SYNTHESIS AND CHARACTERIZATION OF HYDROTHERMAL CARBONS PRODUCED FROM GLUCOSE, STARCH AND CYCLODEXTRIN

2023
MASTER THESIS
CHEMISTRY

MEHBOOB IQBAL

Thesis Advisor
Prof. Dr. Selhan KARAGÖZ

SYNTHESIS AND CHARACTERIZATION OF HYDROTHERMAL CARBONS PRODUCED FROM GLUCOSE, STARCH AND CYCLODEXTRIN

Mehboob IQBAL

Thesis Advisor
Prof. Dr. Selhan KARAGÖZ

T.C.
Karabuk University
Institute of Graduate Programs
Department of Chemistry
Master Thesis
Prepared as

KARABUK
June 2023

I certify that in my opinion the thesis submitted by Mehboob IQBAL titled “SYNTHESIS AND CHARACTERIZATION OF HYDROTHERMAL CARBONS PRODUCED FROM GLUCOSE, STARCH AND CYCLODEXTRIN” is fully adequate in scope and in quality as a thesis for the degree of Master of Science.

Prof. Dr. Selhan KARAGÖZ ....
Thesis Advisor, Department of Chemistry

This thesis is accepted by the examining committee with a unanimous vote in the Department of Chemistry as a Master of Science thesis. 05/06/2023

Examining Committee Members (Institutions)	Signature
Chairman: Prof. Dr. Şaban UYSAL (KBU)	....
Member : Prof. Dr. Selhan KARAGÖZ (KBU)	....
Member : Assoc. Prof. Dr. Soner ÇAKAR (ZBEU)	....

The degree of Master of Science by the thesis submitted is approved by the Administrative Board of the Institute of Graduate Programs, Karabuk University.

Prof. Dr. Müslüm KUZU ....
Director of the Institute of Graduate Programs

“I declare that all the information within this thesis has been gathered and presented in accordance with academic regulations and ethical principles and I have according to the requirements of these regulations and principles cited all those which do not originate in this work as well.”

Mehboob IQBAL

ABSTRACT

M. Sc. Thesis

SYNTHESIS AND CHARACTERIZATION OF HYDROTHERMAL CARBONS PRODUCED FROM GLUCOSE, STARCH AND CYCLODEXTRIN

Mehboob IQBAL

Karabük University
Institute of Graduate Programs
Department of Chemistry

Thesis Advisor:
Prof. Dr. Selhan KARAGÖZ
June 2023, 39 pages

The present thesis aims to investigate the HTC of three different feedstocks, namely glucose, cyclodextrin, and starch. The HTC process was carried out at 180 and 200ºC for 24 h both with and without the use of 2-chloropropionic acid as a catalyst. The effects of various operating conditions and catalysts on hydrochar yields and properties were studied. The obtained hydrochars were characterized using several analytical techniques, including solid-state ^{13}C-NMR, SEM, FTIR, and elemental analysis.

Key Word : Hydrothermal carbonization, glucose, cyclodextrin, starch, 2-chloropropionic acid
Science Code : 20102

ÖZET

Yüksek Lisans Tezi

GLİKOZ, NİŞASTA VE SİKLODEKSTRİNDEN ÜRETİLEN HİDROTERMAL KARBONLARIN SENTEZİ VE KARAKTERİZASYONU

Mehboob IQBAL

Karabük Üniversitesi
Lisansüstü Eğitim Enstitüsü
Kimya Anabilim Dalı

Tez Danışmanı:
Prof. Dr. Selhan KARAGÖZ
Haziran 2023, 39 sayfa

Mevcut tez, glikoz, siklodekstrin ve nişasta olmak üzere üç farklı hammaddenin hidrotermal karbonizasyonunu araştırmayı amaçlamaktadır. HTC İşlemi, katalizör olarak 2-kloropropionik asit kullanılarak ve kullanılmadan 24 saat sürede 180 ve 200°C 'de gerçekleştirildi. Çeşitli çalışma koşullarının ve katalizörlerin hidrokömür verimleri ve özellikleri üzerindeki etkileri incelenmiştir. Elde edilen hidrokömürler, katı hal ^{13}C-NMR, SEM, FTIR ve elementel analizi dahil olmak üzere çeşitli analitik teknikler kullanılarak karakterize edildi.

Anahtar Sözcükler : Hidrotermal karbonizasyon, glikoz, siklodekstrin, nişasta, 2-kloropropiyonik asit

Bilim Kodu : 20102

ACKNOWLEDGEMENT

At first, I would like to thank God for helping me complete this study. As a master's student, I have had the privilege of working with some of the most knowledgeable and supportive individuals in my field. First and foremost, I express my sincere gratitude to my thesis supervisor, Prof. Dr. Selhan KARAGÖZ, for his invaluable guidance and support throughout my research journey. His expertise, insightful feedback, and encouragement have been crucial to the successful completion of this thesis. I am grateful for his patience, kindness, and unwavering commitment to my academic progress.

I would also like to extend my thanks to Dr. Betül ERCAN for her valuable input, encouragement, and support throughout this project. Her expertise, feedback, and guidance have been instrumental in shaping the direction and scope of this thesis. I appreciate her time, dedication, and willingness to share her knowledge and expertise.

I would like to express my deep gratitude to my parents for their unwavering support, encouragement, and the sacrifices they have made for my education. Their belief in me and my abilities has been a constant source of inspiration and motivation. I am forever grateful for their love, care, and unwavering support.

Finally, I would like to acknowledge the support of Dr. Koray ALPER and my colleagues and peers who have contributed to my learning and growth in numerous ways. I am grateful for their friendship, encouragement, and support.

In addition, I would like to thank the KBU-BAP unit for supporting this study with BAP Project No: KBUBAP-22YL-038.

CONTENTS

Pages

APPROVAL ii
ABSTRACT iv
ÖZET v
ACKNOWLEDGEMENT vi
CONTENTS vii
LIST OF FIGURES ix
LIST OF TABLES x
SYMBOLS AND ABBREVITIONS xi

PART 1 1
INTRODUCTION 1
  1.1. CARBOHYDRATES 1
    1.1.1. Monosaccharides 2
    1.1.2. Oligosaccarides 3
    1.1.3. Polysaccharides 4
    1.1.4. Glucose 6
    1.1.5. Starch 6
    1.1.6. Cyclodextrin 7
  1.2. SUBCRITICAL AND SUPERCRITICAL WATER 8
  1.3. HYDROTHERMAL PROCESSES 9
    1.3.1. Hydrothermal Gasification 10
    1.3.2. Hydrothermal Liquefaction 11
    1.3.3. Hydrothermal Carbonization 12

PART 2 16
LITERATURE REVIEW 16

PART 3 20
MATERIALS AND METHODS... 20
    3.1. MATERIALS 20
    3.2. EXPERIMENTAL PROCEDURE.. 20
    3.3. ANALYSIS 21

PART 4 22
RESULTS AND DISCUSSION 22
    4.1. HYDROCHAR YIELDS 22

PART 5 32
CONCLUSIONS... 32

REFERENCES... 33

RESUME 39

LIST OF FIGURES

Pages

Figure 4.1. SEM images of hydrochars produced from glucose, β-cyclodextrin, and starch at 200 °C for 24 h without and with catalysts (a) G-HC3 (b) G-HC4 (c) CD-HC3 (d) CD-HC4. e) S-HC3 (f) S-HC4..................................... 26
Figure 4.2. FT-IR spectra were obtained for: a) Glucose, b) Hydrochars produced from glucose at 180°C without catalyst, c) Hydrochars produced from glucose at 180°C with catalyst, d) Hydrochars produced from glucose at 200°C without catalyst, e) Hydrochars produced from glucose at 200°C with catalyst... 27
Figure 4.3. FTIR spectra were obtained for: a) β-cyclodextrin, b) Hydrochars produced from β-cyclodextrin at 180°C without catalyst, c) Hydrochars produced from β-cyclodextrin at 180°C with catalyst, d) Hydrochars produced from β-cyclodextrin at 200°C without catalyst, e) Hydrochars produced from β-cyclodextrin at 200°C with catalyst. 28
Figure 4.4. FTIR spectra were obtained for: a) starch, b) Hydrochars produced from starch at 180°C without catalyst, c) Hydrochars produced from starch at 180°C with catalyst, d) Hydrochars produced from starch at 200°C without catalyst, e) Hydrochars produced from starch at 200°C with catalyst. ... 29
Figure 4.5. NMR spectra of glucose, β-cyclodextrin, and starch.............................. 30
Figure 4.6. NMR spectra of hydrochars obtained from glucose, β-cyclodextrin, and starch at 200 ºC without and with catalyst. 31

LIST OF TABLES

Pages

Table 1.1. The most common monosaccharides found in nature 3

Table 1.2. Some examples for oligosaccharides 4

Table 1.3. Examples of polysaccharides in nature 5

Table 1.4. Some examples for polysaccharides 6

Table 1.5. The characteristics of water depending on temperature and pressure 8

Table 1.6. Hydrothermal techniques and operating temperatures 9

Table 4.1. Yields of hydrochars produced from glucose, β-Cyclodextrin, and starch at 180 and 200 °C for 24 h without and with catalyst 22

Table 4.2. The pH levels of slurries before and after the HTC process. 23

Table 4.3. Elemental compositions (wt%), H/C, and O/C atomic ratios of glucose, β-cyclodextrin, starch and hydrochars obtained from these raw materials .. 24

SYMBOLS AND ABBREVITIONS

ºC	: degree Celcius
MPa	: megapascal
kJ	: kilojoule
pH	: potential of hydrogen
ε	: dielectric constant
M	: molar
μm	: micrometer
HMF	: 5-Hydroxymethylfurfural
H_2	: Hydrogen gas
HTC	: Hydrothermal carbonization
HTL	: Hydrothermal liquefaction
HTG	: Hydrothermal gasification
^{13}C NMR	: ^{13}Carbon nuclear magnetic resonance
FTIR	: Fourier-transform infrared spectroscopy
SEM	: Scanning electron microscopy

PART 1

INTRODUCTION

Carbon is an essential element that plays a crucial role in the chemistry of life and the environment. While carbon is most commonly associated with living organisms, it is also present in a wide range of materials, including minerals, fuels, and various forms of carbon itself. Among the most well-known carbon-based materials are charcoal, fullerenes, carbon nanotubes, carbon blacks, and activated carbons. These materials have been extensively studied and used in various fields due to their unique properties and applications. In the last two decades, hydrothermal carbons, also known as hydrochars, have gained significant attention from the scientific community due to their unique properties and potential applications. Hydrothermal carbons are relatively easy and inexpensive to produce from a variety of biomass sources, making them a sustainable and eco-friendly alternative to traditional carbon-based materials. Hydrochars are produced through a specialized process known as HTC. The process involves the application of pressure and temperature to biomass in the presence of water, resulting in the formation of a carbon-rich solid product known as hydrochar, which has a range of potential applications, including as a solid fuel, a soil amendment, or a carbon sequestration agent.

In the proposed thesis, the HTC of glucose, cyclodextrin, and starch was carried out without and with the use of a catalyst (2-chloropropionic acid). The effects of feedstock type, temperature, and catalyst on the resulting hydrochars were investigated.

