, and Si. However, the distribution of inorganics in biochar was changed through activation because specific inorganics were concentrated in AB and others were removed from biochar. The total inorganics content of biochar was mostly associated with the high Fe and Si contents of biochar. Conversely, the total inorganics content of AB was mostly connected to the high Fe and K contents of AB. This change in the distribution of inorganics following activation was linked to certain elements like Cu, Fe, Ni, S, and Zn being dissolved by KOH and removed from biochar and K not being completely dissolved by HCl and H_2O and removed from AB during activation [11][36][37]. KOH was converted into different K-containing compounds such as K_2O , K_2CO_3 , and K throughout activation which each modified the biochar C structure in different manners. Yet, KOH was completely turned into K and intercalated into the biochar C structure during activation since biochar was chemically activated with KOH at 800°C [7][9]. K should have then been dissolved by HCl and H_2O and removed from AB but the higher K content of AB compared to that of biochar implied that K was concentrated in AB. Consequently, HCl and H_2O may not have been able to reach most of the intercalated K in AB which allowed a high amount of K to remain in AB after activation. Accordingly, inorganics analysis demonstrated that certain inorganics were removed from biochar and K was concentrated in AB during activation.

Alkalinity of loblolly pine biomass, biochar, and AB is presented in Table 3.5. Alkalinity increased ($p < 0.05$) in AB relative to biochar from 0.14 to 0.65 mmol H^+ /g. This transformation revealed that inorganics that functioned as alkalis were concentrated in AB through activation. Alkalinity is broken apart into separate kinds of alkalinities which each contribute to biochar and AB total alkalinity. Moreover, different sorts of alkalinities dominant the total alkalinity of disparate biochars and ABs. For example, in another study, the total alkalinity of hardwood biochar was chiefly related to the high carbonate alkalinity of the biochar whereas the total alkalinity of red oak biochar was largely associated with the high structural organic and carbonate alkalinities of the biochar [19]. These findings signaled that each of the various types of alkalinities had a prominent influence on biochar total alkalinity. This study also noted that total alkalinity was

Table 3.4. Inorganics analysis of loblolly pine biomass, biochar, and activated biochar.

Loblolly Pine					
Inorganics Analysis (mg/kg, db)					
	Al	Ca	Cu	Fe	K
Biomass	31.69 (17.09)	712.47 (28.59)	1.07 (0.86)	92.19 (30.52)	572.29 (39.54)
Biochar	77.95 (39.16)	2392.83 (580.90)	16.06 (5.62)	3305.49 (901.86)	1527.61 (632.98)
Activated Biochar	68.79 (3.98)	1914.40 (233.02)	6.00 (1.74)	2018.79 (578.60)	6396.96 (3028.11)
Loblolly Pine					
	Mg	Mn	Ni	P	S
Biomass	202.97 (8.75)	92.48 (2.20)	43.51 (10.69)	65.97 (14.65)	70.92 (4.51)
Biochar	663.63 (165.54)	307.41 (71.37)	60.84 (11.27)	234.25 (64.44)	89.71 (15.00)
Activated Biochar	684.19 (100.38)	261.78 (25.88)	42.25 (14.69)	184.13 (62.70)	42.37 (15.58)
Loblolly Pine					
	Si	Zn	Total Inorganics		
Biomass	1021.22 (371.66)	6.64 (0.69)	2913.07 (443.52)		
Biochar	2509.61 (2540.87)	28.29 (17.42)	10979.44 (3234.14)		
Activated Biochar	281.07 (236.21)	2.17 (1.03)	11856.05 (3256.77)		

Values in table are averages with standard deviations in parentheses.

Table 3.5. Alkalinity of loblolly pine biomass, biochar, and activated biochar.

Loblolly Pine	
	Alkalinity (mmol H ⁺ /g)
Biomass	NA
Biochar	0.14 (0.03)
Activated Biochar	0.65 (0.25)

Values in table are averages with standard deviations in parentheses. NA stands for not applicable.

impacted by the presence of base cations with higher amounts of base cations in biochar causing biochar to have a higher total alkalinity [19]. Certain alkalis were removed from our AB during activation because some inorganics in AB were removed during HCl washing which decreased the amount of other inorganic alkalis in AB. However, K was concentrated in AB through activation which increased the amount of other inorganic alkalis in AB. Therefore, the retention of K in the form of intercalated K increased the alkalinity of AB since K is an other inorganic alkali and functions as a base cation and a high amount of K was concentrated in AB during activation. This result contradicted the notion that intercalated K was not removed from AB by HCl and H₂O since the K was unreachable which signified that intercalated K should not have affected the alkalinity of AB. Yet, because alkalinity increased in AB compared to biochar, intercalated K may have been accessible to HCl and H₂O but was not dissolved and removed from AB due to mass transfer limitations. Moreover, these diffusion restrictions may have been overcome when alkalinity was being measured since AB was exposed to HCl for a long time with the mixture being constantly stirred during alkalinity measurement while AB was exposed to HCl for a much shorter time with the mixture being stirred momentarily and subsequently filtered twice during HCl washing. As a result, alkalinity indicated that AB acquired alkalis through activation. Overall, inorganics analysis and alkalinity denoted that K was concentrated in AB during activation which should have provided basic functional groups that could adsorb CO₂.

3.3.5 Thermal Analysis

Mass loss and derivative mass loss thermographs of loblolly pine biomass, biochar, and activated biochar are shown in Figures 3.3 and 3.4, respectively. Mass losses decreased in AB compared to biochar for the most part from 3.00, 13.18, and 25.42 wt. % over approximately 25-100, 200-400, and 400-750°C to 4.32, 1.44, and 11.25 wt. % over 25-100, 200-400, and 400-750°C, respectively. Derivative mass losses also decreased in AB compared to biochar for the most part from 0.07 and 0.16 wt. %/°C at close to 34 and 352°C to 0.16 wt. %/°C at nearly 42°C, respectively. These alterations denoted that volatile matter was removed from biochar during activation which caused AB to have lower mass losses and derivative mass losses with additional heating and higher thermal stability. Mass losses and derivative mass loss maxima or peaks in specific temperature ranges are commonly associated with the removal or thermal decomposition of certain biomass constituents including moisture, cellulose, hemicellulose, and lignin. For example, mass losses from and peaks at <120°C are connected to the removal of moisture, whereas mass losses from and peaks that appear as shoulders at 150-360°C are linked to the decomposition of hemicellulose [20]. Mass losses from and peaks at 360-425°C are related to the decomposition of cellulose and lignin, while mass losses from and peaks at >500°C correspond to the decomposition of lignin. Low derivative mass losses that occur at high temperatures over wide temperature ranges are also associated with the decomposition of lignin because lignin is thermoplastic [20][41]. As a result, the mass losses from 25-100°C and peak at about 34°C for biochar and 42°C for AB exhibited that moisture was removed from biochar and AB with higher mass loss occurring in AB. The mass losses from 200-400 and 400-750°C, peak at close to 352°C for biochar, and lack of a peak near 352°C for AB implied that volatile compounds derived from cellulose, hemicellulose, and lignin were decomposed and removed from biochar and that volatile compounds derived from lignin remained in AB with higher mass losses occurring in biochar because only some of the volatile compounds derived from lignin present in biochar were further degraded and retained in AB following activation. Furthermore, the low derivative mass losses that occurred over broad temperature ranges for biochar and AB signified that volatile compounds

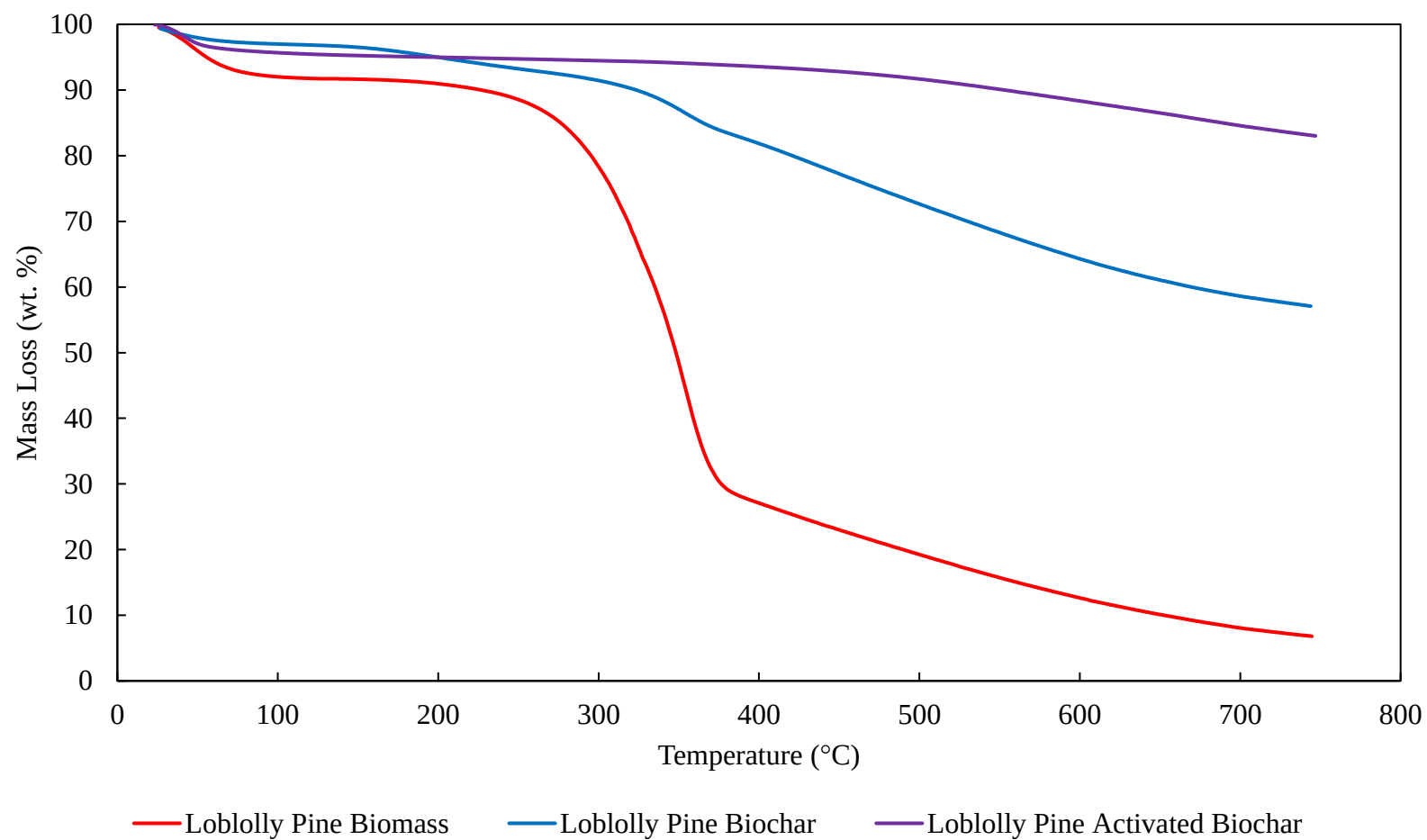


Figure 3.3. Mass loss thermographs of loblolly pine biomass, biochar, and activated biochar.

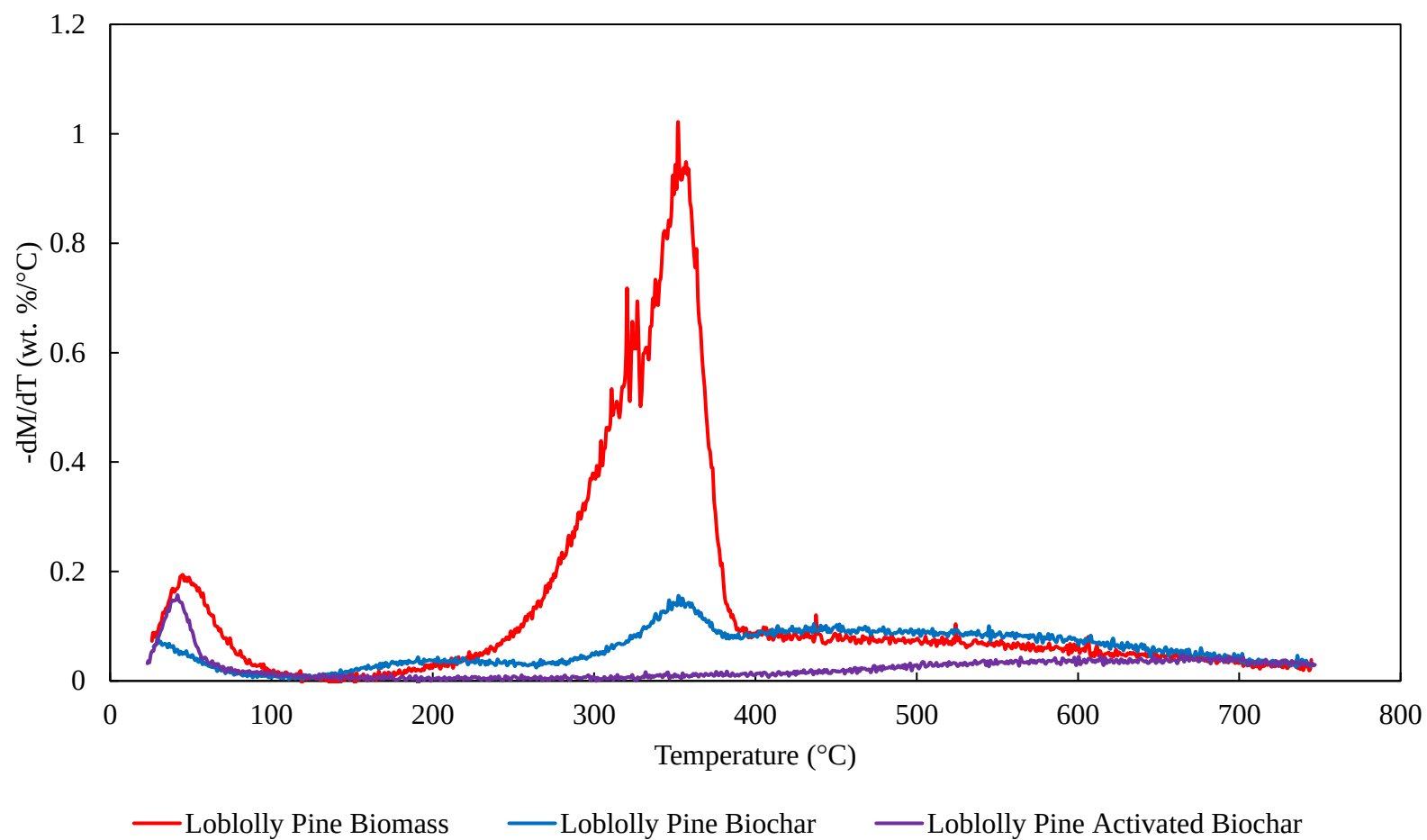


Figure 3.4. Derivative mass loss thermographs of loblolly pine biomass, biochar, and activated biochar.

derived from lignin remained in biochar and AB and continued to decompose up to 750°C [20]. Based on these differences in mass loss between biochar and AB, AB had a higher thermal stability than that of biochar. As such, thermal analysis conveyed that AB became more thermally stable after activation and that most volatile matter that had remained in biochar was removed through activation which supported previous findings.

3.3.6 Fourier-Transform Infrared Spectroscopy

FTIR spectra of loblolly pine biochar and AB are depicted in Figure 3.5. R-OH group stretching peak absorbance at approximately 3424 cm^{-1} became less distinguished in AB which exhibited that carboxylic acids, phenols, or H_2O were removed from AB. Aliphatic and aromatic methyl (R-CH_3) and aliphatic methylene ($\text{R-C(-H}_2\text{)-R'}$) group stretching peak absorbances from about 2959-2847 cm^{-1} became less prominent in AB which expressed that aliphatic compounds and unconjugated rings connected to volatile compounds derived from cellulose and lignin were removed from AB [12][31][32][35][36][41][42][43]. Carbon-oxygen double (C=O) bond stretching peak absorbance at close to 1692 cm^{-1} disappeared in AB which implied that carboxylic acids, esters, ketones, or quinones were removed from AB. Carbon-carbon double (C=C) bond stretching peak absorbance from nearly 1622-1587 cm^{-1} almost completely disappeared in AB which indicated that conjugated or aromatic rings corresponding to volatile compounds derived from lignin were removed from AB [18][31][32][42][43]. Carbon-hydrogen (C-H) bond bending peak absorbances at roughly 1453 and 1367 cm^{-1} disappeared in AB which portrayed that volatile compounds derived from lignin and volatile compounds derived from cellulose and hemicellulose were removed from AB, respectively. Carbon-oxygen single (C-O) bond stretching, ether (R-O-R') group stretching, and R-OH group stretching peak absorbances at about 1259, 1159, and 1107 cm^{-1} , respectively, also disappeared in AB which reinforced that volatile compounds derived from cellulose, hemicellulose, and lignin were removed from AB. C-O bond stretching peak absorbance from approximately 1056-1023 cm^{-1} became less pronounced in AB which supported that volatile compounds derived from cellulose and hemicellulose were removed from AB. C-H bond wagging peak absorbances from close to 867-741 cm^{-1} disappeared in AB which demonstrated that unconjugated rings associated with volatile compounds derived from lignin were removed from AB [10][18][30][31][32]. These alterations signaled that the volatile matter and large assortment of O functional groups that remained in biochar were removed from AB which caused AB to lose most characteristic peaks of volatile compounds derived from cellulose, hemicellulose, and lignin. In addition, these changes suggested that aromatic rings were created through aromatization and aromatic ring clusters were formed through aromatic condensation in AB which resulted in AB losing most characteristic peaks of aromatic R-CH_3 groups and C-H bonds. Based on these findings, peaks associated with aliphatic and labile structures such as volatile compounds derived from biomass constituents either decreased in absorbance or disappeared entirely from the AB spectrum. Consequently, FTIR spectroscopy denoted that biochar was deoxygenated and aromatized through activation and that almost no volatile matter resided in AB which reinforced the results previously noted.

