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Optimization of a Dynamic Hot Water Pretreatment of Switchgrass using Catalysis by Carbonation to Maximize Carbochemical Yields

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Optimization of a Dynamic Hot Water Pretreatment of Switchgrass using Catalysis by Carbonation to Maximize Carbochemical Yields

Optimization of a Dynamic Hot Water Pretreatment of Switchgrass using Catalysis by
Carbonation to Maximize Carbochemical Yields

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Chemical Engineering

By

Rohit Tanaji Dhamdere
University of Mumbai
Bachelor of Engineering in Chemical Engineering, 2007

August 2012
University of Arkansas

Abstract

A bio-refinery is a facility that converts renewable bio-resources into value-added chemicals and products. In this context of a bio-refinery, the production of the carbochemicals such as HMF, furfural and organic acids illustrate that multiple products can be produced from a renewable source such as lignocellulosic biomass (switchgrass). Traditionally, carbochemicals such as furfural and HMF are produced using inorganic acids such as H_2SO_4, HCL, and H_3PO_4. The use of such acids requires the application of high cost materials of construction such as Hastelloy-C, titanium etc.

The objective of this study is to develop a semi-continuous process for the conversion of switchgrass to carbochemicals such as HMF, furfural and organic acids. Moreover, the application of water as a green reaction medium and the utilization of carbonated water as a "green catalyst" were studied in this research. For the purpose of this study, we constructed a semi-continuous flow apparatus using three high precision Isco syringe pumps and a constant temperature oven to allow carbonation of the water over a range of temperatures and pressure to reactively pretreat switchgrass. Carbochemicals (furan-based aldehydes) and acids that were formed were detected using a Waters HPLC employing a Bio-Rad Aminex HPX-87H column with a PDA (photo diode array) detector at wavelengths range of 210 and 280nm. Oligosaccharides were detected using Dionex HPLC employing Bio-Rad Aminex HPX-87P column using a Shodex RI-101 refractive index detector. The kinetics of the formation and degradation of HMF and furfural were studied using the solver function in Microsoft Excel. Carbonated water clearly showed catalytic activity by increasing the yields of the HMF and furfural at temperatures of 220, 250 and 280°C. The highest catalytic activity was observed for HMF formation in carbonated water with a nine-fold increase in yields over that using neat subcritical water.

This thesis is approved for recommendation
to the Graduate Council.

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Acknowledgements

I would like to express my gratitude to my research advisor Dr. Jerry W. King for giving me the opportunity to pursue my graduate research under his mentorship. I am thankful to him for his motivation, support and guidance during the course of this study that has greatly helped me to accomplish my research objective. I would also like to thank Dr. Keerthi Srinivas for his advice and discussions during the course of the research.

I am grateful to the research committee members Dr. Jerry Havens and Dr. Ed Clausen for being a part of the thesis committee. Many thanks to Dr. Chuck West, Dale Bumpers College of Agricultural, Food and Life Sciences, for the switchgrass supply for the study. I would also like to thank Dr. Ya-Jane Wang, Department of Food Science, for biomass comminution and support.

I would like to acknowledge my fellow colleague Yu-Wu Lu for his support and help through the research work. I would like to acknowledge Dr. Mourad Benamara for his guidance for the SEM micrographs study of the biomass samples.

Finally, I would like to thank my mother, father and sister for their continuous support and encouragement through my entire career as a student. Last but not the least, I would like to thank my wife, Sarika Rohit Dhamdere, for her support through the tough times and moments and would like to dedicate the thesis to her.

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Chapter 1. Introduction

Increasing petroleum prices and depleting fossil fuel resources, coupled with an ever growing population, have resulted in an urgent need for alternative resource for energy and chemical industries. Moreover, the recent economic depression coupled with unstable socio-political situation around the world has slowed the overall recovery of world economies. Currently, oil is the primary source of fuel and has a current demand of 85 million barrels per day and projected to be 130 million barrels per day by 2030.[1] Out of this overall demand; an enormous 60% of these resources are used as transportation fuel. With the growth in world population to 9-10 billion by 2040, every effort is being made to find an alternative source for energy needs that is sustainable, renewable and cost effective.[2] Hence, for the purpose of energy security and to provide a major push towards economic recovery, the utilization renewable raw materials for producing fuels and chemicals is critical. Hence, there is a strong necessity for finding an alternative resource that is renewable, cheap, and environmentally-benign with vast availability.