1.1. CARBOHYDRATES

Carbohydrates occur naturally and consist of carbon, hydrogen, and oxygen atoms. Plants manufacture carbohydrates via photosynthesis, a biochemical process that converts light energy from the sun into chemical energy [1]. The process involves transforming carbon dioxide and water into a basic sugar called glucose ($C_6H_{12}O_6$) and molecular oxygen.

However, most naturally occurring carbohydrates are not simple sugars with the empirical formula $C_x(H_2O)_y$. Disaccharides, trisaccharides, and polysaccharides are larger sugars formed by the linkage of two, three, or many monosaccharide units, respectively. Instead, they are oligomers (oligosaccharides), or polymers (polysaccharides) made by joining simple sugars or modified sugars together. Oligosaccharides are composed of two to ten sugar units, while polysaccharides can contain hundreds or thousands of sugar units [2]. Carbohydrates are a large and diverse group of naturally occurring organic compounds that play a fundamental role in many industries and segments of industries. The versatile nature of carbohydrates enables them to be utilized in the production of a wide range of essential materials and goods, spanning from glucose and starch derivatives, to paper, textiles, plastics, and various foodstuffs. Carbohydrates are also used in fermentation processes and in the production of pharmaceuticals, drugs, vitamins, and specialty chemicals, although to a lesser extent [3].

1.1.1. Monosaccharides

Monosaccharides represent the most basic form of carbohydrates, being comprised of a single unit of sugar. They are organic compounds that contain two important chemical functional groups: a carbonyl group (C=O) and at least two carbon atoms that carry hydroxyl (alcohol) groups (-C-OH) [4]. Monosaccharides can be differentiated into two categories: aldoses, which contain an aldehyde functional group as their carbonyl moiety, and ketoses, which feature a ketone functional group as their carbonyl component. Common sugars like glucose and sucrose are examples of monosaccharides and are known as polyhydroxy aldehydes or polyhydroxy ketones owing to the existence of multiple hydroxyl groups. The chemical properties of sugars are determined by the characteristics of alcohols and ketones/aldehydes. However, because sugars contain both functional groups within the same molecule, they also have some unique properties. Table 1.1 displays the most frequently occurring monosaccharides found in nature.

Table 1.1. The most common monosaccharides found in nature [5].

Name	Abbreviation
Glucose	Glc
Mannose	Man
Galactose	Gal
N-Acetylglucosamine	GlcNac
N-Acetylgalatosamine	GalNAc
Fucose	Fuc
Xylose	Xyl
Sialic acid	SA
Glucuronic acid	GlcA
Iduronic acid	IdoA

1.1.2. Oligosaccarides

Oligomers, which are short chains of monomer units, include oligosaccharides, a class of oligomers consisting of 2 to 10 monosaccharide units that are linked by glycosidic bonds. The classification of oligosaccharides can be based on their reducing or non-reducing nature, which depends on whether the terminal monosaccharide unit contains a hemiacetal group or not. Moreover, the oligosaccharides can also be categorized into disaccharides, trisaccharides, and other higher degree of polymerization oligosaccharides, which are formed through successive attachment of glycosyl units. The range of oligosaccharides found in nature is quite restricted, the breakdown of larger polysaccharides into smaller oligosaccharides requires either acid or enzyme as a catalyst. An example of this process is acid-catalyzed hydrolysis, which involves the use of aqueous acid and heat to cleave segments of starch molecules [2,6]. β-amylase enzyme is utilized to cleave maltose disaccharide units from the nonreducing ends of starch polysaccharides, producing maltose through the process of starch hydrolysis. Although it is rare in nature, maltose can be found in the seeds of germinating plants due to the incomplete hydrolysis of starch.

Table 1.2. Some examples for oligosaccharides [6].

Reducing		**Nonreducing**	
Homooligosaccharides	**Heterooligosaccharides**	**Homooligosaccharides**	**Heterooligosaccharides**
Disaccharides		***Disaccharides***	
Maltose	Lactose	Trehalose	Sucrose
Cellobiose	Lactulose	Isotrehalose	Isosucrose
Isomaltose	Melibiose		
Gentiobiose	Turanose		
Trisaccahrides		***Trisaccahrides***	
Maltotriose	Manninotriose		Raffinose
Tetrasaccharides		***Tetrasaccharides***	
Maltotetraose			Stachyose
Pentasaccharides			
Hexasaccahrides			
Heptasaccharides			
Octasaccahrides			
Nonasaccahrides			
Decasaccahrides			
Conjugate oligosaccahrides		*Conjugate oligosaccahrides*	
		Glycolipids	
		Gangliosides	

1.1.3. Polysaccharides

The term used to refer to polysaccharides is glycan, which derives from the Greek word "glyc-" meaning sweet or sugar, and the suffix "-an" indicating a polymer. Carbohydrate molecules known as polysaccharides are large molecules with high molecular weight that are made up of multiple monosaccharide units. These molecules primarily consist of chains of monosaccharides that are linked together through glycosidic bonds to form polymers. Polysaccharides make up most of the organic matter on Earth, with estimates suggesting that over 90% of all carbohydrates found in nature exist as polysaccharides [2]. These complex carbohydrates are widely distributed in the natural world and are an essential component of the biomass of living organisms, including plants, animals, fungi, and bacteria. Table 1.3 demonstrates some commonly occurring polysaccharides that are representative of those found in nature [5].

Table 1.3. Examples of polysaccharides in nature [5].

Origin	**Polysaccharides**
Animal	Chitin, Chitosan
Algal Biomass	Alginate,Agarose
Plant	Starch, Cellulose
Microbial	Cyclodextrin, dextran

The degree of polymerization (DP) of a polysaccharide, which refers to the number of monosaccharide units it contains, can vary based on the polysaccharide type. They are much larger than oligosaccharides, with varying degrees of polymerization. The majority of naturally occurring polysaccharides have DPs between 200 to 3000. Polysaccharides with degrees of polymerization under 100 are rare in natural occurrences. Some of the largest known polysaccharides include cellulose, with DPs of 7000 to 15.000, and amylopectin, a component of starch, which can have an average DPs more than 100.000 [2]. Polysaccharides are diverse in their chemical structures and can be classified based on multiple features, including the sugar units that are linked, the chain length, the type of linkages between the units, and the level of branching. When a polysaccharide is composed of a single type of sugar monomer, it is referred to as a homopolysaccharide. Examples of homopolysaccharides include glucan and mannan. Glucose homopolymers, such as starch in plants and glycogen in animals, function as storage forms of glucose. Cellulose and chitin are examples of homopolysaccharides that play a crucial role in providing mechanical support to plant cell walls and animal exoskeletons, respectively. Heteropolysaccharides, on the other hand, are made up of two or more kinds of sugar subunits. Since the shape of polymers plays a crucial role in determining their physical properties, each of these types of polymers is further classified as either linear or branched polysaccharides [6].

Table 1.4. Some examples for polysaccharides [6].

Homopolysaccharides		**Heteropolysaccharides**	
Linear	Branched	Linear	Branched
Simple polysaccharides			
Amylose	Amylopectin	Mannass	Gums
Cellulose	Glycogen	Xylans	Mucilages
Chitin			Pectins
			Algin
			Agar
			Bacterial polysaccahrides
			Peptidoglycans
			Glycoproteins
			Lectins

1.1.4. Glucose

Glucose, a ubiquitous monosaccharide, plays a vital role in providing energy to living organisms. It is also known as dextrose and is classified as an aldohexose because it has six carbon atoms and an aldehyde functional group (-CHO). D-glucose commonly exists in the form of α-D-glucopyranose, but when it is dissolved in water, it undergoes equilibration, resulting in the formation of six different isomers. The various isomers of glucose that exist in aqueous solution include two isomers in the furanose form, two in the pyranose form, an acyclic carbonyl form, and a hydrated carbonyl form [6]. Glucose is commonly found in fruits, vegetables, and honey, and it is also a product of photosynthesis in plants. Glucose plays a vital role in various metabolic pathways of living organisms.

1.1.5. Starch

Starch is a natural biopolymer made up of numerous glucose units joined together by glycosidic bonds. It is a crucial carbohydrate in the human diet, serving as the primary source of energy for most living organisms, and has been used for centuries. Starch is produced by plants as a reserve food material and is stored in various plant organs.

There are two types of glucose polymers in starch, amylose, which is a linear chain of glucose units, and amylopectin, which is a branched polymer with both linear and highly branched regions. Different types of starches have varying amylose to amylopectin ratios. Enzymes in the human digestive system break down the glycosidic bonds between glucose units, releasing glucose molecules that the body uses to produce energy. The digestion of starch begins in the mouth with the enzyme amylase breaking down the starch into smaller fragments. Starch has a broad range of industrial applications. Starch is also utilized in the production of bioplastics, textiles, paper, and adhesives [1,5,7,8]. Starch is an important storage carbohydrate in many plant species, and it can be obtained from several plant sources. Many crops such as potato, corn, wheat, rice, cassava, barley, and oat are commonly used to produce starch. However, there are also other unconventional sources of starch, such as fruits and medicinal plants, that can be utilized for starch extraction [7]. Starches obtained from various sources exhibit dissimilarities in terms of their chemical composition and structural characteristics. For example, the ratio of amylose to amylopectin, two major components of starch, can vary between different sources of starch. Additionally, the degree of branching, chain length distribution, and degree of polymerization of the starch molecules can also differ between different sources of starch. The chemical composition of starch can also vary within the same source depending on factors such as plant variety, growing conditions, and processing methods [8].

1.1.6. Cyclodextrin

Cyclodextrins (CDs) are a class of cyclic carbohydrates containing glucose parts. They are synthesized through the degradation of starch by the enzyme cyclomaltodextrin glucanotransferase (CGTase), which causes the breaking of glycosidic bonds within the starch molecule [9]. The three common types of cyclodextrins are α-CD, β-CD, and γ-CD, each consisting of 6, 7, and 8 glucose units, respectively.

Within the cyclodextrin structure, the numbering system of α-1, β-2, and γ-3 indicates the precise location of the glycosidic bond between the glucose units [10]. Cyclodextrins (CDs) are widely used in chromatography due to their ability to selectively interact with molecules based on their size and shape [9]. CDs have found widespread use in various industries, including pharmaceuticals, food, cosmetics, and agriculture. Some common uses of CDs are: 1) Improving solubility [11,12] 2) Masking odors and flavors [13] 3) Applications in the textile industry [14] 4) Environmental applications [15] 5) Pharmaceutical applications [16].

1.2. SUBCRITICAL AND SUPERCRITICAL WATER

Water can exist under various conditions of temperature and pressure. When water is maintained at a temperature range of 100-374°C under enough pressure, it is called subcritical water. In contrast, supercritical water refers to the state of water that exists above 374°C and 22.1 MPa pressure, and it has unique physical and chemical properties compared to subcritical water [17]. Under high temperature and pressure conditions, water can serve as a suitable medium for organic reactions that require acid-base catalysis. Furthermore, water under hydrothermal conditions can actively participate in hydrolysis reactions and act as a potential source of hydrogen. The unique properties of water can be modulated by adjusting temperature and pressure levels, allowing for diverse applications in various fields of study. Table 1.5 provides insight into how changes in these variables affect water's properties. The characteristics of water depending on temperature and pressure.