3.3.7 X-Ray Diffraction

XRD diffractograms of loblolly pine biomass, biochar, and AB are displayed in Figure 3.6. Peaks at 18, 23, 43, and 79° 2 θ were assigned to the turbostratic or graphitic C crystalline phase. Reflections at 18, 23, 43, and 79° 2 θ were indexed with the γ band and (002), (100), and (110) crystallographic planes of graphite, respectively [10][21][22][23][24][25][36][44][45][46]. The

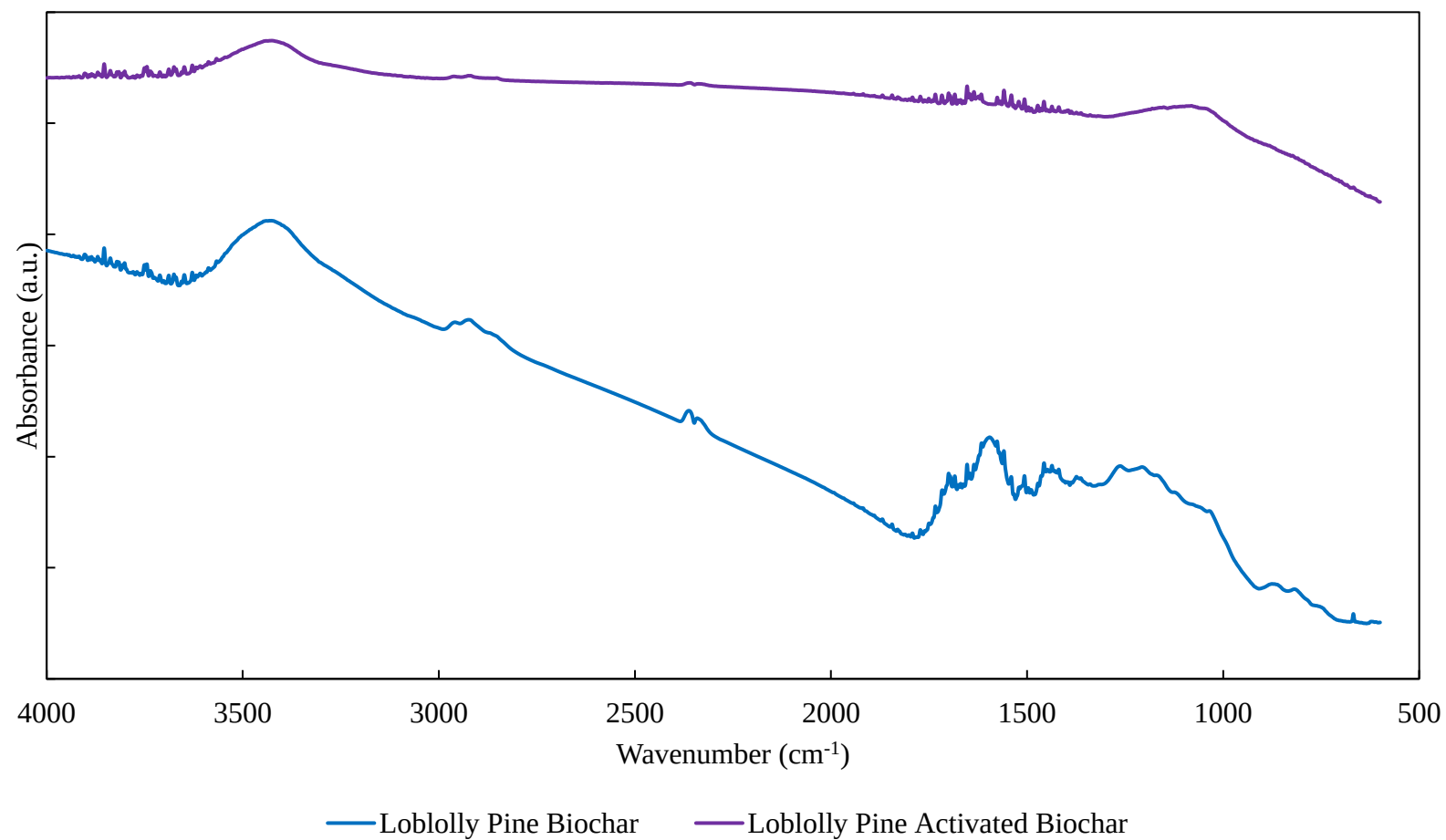


Figure 3.5. FTIR spectra of loblolly pine biochar and activated biochar.

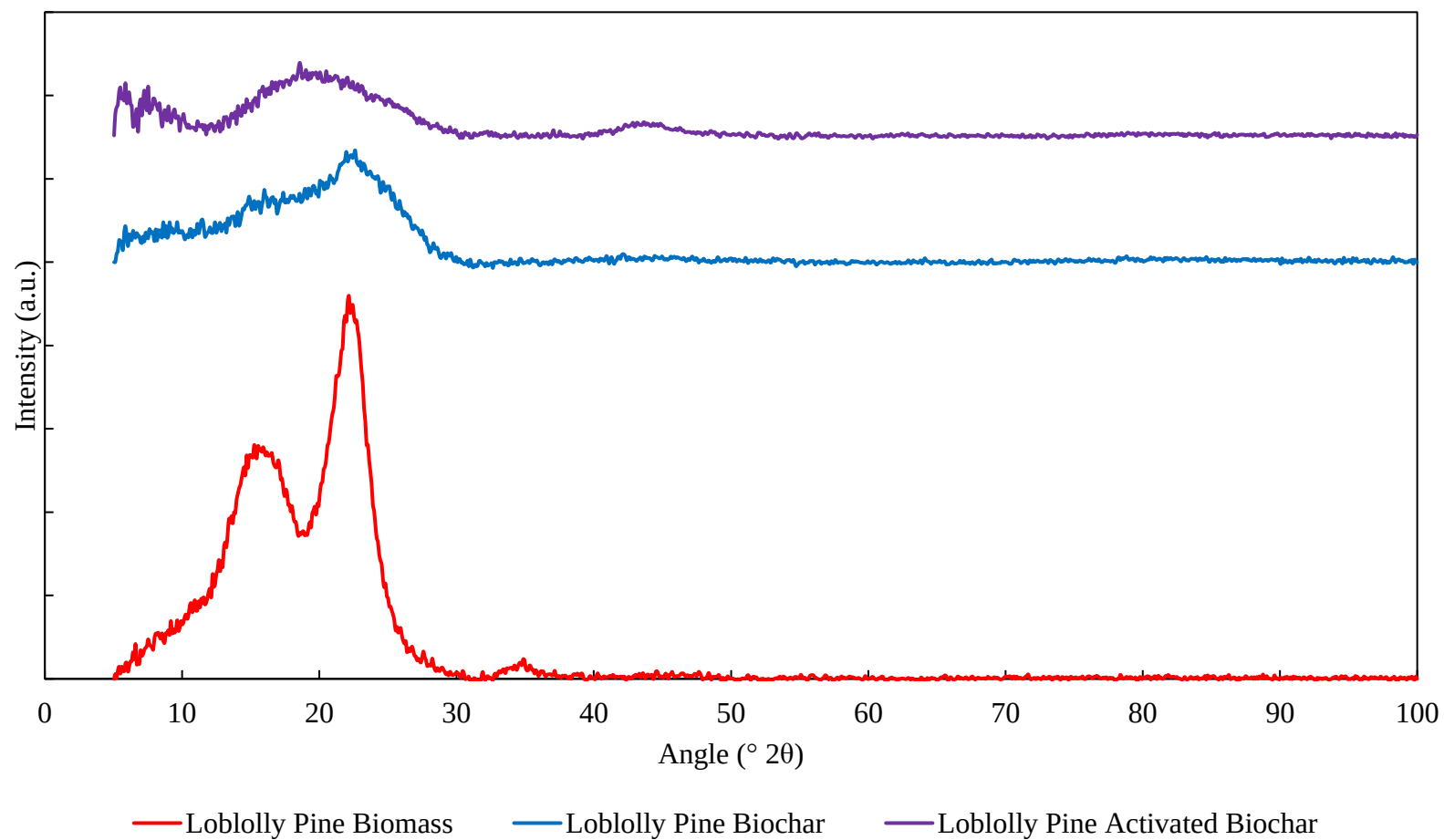


Figure 3.6. XRD diffractograms of loblolly pine biomass, biochar, and activated biochar.

graphite crystallographic planes faintly differed between biochar and AB with the γ band and (002), (100), and (110) planes ranging from 17.01-17.13, 22.55-22.91, 42.93-43.50, and 78.12-79.60° 2θ for biochar and 17.29-17.80, 20.20-21.03, 43.55-43.75, and 79.53-80.70° 2θ for AB, respectively. Graphitic C crystalline peak broadenings and intensities somewhat varied between biochar and AB which demonstrated that biochar and AB had slightly different graphitic C structures. Aliphatic interchain spacing, aromatic interlayer spacing, aromatic stacking diameter, aromatic sheet diameter, number of stacked aromatic sheets, and aromaticity of loblolly pine biochar and AB are expressed in Table 3.6. Aliphatic interchain spacing or the distance between aliphatic side chains attached to aromatic ring clusters remained constant between biochar and AB at 5 Å which illustrated that branching in the form of aliphatic side chains attached to aromatic sheets in AB was negligible and probably only encompassed R-CH₃ and ethyl (R-C(H₂)-CH₃) groups [21][22]. Aromatic interlayer spacing or the distance between aromatic C sheets in graphitic C crystallites also remained constant between biochar and AB at 4 Å which implied that AB contained condensed and ordered aromatic sheet clusters since the AB C structure was not saturated and contained almost no heteroatoms which would otherwise prevent aromatic sheets in AB from being closely stacked. Aromatic stacking diameter or the distance of aromatic sheet clusters or the height of graphitic C crystallites decreased ($p < 0.05$) in AB relative to biochar from 14 to 8 Å which indicated that AB contained shorter graphitic C crystallites compared to those in biochar since K intercalated into the biochar C structure through activation and widened the spaces between aromatic sheets in graphitic C crystallites in AB [21][22][25][45][47][48].

This transformation was supported by the lower volatile matter content and H/C and O/C atomic ratios of AB relative to those of biochar. Aromatic sheet diameter or the distance of aromatic sheets or the width of graphitic C crystallites increased ($p < 0.05$) in AB compared to biochar from 16 to 28 Å which portrayed that AB contained wider graphitic C crystallites than those in biochar which was ascribed to the higher temperature applied for activation compared to that used for pyrolysis causing aromatic sheets in biochar to expand during activation through aromatic condensation creating larger aromatic sheets in AB [21][22][25][45][47][48]. Number of stacked aromatic sheets or the number of ordered aromatic sheets in an aromatic sheet cluster or graphitic C crystallite decreased ($p < 0.05$) in AB relative to biochar from 4 to 2 which reinforced that the intercalation of K into the biochar C structure through activation resulted in aromatic sheets in graphitic C crystallites being farther apart and shortening of graphitic C crystallites in AB. Aromaticity or the fraction of ordered or aromatic C atoms in graphitic C crystallites ranged from 74.18 to 81.19% but was not different between biochar and AB ($p > 0.05$). This finding contradicted the other structural results obtained for AB since biochar and AB C structures displayed differences. Based on these findings, peaks associated with the graphitic C crystalline phase which were present in the biochar diffractogram narrowed and increased in intensity in the AB diffractogram. Therefore, XRD conveyed that biochar became more ordered as graphitic C structures were further developed in biochar through activation. These crystallites should provide pores in AB that could adsorb CO₂ because CO₂ can diffuse through the aromatic interlayer spacings of these crystallites.

3.3.8 CO₂ Adsorption

CO₂ breakthrough curves of loblolly pine biochar and AB are illustrated in Figure 3.7. Breakthrough curves are used to portray the saturation of an adsorbent bed in an adsorption column from the column inlet to outlet as an adsorbate like CO₂ is slowly adsorbed over time until the bed is completely saturated. Breakthrough refers to the point during adsorption when the part of the

Table 3.6. Aliphatic interchain spacing, aromatic interlayer spacing, aromatic stacking diameter, aromatic sheet diameter, number of stacked aromatic sheets, and aromaticity of loblolly pine biochar and activated biochar.

Loblolly Pine			
	Aliphatic Interchain Spacing (Å)	Aromatic Interlayer Spacing (Å)	Aromatic Stacking Diameter (Å)
Biochar	5 (0)	4 (0)	14 (0)
Activated Biochar	5 (0)	4 (0)	8 (0)
Loblolly Pine			
	Aromatic Sheet Diameter (Å)	Number of Stacked Aromatic Sheets	Aromaticity (%)
Biochar	16 (2)	4 (0)	74.18 (3.63)
Activated Biochar	28 (2)	2 (0)	81.19 (3.94)

Values in table are averages with standard deviations in parentheses.

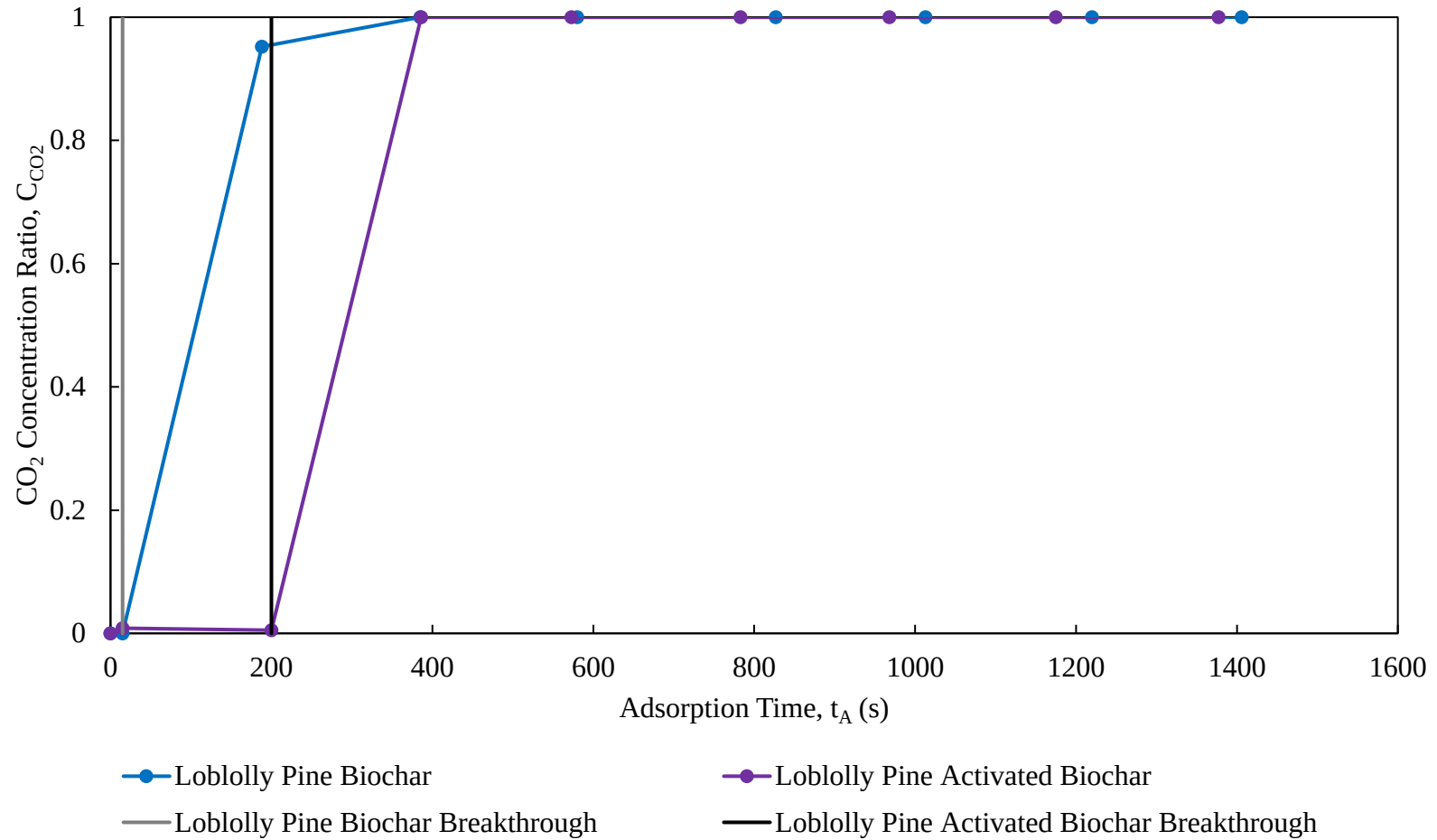


Figure 3.7. CO₂ adsorption breakthrough curves of loblolly pine biochar and activated biochar.

bed closest to the column inlet becomes saturated which causes the section of the bed where mass transfer of CO₂ into the bed is occurring to transition down the bed and the concentration of CO₂ at the column outlet to increase as the bed approaches total saturation [26]. The breakthroughs of loblolly pine biochar and AB as shown by the straight lines in Figure 3.7 signified that AB had a slower breakthrough than that of biochar with biochar and AB beginning to be saturated by about 15 and 200 s, respectively. This finding suggested that the inlet section of the AB bed took longer to become saturated compared to the inlet section of the biochar bed which was ascribed to AB assumedly having a much higher specific surface area and total pore volume relative to those of biochar. Accordingly, the CO₂ breakthrough curves signaled that AB absorbed a higher amount of CO₂ than the amount adsorbed by biochar. CO₂ adsorption, desorption, and working capacities and regenerability of loblolly pine biochar and AB are depicted in Table 3.7. CO₂ adsorption, desorption, and working capacities increased ($p < 0.05$) in AB compared to biochar from 0.18, 0.14, and 0.05 to 0.51, 0.34, and 0.17 mmol/g, respectively, whereas regenerability varied from 67.03-73.51% but was not different between biochar and AB ($p > 0.05$). These alterations denoted that AB adsorbed more CO₂ than that adsorbed by biochar which was attributed to AB having a higher specific surface area, total pore volume, and amount of basic functional groups relative to those of biochar since these biochar physicochemical characteristics govern CO₂ adsorption mechanisms. Such changes also signified that the same proportion of CO₂ that was adsorbed onto biochar and AB was not removed through desorption which conveyed that either the same mass transfer limitations or the generation of strong intermolecular interactions between biochar and AB surfaces and CO₂ molecules inhibited complete desorption. As a result, CO₂ adsorption, desorption, and working capacities and regenerability demonstrated that AB adsorbed a higher amount of CO₂ than that adsorbed by biochar but that some adsorbed CO₂ was still conserved on AB following desorption similar to that retained on biochar.

3.4 Conclusions

The impact of KOH activation on the physicochemical characteristics and CO₂ adsorption behavior of loblolly pine AB compared to those of loblolly pine biochar was investigated using loblolly pine biochar activated through KOH activation at 800°C. Most physicochemical characteristics of loblolly pine AB activated under these conditions differed ($p < 0.05$) from those of loblolly pine biochar and favored CO₂ adsorption. Loblolly pine AB adsorbed a higher amount of CO₂ than that adsorbed by loblolly pine biochar because of the higher specific surface area, total pore volume, and alkalinity of loblolly pine AB relative to those of loblolly pine biochar which are characteristics that are known to control CO₂ adsorption. Accordingly, KOH activation is a useful process for enhancing the physicochemical characteristics of biochar for CO₂ adsorption and improving the CO₂ adsorption behavior of biochar. Future research should alter the KOH/biochar mass ratio and activation temperature used to activate loblolly pine biochar since the values of these parameters used in our study may have not been ideal for loblolly pine biochar.

Table 3.7. CO₂ adsorption, desorption, and working capacities and regenerability of loblolly pine biochar and activated biochar.

Loblolly Pine				
	CO ₂ Adsorption Capacity (mmol/g)	CO ₂ Desorption Capacity (mmol/g)	CO ₂ Working Capacity (mmol/g)	Regenerability (%)
Biochar ¹	0.18	0.14	0.05	73.51
Activated Biochar	0.51 (0.02)	0.34 (0.04)	0.17 (0.03)	67.03 (6.22)

Values in table are averages with standard deviations in parentheses. ¹Values are based on 1 CO₂ adsorption experiment.

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Appendices

Appendix A. Biochar Activation

Table 3.8. Activated biochar yields of loblolly pine biochar potassium hydroxide activation experiments.

Loblolly Pine			
	Sample	Run	Activated Biochar Yield (wt. %, db)
Biochar	1	1	41.70
		2	53.08
		3	52.91
	2	1	45.00
		2	43.24
		3	47.40
	3	1	42.90
		2	47.81
		3	48.60

Appendix B. Activated Biochar Characterization

Table 3.9. Proximate analyses of loblolly pine activated biochars.

Loblolly Pine					
Sample		Proximate Analysis			
		Moisture (wt. %, wb)	Ash (wt. %, db)	Volatile Matter (wt. %, db)	Fixed Carbon (wt. %, db)
Activated Biochar	1	5.34	0.11	5.74	88.82
	2	5.93	1.12	5.44	87.51
	3	5.23	2.10	6.35	86.32

Table 3.10. Ultimate analyses of loblolly pine activated biochars.

Loblolly Pine					
Sample		Ultimate Analysis (wt. %, dafb)			
		C	H	N	O
Activated Biochar	1	93.22	0.47	1.17	5.54
	2	94.26	0.01	1.32	5.54
	3	NM	NM	NM	NM

NM stands for not measured.

Table 3.11. Atomic ratios of loblolly pine activated biochars.

Loblolly Pine					
Sample		Atomic Ratios			
		H/C	O/C	(O+N)/C	
Activated Biochar	1	0.06	0.04	0.06	
	2	0.00	0.04	0.06	
	3	NM	NM	NM	

NM stands for not measured.

Table 3.12. Bulk and particle densities and bulk porosities of loblolly pine activated biochars.

Loblolly Pine				
	Sample	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Bulk Porosity (vol. %)
Activated Biochar	1	0.16	2.21	92.96
	2	0.15	2.17	92.85
	3	0.15	2.10	92.64

Table 3.13. Inorganics analyses of loblolly pine activated biochars.

Loblolly Pine									
	Sample	Subsample	Inorganics Analysis (mg/kg, db)						
			Al	Ca	Cu	Fe	K	Mg	Mn
Activated Biochar	1	1	68.98	1642.72	5.16	1456.36	2618.20	785.67	254.81
		2	75.26	1606.56	5.21	1463.14	2614.88	776.85	257.51
	2	1	68.62	1999.56	4.75	2738.27	7467.12	714.81	294.12
		2	67.98	1982.40	4.48	2716.11	7384.17	704.90	292.01
	3	1	69.16	2136.16	8.54	1881.54	9141.12	562.11	237.56
		2	62.75	2119.00	7.86	1857.30	9156.27	560.81	234.64
	Sample	Subsample	Inorganics Analysis (mg/kg, db)						
			Ni	P	S	Si	Zn	Total Inorganics	
Activated Biochar	1	1	26.33	267.70	53.88	636.28	3.40	7819.49	
		2	26.58	253.68	56.61	378.08	3.51	7517.85	
	2	1	59.21	171.97	53.50	236.34	1.91	13810.17	
		2	59.26	163.55	20.77	113.25	1.31	13510.19	
	3	1	41.39	120.71	44.03	41.42	1.68	14285.40	
		2	40.70	127.19	25.47	ND	1.23	14193.22	

ND stands for not detected.

Table 3.14. Alkalinities of loblolly pine activated biochars.

Loblolly Pine		
	Sample	Alkalinity (mmol H ⁺ /g)
Activated Biochar	1	0.57
	2	0.46
	3	0.94

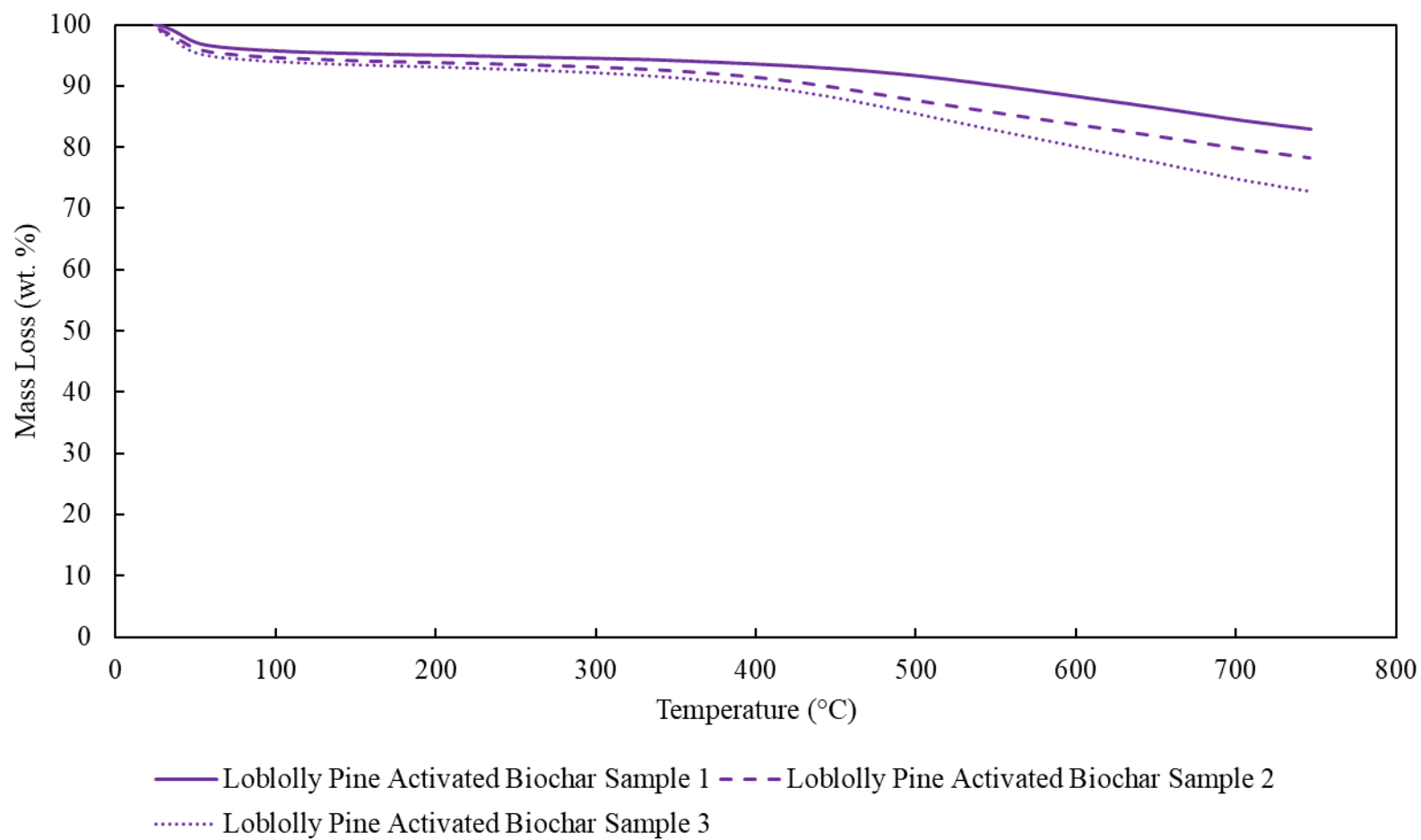


Figure 3.8. Mass loss thermographs of loblolly pine activated biochars.

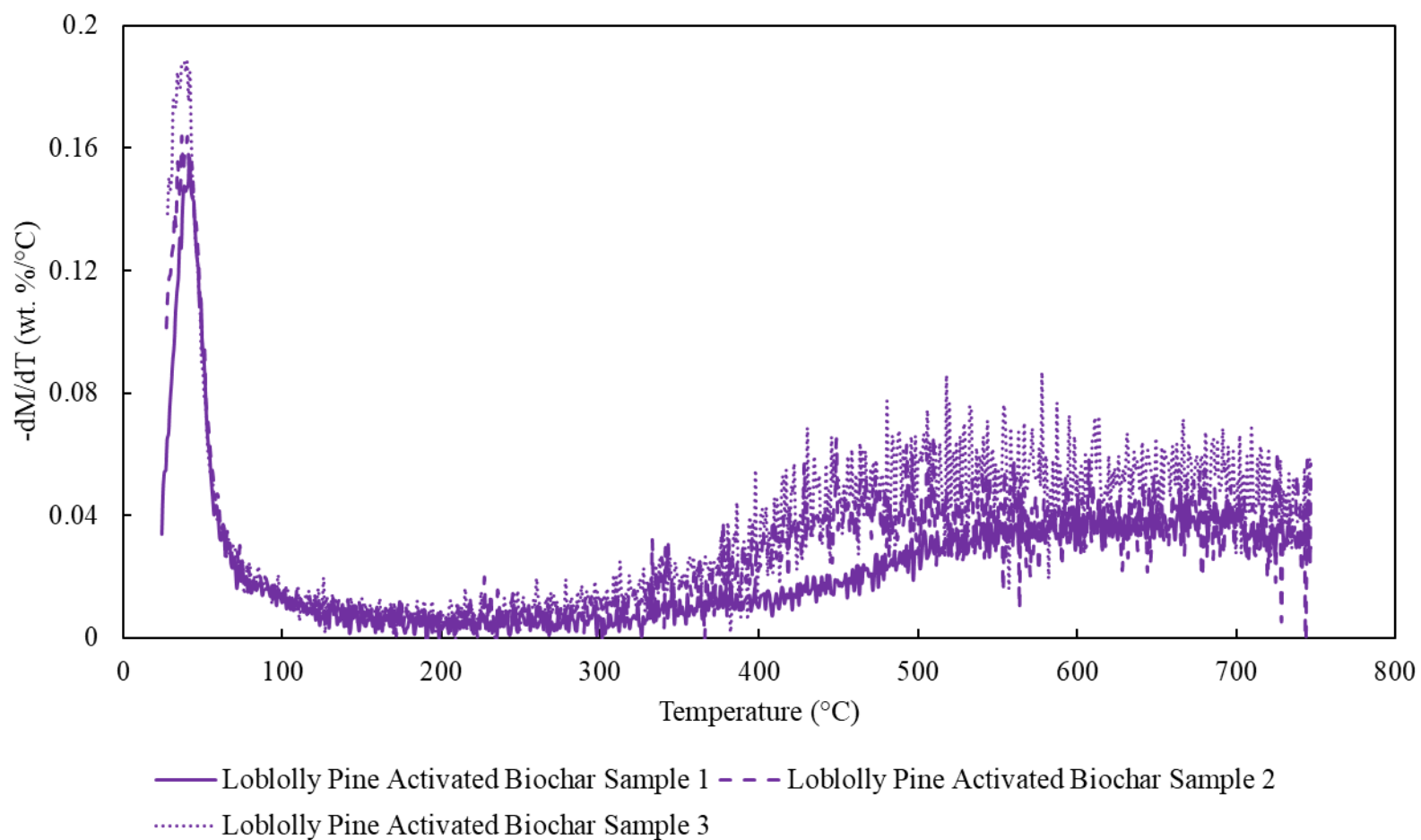


Figure 3.9. Derivative mass loss thermographs of loblolly pine activated biochars.

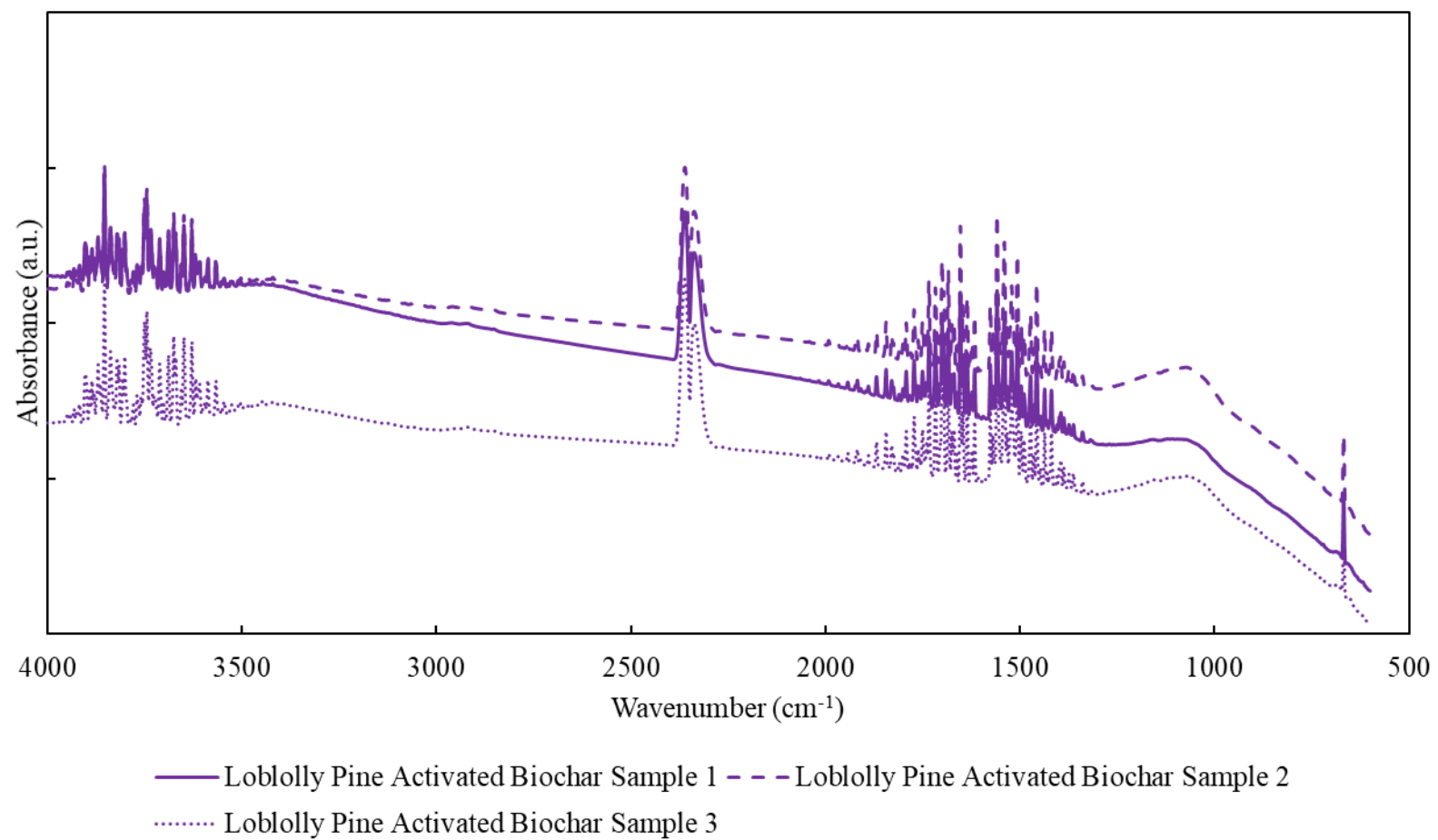


Figure 3.10. FTIR spectra of loblolly pine activated biochars.

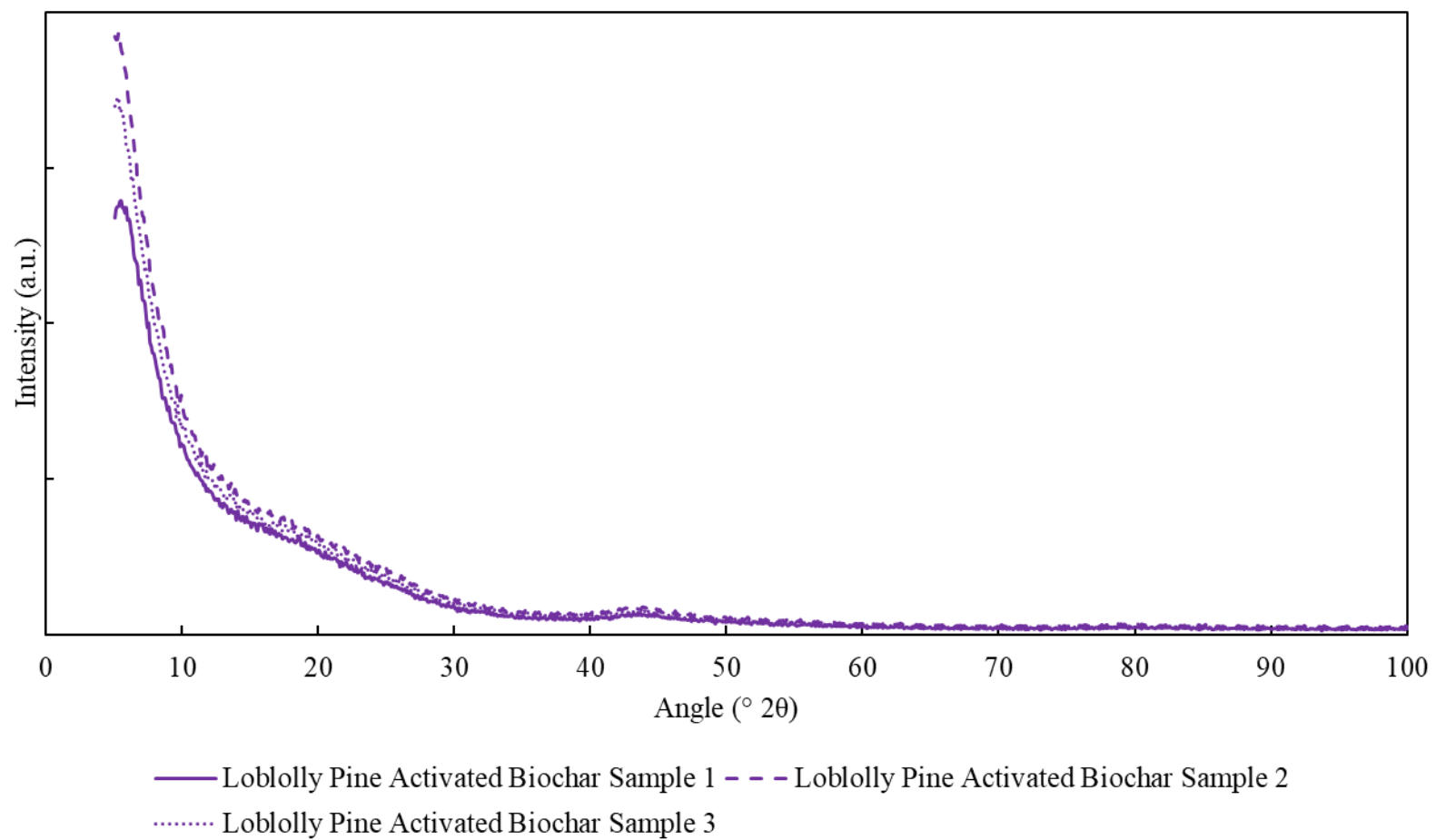


Figure 3.11. XRD diffractograms of loblolly pine activated biochars.

Table 3.15. Aliphatic interchain spacings, aromatic interlayer spacings, aromatic stacking diameters, aromatic sheet diameters, numbers of stacked aromatic sheets, and aromaticities of loblolly pine activated biochars.