Table 1.5. The characteristics of water depending on temperature and pressure [18].

	Ambient Water	**Subcritical Water**	**Supercritical Water**	
Temperature (°C)	25	250	400	400
Pressure (MPa)	0.1	5	25	50
Density ($g.cm^{-3}$)	0.997	0.80	0.17	0.58
Dielectric constant (ε)	78.5	27.1	5.9	10.5
pKwater	14.0	11.2	19.4	11.9
Heat capacity ($kJ.kg^{-1}$)	4.22	4.86	13	6.8
Viscosity (m.Pa.s)	0.89	0.11	0.03	0.07
Thermal conductivity ($Mw.m^{-1}.K^{-1}$)	608	620	160	438

As water approaches its critical point, its properties undergo significant changes. At ambient temperature, water has a high dielectric constant (ε≈79) due to hydrogen bonding. However, as it is heated to its critical point, its dielectric constant decreases (ε≈6.0), changing its solvent behavior [17]. It is noteworthy that the density of water at the supercritical point can vary based on temperature and pressure. The density of water at ambient temperature is roughly 1 g/cm^3, but at the supercritical point, it reduces to about 0.58 g/cm^3. Subcritical and supercritical water possess exceptional properties that can confer significant advantages in diverse hydrothermal processes.

1.3. HYDROTHERMAL PROCESSES

Hydrothermal processes are a set of conversion methods that involve the use of water as a reactant, solvent, and catalyst at high temperatures and pressures. Hydrothermal processes are similar to natural geological processes that occur deep in the Earth's crust to create fossil fuels. The processes involve the application of high pressure and temperature conditions to materials, resulting in the transformation of the starting materials into different products [17]. While hydrothermal processes are used in industry to modify or transform organic materials on a much shorter time scale, the geological processes that create fossil fuels occur naturally over millions of years. The hydrothermal process offers advantages over traditional methods such as gasification and pyrolysis, as they eliminate the need to dry biomass before processing it, which saves time and cost [19]. Different types of products can be generated through the hydrothermal process, which include liquefied, solidified, and gaseous forms, depending on the chosen method, such as HTC, HTL and HTG. The selection of the most suitable method is based on the desired output. Table 1.6 shows operating temperatures based on the desired product.

Table 1.6. Hydrothermal techniques and operating temperatures [20,21].

Types of Hydrothermal Processes	Operating Temperatures (°C)
Hydrothermal Carbonization (HTC)	180-250
Hydrothermal Liquefaction (HTL)	280-380
Hydrothermal Gasification (HTG)	400-700

1.3.1. Hydrothermal Gasification

High-temperature and high-pressure conditions in the presence of water can be used in the process of HTG to convert organic matter into gaseous products [22]. HTG is a versatile process that can effectively convert various feedstocks such as agricultural waste, energy crops, and wastewater sludge into valuable gaseous products. In HTG, organic matter is first dissolved in water, and the resulting slurry is pressurized and heated to a specific temperature. Under these conditions, the organic matter decomposes and reacts with water to produce gaseous products [23]. The HTG process also produces a liquid fraction, which can be further treated to produce fuels or chemicals. The process of HTG can be divided into three different regions that are defined by the pressure and temperature at which they occur [24]. The first region, which is known as catalytic gasification, occurs below the temperature of 374°C. In this region, a catalyst is typically used to facilitate the conversion of organic matter into useful gases.

The second region, called supercritical gasification, occurs at higher temperatures between 374 and 500°C. Under these conditions, water becomes supercritical and exhibits unique properties that enhance the gasification process. The third and final region, high-temperature gasification, occurs at temperatures between 500 and 700°C. This region typically produces the highest quality gas, which can be used directly in power generation or as a feedstock for chemical synthesis. The production of methane (CH_4) and hydrogen (H_2) during HTG is influenced by the operating temperature. The selection of temperature is a critical factor in controlling the composition and quality of the gas product. Specifically, lower temperatures in the range of 350-500°C tend to favor the production of CH_4, while higher temperatures between 400-600°C promote the production of H_2 [25]. HTG stands out among other methods of converting biomass due to its numerous benefits. These include high rates of conversion, minimal emissions, and the capacity to utilize diverse types of biomasses. The HTG process also produces a high-quality gas that can be used directly in power generation or as a feedstock for chemical synthesis.

1.3.2. Hydrothermal Liquefaction

HTL is conducted in the presence of hot-compressed water under high pressure and temperature [26]. As pressure and temperature increase in hydrothermal conditions, water properties change dramatically. For instance, dielectric constant and density of water decrease while its solubility increases, rendering it a good solvent for hydrocarbons. Additionally, the water at high pressure allows it to stay in a liquid state, enabling the process to proceed. The process of HTL involves the conversion of biomass into high-energy liquid products, which is typically achieved using subcritical water under high pressure [17]. The outcome of HTL is influenced by multiple factors, which include temperature, pressure, reaction time, particle size, feedstock type, solvent-to-biomass ratio, and the presence of reducing agents or catalysts. These factors affect the yield of the final products, including bio-oil, bio-char, and gas, as well as their properties such as composition, heating value, and acidity [17]. The HTL of organic matter yields four main products, namely biocrude, dissolved chemicals in the aqueous phase, solid residue, and gas. Biocrude is a dark, viscous liquid that is produced during the HTL process of organic matter, such as biomass.

The chemical composition of bio-oil is highly dependent on the type of feedstock used in hydrothermal liquefaction, but it typically consists of a diverse range of organic compounds, including oxygenated hydrocarbons, phenolic compounds, aldehydes, ketones, and carboxylic acids. Additionally, the presence of nitrogen and sulfur-containing compounds can also vary depending on the feedstock [27]. Biocrude, derived from hydrothermal liquefaction, is a promising source of renewable energy that can be transformed into a variety of useful products such as transportation fuels, chemicals, and other high-value products. Additionally, the aqueous phase generated during HTL can contain dissolved organic compounds and be utilized for a variety of purposes, including gasification [17,19]. Solid product is primarily made up of organic compounds, including carbon, hydrogen, and oxygen, along with inorganic materials like ash [17]. There are multiple potential uses for the solid products produced during hydrothermal liquefaction. One option is carbon sequestration, while another is using them to synthesize carbon-based materials. The composition of the gas products typically consists of high levels of carbon dioxide (CO_2), along with smaller quantities of other gaseous compounds [21].

1.3.3. Hydrothermal Carbonization

HTC is a method that involves using high temperature and pressure conditions to convert biomass into a solid substance that resembles coal. Despite being studied for nearly a century, this process has recently garnered attention as a promising technology for converting biomass [28]. During the HTC process, hydrochars, liquids, and gases are produced. However, because the process operates at low temperatures (generally 180-250°C, the yield of gas products is not as high compared to other processes [29,30]. The gas products from the HTC typically contain a high proportion (70-90%) of carbon dioxide, along with trace amounts of carbon monoxide, methane, and hydrogen [31,32]. The liquid products generated during the HTC process are typically acidic and contain both organic and inorganic compounds. These liquids may also contain nitrogen, phosphorus, and other mineral matter originating from the raw material. The exact composition of the liquid and gas products depends on several factors, such as the type of feedstock used, the operating conditions, and the pH of solution. After undergoing the HTC process, a solid material called hydrochar or hydrothermal carbon is typically produced. This main product usually has a black or dark brown coloration [33]. It contains carbon, hydrogen, and oxygen, as well as ash. The presence of heteroatoms, such as nitrogen and sulfur, is also possible in the hydrochars depending on its source. This process has been studied for almost a century and has gained interest in recent years as a potential biomass conversion technology. The HTC process can be applied to a wide range of feedstocks, including various types of biomass such as wood, plant residues, and coal [34].

1.3.3.1. Influence of Operating Parameters

The operating parameters of the HTC process can significantly influence the yield, quality, and properties of the resulting hydrochar. Some of the key operating parameters that can impact the HTC process are temperature, residence time, pressure, solid load, pH of reaction mixture [28,35].

Temperature

Achieving optimal temperature is vital in the HTC process since it directly influences the quality, yield, and properties of the final hydrochar product. Thus, the operating temperature is crucial for achieving desirable results in the process [28]. Higher temperatures can decrease the hydrochar yield while increasing carbon content and heating value. However, excessively high temperatures can also cause the formation of unwanted byproducts like tar and ash. Conversely, lower temperatures lead to higher hydrochar yield but lower carbon content and heating value. The ideal temperature for HTC depends on the feedstock and desired properties of the hydrochar. HTC decomposition mechanisms are akin to those present in dry pyrolysis, but hydrolysis plays a more important role. The hydrolysis reaction is typically the first step in the process, as it has a lower activation energy compared to pyrolysis reactions. Under hydrothermal conditions, the biomass components become less stable, ultimately resulting in lower decomposition temperatures [35].

Residence time

The residence time during the HTC process is a critical factor that affects the severity of the reaction, product yield, and quality. Typically, the reaction time for HTC ranges from a few hours to several days. Longer residence times lead to increased reaction severity because the biomass has more time to react with hot water, undergo decomposition, and carbonization.

Research has shown that longer reaction times can increase the production of hydrochar, as it allows for more complete conversion of biomass into solid hydrochar. The process allows for an extended reaction time, which facilitates the reaction and polymerization of soluble fragments present in the liquid phase. This ultimately leads to the generation of insoluble solids as the end product [35].

Pressure

Experimental studies have shown that the effect of pressure on HTC and natural coalification is relatively low compared to other factors such as temperature and time. The pressure in the HTC process can affect the reaction network according to LeChatelier's principle. As the reaction pressure increases, the equilibrium shifts towards the solid and liquid phases, as well as towards reactants with a lower number of moles. This can result in a depression of dehydration and decarboxylation, which are the primary overall reactions. Higher reaction pressure is believed to favor liquefied products [35].

The ratio of feedstock to water

The ratio of feedstock to water is an important parameter in the HTC process, as it can significantly influence the yield and properties of the resulting products. In general, increasing the feedstock-to-water ratio in the HTC process can lead to higher yields of solid carbonaceous products, as more organic material is available to react with the water and form carbonaceous compounds [36,37]. However, higher feedstock-to-water ratios can also lead to lower carbon conversion efficiency, as well as lower heating values in the resulting products [38]. The feedstock-to-water ratio is a critical parameter in the HTC process, as it can impact the yield and quality of the hydrochar produced. The optimum ratio depends on the characteristics of the feedstock as well as the desired properties of the hydrochar, such as its carbon content and heating value. Higher ratios of feedstock to water can result in a higher yield of hydrochar, but with lower carbon content and heating value. On the other hand, lower ratios of feedstock to water can lead to a higher carbon content and heating value, but with a lower yield of hydrochar. Thus, the selection of the appropriate feedstock-to-water ratio is crucial in optimizing the HTC process for a particular feedstock and desired product.

pH of reaction mixture

During HTC, a drop in pH is commonly observed due to the formation of various organic acids, including acetic, formic, lactic, and levulinic acid. To replicate natural coal formation, a slightly acidic to neutral environment is required. The pH of the reaction mixture is a crucial factor that can influence both the quantity and quality of the final products. The role of acidic conditions in HTC is still not fully understood, especially in relation to reaction mechanisms. However, recent studies have indicated that mildly acidic conditions can accelerate the rate of reaction in HTC [28].