Loblolly Pine				
	Sample	Aliphatic Interchain Spacing (Å)	Aromatic Interlayer Spacing (Å)	Aromatic Stacking Diameter (Å)
Activated Biochar	1	5	4	8
	2	5	4	8
	3	5	4	8
	Sample	Aromatic Sheet Diameter (Å)	Number of Stacked Aromatic Sheets	Aromaticity (%)
Activated Biochar	1	27	2	85.30
	2	30	2	77.45
	3	28	2	80.83

Appendix C. CO₂ Adsorption

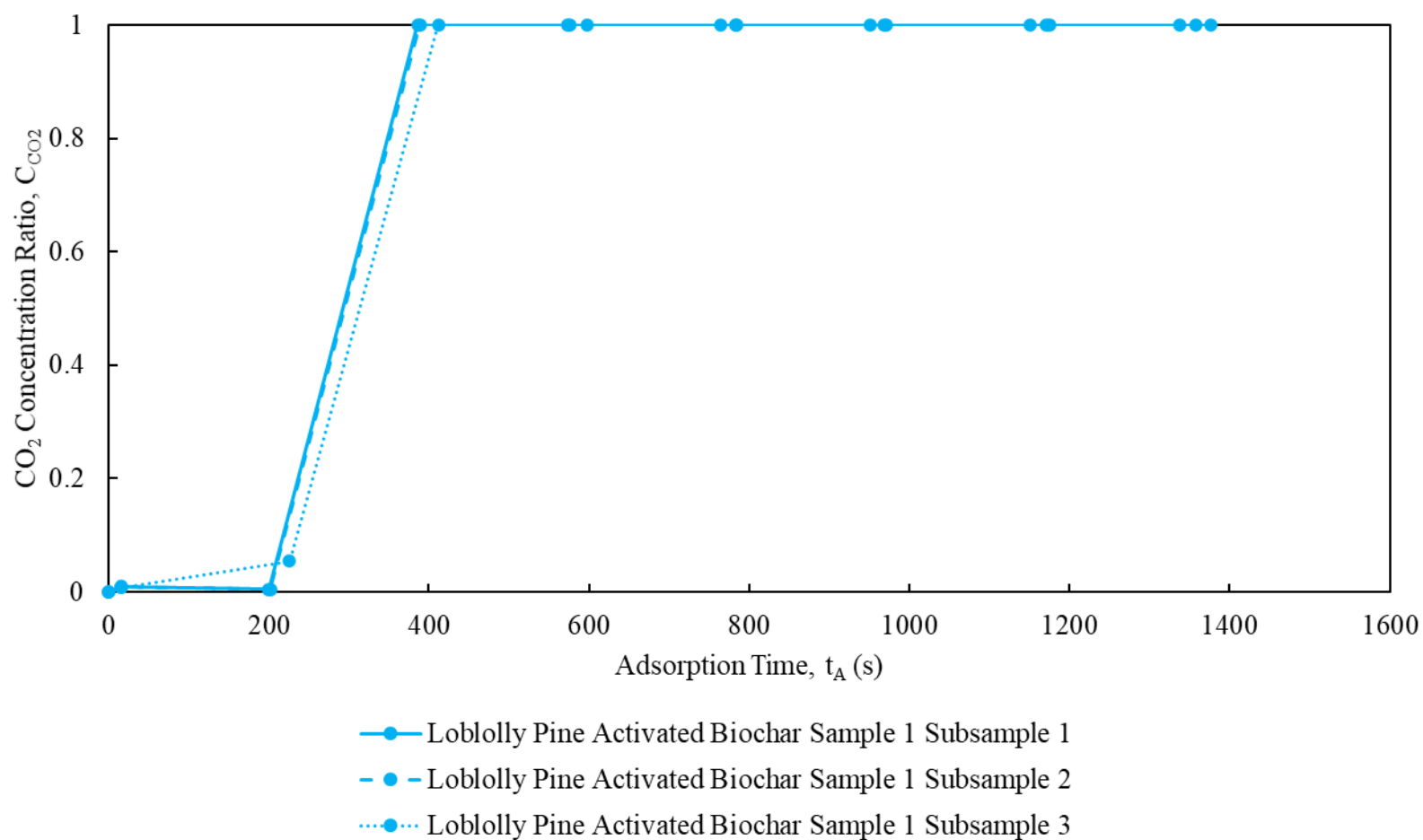


Figure 3.12. CO₂ breakthrough curves of loblolly pine activated biochars (sample 1).

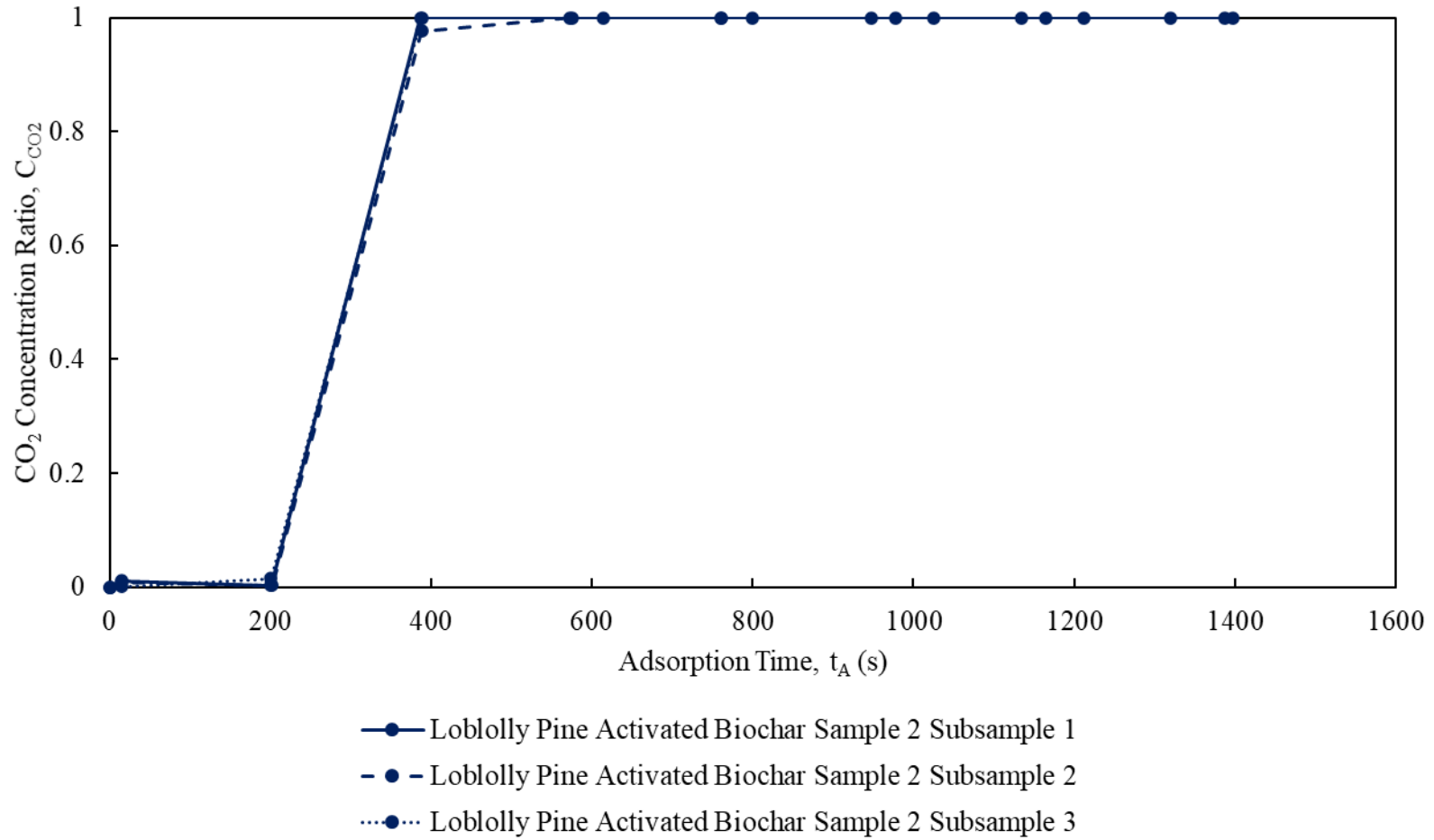


Figure 3.13. CO₂ breakthrough curves of loblolly pine activated biochars (sample 2).

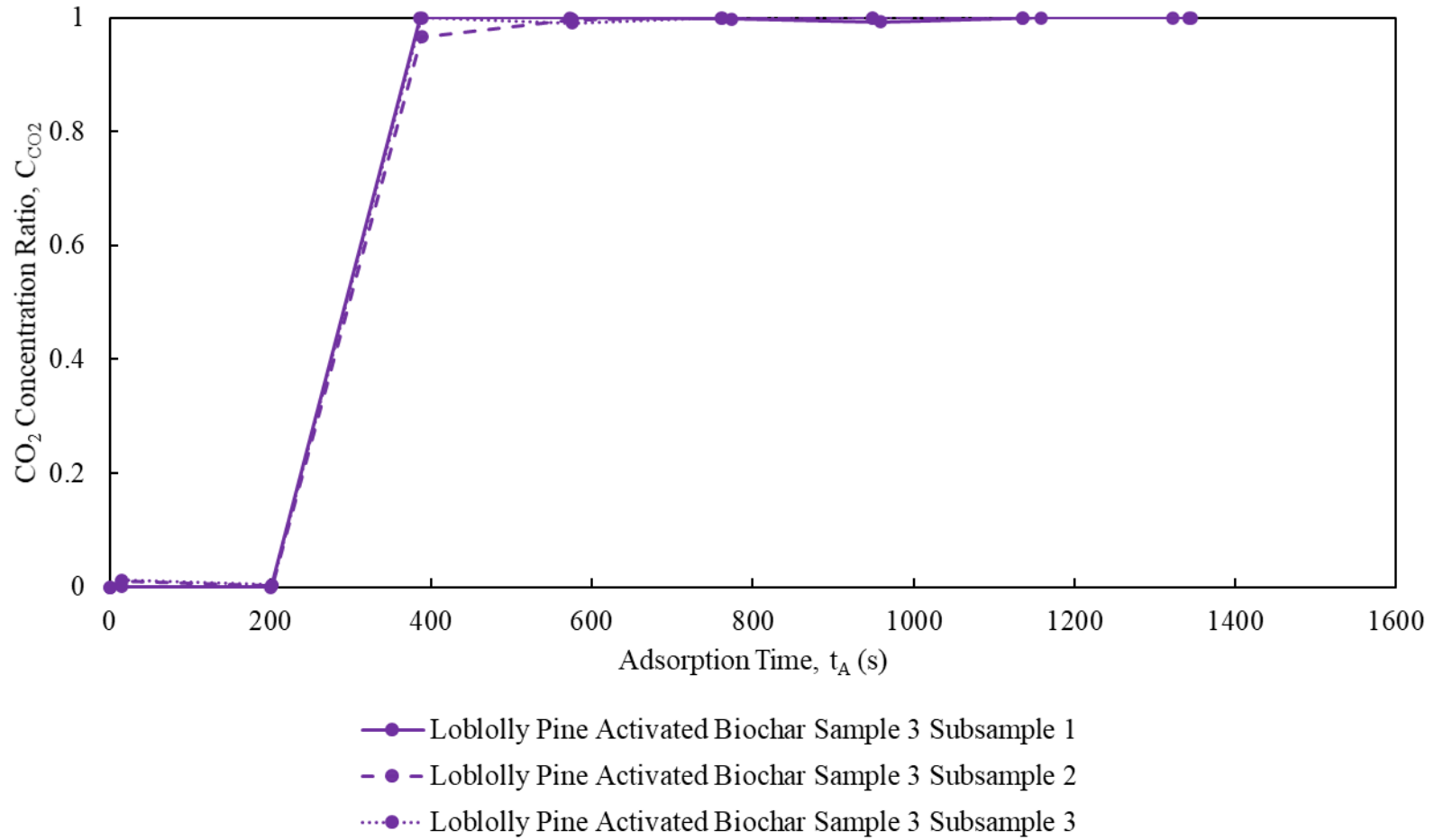


Figure 3.14. CO₂ breakthrough curves of loblolly pine activated biochars (sample 3).

Table 3.16. CO₂ adsorption, desorption, and working capacities and regenerabilities of loblolly pine activated biochars.

Loblolly Pine						
	Sample	Subsample	CO ₂ Adsorption Capacity (mmol/g)	CO ₂ Desorption Capacity (mmol/g)	CO ₂ Working Capacity (mmol/g)	Regenerability (%)
Activated Biochar	1	1	0.53	0.37	0.16	69.94
		2	0.52	0.37	0.15	71.32
		3	0.54	0.35	0.19	64.86
	2	1	0.49	0.30	0.19	60.61
		2	0.50	0.29	0.20	59.50
		3	0.48	0.29	0.20	59.47
	3	1	0.49	0.38	0.12	76.14
		2	0.50	0.34	0.16	68.17
		3	0.50	0.36	0.13	73.26

**Chapter 4. The Significance of Metal-Organic
Framework/Activated Biochar Composite Solvothermal
Synthesis on Activated Biochar Physicochemical
Characteristics and CO₂ Adsorption**

Abstract

Carbon- and metal-based porous solids such as metal-organic frameworks (MOF) and graphene oxides (GO) have difficulties in separating carbon dioxide (CO₂) from gas mixtures like flue gas. However, the creation of mixed porous solids or composites synthesized from MOFs and GO can be performed to overcome these challenges since such porous solids exhibit synergism when merged into composites. This study sought to identify the significance of MOF/activated biochar (AB) composite solvothermal synthesis on the physicochemical characteristics and CO₂ adsorption behavior of magnesium-metal-organic framework-74 (Mg-MOF-74)/loblolly pine AB composites compared to those of Mg-MOF-74 and loblolly pine AB. MOF/AB composite synthesis experiments were conducted by growing Mg-MOF-74 crystals in the presence of loblolly pine AB in a *N,N*-dimethylformamide (DMF), ethanol, and deionized (DI) water mixture with a DMF/ethanol/DI water volume ratio of 15/1/1 at 125°C. Physicochemical characteristics of loblolly pine AB, Mg-MOF-74, and Mg-MOF-74/loblolly pine AB composite including carbon (C) and hydrogen (H) contents and MOF crystallite size were measured or obtained using standard or published techniques. CO₂ adsorption and desorption experiments were performed in a CO₂ adsorption system at 35°C using 5 vol. % CO₂ balanced with nitrogen gas (N₂) flowing at 50 mL/min. H content increased in Mg-MOF-74/loblolly pine AB composite compared to loblolly pine AB from 0.23 to 1.35 wt. %, wet basis (wb) indicating that Mg-MOF-74 crystals were grown on loblolly pine AB. MOF crystallite size varied from 328–374 Å but did not differ between loblolly pine AB and Mg-MOF-74/loblolly pine AB composite revealing that loblolly pine AB did not affect Mg-MOF-74 crystal growth. Therefore, CO₂ adsorption capacity increased in Mg-MOF-74/loblolly pine AB composite relative to loblolly pine AB from 0.51 to 0.59 mmol/g representing a 16% enhancement in CO₂ adsorption capacity. The results illustrated that AB CO₂ adsorption capacity was upgraded by MOF/AB composite synthesis.

4.1 Introduction

Adsorption is a gas separation process that has been gaining increasing attention as a means of developing carbon capture and storage (CCS) technologies for separating CO₂ from the gas mixture referred to as flue gas emitted from coal-fired power plants into Earth's atmosphere. This process is favored because adsorption can be used in a wide range of operating pressures and temperatures and has low energy requirements and process costs [1][2]. However, these benefits depend on the process using adsorbents that have high CO₂ adsorption capacities, CO₂ adsorption selectivities, thermal stabilities, and chemical stabilities and can be effortlessly regenerated for reuse over multiple adsorption cycles. As such, many kinds of adsorbents or porous solids such as activated carbons (AC), GO, MOF, metal oxides (MO), silicas, and zeolites have been created and researched to assess their aptitudes for effectively separating CO₂ from flue gas [1][2][3]. Among these different porous solids, ACs have been used extensively for CO₂ adsorption because of the many advantages ACs have over other porous solids. These disparate advantages include ACs having high CO₂ adsorption capacities at ambient pressures, acceptable CO₂ adsorption behaviors over a wide range of operating conditions, high specific surface areas, easily manipulated pore structures, high thermal stabilities, adequate chemical stabilities, low energy requirements, high regenerabilities, ample precursor or feedstock availabilities, and low production costs [2]. Nevertheless, the use of ACs in CCS technologies is not ideal since ACs are still predominantly produced from fossil fuels like coal which makes ACs less environmentally friendly and sustainable than other porous solids. Conversely, biochar is an alternative carbon-based porous solid or porous carbon to AC that has a higher feedstock availability than that of AC and is more

environmentally friendly than AC. Such discrepancies are associated with biochar being generated from different biomasses and wastes through pyrolysis whereas AC is produced from coal, lignite, peat, polymers, and wood through carbonization and activation [1][3][4][5][6][7]. Yet, despite biochar having these benefits over AC, biochar has a much lower CO₂ adsorption capacity than that of AC which means that AC is more effective at separating CO₂ from flue gas. The poor CO₂ adsorption behavior of biochar can be improved by activating biochar through chemical activation using a suitable chemical activating agent such as potassium hydroxide (KOH) which greatly improves the porosity and, consequently, CO₂ adsorption capacity of biochar [1][2][4][5][8]. Regardless of this improvement, AB has a low CO₂ adsorption selectivity and the CO₂ adsorption capacity of AB decreases with increasing temperature which are disadvantageous characteristics that are common to most carbonaceous materials or carbons. Because of these drawbacks, AB is not effective at separating CO₂ from flue gas since this gas mixture has a low CO₂ concentration and is emitted from the flues of coal-fired power plants at about 150°C [2][9]. Other porous carbons also face such challenges with effectively separating CO₂ from flue gas which indicates that metal-based porous solids like MOs and MOFs may be more appropriate for this application.

MOFs are metal-based organic-inorganic porous solids that are constituted of organic ligands and metal ions or clusters called secondary building units (SBU) which are coordinated to each other through covalent bonding. The coordination that develops between these constituents creates highly ordered, three-dimensional porous structures in the form of MOFs. Because MOFs have such regular structures and can be produced from a wide variety of metal ions and organic ligands, MOFs are crystalline materials that have high specific surface areas, high porosities, consistent pore structures, easily modified pore sizes, and tailorable surface functional groups or functionalities [10][11][12][13][14][15]. These beneficial physicochemical characteristics result in many MOFs having high CO₂ adsorption capacities and selectivities. Additionally, by using certain metal ions and organic ligands during synthesis, MOFs can be customized to have higher affinities for CO₂ and, therefore, be more favorable for CO₂ adsorption [12][13][15][16][17]. For example, the metal-metal-organic framework-74 (M-MOF-74) series of MOFs where M denotes different metals has gained extensive attention in research related to CO₂ adsorption because MOFs in this specific family have high specific surface areas and CO₂ adsorption capacities. Such MOFs are composed of either magnesium(II) (Mg²⁺), manganese(II) (Mn²⁺), iron(II) (Fe²⁺), cobalt(II) (Co²⁺), nickel(II) (Ni²⁺), copper(II) (Cu²⁺), or zinc(II) (Zn²⁺) ions in the form of divalent metal oxide clusters (M₃O₃) arranged in infinite rods and 2,5-dioxidoterephthalate (C₈H₂O₆⁴⁻) anions as organic ligands. Each metal ion in MOFs of this series is coordinated to three carboxyl (R-C(=O)-OH) groups, two hydroxyl (R-OH) groups, and a coordinated ligand in the form of either DMF or water (H₂O) [14][17][18][19][20]. Among the MOFs of this series, Mg-MOF-74 has an exceptional affinity for CO₂ under ambient conditions with Mg-MOF-74 having a CO₂ adsorption capacity of 8.61 mmol/g at 1 atm and 25°C. This strong affinity for CO₂ at low pressure and temperature is linked to the high specific surface area of 1174 m²/g and low average pore size of 1.02 nm of Mg-MOF-74 and the strong interaction between coordinatively unsaturated Mg²⁺ ions in Mg-MOF-74 and oxygen (O) lone pair orbitals of CO₂ molecules [11][14][15][17][18].

However, despite the extraordinary CO₂ adsorption behaviors of MOFs, these porous solids have several challenges that limit the use of MOFs for CO₂ adsorption. For instance, MOFs have low CO₂ adsorption capacities at low pressure since these porous solids heavily rely on the development of van der Waals interactions to adsorb CO₂ [12]. Furthermore, MOFs have low water resistance which causes the crystal structures of MOFs to deteriorate in the presence of water vapor (H₂O_v). Such diminished stability is connected to H₂O_v destroying the covalent bonds

between metal ions and organic ligands in MOFs as H_2O_v is adsorbed which results in MOFs falling apart and being unable to adsorb CO_2 . MOFs also have low thermal stabilities compared to those of other porous solids like ACs and zeolites which corresponds to the organic ligands in MOFs typically decomposing in the temperature range of about 300-600°C [2][10][15][19][21]. To make matters worse, MOFs usually have high production costs linked to the specific organic ligands and solvents that must be used to create certain MOFs. Regardless of these difficulties, researchers are exploring the substitution of metal ions and organic ligands in MOFs, impregnation of MOFs with other materials, MOF carbonization, surface functionalization of MOFs, and MOF mixed porous solid or composite synthesis as means of overcoming these limitations by altering the physicochemical characteristics of MOFs [12][13][15][16][17][22][23][24][25][26][27]. Of note, MOF composites synthesized with GO are gaining interest among researchers since such composites acquire beneficial physicochemical characteristics from MOFs and GO which causes MOF/GO composites to have improved CO_2 adsorption behaviors. For example, MOFs have low atomic densities and largely open structures whereas GO has a high atomic density and contains many different surface functionalities. Accordingly, the incorporation of GO into MOF composites drastically increases dispersive forces such as van der Waals interactions between MOF/GO composite surfaces and CO_2 molecules which enhance CO_2 adsorption [12][13][15][16][26]. In addition, the presence of GO in MOF composites improves the water resistance of MOFs since O functional groups in GO coordinate with metal ions in MOFs through covalent bonds which results in the aromatic C rings that compose the graphene sheets in GO surrounding metal ions in MOFs and forming hydrophobic covers around metal ions. This coordination prevents H_2O_v from interacting with metal ions in MOFs and, thereby, improves the stability of MOFs [15][25].

Nevertheless, GO is less environmentally friendly and sustainable than other porous carbons because GO is made from graphite which is obtained from mining. The transformation of graphite into GO also uses nitric acid (HNO_3) and sodium nitrate ($NaNO_3$) based on Hummer's method which cause the reaction to be violent and pose serious safety risks although other methods are available [28]. Because of these drawbacks, MOF composites synthesized with other porous carbons like AB may result in the creation of MOF composites that have magnified CO_2 adsorption behaviors and are environmentally friendly and sustainable. AB and GO are similar in that both porous carbons have carbonaceous structures constituted of disordered graphene sheet segments and various O surface functionalities. However, there have not been any studies reported in the literature to date that have created MOF/AB composites from MOFs and AB and investigated the CO_2 adsorption behaviors of such MOF composites. Consequently, this study aims to identify the significance of MOF/AB composite solvothermal synthesis using Mg-MOF-74 and loblolly pine AB on the physicochemical characteristics and CO_2 adsorption performance of Mg-MOF-74/loblolly pine AB composites relative to those of Mg-MOF-74 and loblolly pine AB.

4.2 Materials and Methodology

4.2.1 Materials and MOF and MOF/AB Composite Syntheses

Ultra high purity (UHP) grade N_2 and a 5 vol. % CO_2 balanced with N_2 mixture were purchased from Airgas Inc. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) (98+%, American Chemical Society (ACS) reagent, Thermo Scientific), 2,5-dihydroxyterephthalic acid (DHTA) (97%, Thermo Scientific), and DMF (ACS reagent, $\geq 99.8\%$) were purchased from Fisher Scientific. 200 mL hydrothermal synthesis autoclave reactors with Teflon lined vessels were purchased from Huanyu. Ethanol (pure, 190 proof, high-performance liquid chromatography

(HPLC)), methanol (suitable for HPLC, $\geq 99.9\%$), potassium bromide (KBr) (Fourier-transform infrared (FTIR) grade, $\geq 99\%$ trace metals basis), and a molecular sieve adsorbent (0.425-0.600 mm particle size, 5 Å pore size) were purchased from Sigma-Aldrich. In terms of AB, loblolly pine biochar was produced by pyrolyzing loblolly pine biomass through intermediate pyrolysis in a semi-pilot scale auger pyrolysis system at 500°C and 350°C/h under N₂ flowing at 10 L/min with a residence time of about 13 min. Loblolly pine AB was then developed by activating loblolly pine biochar through KOH activation at a KOH/biochar mass ratio of 3 and 800°C for 2 h under N₂ flowing at 25 mL/min. For each MOF/AB composite synthesis experiment, approximately 0.66-0.67 g of Mg(NO₃)₂·6H₂O and 0.15-0.16 g of DHTA were dissolved in a solvent mixture of DMF, ethanol, and DI water with a DMF/ethanol/DI water volume ratio of 15/1/1 and mixture volume of close to 76.5 mL through sonication at 25°C for 30 min [11][17][19]. Nearly 0.29-0.30 g of loblolly pine AB was then loaded into a Teflon lined vessel. After sonication, the solution was poured into the loaded Teflon lined vessel along the walls of the vessel to carry any loblolly pine AB particles attached to the walls to the bottom of the vessel. The loaded Teflon lined vessel was capped, placed into a 200 mL hydrothermal synthesis autoclave reactor, and heated at 125°C for 26 h [11][17][19]. Following MOF/AB composite synthesis, the reactor was cooled to 25°C before being opened. The liquor inside of the vessel was then decanted and replaced with roughly 76.5 mL of methanol to dissolve and remove any unreacted Mg(NO₃)₂·6H₂O and DHTA from the Mg-MOF-74/loblolly pine AB composite. The methanol was decanted and replaced five times over 72 h [11][17][19]. Once the methanol had been replaced five times, the contents of the vessel were filtered using 5 µm filter paper while being washed with additional methanol. The MOF/AB composite was then dried at 25°C for 24 h, weighed, and stored in a plastic bag. A small amount of MOF/AB composite was collected from the bag as a sample and stored for characterization.

MOF/AB composite yield ($Yield_{MOF/AB Composite}$) (wt. %, wet basis (wb)) was then calculated using the following formula:

$$F4.1: Yield_{MOF/AB Composite} = \frac{Mass_{MOF/AB Composite}}{Mass_{Mg(NO_3)_2} + Mass_{DHTA} + Mass_{AB}} \times 100 \quad (1)$$

where $Mass_{MOF/AB Composite}$ is the mass of Mg-MOF-74/loblolly pine AB composite (g), $Mass_{Mg(NO_3)_2}$ is the mass of Mg(NO₃)₂ (g), $Mass_{DHTA}$ is the mass of DHTA (g), and $Mass_{AB}$ is the mass of loblolly pine AB (g). For each MOF synthesis experiment, the same procedure previously discussed for MOF/AB composite synthesis was followed except that no loblolly pine AB was loaded into the Teflon lined vessel. MOF yield ($Yield_{MOF}$) (wt. %, wb) was then calculated using the following formula:

$$F4.2: Yield_{MOF} = \frac{Mass_{MOF}}{Mass_{Mg(NO_3)_2} + Mass_{DHTA}} \times 100 \quad (2)$$

where $Mass_{MOF}$ is the mass of Mg-MOF-74 (g). Septuplicate experiments were conducted using loblolly pine AB created over 3 activation experiments and combined because of the low amount of MOF/AB composite synthesized in each experiment whereas triplicate experiments were performed without using loblolly pine AB resulting in 3 samples of AB, 3 samples of MOF/AB composite, and 1 sample of MOF being obtained for characterization. As a result, characterization was completed on 3 samples of AB, 3 samples of MOF/AB composite, and 1 sample of MOF resulting in 3 measurements per characterization technique for AB and MOF/AB composite and 1 measurement per characterization technique for MOF unless otherwise stated. Before each

experiment was conducted, the Teflon lined vessel was scrubbed extensively and washed with H₂O to remove any residual MOF/AB composite or MOF and minimize cross-contamination.

4.2.2 AB, MOF, and MOF/AB Composite Characterization

Loblolly pine AB, Mg-MOF-74, and Mg-MOF-74/loblolly pine AB composite were characterized according to the following analyses and measurements on a wb where appropriate. Ultimate analysis including C, H, and nitrogen (N) contents (wt. %, wb) was accomplished by having Hazen Research, Inc. analyze the AB, MOF, and MOF/AB composite. Atomic ratios including H/C and N/C were computed after ultimate analysis. FTIR spectroscopy was conducted by grinding about 1 mg of AB, MOF, or MOF/AB composite using a mortar and pestle, mixing the ground AB, MOF, or MOF/AB composite with approximately 220-250 mg of KBr, pressing the mixture into a pellet using a 13 mm die set and hydraulic press, and analyzing each KBr-pelleted AB, MOF, or MOF/AB composite using a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with a KBr beamsplitter and deuterated triglycine sulfate (DTGS) detector. Pellets were also made using only KBr and analyzed as blanks. FTIR spectra were collected by accumulating 64 scans in transmission mode from 4000-600 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and converted from transmittance to absorbance for analysis. XRD was performed by putting close to 0.1 g of AB, MOF, or MOF/AB composite into a powder sample holder and analyzing the AB, MOF, or MOF/AB composite using a Malvern Panalytical Empyrean x-ray diffractometer equipped with a PIXcel^{3D} Medipix3 1x1 detector and Ni β filter. X-ray diffractograms were obtained at 45 kV and 40 mA from 5-100° 2θ using Cu Kα radiation at a scan speed of nearly 13 s per 0.09° 2θ step. After collection, x-ray diffractograms were processed through baseline subtraction and peak deconvolution using HighScore Plus 5.1. The deconvoluted peaks at roughly 7, 12, 15, 17, 18, 19, 20, 22, 24, 25, 26, 27, 28, 30, 31, and 34° 2θ were assigned to the Mg-MOF-74 crystalline phase, whereas the deconvoluted peaks at about 23, 43, and 79° 2θ were identified as the graphite crystalline phase [14][17][19][24][29][30][31][32][33]. The deconvoluted peaks were fit using a pseudo-voigt function. MOF crystallite size ($L_{c,MOF}$) (Å) was calculated using the following formula based on the Scherrer equation [14]:

$$\text{F4.3: } L_{c,MOF} = \frac{K_s \lambda}{\beta_{110} \cos \theta_{110}} \quad (3)$$

where K_s is the crystallite shape factor (0.9 assumed for MOF), λ is the wavelength of the incident beam (Å), β_{110} is the full width at half maximum (FWHM) of the 7° 2θ peak (° 2θ), and θ_{110} is the position of the 7° 2θ peak (° 2θ).

4.2.3 CO₂ Adsorption

CO₂ adsorption using loblolly pine AB and Mg-MOF-74/loblolly pine AB composite was performed with a CO₂ adsorption system composed of a stainless-steel adsorption column, Lindberg 70-SV tube furnace, Digi-Sense TC9500 advanced multiparameter temperature controller, OMEGA type K thermocouple sensor, and a Thermo Scientific TRACE 1310 gas chromatograph (GC) as illustrated in Figure 4.1. For each adsorption experiment, close to 1 g of AB or MOF/AB composite was loaded into the adsorption column in between pieces of glass wool. The loaded adsorption column was then outgassed at 100°C under N₂ flowing at 150 mL/min for 24 h. After outgassing, the loaded adsorption column was cooled and 5 vol. % CO₂ balanced with N₂ was passed through a line bypassing the adsorption system at 25°C and 50 mL/min to the GC. Five gas chromatograms were collected and used to determine the inlet CO₂ concentration ($C_{CO_2,In}$).

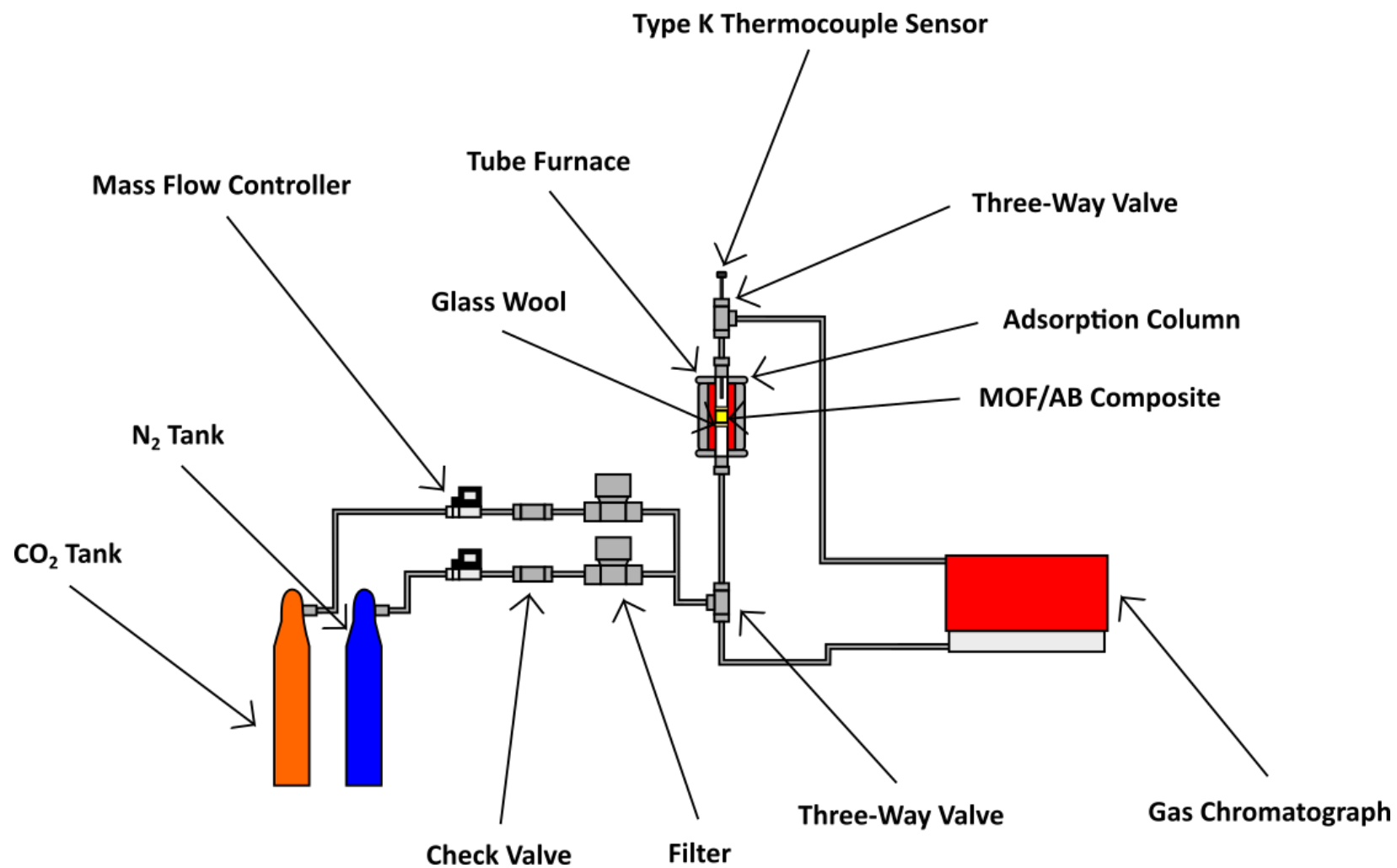


Figure 4.1. CO₂ adsorption system used to adsorb CO₂ onto and desorb CO₂ from loblolly pine activated biochar and magnesium-metal-organic framework-74/loblolly pine activated biochar composite.

(vol. %). N₂ was then passed through the adsorption system at 150 mL/min to remove CO₂ from the adsorption system prior to the experiment. Once CO₂ had been removed, the loaded adsorption column was heated to 35°C and 5 vol. % CO₂ balanced with N₂ was passed through the loaded adsorption column at 50 mL/min which denoted the beginning of the experiment [34][35]. The outlet CO₂ concentration ($C_{CO_2,out}$) (vol. %) was monitored by the GC nearly every 4 min. When $C_{CO_2,out}$ was roughly equal to $C_{CO_2,in}$, the AB or MOF/AB composite in the adsorption column was saturated which marked the end of adsorption. CO₂ concentration ratio (C_{CO_2}) was calculated using the following formula [34][36]:

$$F4.4: C_{CO_2} = \frac{C_{CO_2,out}}{C_{CO_2,in}} \quad (4)$$

CO₂ breakthrough curves were created by plotting C_{CO_2} versus adsorption time (t_A) (s). Adsorbed CO₂ concentration ratio ($C_{CO_2,A}$) was determined using the following formula:

$$F4.5: C_{CO_2,A} = 1 - \frac{C_{CO_2,out}}{C_{CO_2,in}} \quad (5)$$

CO₂ adsorption volume ($V_{CO_2,A}$) (mL) and CO₂ adsorption capacity ($Q_{CO_2,A}$) (mmol/g) were calculated using the following formulas, respectively [36][37]:

$$F4.6: V_{CO_2,A} = \int_0^{t_A} F_A C_{CO_2,A} dC_{CO_2,A} \quad (6)$$

$$F4.7: Q_{CO_2,A} = \frac{P_A V_{CO_2,A}}{m_{MOF/AB} RT} \quad (7)$$

where F_A is the flow rate of 5 vol. % CO₂ balanced with N₂ (mL/min), P_A is the pressure during adsorption (atm), $m_{MOF/AB}$ is the mass of the AB or MOF/AB composite in the adsorption column (g), and R is the universal gas constant (atm·L/mol·K).

Following adsorption, N₂ was passed through a line bypassing the adsorption column at 150 mL/min to remove CO₂ from the adsorption system before continuing the experiment. Once CO₂ had been removed, the loaded adsorption column was heated to 35°C and N₂ was passed through the loaded adsorption column at 50 mL/min which indicated the beginning of desorption. $C_{CO_2,out}$ was monitored by the GC about every 4 min. When $C_{CO_2,out}$ was approximately 0, the AB or MOF/AB composite in the adsorption column was regenerated which signified the end of the experiment. Desorbed CO₂ concentration ratio ($C_{CO_2,D}$) was found using the following formula:

$$F4.8: C_{CO_2,D} = C_{CO_2} \quad (8)$$

CO₂ desorption volume ($V_{CO_2,D}$) (mL) and CO₂ desorption capacity ($Q_{CO_2,D}$) (mmol/g) were determined using the following formulas, respectively:

$$F4.9: V_{CO_2,D} = \int_0^{t_D} F_D C_{CO_2,D} dC_{CO_2,D} \quad (9)$$

$$F4.10: Q_{CO_2,D} = \frac{P_D V_{CO_2,D}}{m_{MOF/AB} RT} \quad (10)$$

where F_D is the flow rate of N_2 (mL/min), P_D is the pressure during desorption (atm), and t_D is the desorption time (s). CO_2 working capacity (ΔQ_{CO_2}) (mmol/g) and regenerability (R_A) (%) were calculated using the following formulas, respectively [37]:

$$F4.11: \Delta Q_{CO_2} = Q_{CO_2,A} - Q_{CO_2,D} \quad (11)$$

$$F4.12: R_A = 100 - \left(\frac{\Delta Q_{CO_2}}{Q_{CO_2,A}} \times 100 \right) \quad (12)$$

After being cooled, spent AB or MOF/AB composite was removed from the adsorption column and stored in a plastic bag. Triplicate experiments were carried out using loblolly pine AB and singlet experiments were conducted using MOF/AB composite. An experiment using a molecular sieve adsorbent was accomplished as a standard. Differences in loblolly pine AB, Mg-MOF-74, and Mg-MOF-74/loblolly pine AB composite characterization and CO_2 adsorption data were analyzed through significance testing by performing analysis of variance (ANOVA) using Microsoft Excel.