PART 2

LITERATURE REVIEW

In a study conducted by Elaigwu and Greenway, the microwave-assisted HTC of glucose was investigated to determine the energy properties of the hydrochars produced [39]. The HTC process was conducted at 200°C for 5-60 min. The findings showed that this method significantly reduced the processing time compared to traditional HTC, while also yielding hydrochars with higher heating values than previously reported values [39].

Demir-Cakan and co-workers sythesized novel type of functional carbon microparticles through a straightforward HTC process using glucose and acrylic acid monomer [40]. The final products exhibited high thermal and chemical stability due to their amorphous carbon framework, while the incorporated monomer imparted additional functionality [40].

Ischia and colleagues carried out an investigation on the HTC of a glucose solution (1.1 M, 25 wt%) under various operating conditions (180-270°C and 0-8 h) and evaluated the characteristics of the solid and liquid products [41]. The temperature had a significant impact on hydrochar yield only at 180°C, whereas at higher temperatures (220-270°C), the yield remained relatively constant at 47-50% [41].

Simsir et al. carried out hydrothermal treatment of glucose and cellulose with acidic and alkaline catalysts [42]. The experiments were carried out for 4 h at 200°C to evaluate the impact of the catalyst type on the yield and properties of hydrochar. The results showed that the use of $Al(OTf)_3$ catalyst resulted in decreased hydrochar yields for both feedstocks, whereas the use of NaOTf catalyst led to an increase in hydrochar yields [42].

Sevilla and Fuertes carried out a study on the production of hydrothermal carbons from cellulose, using hydrothermal conditions at temperatures ranging from 220-250°C for either 2 h or 4 h [43]. The resultant hydrochars were made up of clusters of carbon microspheres that were agglomerated, with a size of roughly 2-5 μm. Further analysis of the solid product revealed that it comprised small groups of condensed benzene rings that formed stable clusters with oxygen located at the core. Meanwhile, the shell of the microspheres possessed more reactive and hydrophilic oxygen functionalities [43].

Modugno and Titirici produced hydrothermal carbons by subjecting fructose (10% w/w) to temperatures of 200°C for 2-12 h, with and without concentrated acids [44]. They found that both strong and weak acids expedite the conversion of fructose, and that levulinic acid is formed more quickly than hydrothermal carbon in acidic conditions [44].

In a study conducted by Yao and colleagues, the HTC of glucose and fructose was examined at various temperatures from 120°C to 180°C [45]. The hydrothermal treatment of an aqueous glucose solution resulted in the formation of carbon spheres through an intermolecular dehydration process without the formation of HMF at 170-180°C, while an aqueous fructose solution formed HMF by intramolecular dehydration at 120-140°C [45].

Sevilla and Fuertes conducted HTC of glucose (C=05-1 M), sucrose (C=0.5 M), and starch (C=0.1-0.5 M) at 170-240°C for 0.5-15 h [46]. By adjusting the operational parameters, the diameter of the hydrochar microspheres could be controlled. The mean diameter of the microparticles increased with the rise in reaction temperature, concentration of the reaction mixture, or reaction time, irrespective of the type of saccharide used. In terms of mean diameter, the hydrochar particles exhibited the following trend: glucose < starch < sucrose [46].

Titirici group performed HTC at 180°C for 24 hours on a range of materials, such as glucose, xylose, maltose, sucrose, amylopectin, and starch, with a fixed biomass to water ratio of 1.5 g feedstock/13.5 ml water [47]. The resulting carbon materials exhibited noticeable differences in structure and morphology between pentoses and hexoses, but intriguingly, regardless of the specific hexose sugar used, all carbon materials showed remarkable similarities [47].

Liang et al. synthesized carbon microspheres by subjecting starch to HTC at different solution pH values and temperatures of 210°C for a duration of 1 h to 6 h [48]. It was reported that the optimal solution pH range for HTC was determined to be between 3 and 7. However, a starting pH of 1 was observed to expedite the hydrolysis of starch and the formation of microspheres only during the initial stages of the reaction [48].

Paksung and co-workers prepared hydrothermal carbons from microcrystalline cellulose and α-cellulose at 180-240°C for 0-240 min [49]. The study revealed that hydrolysis of the amorphous fraction of cellulose occurred upon subjecting it to a temperature of up to 200°C, while the crystalline fraction remained unaffected by water, resulting in a higher char yield for microcrystalline cellulose. However, at temperatures exceeding 220°C, the impact of crystallinity decreased, leading to a reduced extent of pyrolysis in microcrystalline cellulose [49].

Zhao et al. conducted the HTC of cellulose with citric acid at 200-240°C for 6-12 h [50]. It was reported that, the optimal conditions were detected for the synthesis of carbon spheres with a smooth and regular morphology. The resulting carbon spheres were composed of both aliphatic and aromatic structures and had abundant oxygen-containing functional groups on their surface [50].

Lu and Berge performed HTC on diverse feedstocks (such as cellulose, starch, lignin, glucose, and xylose) at 250°C for 96 h, utilizing a constant feedstock to water ratio of 8 g feedstock/32 g water [51]. It was reported that the properties of the feedstock had an impact on the properties of the resulting carbonization product. Predictions regarding the characteristics of the carbonization product were made based on the results obtained from carbonizing pure compounds. These predictions indicated that the energy content of the recovered solids could be more accurately projected than the solid yields and the amount of carbon in each phase. Additionally, it was also reported that surface functional groups on the solids were harder to predict using this linear approach [51].

Carbon spheres were synthesized by Shin and colleagues via hydrothermal treatment of aqueous solutions that contained α-, β-, and γ-cyclodextrin (CD) at 160°C for 16 h [9]. The cyclodextrin to water ratio was fixed at 2 g CD/20 mL water. Under hydrothermal conditions, it was observed that cyclodextrin underwent hydrolysis into glucose, followed by dehydration into HMF. Subsequently, it transformed into porous carbon spheres. Furthermore, it was reported that the carbon spheres synthesized from γ-CD exhibited a significantly higher amount of aromatic carbon compared to those generated from other CDs [9].

PART 3

MATERIALS AND METHODS

3.1. MATERIALS

Anhydrous D (+)-glucose (CAS-No: 50-99-7) was purchased from Merck, Germany. β-cyclodextrin (CAS-No: 7585-39-9) was purchased from Sigma-Aldrich, USA. Starch (Cas No: 9005-44-9) Isolab, Germany. 2-chloropropionic acid (CAS No:598-78-7) was purchased from Sigma-Aldrich, USA.

3.2. EXPERIMENTAL PROCEDURE

To conduct the HTC experiments, PPL-lined stainless-steel hydrothermal autoclaves were used. In non-catalytic runs, 2 g of the sample were added to a PPL container with 20 ml of deionized water. The container was then placed in a steel reactor, tightly closed, and put into a preheated oven. Reactions were carried out at 180°C and 200°C for 24 h. For catalytic runs, 2 g of the sample were weighed and added to a PPL container with 20 ml of 0.5 M 2-chloropropionic acid as a solvent. For cyclodextrin and starch, samples and water were stirred at 60°C for 3 h at 700 rpm. The operating temperature and reaction time were the same as in non-catalytic runs. After adding the catalyst, the solutions were stirred for 5 min in an ultrasound bath. Once the reaction was completed, the resulting product was collected in a centrifuge plastic tube and centrifuged at 3500 rpm to separate the solid and liquid products. The resulting liquid product was collected separately for pH measurement. The solid product was washed three times with 50 ml of deionized water and dried in an oven at 105°C for 24 h. The yields of hydrochars were calculated using the equation below:

$$Hydrochar\ yields(wt\%) = \frac{mass\ yields\ of\ recovered\ solid\ products(g)}{mass\ yield\ of\ feedstock} x100$$

3.3. ANALYSIS

The morphologies of the hydrochars were studied using a Carl Zeiss Ultra Plus Gemini FESEM. ^{13}C NMR spectra of the samples were recorded with a JEOL ECZ 500R NMR spectrometer. The functional groups present in the starting materials and hydrochars were analyzed using a Thermo Scientific Nicolet iS50 FTIR-ATR spectrometer. Additionally, samples of glucose, starch, and cyclodextrin, as well as the resulting hydrochars from these materials, were analyzed for their elemental composition using an elemental analyzer (LECO CHNS-932). The pH of the reaction medium was measured using a Mettler Toledo SE 5470-K type pH meter.

PART 4

RESULTS AND DISCUSSION

4.1. HYDROCHAR YIELDS

The yields of hydrochars produced from different materials at different temperatures are shown in Table 4.1. For the glucose, the hydrochar yields from the non-catalytic runs were 29.05 and 39.76 wt%, at 180 and 200°C, respectively.

Table 4.1. Yields of hydrochars produced from glucose, β-Cyclodextrin, and starch at 180 and 200°C for 24 h without and with catalyst (2-chloropropionic acid).

Sample	**Raw material**	**Temperature (°C)**	**Catalyst**	**Yield (wt%)**
G-HC1	Glucose	180	-	29.05
G-HC2	Glucose	180	+	18.45
G-HC3	Glucose	200	-	39.76
G-HC4	Glucose	200	+	18.06
CD-HC1	β-cyclodextrin	180	-	20.77
CD-HC2	β-cyclodextrin	180	+	20.53
CD-HC3	β-cyclodextrin	200	-	42.42
CD-HC4	β-cyclodextrin	200	+	20.54
S-HC1	Starch	180	-	25.54
S-HC2	Starch	180	+	22.31
S-HC3	Starch	200	-	38.20
S-HC4	Starch	200	+	21.18

The increase in temperature resulted in increased hydrochar yields. Sevilla and Fuertes also conducted HTC on a glucose solution with a concentration of 0.5 mol/L at 180 and 210ºC for 4.5 h, yielding 5.1 weight percent hydrochar at 180ºC, but a sharply increased yield of 28 wt% at 210ºC [46]. In a study by Falco et al., glucose (C=10%) was subjected to HTC at 180 and 200ºC for 24 h, resulting in a hydrochar yield of approximately 33 wt%, which increased to around 39 wt% at 200ºC [52]. In another study, Ischia and co-workers investigated HTC of glucose (C = 1.11 M) at different operating conditions (T=180-270ºC, t=0-8 h) [41]. The hydrochar yield was 39.2 wt% at 180ºC for 8 h and increased to 49.5 wt% at 220ºC. All the above-mentioned studies demonstrated that an increase in HTC temperature led to the production of higher mass yields of hydrochars [41,46,52]. Notably, hydrochar yields remain stable after 180ºC [41]. For glucose, the use of a catalyst reduced the hydrochar yields both at 180 and 200ºC. It is known that acid catalysts promote hydrolysis reactions in hydrothermal media and increase soluble products [53,54]. The addition of acid catalysts during the HTC process is believed to cause increased biomass degradation, leading to the production of smaller or water-soluble products. This, in turn, may result in decreased yields of hydrochars. Notably, the use of a catalyst did not significantly change the hydrochar yields produced from starch and β-cyclodextrin at 180°C but did significantly reduce the yields at 200°C. One can conclude that the catalytic effect is more pronounced at 200°C for oligosaccharide and polysaccharides.