4.3 Results and Discussion

4.3.1 MOF and MOF/AB Composite Yields and Ultimate Analysis

MOF and MOF/AB composite yields and ultimate analysis of loblolly pine AB, Mg-MOF-74, and Mg-MOF-74/loblolly pine AB composite are depicted in Table 4.1. MOF yield was 25.75 wt. %, wb whereas MOF/AB composite yield was 38.18 wt. %, wb. Both yields slightly differed across MOF and MOF/AB composite syntheses experiments because of subtle variations in the surface area of the Teflon lined vessel submerged in the solvent mixture which was where Mg-MOF-74 crystals formed. The yields also varied due to some loblolly pine AB loss associated with static electricity causing loblolly pine AB particles to be ejected from the vessel before the vessel could be closed and keeping loblolly pine AB particles from being submerged in the solvent mixture. The difference between the MOF and MOF/AB composite yields was ascribed to the product being collected from the bottom and walls of the vessel for MOF synthesis experiments since the products from both locations were Mg-MOF-74 crystals while the product was only retrieved from the bottom of the vessel for MOF/AB composite synthesis experiments because only the product from the bottom of the vessel was Mg-MOF-74 crystals grown on loblolly pine AB or Mg-MOF-74/loblolly pine AB composite. The discrepancy was also attributed to loblolly pine AB being used for MOF/AB composite synthesis experiments and not being used for MOF synthesis experiments. H content increased ($p < 0.05$) in Mg-MOF-74/loblolly pine AB composite compared to loblolly pine AB from 0.23 to 1.35 wt. %, wb, while C and N contents ranged from 73.80 and 1.19 to 89.56 and 1.74 wt. %, wb, respectively, but were not different between loblolly pine AB and Mg-MOF-74/loblolly pine AB composite ($p > 0.05$). These alterations denoted that Mg-MOF-74 crystals were grown on loblolly pine AB since Mg-MOF-74 has a higher H content than that of loblolly pine AB ($p < 0.05$) which denoted that the presence of Mg-MOF-74 crystals on loblolly pine AB should increase H content in Mg-MOF-74/loblolly pine AB composite. H/C increased ($p < 0.05$) in Mg-MOF-74/loblolly pine AB composite compared to loblolly pine AB from 0.03 to 0.22 which supported that Mg-MOF-74 crystals were grown on loblolly pine AB.

Table 4.1. Metal-organic framework and metal-organic framework/activated biochar composite yields and ultimate analysis and atomic ratios of loblolly pine activated biochar, magnesium-metal-organic framework-74, and magnesium-metal-organic framework-74/loblolly pine activated biochar composite.

Porous Solid				
	MOF or MOF/AB Composite Yield (wt. %, wb)	Ultimate Analysis (wt. %, wb)		
		C	H	N
Loblolly Pine AB ¹	NA	89.56 (0.53)	0.23 (0.31)	1.19 (0.08)
Mg-MOF-74 ²	25.75 (1.69)	33.76 (0.00)	3.06 (0.00)	1.74 (0.00)
Mg-MOF-74/ Loblolly Pine AB Composite ¹	38.18 (1.22)	73.80 (7.31)	1.35 (0.18)	1.28 (0.18)
Porous Solid				
	Atomic Ratios			
	H/C		N/C	
Loblolly Pine AB ¹	0.03 (0.04)		0.01 (0.00)	
Mg-MOF-74 ²	1.08 (0.00)		0.04 (0.00)	
Mg-MOF-74/ Loblolly Pine AB Composite ¹	0.22 (0.01)		0.01 (0.00)	

Values in table are averages with standard deviations in parentheses. NA stands for not applicable.

¹Values are based on 2 measurements. ²Values are based on 1 measurement.

Accordingly, ultimate analysis conveyed that Mg-MOF-74 crystals were grown on loblolly pine AB during MOF/AB composite synthesis which should provide pores that can adsorb CO₂.

4.3.2 Fourier-Transform Infrared Spectroscopy

FTIR spectra of loblolly pine AB, Mg-MOF-74, and Mg-MOF-74/loblolly pine AB composite are illustrated in Figure 4.2. Hydroxyl (R-OH) group stretching peak absorbance from nearly 3424-3381 cm⁻¹ became drastically more distinguished in Mg-MOF-74/loblolly pine AB composite which portrayed that carboxyl (R-C(=O)-OH) groups like those found in DHTA within Mg-MOF-74 crystals and H₂O were present in Mg-MOF-74/loblolly pine AB composite. Carbon-oxygen double (C=O), carbon-carbon double (C=C), carbon-oxygen single (C-O), aromatic carbon-hydrogen (C-H), and aromatic C-O bond stretching peak absorbances from roughly 1590-1416, 1372-1371, 1237-1236, 1212-1210, and 1127-1120 cm⁻¹, respectively, appeared in Mg-MOF-74/loblolly pine AB composite which revealed that aromatic rings with C=O bonds such as those present in DHTA within Mg-MOF-74 crystals were present in Mg-MOF-74/loblolly pine AB composite. Aromatic C-H bond wagging peak absorbances from about 887-818 cm⁻¹ also appeared in Mg-MOF-74/loblolly pine AB composite which reinforced that aromatic rings like those found in DHTA within Mg-MOF-74 crystals resided in Mg-MOF-74/loblolly pine AB composite [17][38][39]. These transformations signaled that Mg-MOF-74 crystals were grown on loblolly pine AB, yet the absorbances of each of the previously mentioned peaks were less prominent compared to those in Mg-MOF-74. These differences signified the presence of loblolly pine AB in Mg-MOF-74/loblolly pine AB composite. Furthermore, the coordination of carboxylate (R-C(-O)-O⁻) ions with Mg²⁺ ions in Mg-MOF-74 crystals is indicated by the separation of the symmetric and asymmetric C=O bond stretching peaks at approximately 1590 and 1430 cm⁻¹, respectively [17]. Separation values >200 and <110 cm⁻¹ convey that monodentate and bidentate ligands control the coordination, respectively, whereas values of 200-138 cm⁻¹ demonstrate that bridging ligands dictate the coordination. The separation values of Mg-MOF-74 and Mg-MOF-74/loblolly pine AB composite were close to 167 and 161 cm⁻¹, respectively, which were similar to those of Mg-MOF-74 and Mg-MOF-74/carbon nanotube and Mg-MOF-74/GO composites that were reported in another study [17]. Such results indicated that bridging ligands were responsible for the coordination in Mg-MOF-74 and Mg-MOF-74/loblolly pine AB composite. Based on these findings, peaks associated with Mg-MOF-74 structures appeared in the Mg-MOF-74/loblolly pine AB composite spectrum. As a result, FTIR spectroscopy indicated that Mg-MOF-74 crystals were grown on loblolly pine AB through MOF/AB composite synthesis which supported the results previously discussed.

4.3.3 XRD

XRD diffractograms of loblolly pine AB, Mg-MOF-74, and Mg-MOF-74/loblolly pine AB composite are portrayed in Figures 4.3 and 4.4. For Mg-MOF-74 and Mg-MOF-74/loblolly pine AB composite diffractograms, peaks at 7, 12, 15, 17, 18, 19, 20, 22, 24, 25, 26, 27, 28, 30, 31, and 34° 2θ were assigned to the Mg-MOF-74 crystalline phase. Reflections at 7, 12, 17, 18, 20, 22, 25, and 26° 2θ were indexed with the (110), (300), (12 $\bar{1}$), (410), (401), (23 $\bar{1}$), (520), and (15 $\bar{1}$) crystallographic planes of Mg-MOF-74, respectively [17][19][24]. The Mg-MOF-74 crystallographic planes faintly varied between Mg-MOF-74 and Mg-MOF-74/loblolly pine AB composite with the (110), (300), (12 $\bar{1}$), (410), (401), (23 $\bar{1}$), (520), and (15 $\bar{1}$) planes being located at 6.78, 11.79, 16.60, 18.02, 20.45, 21.56, 24.71, and 26.17° 2θ for Mg-MOF-74 and ranging from 6.75-6.77, 11.74-11.77, 16.64-16.68, 17.97-18.03, 20.44-20.46, 21.56-21.60, and

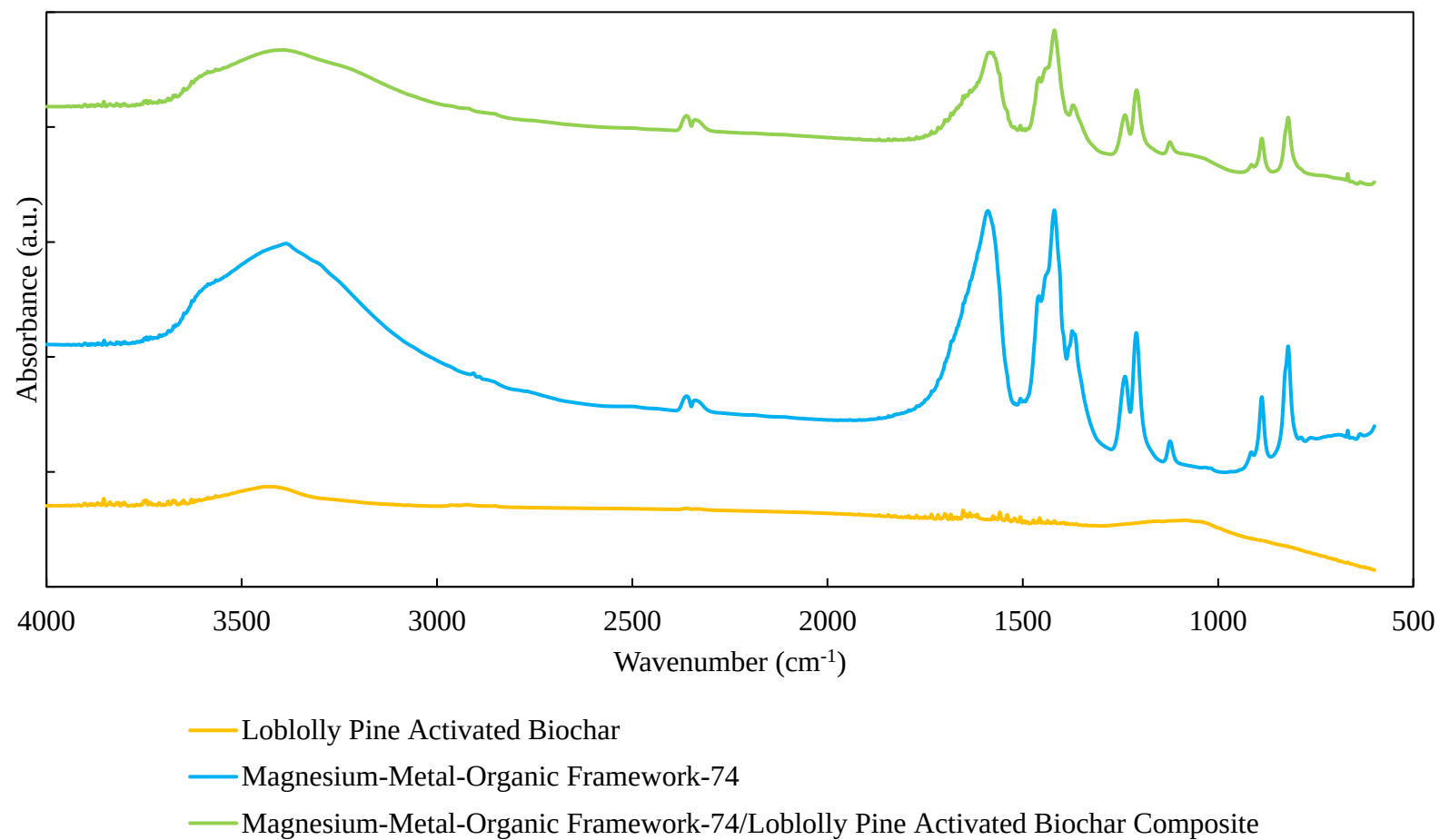


Figure 4.2. FTIR spectra of loblolly pine activated biochar, magnesium-metal-organic framework-74, and magnesium-metal-organic framework-74/loblolly pine activated biochar composite.

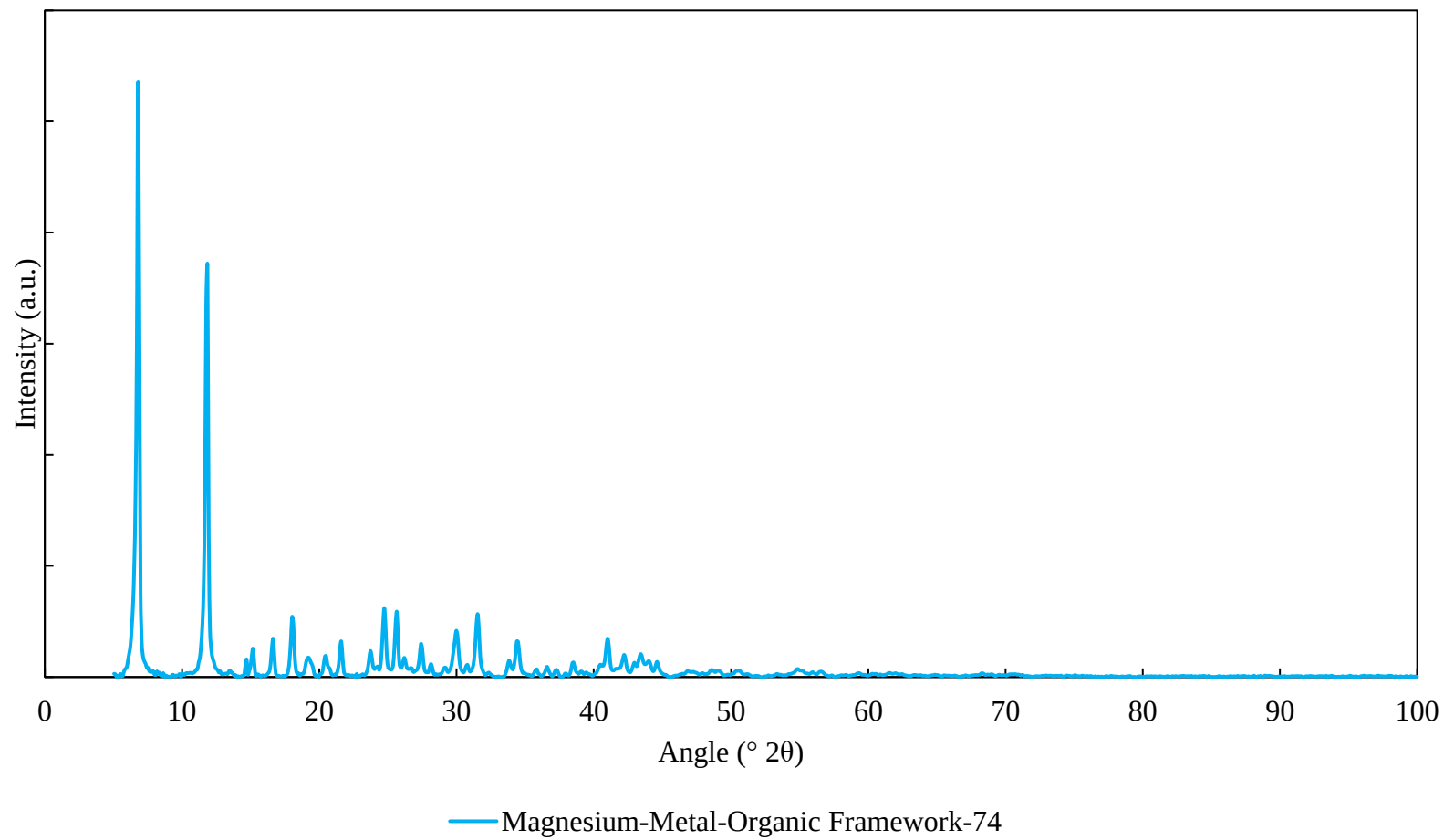


Figure 4.3. XRD diffractogram of magnesium-metal-organic framework-74.

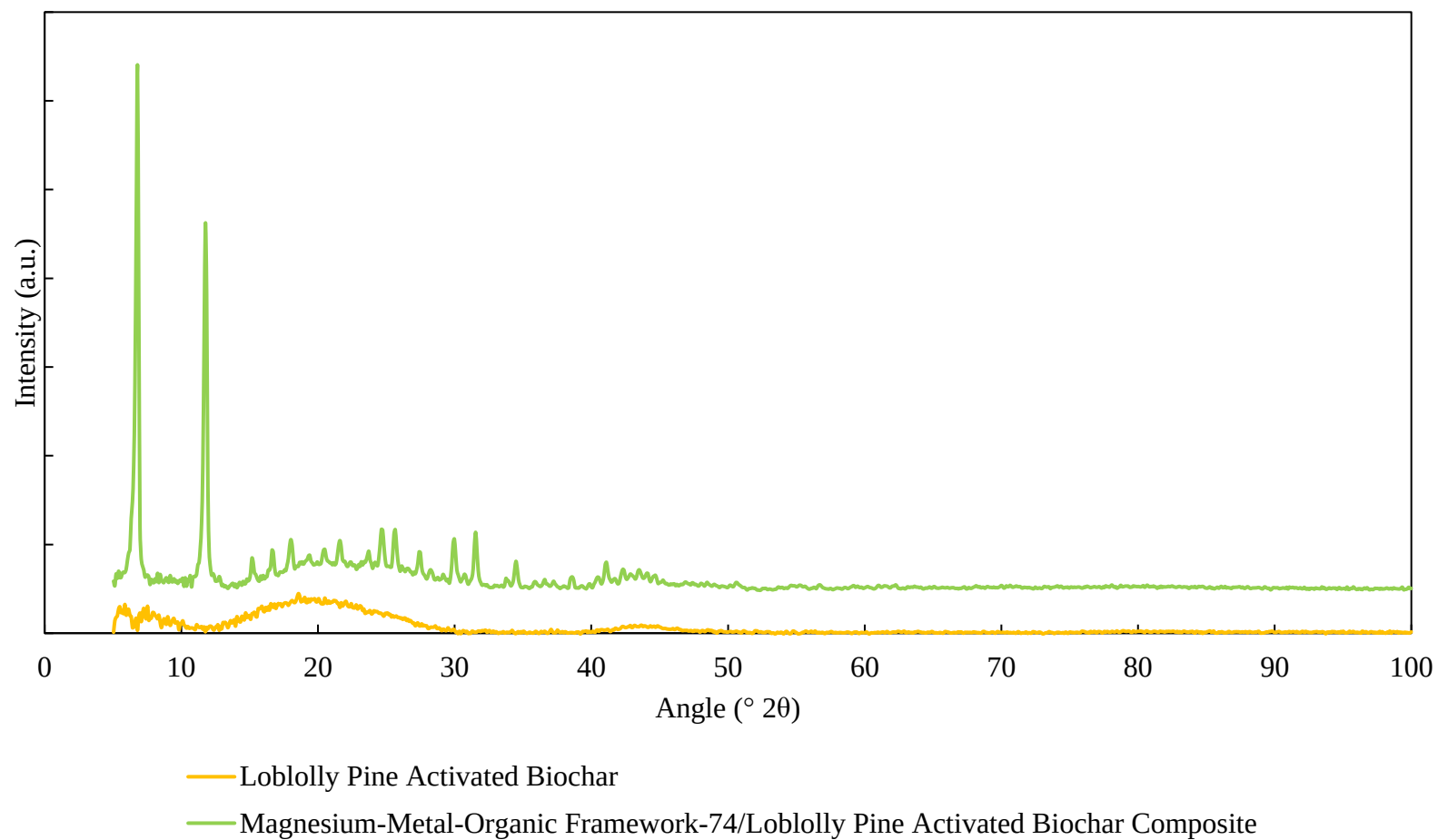


Figure 4.4. XRD diffractograms of loblolly pine activated biochar and magnesium-metal-organic framework-74/loblolly pine activated biochar composite.

24.65-24.68° 2 θ for Mg-MOF-74/loblolly pine AB composite, respectively. Mg-MOF-74 crystalline peak intensities differed between Mg-MOF-74 and Mg-MOF-74/loblolly pine AB composite which was ascribed to loblolly pine AB in Mg-MOF-74/loblolly pine AB composite restricting the degrees of freedom of Mg-MOF-74 crystal growth [16]. MOF crystallite size expresses the size of Mg-MOF-74 crystallites in Mg-MOF-74 and Mg-MOF-74/loblolly pine AB composite. MOF crystallite size of Mg-MOF-74 and Mg-MOF-74/loblolly pine AB composite are represented in Table 4.2. MOF crystallite size varied from 328-374 Å but were not different between Mg-MOF-74 and Mg-MOF-74/loblolly pine AB composite ($p > 0.05$). This lack of variation expressed that loblolly pine AB did not affect the nucleation rate of Mg-MOF-74 crystals since differences in nucleation rates lead to the formation of different Mg-MOF-74 crystals sizes. In addition, these MOF crystallite sizes were comparable to those reported in another study that used a DMF/ethanol/DI water volume ratio of 16/2/2 [14]. In terms of loblolly pine AB and Mg-MOF-74/loblolly pine AB composite diffractograms, peaks at 23, 43, and 79° 2 θ were assigned to the graphitic C crystalline phase. Reflections at 23, 43, and 79° 2 θ were indexed with the (002), (100), and (110) crystallographic planes of graphite, respectively [29][30][31][32][33]. The graphite crystallographic planes slightly differed between loblolly pine AB and Mg-MOF-74/loblolly pine AB composite with the (002), (100), and (110) planes fluctuating from 20.20-21.03, 43.55-43.75, and 79.53-80.70° 2 θ for loblolly pine AB and ranging from 21.83-24.35, 42.99-43.18, and 79.02-79.37° 2 θ for Mg-MOF-74/loblolly pine AB composite, respectively. Graphitic C crystalline peak broadenings and intensities were comparable between loblolly pine AB and Mg-MOF-74/loblolly pine AB composite which implied that the graphitic C structure in loblolly pine AB was retained through MOF/AB composite synthesis. Based on these findings, peaks connected to the Mg-MOF-74 crystalline phase which were not found in the loblolly pine AB diffractogram appeared in the Mg-MOF-74/loblolly pine AB composite diffractogram, whereas peaks corresponding to the graphitic C crystalline phase which were present in the loblolly pine AB diffractogram slightly shifted in the Mg-MOF-74/loblolly pine AB composite diffractogram. As such, XRD denoted that Mg-MOF-74 crystals were grown on loblolly pine AB during MOF/AB composite synthesis and that Mg-MOF-74 and graphitic C crystal structures was largely unaffected by MOF/AB composite synthesis.

4.3.4 CO₂ Adsorption

CO₂ breakthrough curves of loblolly pine AB and Mg-MOF-74/loblolly pine AB composite are shown in Figure 4.5. Breakthrough curves are used to reveal the saturation of an adsorbent bed in an adsorption column from the column inlet to outlet as an adsorbate such as CO₂ is gradually adsorbed over time until the bed is completely saturated. Breakthrough distinguishes the point during adsorption when the section of the bed nearest to the column inlet becomes saturated which results in the portion of the bed where mass transfer of CO₂ into the bed is occurring to shift down the bed and the concentration of CO₂ at the column outlet to increase as the bed nears total saturation [34]. The breakthroughs of loblolly pine AB and Mg-MOF-74/loblolly pine AB composite as depicted by the straight lines in Figure 4.5 signaled that Mg-MOF-74/loblolly pine AB composite had a faster breakthrough than that of loblolly pine AB with loblolly pine AB and Mg-MOF-74/loblolly pine AB composite starting to be saturated by about 200 and 15 s, respectively. This difference signified that the inlet part of the loblolly pine AB bed took longer to become saturated compared to the inlet section of the Mg-MOF-74/loblolly pine AB composite bed. Moreover, the mass transfer zone width of Mg-MOF-74/loblolly pine AB composite as represented by the curvature and slope of the breakthrough curve was greater than

Table 4.2. Metal-organic framework crystallite size of magnesium-metal-organic framework-74 and magnesium-metal-organic framework-74/loblolly pine activated biochar composite.

Porous Solid	
	MOF Crystallite Size (Å)
Mg-MOF-74	374 (0)
Mg-MOF-74/Loblolly Pine AB Composite	328 (17)

Values in table are averages with standard deviations in parentheses.

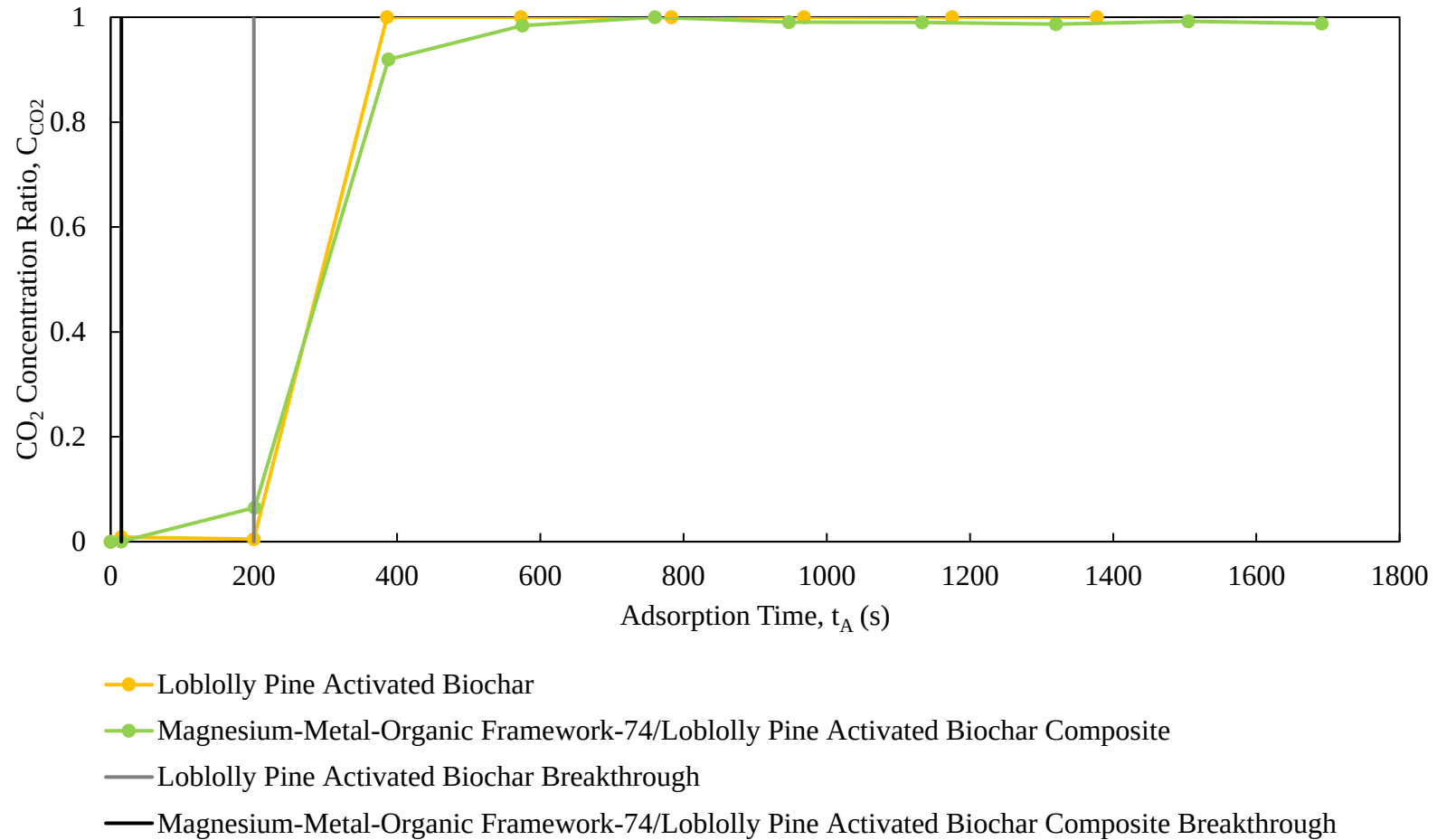


Figure 4.5. CO₂ adsorption breakthrough curves of loblolly pine activated biochar and magnesium-metal-organic framework-74/loblolly pine activated biochar composite.

that of loblolly pine AB. This discrepancy suggested that mass transfer of CO₂ into the Mg-MOF-74/loblolly pine AB composite bed following saturation of the inlet portion occurred slower than that of the loblolly pine AB bed. Such variations in breakthrough and mass transfer zone width between loblolly pine AB and Mg-MOF-74/loblolly pine AB composite demonstrated that mass transfer resistance more strongly influenced CO₂ adsorption onto Mg-MOF-74/loblolly pine AB composite than loblolly pine AB [34][40][41]. Consequently, this difference in mass transfer resistance denoted that loblolly pine AB and Mg-MOF-74/loblolly pine AB composite pore structures may have differed. Different pore sizes control separate aspects of CO₂ adsorption onto porous solids with mesopores chiefly dictating CO₂ adsorption kinetics and micropores mainly impacting CO₂ adsorption capacity [15][42]. Therefore, the CO₂ breakthrough curves indicated that Mg-MOF-74/loblolly pine AB composite adsorbed a higher amount of CO₂ than the amount adsorbed by loblolly pine AB and adsorbed CO₂ at a slower rate than that of loblolly pine AB. Such results exhibited that loblolly pine AB may have had mostly mesopores whereas Mg-MOF-74/loblolly pine AB composite may have had mesopores and micropores.

CO₂ adsorption, desorption, and working capacities and regenerability of loblolly pine AB and Mg-MOF-74/loblolly pine AB composite are displayed in Table 4.3. CO₂ adsorption and desorption capacities and regenerability increased ($p < 0.05$) in Mg-MOF-74/loblolly pine AB composite compared to loblolly pine AB from 0.51 and 0.34 and 67.03 to 0.59 and 0.47 mmol/g and 79.85%, respectively, while CO₂ working capacity decreased ($p < 0.05$) in Mg-MOF-74/loblolly pine AB composite relative to loblolly pine AB from 0.17 to 0.12 mmol/g. These alterations supported the variations in loblolly pine AB and Mg-MOF-74/loblolly pine AB composite pore structures previously suggested since a higher amount of micropores in Mg-MOF-74/loblolly pine AB composite should result in Mg-MOF-74/loblolly pine AB composite having a higher CO₂ adsorption capacity than that of loblolly pine AB ($p < 0.05$) [15][42]. Additionally, the higher CO₂ desorption capacity and regenerability and lower CO₂ working capacity of Mg-MOF-74/loblolly pine AB composite compared to those of loblolly pine AB ($p < 0.05$) implied that these improvements to CO₂ adsorption and desorption obtained through MOF/AB composite synthesis corresponded to enhancements in physical characteristics which control CO₂ physisorption rather than chemical characteristics which impact CO₂ chemisorption. Such an insinuation was based on CO₂ chemisorption causing the creation of stronger intermolecular interactions in the form of covalent bonds between porous solid surfaces and CO₂ molecules and CO₂ physisorption resulting in the development of weaker intermolecular interactions in the form of van der Waals interactions between porous solid surfaces and CO₂ molecules [2][4][43]. Accordingly, CO₂ adsorption, desorption, and working capacities and regenerability expressed that Mg-MOF-74/loblolly pine AB composite adsorbed a higher amount of CO₂ than that adsorbed by loblolly pine AB and that less adsorbed CO₂ was retained on Mg-MOF-74/loblolly pine AB composite after desorption than on loblolly pine AB.

4.4 Conclusions

The significance of MOF/AB composite solvothermal synthesis on the physicochemical characteristics and CO₂ adsorption behavior of Mg-MOF-74/loblolly pine AB composites relative to those of Mg-MOF-74 and loblolly pine AB was researched using Mg-MOF-74 grown on loblolly pine AB in a DMF, ethanol, and DI water mixture with a DMF/ethanol/DI water volume ratio of 15/1/1 at 125°C. Many physicochemical characteristics of Mg-MOF-74/loblolly pine AB composites synthesized under these conditions varied from those of loblolly pine AB and indicated that Mg-MOF-74 crystals had been grown on loblolly pine AB. Mg-MOF-74/loblolly pine AB

Table 4.3. CO₂ adsorption, desorption, and working capacities and regenerability of loblolly pine activated biochar and magnesium-metal-organic framework-74/loblolly pine activated biochar composite.

	Porous Solid			
	CO ₂ Adsorption Capacity (mmol/g)	CO ₂ Desorption Capacity (mmol/g)	CO ₂ Working Capacity (mmol/g)	Regenerability (%)
Loblolly Pine AB	0.51 (0.02)	0.34 (0.04)	0.17 (0.03)	67.03 (6.22)
Mg-MOF-74/ Loblolly Pine AB Composite	0.59 (0.02)	0.47 (0.05)	0.12 (0.03)	79.85 (5.73)

Values in table are averages with standard deviations in parentheses.

composite adsorbed a higher amount of CO₂ than that adsorbed by loblolly pine AB because of the assumed higher specific surface area, total pore volume, and amount of micropores of Mg-MOF-74/loblolly pine AB composite compared to those of loblolly pine AB which are characteristics that are known to influence CO₂ adsorption. As a result, MOF/AB composite solvothermal synthesis is an effective process for improving the physicochemical characteristics of MOFs and AB for CO₂ adsorption and upgrading the CO₂ adsorption performances of MOFs and AB. Future research should adjust the DMF/ethanol/DI water volume ratio used to grow Mg-MOF-74 crystals on loblolly pine AB since changing this value should alter the shape and size of Mg-MOF-74 crystals grown on loblolly pine AB [14]. By changing Mg-MOF-74 crystal morphology and size, MOF/AB composite solvothermal synthesis can be optimized to create more hierarchical pore structures in Mg-MOF-74/loblolly pine AB composites which should enhance the synergism of Mg-MOF-74 and loblolly pine AB and, therefore, promote CO₂ adsorption.

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Appendices

Appendix A. Metal-Organic Framework/Activated Biochar Composite Synthesis

Table 4.4. Metal-organic framework yields of magnesium-metal-organic framework-74 synthesis experiments.

Metal-Organic Framework		
	Run	MOF Yield (wt. %, wb)
Mg-MOF-74	1	26.78
	2	26.68
	3	23.80

Table 4.5. Metal-organic framework/activated biochar composite yields of magnesium-metal-organic framework-74/loblolly pine activated biochar composite synthesis experiments.

Metal-Organic Framework/Activated Biochar Composite			
	Sample	Run	MOF/AB Yield (wt. %, wb)
Mg-MOF-74/Loblolly Pine AB Composite	1	1	37.67
		2	37.63
		3	38.23
		4	39.15
		5	38.34
		6	39.59
		7	40.62
	2	1	37.31
		2	38.94
		3	39.66
		4	38.12
		5	39.02
		6	39.19
		7	37.34

(Table 4.5. Continued)

Metal-Organic Framework/Activated Biochar Composite			
	Sample	Run	MOF/AB Yield (wt. %, wb)
Mg-MOF-74/Loblolly Pine AB Composite	3	1	37.13
		2	35.97
		3	39.05
		4	37.69
		5	35.84
		6	38.56
		7	36.76

Appendix B. Metal-Organic Framework/Activated Biochar Composite Characterization

Table 4.6. Ultimate analyses of magnesium-metal-organic framework-74 and magnesium-metal-organic framework-74/loblolly pine activated biochar composites.

Porous Solid				
	Sample	Ultimate Analysis (wt. %, wb)		
		C	H	N
Mg-MOF-74	1	33.76	3.06	1.74
Mg-MOF-74/Loblolly Pine AB Composite	1	78.97	1.47	1.41
	2	68.63	1.22	1.15
	3	NM	NM	NM

NM stands for not measured.

Table 4.7. Atomic ratios of magnesium-metal-organic framework-74 and magnesium-metal-organic framework-74/loblolly pine activated biochar composites.

Porous Solid			
	Sample	Atomic Ratios	
		H/C	N/C
Mg-MOF-74	1	1.08	0.04
Mg-MOF-74/Loblolly Pine AB Composite	1	0.22	0.02
	2	0.21	0.01
	3	NM	NM

NM stands for not measured.

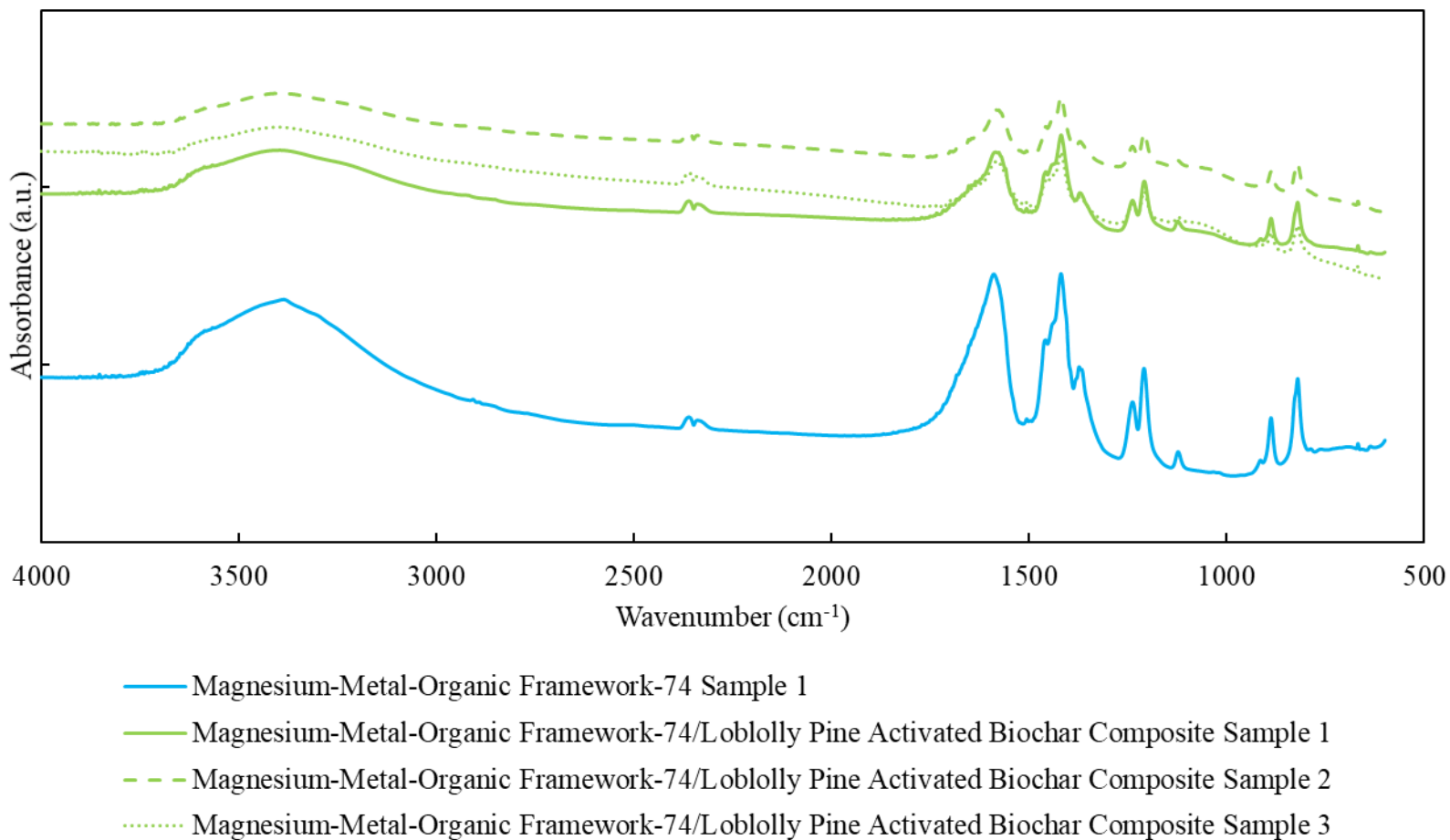


Figure 4.6. FTIR spectra of magnesium-metal-organic framework-74 and magnesium-metal-organic framework-74/loblolly pine activated biochar composites.