The pH value of the reaction mixture can significantly affect the yield and properties of the resulting hydrochars. The pH values of the slurries before and after the HTC process were measured, and the results are presented in Table 4.2.

Table 4.2. The pH levels of slurries before and after the HTC process.

Feedstock	**Temperature (ºC)**	**Catalyst**	**pH (before the HTC)**	**pH (after the HTC)**
Glucose	180	-	4.74	2.30
	180	+	1.55	0.49
	200	-	4.74	2.31
	200	+	1.55	0.51
β-Cyclodextrin	180	-	5.78	2.34
	180	+	1.60	0.51
	200	-	5.78	2.34
	200	+	1.60	0.59
Starch	180	-	7.30	2.25
	180	+	2.02	0.55
	200	-	7.30	2.19
	200	+	2.02	0.53

The pH levels of the slurries were affected by the type of feedstock used in both catalytic and non-catalytic runs. The pH levels of all the runs decreased after the HTC process. This decrease is a common trend in HTC because of the generation of various organic acids such as acetic, formic, lactic, and levulinic acid [28]. After the HTC process, there was a noticeable decrease in pH levels for both non-catalytic and catalytic runs. The pH levels ranged from 2.19 to 2.34 for non-catalytic runs, while for catalytic runs, the pH levels were even lower, ranging from 0.49 to 0.55.

Table 4.3. Elemental compositions (wt%), H/C, and O/C atomic ratios of glucose, β-cyclodextrin, starch, and hydrochars obtained from these raw materials.

Sample	**T (°C)**	**Catalyst**	**C (wt%)**	**H (wt%)**	**O[a] (wt%)**	**H/C[b]**	**O/C[b]**
Glucose	-	-	39.50	6.37	54.13	1.94	1.03
G-HC1	180	-	64.20	4.51	31.29	0.84	0.37
G-HC2	180	+	65.10	4.78	30.12	0.88	0.35
G-HC3	200	-	66.60	4.56	28.84	0.82	0.32
G-HC4	200	+	66.30	5.12	28.58	0.93	0.32
β-cyclodextrin	-	-	39.20	6.46	54.34	1.98	1.04
CD-HC1	180	-	65.00	4.42	30.58	0.82	0.35
CD-HC2	180	+	66.60	4.59	28.81	0.83	0.32
CD-HC3	200	-	66.60	4.50	28.90	0.81	0.33
CD-HC4	200	+	64.20	4.97	30.83	0.93	0.36
Starch	-	-	35.07	6.04	58.89	2.07	1.26
S-HC1	180	-	63.30	4.41	32.29	0.84	0.38
S-HC2	180	+	62.60	4.84	32.56	0.93	0.39
S-HC3	200	-	66.00	4.38	29.62	0.80	0.34
S-HC4	200	+	64.40	5.15	30.45	0.96	0.35

[a] By difference
[b] atomic ratio

Table 4.3 demonstrates elemental compositions, O/C and H/C atomic ratios of hydrochars produced from glucose, β-cyclodextrin, and starch at 180 and 200°C. The HTC process predominantly decreases the amount of oxygen and hydrogen present in the feed, which can be measured by the O/C and H/C ratios. This reduction occurs mainly through two mechanisms: dehydration and decarboxylation [28]. Dehydration eliminates oxygen by removing water molecules, while decarboxylation eliminates oxygen in the form of carbon dioxide [21]. The O/C and H/C ratios of the feedstock decreased after HTC, irrespective of the feedstock used. The primary reactions that occurred during the process were found to be dehydration and decarboxylation at 180 and 200ºC. However, the use of a catalyst suppressed the dehydration reactions, resulting in hydrochars with higher H/C ratios. Comparing catalytic and non-catalytic runs, it was observed that the dehydration reactions were less prominent in the former, leading to the formation of hydrochars with a higher H/C ratio.

Examination of the surface morphology of the hydrochars was carried out through scanning electron microscopy (SEM). The SEM images of hydrochars derived from glucose, β-cyclodextrin, and starch, both with and without the presence of a catalyst at 200°C, are depicted in Figure 4.1. Carbon spheres were found to be produced in all hydrochars, with their sizes considerably influenced using catalyst. The diameter of carbon spheres in all feedstocks increased when a catalyst was employed. The hydrochars produced from glucose, with and without catalyst, had interconnected carbon sphere particles. The diameter of the spherical carbon particles from non-catalytic HTC of glucose ranged from 1 to 3 µm, while the diameter of the carbon spheres from glucose with catalyst ranged from 3.5 to 6 µm. The size of the carbon spheres in the hydrochars obtained from the non-catalytic HTC of β-cyclodextrin varied between 538 nm to 1.3 µm, with an average diameter of 850 nm. On the other hand, the hydrochars obtained from the catalytic HTC of β-cyclodextrin had larger carbon spheres with a diameter ranging from 5 to 9 µm. The results suggest that the presence of a catalyst can significantly impact the particle size of the carbon spheres in the hydrochar obtained. The diameter of carbon spheres produced from starch ranged from 1.2 to 5.0 µm for the non-catalytic run and from 2.0 to 8.0 µm for the catalytic run.

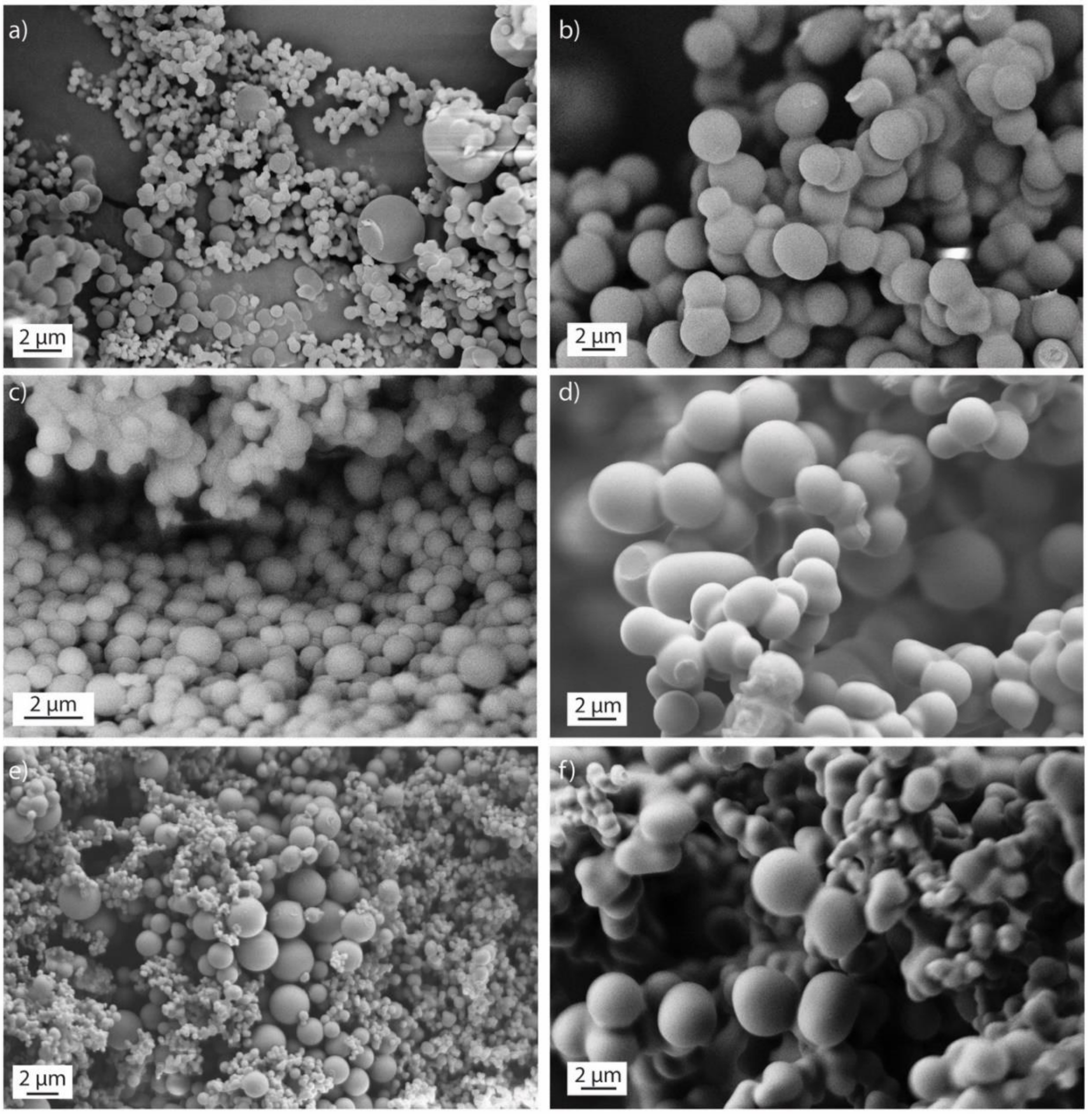

Figure 4.1. SEM images of hydrochars produced from glucose, β-cyclodextrin, and starch at 200°C for 24 h without and with catalysts (a) G-HC3 (b) G-HC4 (c) CD-HC3 (d) CD-HC4. e) S-HC3 (f) S-HC4.

Figure 4.2 displays the FTIR spectra of glucose and hydrochars obtained from glucose. The spectra of glucose exhibited characteristic peaks at 3204 cm^{-1}, 2943 cm^{-1}, 2913 cm^{-1}, 1458 cm^{-1}, 1103 cm^{-1}, 1048 cm^{-1}, 995 cm^{-1}, 837 cm^{-1}, 774 cm^{-1}, and 612 cm-1, which correspond to -O-H stretching, -C-H of C2, -C-H of C1, CH2+ O-C-H+C-C-H bending, C-O vibrations, -C-O and -C-C vibrations, C-H bending, C-C-O+C-C-H bending, and CH_2, respectively [55]. In the hydrochars, the intensity of the peak at around 3300 cm^{-1} corresponding to -OH group decreased, indicating dehydration. The presence of a new absorption band at around 1700 cm^{-1}

was assigned to C=O groups, which was also confirmed by the elemental analysis results presented in Table 4.3. Two new peaks at around 1605 cm^{-1} and 1511 cm^{-1} were observed in hydrochars, indicating the aromatization of the samples [56]. The presence of the 1605 and 1511 cm^{-1} bands indicated that the samples have undergone aromatization. The peak at around 800 cm^{-1} was assigned to aromatic C-H out-of-plane bending vibrations [43]. The peak at around 800 cm^{-1} was assigned to aromatic C-H out-of-plane bending vibrations.