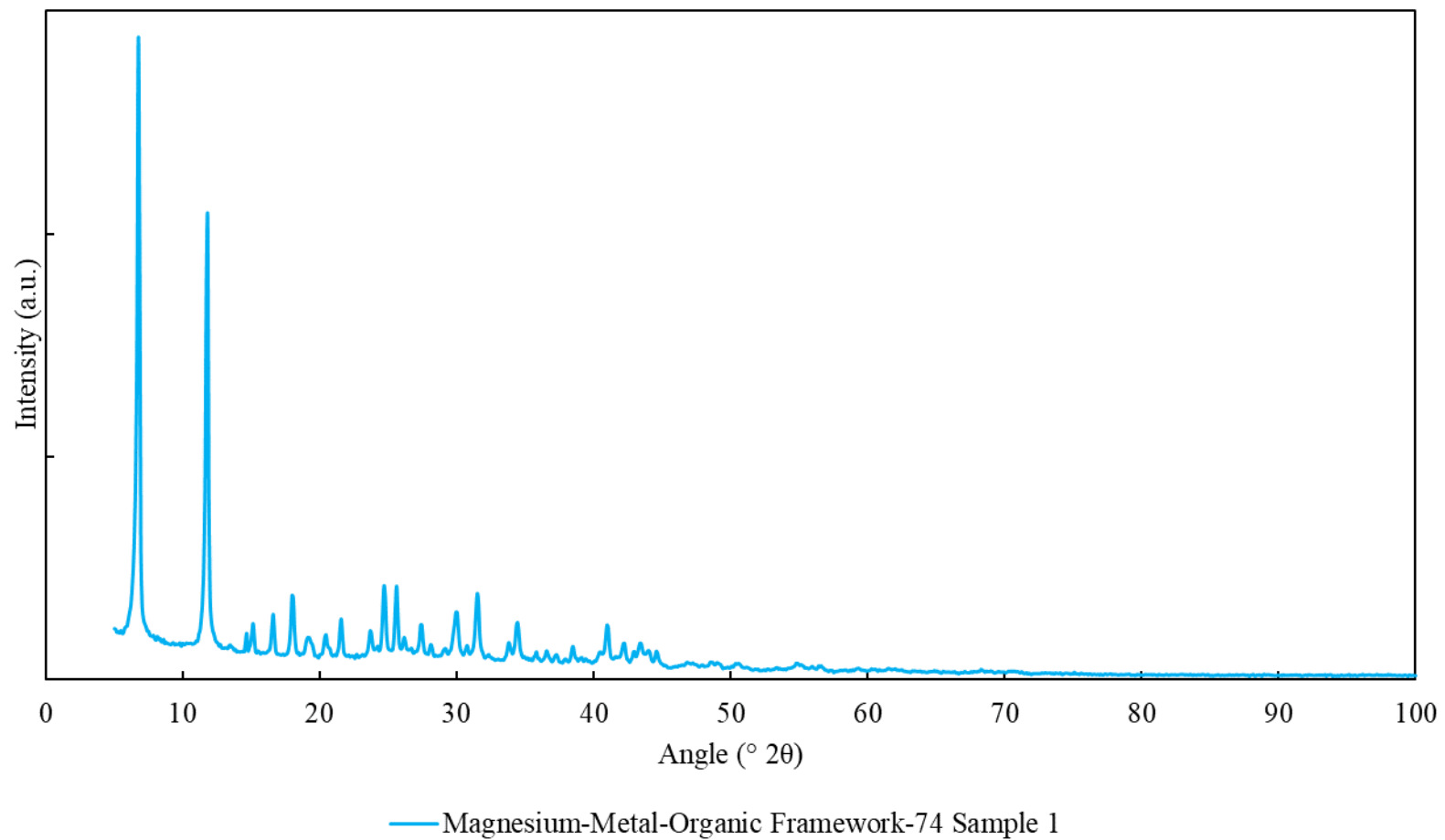


Figure 4.7. XRD diffractogram of magnesium-metal-organic framework-74.

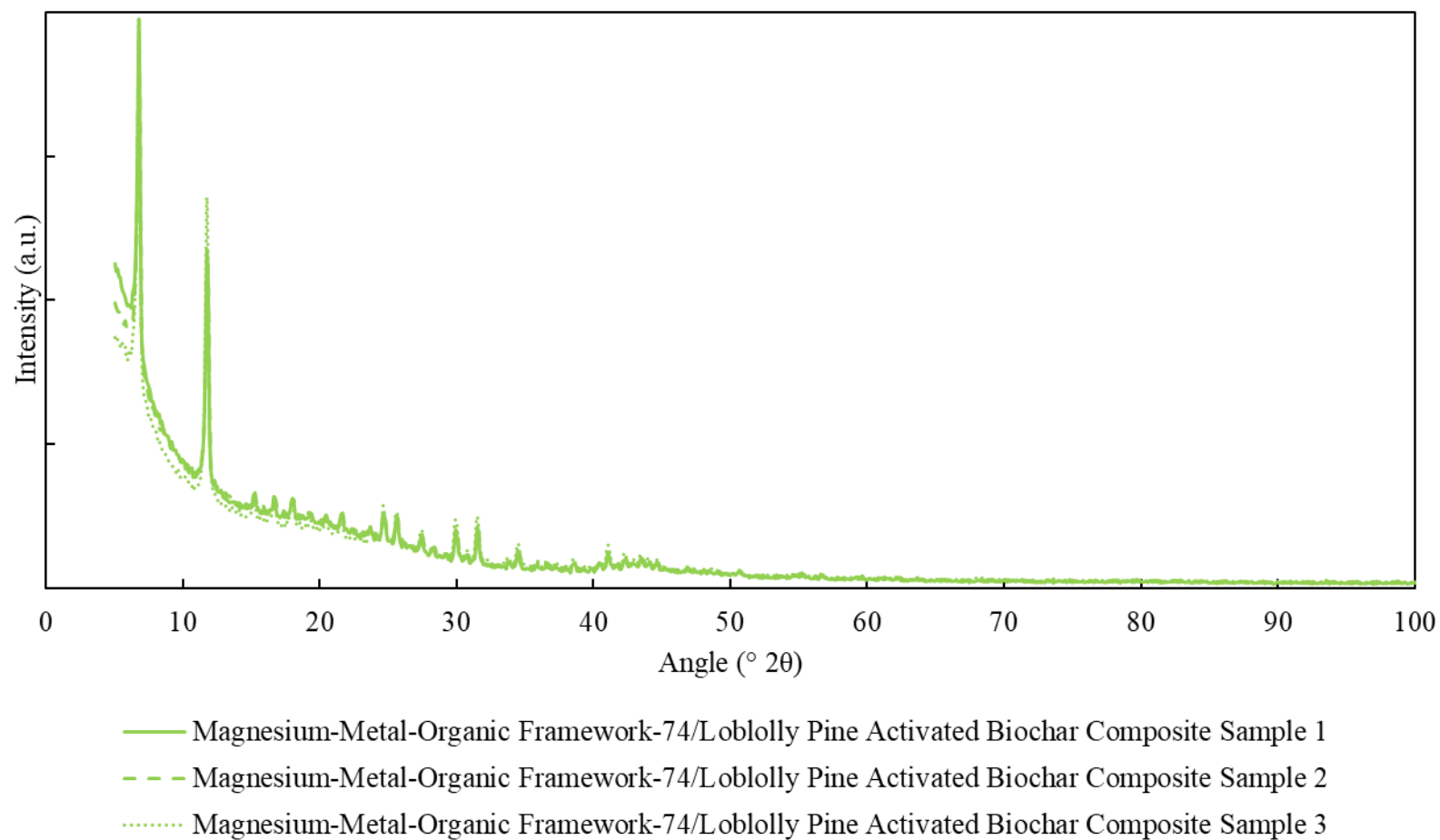


Figure 4.8. XRD diffractograms of magnesium-metal-organic framework-74/loblolly pine activated biochar composites.

Table 4.8. Metal-organic framework crystallite sizes of magnesium-metal-organic framework-74 and magnesium-metal-organic framework-74/loblolly pine activated biochar composites.

Porous Solid		
	Sample	MOF Crystallite Size (Å)
Mg-MOF-74	1	374
Mg-MOF-74/Loblolly Pine AB Composite	1	341
	2	308
	3	333

Appendix C. CO₂ Adsorption

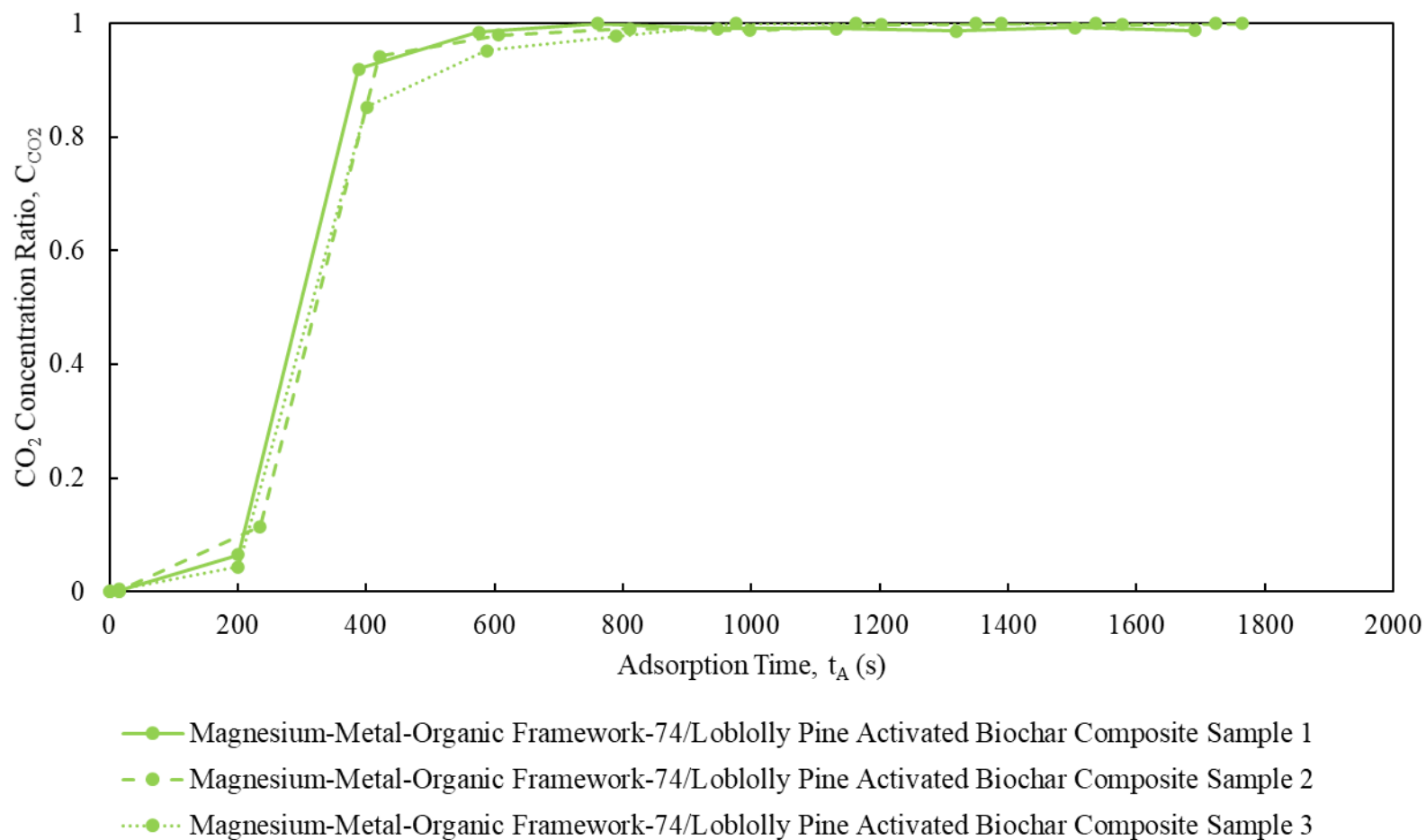


Figure 4.9. CO₂ breakthrough curves of magnesium-metal-organic framework-74/loblolly pine activated biochar composites.

Table 4.9. CO₂ adsorption, desorption, and working capacities and regenerabilities of magnesium-metal-organic framework-74/loblolly pine activated biochar composites.

Metal-Organic Framework/Activated Biochar Composite					
	Sample	CO ₂ Adsorption Capacity (mmol/g)	CO ₂ Desorption Capacity (mmol/g)	CO ₂ Working Capacity (mmol/g)	Regenerability (%)
Mg-MOF-74/Loblolly Pine AB Composite	1	0.57	0.43	0.15	74.65
	2	0.59	0.46	0.12	78.91
	3	0.60	0.52	0.08	85.99

Conclusions and Future Work

This research project synthesized metal-organic framework (MOF)/activated biochar (AB) composites with appropriate physicochemical characteristics and carbon dioxide (CO₂) adsorption capacities for adsorbing CO₂ from flue gas and other important industrial gas mixtures using magnesium-metal-organic framework-74 (Mg-MOF-74) and AB derived from loblolly pine. Mg-MOF-74/loblolly pine AB composites combine beneficial physicochemical characteristics from Mg-MOF-74 and loblolly pine AB for CO₂ adsorption and accomplish the goal of this research project by synthesizing MOF/AB composites that can effectively adsorb CO₂. However, this goal was completed through three objectives. In objective 1, biochars were created from hybrid poplar, loblolly pine, and switchgrass through intermediate pyrolysis at 500°C and used to adsorb CO₂ at 35°C from a 5 vol. % CO₂ balanced with nitrogen gas (N₂) mixture flowing at 50 mL/min. All biochars had low CO₂ adsorption capacities ranging from 0.17-0.18 mmol/g which was attributed to the low specific surface areas, total pore volumes, and alkalinities of biochars because these physicochemical characteristics control CO₂ adsorption. Accordingly, loblolly pine biochar was chosen for subsequent use in the other objectives since loblolly pine is more widely available than hybrid poplar and switchgrass which is a factor that must be considered when synthesizing MOF/AB composites from AB made from lignocellulosic biomass. Yet, biochars produced at higher pyrolysis temperatures are anticipated to have higher specific surface areas, total pore volumes, and alkalinities which could enhance CO₂ adsorption onto such biochars. In objective 2, ABs were formed from loblolly pine biochar through potassium hydroxide (KOH) activation at 800°C and used to adsorb CO₂ at 35°C from a 5 vol. % CO₂ balanced with N₂ mixture flowing at 50 mL/min. Loblolly pine AB had an increased CO₂ adsorption capacity of 0.51 mmol/g compared to 0.18 mmol/g for loblolly pine biochar which was connected to the higher specific surface area, total pore volume, and alkalinity and lower average pore width of loblolly pine AB relative to those of loblolly pine biochar. However, part of this explanation was assumed since textural analysis was not performed on loblolly pine AB. Consequently, KOH activation was demonstrated as being an important process for improving the physicochemical characteristics of biochar to favor CO₂ adsorption. Nevertheless, ABs created under different KOH activation conditions may have higher specific surface areas, total pore volumes, and alkalinities than those of the AB produced in this research project which could improve CO₂ adsorption onto such ABs since KOH activation was not optimized for loblolly pine biochar.

In objective 3, MOF/AB composites were synthesized from Mg-MOF-74 and loblolly pine AB by growing Mg-MOF-74 crystals in the presence of loblolly pine AB through solvothermal synthesis at 125°C and used to adsorb CO₂ at 35°C from a 5 vol. % CO₂ balanced with N₂ mixture flowing at 50 mL/min. Mg-MOF-74/loblolly pine AB composites had an increased CO₂ adsorption capacity of 0.59 mmol/g relative to 0.51 mmol/g for loblolly pine AB which was linked to the higher amount of micropores of Mg-MOF-74/loblolly pine AB composites compared to that of loblolly pine AB. Yet, part of this reasoning was assumed because textural analysis was not performed on Mg-MOF-74/loblolly pine AB composites. Therefore, MOF/AB composite synthesis was shown as being a pivotal process for magnifying the physicochemical characteristics of AB to promote CO₂ adsorption. However, MOF/AB composites formed in *N,N*-dimethylformamide (DMF), ethanol, and deionized (DI) water mixtures containing more DMF are expected to have higher specific surface areas and total pore volumes which could upgrade CO₂ adsorption onto such MOF/AB composites. All in all, this research project revealed that synthesizing MOF/AB composites with suitable physicochemical characteristics and CO₂ adsorption capacities for adsorbing CO₂ from gas mixtures was attainable. Moving forward, CO₂

adsorption and desorption experiments with different bed loadings and gas mixture flow rates will be performed to enhance breakthrough for biochar, AB, and MOF/AB composites. By reducing the gas mixture flow rate to a sufficient extent, MOF/AB composites may be revealed to have a higher CO₂ adsorption capacity since mass transfer into micropores will not be limited under such conditions. Additional work is also needed related to MOF/AB composite synthesis to take advantage of the synergism between MOFs and AB for CO₂ adsorption more effectively. Future work will examine MOF synthesis methodologies other than solvothermal synthesis like layer-by-layer (LBL) assembly and secondary growth to optimize the growth of MOFs on AB and maximize the specific surface areas and total pore volumes of MOF/AB composites. Moreover, surface functionalization of MOF/AB composites using nitrogenous compounds in the form of diaminoalkanes such as 1,4-butanediamine or putrescine, 1,7-heptanediamine, and bis(3-aminopropyl)amine or norspermidine will be explored to further improve the CO₂ adsorption capacities of MOF/AB composites.

Vita

Conner Pope was born in Birmingham, Alabama. After finishing high school, he attended Auburn University and graduated cum laude with a Bachelor of Biosystems Engineering degree in May 2019. Before graduation, Conner worked as an undergraduate research assistant under Dr. Sushil Adhikari on the catalytic upgrading of *Brassica carinata* oil to produce sustainable aviation fuel which was later published. He is currently finishing his Master of Science in Biosystems Engineering degree at The University of Tennessee, Knoxville and plans to graduate in May 2022. His research interests focus on creating carbon-based materials from lignocellulosic biomass and advancing the study of carbon capture. Following graduation, Conner will pursue a Doctor of Philosophy in Biosystems Engineering degree at The University of Tennessee, Knoxville. He is very grateful for the support from his wife, dog, and family as he continues his higher education.