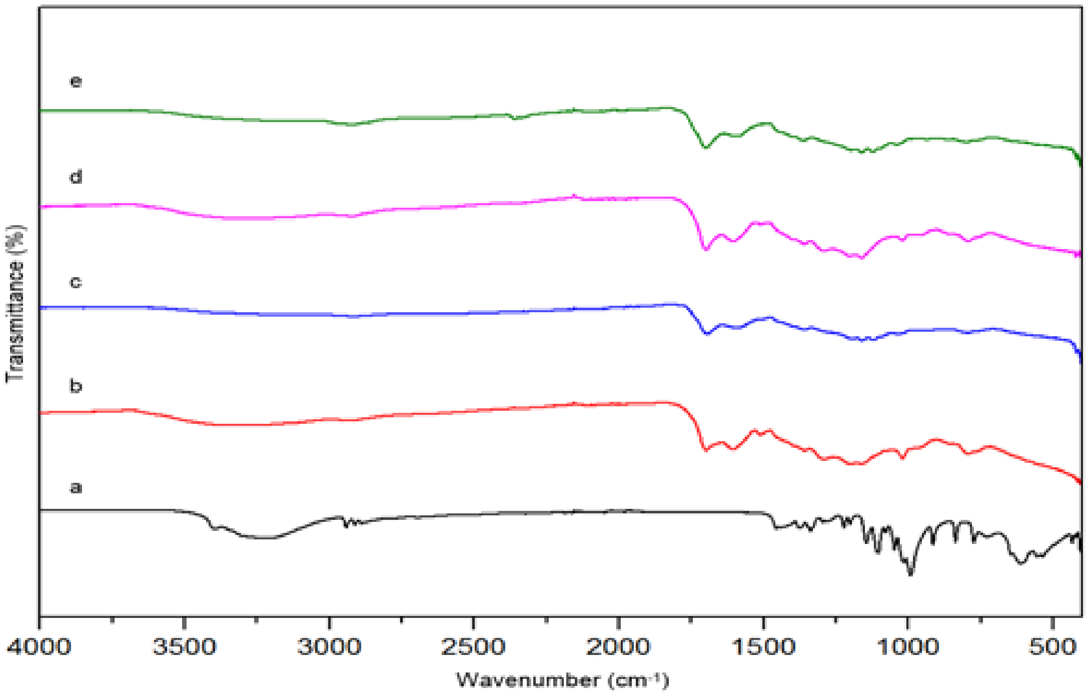

Figure 4.2. FT-IR spectra were obtained for: a) Glucose, b) Hydrochars produced from glucose at 180°C without catalyst, c) Hydrochars produced from glucose at 180°C with catalyst, d) Hydrochars produced from glucose at 200°C without catalyst, e) Hydrochars produced from glucose at 200°C with catalyst.

FT-IR spectra of β-cyclodextrin and hydrochars from β-cyclodextrin are shown in Figure 4.3. The FTIR spectrum of β-cyclodextrin was analyzed to identify key molecular characteristics. The peak observed at 3250 cm^{-1} was attributed to OH stretching, while the peaks at 2920 cm^{-1} corresponded to CH stretching. Other distinctive peaks were observed at 1645 cm^{-1}, 1157 cm^{-1}, 1030 cm^{-1}, and 851 cm^{-1}, which indicated the presence of H–O–H, C–O, C–O–C glucose units, and C–O–C rings, respectively, in the β-cyclodextrin molecule. These peaks provide important information about the molecular structure of the β-cyclodextrin feedstock [57,58]. The FT-IR analysis of hydrochars obtained from β-cyclodextrin, with and without catalysts, revealed unique features of the hydrochars. The spectra showed two major peaks, corresponding to O-H absorption in the range of 3700 to 2800 cm^{-1} and carbon stretching absorption at 1700 cm^{-1}. Furthermore, the FT-IR spectra of hydrochars produced from β-cyclodextrin indicated the presence of several groups such as aliphatic hydrocarbon (-C-H) at 2920 cm^{-1}, -C=C at 1590-1607 cm^{-1}, and -C-O at 1020 cm^{-1}. The intensity of the -O-H group was lower in hydrochars produced from catalytic runs compared to those from non-catalytic runs at the same conditions.

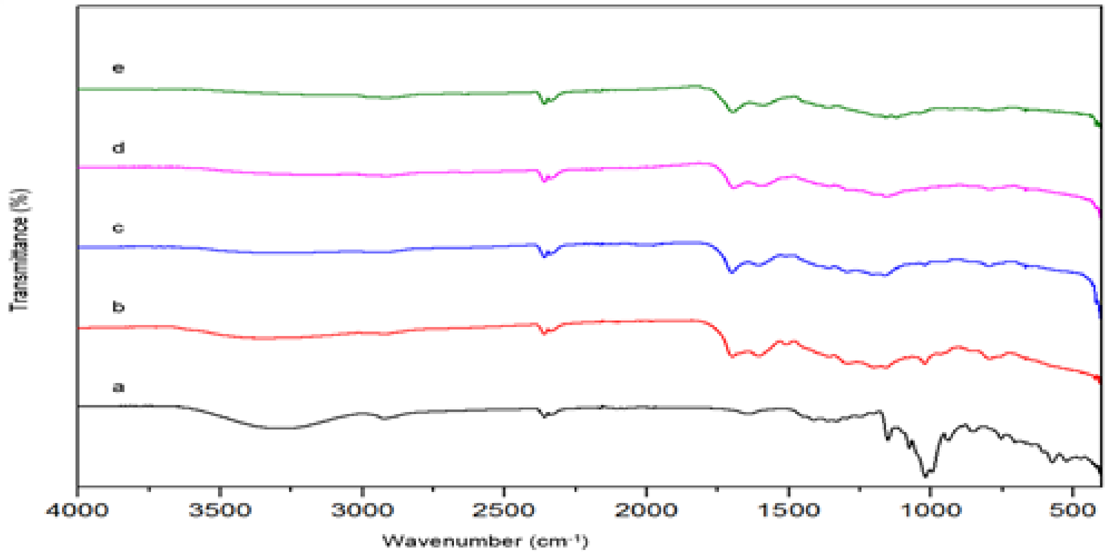

Figure 4.3. FTIR spectra were obtained for: a) β-cyclodextrin, b) Hydrochars produced from β-cyclodextrin at 180°C without catalyst, c) Hydrochars produced from β-cyclodextrin at 180°C with catalyst, d) Hydrochars produced from β-cyclodextrin at 200°C without catalyst, e) Hydrochars produced from β-cyclodextrin at 200°C with catalyst.

FT-IR spectra of starch and hydrochars from starch are shown in Figure 4.4. The FT-IR spectra of starch and hydrochars produced from starch were analyzed to identify distinctive peaks that provide insight into the molecular structure of the samples. The starch spectrum displayed the -O-H stretching peak at 3270 cm^{-1}, the C-H stretching peak at 2927 cm^{-1}, and several other peaks corresponding to C-O, C-C, and C-O-H stretching [59,60]. The FTIR spectra of hydrochars produced from starch with and without catalysts showed absorption bands between 3700 and 2800 cm^{-1} corresponding to O-H stretching, 2927 cm^{-1} corresponding to C-H stretching, and 1700 cm^{-1} corresponding to C=O groups. Additionally, the spectra displayed peaks at 1600 cm^{-1} corresponding to C=C stretching and between 1350 and 1500 cm^{-1} corresponding to aliphatic C-H deformation vibration. Finally, the peaks around 800 cm^{-1} indicated the presence of aromatic C-H out-of-plane bending vibrations [61]. Overall, the FTIR spectra indicated the presence of functional groups in the hydrochars outer layers, indicating the presence of aromatic cores in samples produced from glucose, β-cyclodextrin, and starch.

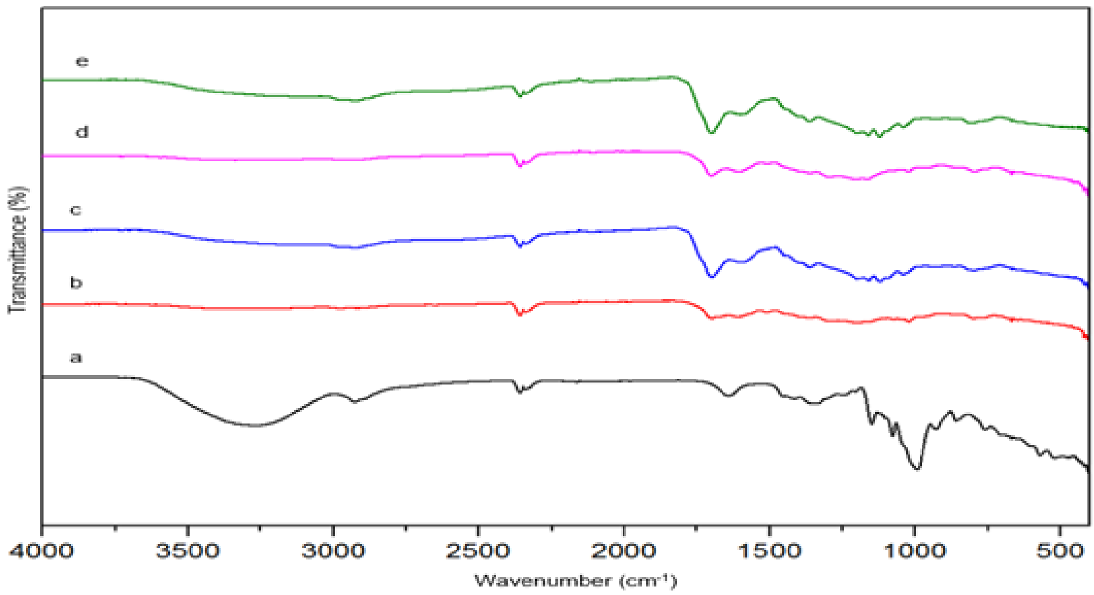

Figure 4.4. FTIR spectra were obtained for: a) starch, b) Hydrochars produced from starch at 180°C without catalyst, c) Hydrochars produced from starch at 180°C with catalyst, d) Hydrochars produced from starch at 200°C without catalyst, e) Hydrochars produced from starch at 200°C with catalyst.

The chemical structures of glucose, β-cyclodextrin, and starch were analyzed using NMR spectroscopy, as shown in Figure 4.5. The NMR spectra of glucose, β-cyclodextrin, and starch displayed unique chemical shifts. The NMR spectrum of glucose revealed chemical shifts between 60 and 110 ppm [62–64]. The C6 carbon peak was observed at 65.93 ppm, while the C5 peak was seen at 72.73 ppm in the

^{13}C NMR spectrum. In addition, the C3 and C2 peaks were observed at 74.88 ppm and 75.24 ppm, respectively. The C4 peak was observed at 73.84 ppm, while the C1 peak was observed at 95.22 ppm, as revealed in the NMR spectra [65]. The peak assignments for β-cyclodextrin were performed and revealed the peaks for C6 between 60-70 ppm, and for C3, C2, and C5 between 70-78 ppm. The peak for C4 was identified between 80-86 ppm, while the peak for C1 was located between 103-106 ppm [66]. Similarly, peak assignments were conducted on the NMR spectrum of starch, which resulted in the same identified peaks for C6, C3, C2, C5, C4, and C1 as those observed for β-cyclodextrin [67].

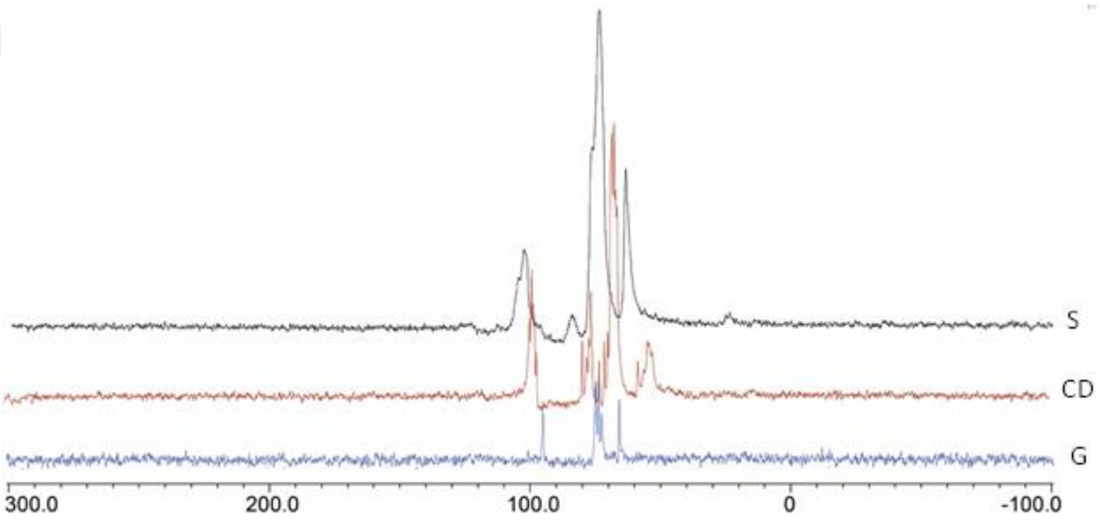

Figure 4.5. NMR spectra of glucose, β-cyclodextrin, and starch

The NMR spectra of hydrochars obtained from glucose, β-cyclodextrin, and starch were analyzed at 200ºC, both with and without a catalyst, as shown in Figure 4.6. In the chemical analysis of the material, the presence of sp^3 carbon atoms was identified from a peak observed between 0 and 90 ppm, as reported in [68,69]. Peaks in the range of 100-160 ppm were attributed to the presence of sp^2 carbon atoms in C=C double bonds, with the signals between 140 and 160 ppm indicating the presence of oxygen-bound O−C=C. Resonance signals were observed between 170-225 ppm, indicating the presence of C=O groups that could be in carboxylic acid moieties (177 ppm) or ketones and aldehydes (200-220 ppm) [68,69]. The main differences in the hydrochars produced from the non-catalytic runs and catalytic runs were the presence of a peak corresponding to unreacted glucose (68.80 ppm) in the hydrochars obtained from the catalytic runs. Moreover, the intensities of peaks observed at 177 ppm in hydrochars obtained from catalytic runs were higher than those obtained from non-catalytic runs.

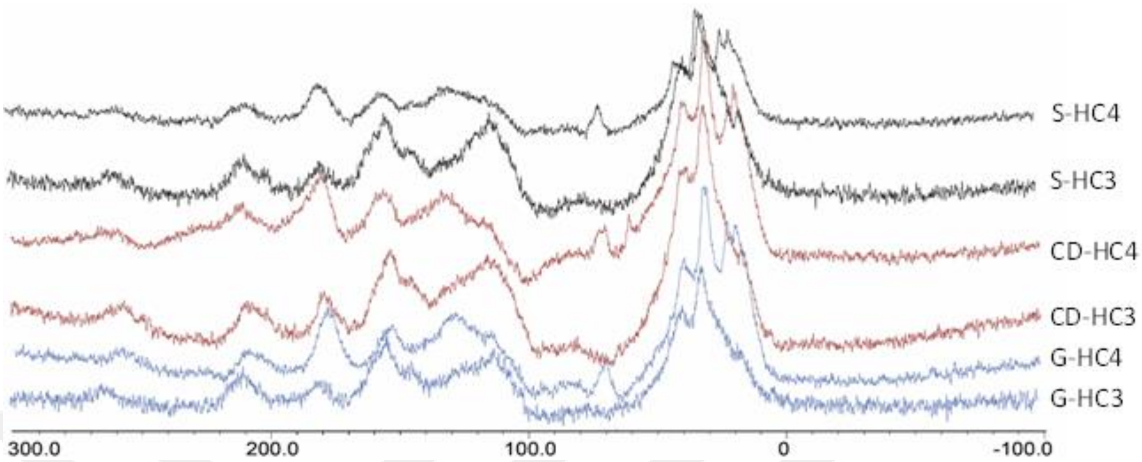

Figure 4.6. NMR spectra of hydrochars obtained from glucose, β-cyclodextrin, and starch at 200ºC without and with catalyst.

PART 5

CONCLUSIONS

In summary, the present study investigated the effects of temperature and the use of a catalyst on the HTC of three feedstocks: glucose, β-cyclodextrin, and starch. The results showed that hydrochar yields increased with increasing temperature in non-catalytic runs but decreased with the use of a catalyst at both temperatures. The carbon and oxygen content of hydrochars from each feedstock were similar, and the HTC process led to a reduction in the O/C and H/C ratios, regardless of the feedstock type. The use of a catalyst resulted in an increase in the diameter of carbon spheres in each feedstock. The hydrochars from both non-catalytic and catalytic runs exhibited characteristic peaks, with higher intensities observed at 177 ppm in hydrochars from catalytic runs. These findings provide valuable insights into the optimization of the HTC process for producing hydrochars with desirable properties.

REFERENCES

1. Robyt, J. F., "Essentials of Carbohydrate Chemistry", ***Springer New York***, New York, NY, 1-410 (1998).

2. BeMiller, J. N., "Carbohydrate Chemistry for Food Scientists", 3rd edition. Ed., ***Elsevier***, Cambridge, MA, 1-420 (2018).

3. Bonner, W. A., "The Carbohydrates. Chemistry, Biochemistry, Physiology.", ***Journal of The American Chemical Society***, 80 (10): 2598–2598 (1958).

4. "Introduction to Biochemistry-Chapter 13- Carbohydrate Chemistry: Simple Sugars, Rings and Glycosides", https://ecampusontario.pressbooks.pub/bioc2580/chapter/carbohydratechemistry-simple-sugars-rings-and-glycosides/. accessed 1 March 2023.

5. Song, E.-H., Shang, J., and Ratner, D. M., "Polysaccharides", Polymer Science: A Comprehensive Reference, ***Elsevier***, 137–155 (2012).

6. "Carbohydrates", ***Carbohydrates in Encyclopedia of Physical Science and Technology***, 369-416 (2003).

7. "Starch Structure, Functionality and Application in Foods", ***Springer,*** Singapore, (2020).

8. Cornejo-Ramírez, Y. I., Martínez-Cruz, O., Del Toro-Sánchez, C. L., Wong-Corral, F. J., Borboa-Flores, J., and Cinco-Moroyoqui, F. J., "The structural characteristics of starches and their functional properties", ***CyTA - Journal of Food***, 16 (1): 1003–1017 (2018).

9. Shin, Y., Wang, L.-Q., Bae, I.-T., Arey, B. W., and Exarhos, G. J., "Hydrothermal syntheses of colloidal carbon spheres from cyclodextrins", ***The Journal of Physical Chemistry C***, 112 (37): 14236–14240 (2008).

10. Dodziuk, H., "Molecules with holes–cyclodextrins", ***Cyclodextrins and Their Complexes: Chemistry, Analytical Methods, Applications***, 1–30 (2006).

11. Amiri, S. and Rahimi, A., "Poly (ε-caprolactone) electrospun nanofibers containing curcumin nanocontainers: Enhanced solubility, dissolution and physical stability of curcumin via formation of inclusion complex with cyclodextrins", ***International Journal of Polymeric Materials and Polymeric Biomaterials***, 68 (11): 669–679 (2019).

12. Kalepu, S. and Nekkanti, V., "Insoluble drug delivery strategies: review of recent advances and business prospects", ***Acta Pharmaceutica Sinica B***, 5 (5): 442–453 (2015).

13. Mourtzinos, I., Makris, D. P., Yannakopoulou, K., Kalogeropoulos, N., Michali, I., and Karathanos, V. T., "Thermal stability of anthocyanin extract of Hibiscus sabdariffa L. in the presence of β-cyclodextrin", J***ournal of Agricultural and Food Chemistry***, 56 (21): 10303–10310 (2008).

14. Bezerra, F. M., Lis, M. J., Firmino, H. B., Dias da Silva, J. G., Curto Valle, R. de C. S., Borges Valle, J. A., Scacchetti, F. A. P., and Tessaro, A. L., "The role of β-cyclodextrin in the textile industry", ***Molecules***, 25 (16): 3624 (2020).

15. Morin-Crini, N. and Crini, G., "Environmental applications of water-insoluble β-cyclodextrin–epichlorohydrin polymers", ***Progress In Polymer Science***, 38 (2): 344–368 (2013).

16. Loftsson, T. and Brewster, M. E., "Pharmaceutical applications of cyclodextrins: basic science and product development", ***Journal of Pharmacy and Pharmacology***, 62 (11): 1607–1621 (2010).

17. Tekin, K., Karagöz, S., and Bektaş, S., "A review of hydrothermal biomass processing", ***Renewable and Sustainable Energy Reviews***, 40: 673–687 (2014).

18. Onwudili, J. A. and Williams, P. T., "Hydrothermal gasification and oxidation as effective flameless conversion technologies for organic wastes", ***Journal of The Energy Institute***, 81 (2): 102–109 (2008).

19. Alper, K., Tekin, K., Karagöz, S., and Ragauskas, A. J., "Sustainable energy and fuels from biomass: a review focusing on hydrothermal biomass processing", ***Sustainable Energy & Fuels***, 4 (9): 4390–4414 (2020).

20. Mumme, J., Eckervogt, L., Pielert, J., Diakité, M., Rupp, F., and Kern, J., "Hydrothermal carbonization of anaerobically digested maize silage", ***Bioresource Technology***, 102 (19): 9255–9260 (2011).

21. Peterson, A. A., Vogel, F., Lachance, R. P., Fröling, M., Antal Jr, M. J., and Tester, J. W., "Thermochemical biofuel production in hydrothermal media: a review of sub-and supercritical water technologies", ***Energy & Environmental Science***, 1 (1): 32–65 (2008).

22. Azadi, P. and Farnood, R., "Review of heterogeneous catalysts for sub-and supercritical water gasification of biomass and wastes", ***International Journal of Hydrogen Energy***, 36 (16): 9529–9541 (2011).

23. Okolie, J. A., Epelle, E. I., Nanda, S., Castello, D., Dalai, A. K., and Kozinski, J. A., "Modeling and process optimization of hydrothermal gasification for hydrogen production: A comprehensive review", ***The Journal of Supercritical Fluids***, 173: 105199 (2021).

24. Elliott, D. C., "Catalytic hydrothermal gasification of biomass", ***Biofuels, Bioproducts and Biorefining***, 2 (3): 254–265 (2008).

25. Savage, P. E., Levine, R. B., and Huelsman, C. M., "Hydrothermal processing of biomass", Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals, ***Royal Society of Chemistry London***, 192–221 (2010).

26. Dimitriadis, A. and Bezergianni, S., "Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review", ***Renewable and Sustainable Energy Reviews***, 68: 113–125 (2017).

27. Tekin, K. and Karagöz, S., "Non-catalytic and catalytic hydrothermal liquefaction of biomass", ***Research on Chemical Intermediates***, 39: 485–498 (2013).

28. Funke, A. and Ziegler, F., "Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering", ***Biofuels, Bioproducts and Biorefining***, 4 (2): 160–177 (2010).

29. Hasan, R. O., Ercan, B., Acikkapi, A. N., Ucar, S., and Karagöz, S., "Effects of metal chlorides on the hydrothermal carbonization of grape seeds", ***Energy & Fuels***, 35 (10): 8834–8843 (2021).

30. Lachos-Perez, D., Torres-Mayanga, P. C., Abaide, E. R., Zabot, G. L., and De Castilhos, F., "Hydrothermal carbonization and Liquefaction: Differences, progress, challenges, and opportunities", ***Bioresource Technology***, 343: 126084 (2022).

31. Oliveira, I., Blöhse, D., and Ramke, H.-G., "Hydrothermal carbonization of agricultural residues", ***Bioresource Technology***, 142: 138–146 (2013).

32. Yay, A. S. E., Birinci, B., Açıkalın, S., and Yay, K., "Hydrothermal carbonization of olive pomace and determining the environmental impacts of post-process products", ***Journal of Cleaner Production***, 315: 128087 (2021).

33. Ercan, B., Ajagbe, Y. O., Uçar, S., Tekin, K., and Karagöz, S., "Production of Hydrochars from Lignocellulosic Biomass with and without Boric Acid", ***Chemical Engineering & Technology***, 45 (11): 2112–2122 (2022).

34. Khan, T. A., Saud, A. S., Jamari, S. S., Ab Rahim, M. H., Park, J.-W., and Kim, H.-J., "Hydrothermal carbonization of lignocellulosic biomass for carbon rich material preparation: A review", ***Biomass and Bioenergy***, 130: 105384 (2019).

35. Libra, J. A., Ro, K. S., Kammann, C., Funke, A., Berge, N. D., Neubauer, Y., Titirici, M.-M., Fühner, C., Bens, O., and Kern, J., "Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis", ***Biofuels***, 2 (1): 71–106 (2011).

36. Román, S., Nabais, J. M. V., Laginhas, C., Ledesma, B., and González, J. F., "Hydrothermal carbonization as an effective way of densifying the energy content of biomass", ***Fuel Processing Technology***, 103: 78–83 (2012).

37. Soroush, S., Ronsse, F., Verberckmoes, A., Verpoort, F., Park, J., Wu, D., and Heynderickx, P. M., "Production of solid hydrochar from waste seaweed by

hydrothermal carbonization: effect of process variables", ***Biomass Conversion and Biorefinery***, 1–15 (2022).

38. Pauline, A. L. and Joseph, K., "Hydrothermal carbonization of organic wastes to carbonaceous solid fuel–A review of mechanisms and process parameters", ***Fuel***, 279: 118472 (2020).

39. Elaigwu, S. E. and Greenway, G. M., "Chemical, structural and energy properties of hydrochars from microwave-assisted hydrothermal carbonization of glucose", ***International Journal Of Industrial Chemistry***, 7 (4): 449–456 (2016).

40. Demir-Cakan, R., Baccile, N., Antonietti, M., and Titirici, M.-M., "Carboxylate-rich carbonaceous materials via one-step hydrothermal carbonization of glucose in the presence of acrylic acid", ***Chemistry of Materials***, 21 (3): 484–490 (2009).

41. Ischia, G., Cutillo, M., Guella, G., Bazzanella, N., Cazzanelli, M., Orlandi, M., Miotello, A., and Fiori, L., "Hydrothermal carbonization of glucose: Secondary char properties, reaction pathways, and kinetics", ***Chemical Engineering Journal,*** 449: 137827 (2022).

42. Simsir, H., Eltugral, N., and Karagoz, S., "Effects of acidic and alkaline metal triflates on the hydrothermal carbonization of glucose and cellulose", ***Energy & Fuels***, 33 (8): 7473–7479 (2019).

43. Sevilla, M. and Fuertes, A. B., "The production of carbon materials by hydrothermal carbonization of cellulose", ***Carbon***, 47 (9): 2281–2289 (2009).

44. Modugno, P. and Titirici, M.-M., "Influence of reaction conditions on hydrothermal carbonization of fructose", ***ChemSusChem***, 14 (23): 5271–5282 (2021).

45. Yao, C., Shin, Y., Wang, L.-Q., Windisch, C. F., Samuels, W. D., Arey, B. W., Wang, C., Risen, W. M., and Exarhos, G. J., "Hydrothermal dehydration of aqueous fructose solutions in a closed system", ***The Journal Of Physical Chemistry*** C, 111 (42): 15141–15145 (2007).

46. Sevilla, M. and Fuertes, A. B., "Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides", ***Chemistry–A European Journal***, 15 (16): 4195–4203 (2009).

47. Titirici, M.-M., Antonietti, M., and Baccile, N., "Hydrothermal carbon from biomass: a comparison of the local structure from poly-to monosaccharides and pentoses/hexoses", ***Green Chemistry***, 10 (11): 1204–1212 (2008).

48. Liang, J., Liu, Y., and Zhang, J., "Effect of solution pH on the carbon microsphere synthesized by hydrothermal carbonization", ***Procedia Environmental Sciences***, 11: 1322–1327 (2011).

49. Paksung, N., Pfersich, J., Arauzo, P. J., Jung, D., and Kruse, A., "Structural effects of cellulose on hydrolysis and carbonization behavior during hydrothermal treatment", ***ACS Omega***, 5 (21): 12210–12223 (2020).

50. Zhao, Y., Li, W., Zhao, X., Wang, D. P., and Liu, S. X., "Carbon spheres obtained via citric acid catalysed hydrothermal carbonisation of cellulose", ***Materials Research Innovations***, 17 (7): 546–551 (2013).

51. Lu, X. and Berge, N. D., "Influence of feedstock chemical composition on product formation and characteristics derived from the hydrothermal carbonization of mixed feedstocks", ***Bioresource Technology***, 166: 120–131 (2014).

52. Falco, C., Baccile, N., and Titirici, M.-M., "Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons", ***Green Chemistry***, 13 (11): 3273–3281 (2011).

53. Huang, Y.-B. and Fu, Y., "Hydrolysis of cellulose to glucose by solid acid catalysts", ***Green Chemistry***, 15 (5): 1095–1111 (2013).

54. García-Bordejé, E., Pires, E., and Fraile, J. M., "Parametric study of the hydrothermal carbonization of cellulose and effect of acidic conditions", ***Carbon***, 123: 421–432 (2017).

55. Ibrahim, M., Alaam, M., El-Haes, H., Jalbout, A. F., and Leon, A. de, "Analysis of the structure and vibrational spectra of glucose and fructose", ***Ecletica Quimica***, 31: 15–21 (2006).

56. Bağ, Ö. and Tekin, K., "Production and characterization of hydrothermal carbon from waste lignocellulosic biomass", J***ournal of The Faculty of Engineering and Architecture of Gazi University***, 35 (2): 1063–1076 (2019).

57. Xu, R., Lin, X., Xu, J., and Lei, C., "Controlling the water absorption and improving the high C-rate stability: A coated Li-ion battery separator using β-cyclodextrin as binder", ***Ionics***, 26: 3359–3365 (2020).

58. Amani, S., Garmarudi, A. B., Rahmani, N., and Khanmohammadi, M., "The β-cyclodextrin-modified nanosized ZSM-5 zeolite as a carrier for curcumin", ***RSC Advances***, 9 (55): 32348–32356 (2019).

59. Warren, F. J., Gidley, M. J., and Flanagan, B. M., "Infrared spectroscopy as a tool to characterise starch ordered structure—a joint FTIR–ATR, NMR, XRD and DSC study", ***Carbohydrate Polymers***, 139: 35–42 (2016).

60. Pozo, C., Rodríguez-Llamazares, S., Bouza, R., Barral, L., Castaño, J., Müller, N., and Restrepo, I., "Study of the structural order of native starch granules using combined FTIR and XRD analysis", ***Journal Of Polymer Research***, 25: 1–8 (2018).

61. Shi, N., Liu, Q., He, X., Wang, G., Chen, N., Peng, J., and Ma, L., "Molecular structure and formation mechanism of hydrochar from hydrothermal carbonization of carbohydrates", ***Energy & Fuels***, 33 (10): 9904–9915 (2019).

62. Bubb, W. A., "NMR spectroscopy in the study of carbohydrates: Characterizing the structural complexity", ***Concepts In Magnetic Resonance Part A: An Educational Journal***, 19 (1): 1–19 (2003).

63. Fort, D. A., Swatloski, R. P., Moyna, P., Rogers, R. D., and Moyna, G., "Use of ionic liquids in the study of fruit ripening by high-resolution 13C NMR spectroscopy: ‘green’ solvents meet green bananas", ***Chemical Communications***, (7): 714–716 (2006).

64. Patil, N. V. and Netravali, A. N., "Enhancing strength of wool fiber using a soy flour sugar-based “green” cross-linker", ***ACS Omega***, 4 (3): 5392–5401 (2019).

65. Alexandersson, E. and Nestor, G., "Complete 1H and 13C NMR spectral assignment of D-glucofuranose", ***Carbohydrate Research***, 511: 108477 (2022).

66. Koito, Y., Yamada, K., and Ando, S., "Solid-state NMR and wide-angle X-ray diffraction study of hydrofluoroether/β-cyclodextrin inclusion complex", ***Journal of Inclusion Phenomena and Macrocyclic Chemistry***, 76: 143–150 (2013).

67. Zhang, X., Golding, J., and Burgar, I., "Thermal decomposition chemistry of starch studied by ^{13}C high-resolution solid-state NMR spectroscopy", ***Polymer***, 43 (22): 5791–5796 (2002).

68. Baccile, N., Laurent, G., Babonneau, F., Fayon, F., Titirici, M.-M., and Antonietti, M., "Structural characterization of hydrothermal carbon spheres by advanced solid-state MAS ^{13}C NMR investigations", ***The Journal Of Physical Chemistry C***, 113 (22): 9644–9654 (2009).

69. Tekin, K., Pileidis, F. D., Akalin, M. K., and Karagöz, S., "Cellulose-derived carbon spheres produced under supercritical ethanol conditions", ***Clean Technologies and Environmental Policy***, 18: 331–338 (2016).

RESUME

Mehboob IQBAL completed his primary and elementary education in Lodhran, Pakistan. He graduated from Allama Iqbal High School and then, in 2015, he began his BS in Chemistry at the Federal Urdu University of Arts, Science, and Technology in Pakistan. In October 2020, he started his M.Sc. in the Department of Chemistry at Karabük University in Turkey.