Considering these constraints, lignocellulosic biomass, available at ~1.4 bn dry tons/year as shown in Figure 1.1 can prove to be an alternative resource to substitute for fossil-based fuel.[3] Current technologies for the production of fuels and chemicals from renewable resources are primarily focused towards the synthesis of ethanol, butanol, and biodiesel. These low-value high-volume products result in an incomplete or partial utilization of carbon from the lignocellulosic biomass substrate. Hence an alternative route for an integrated approach towards implementing bio-based resources should be found. Current technology for the production of biofuels needs to be further optimized with respect to cost and processing efficiency.
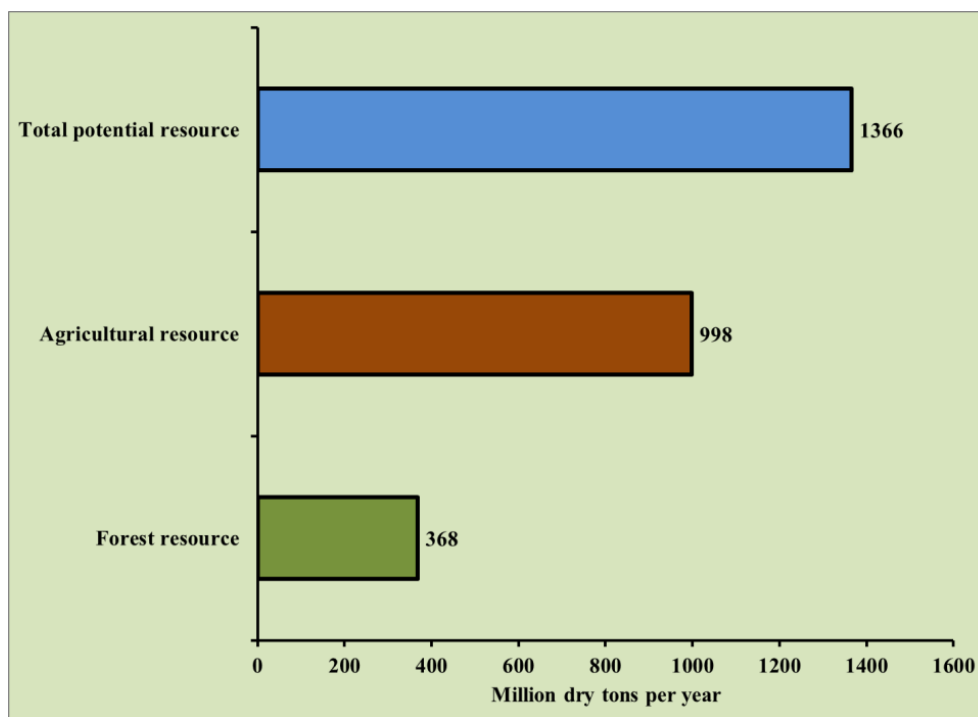
Figure 1.1: Available biomass resources[3]

An integrated bio-refinery approach can play a vital role towards the development of bio-based fuels and chemicals. A bio-refinery is defined by NREL (National Renewable Energy Laboratory) is as "A facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass". The bio-refinery concept is analogous to today's petroleum refinery, which produces a multiple range of products such as fuels and chemicals. DOE's (Department of Energy) definition of a bio-refinery is "A bio-refinery is an overall concept of a processing plant where biomass feedstock are converted and extracted into a spectrum of valuable products"

The conversion of biomass can be defined according to first-generation biofuels and second-generation biofuels. First generation biofuels are those fuels produced by the conversion of bio-resources such as cereals, grains, seeds.[4] These materials are primarily starch-derived

feedstocks. In the process of conversion, the starch is extracted from the biomass matrix and further converted to its constituent sugars. These sugars are then fermented to ethanol using enzymes and chemical catalysts. Currently, the US is the largest producer of ethanol in the world with capacities ranging from 175 million gallons in 1980 to 13.9 billion gallons in 2010, mostly produced from the conversion of corn.[5]

One major drawback of using starch-based feedstock is that these resources are produced from food crops. The cost of corn for example, has risen from less than $3/bushel to nearly $7/bushel in just few years. As the production capacities for the biofuel production are increased, all the resources will be directed towards the production of fuels leading to a scarcity and cost increase of food products. Hence, an alternative resource to the use of food crop feedstock is essential, and these factors have led to the development of second generation biofuels.

Second generation biofuels are those fuels that are produced using non-food crops and resources such as agricultural and municipal wastes, forest resources, and dedicated energy crops, such as switchgrass, primarily known as lignocellulosic biomass. The concept of bio-refinery can be implemented provided there is a constant supply of raw material for processing. Lignocellulosic biomass can provide a valuable opportunity for full-scale implementation of the bio-refinery concept.

1.1. Lignocellulosic Biomass: Switchgrass as a Potential Bio-fuel Crop

The production of biofuels and bio-chemicals from biomass depends on year-round availability. Switchgrass (i.e. *Panicum virgatum*) is a tall growing, warm season grass found in North America.[6,7] Switchgrass is a promising alternative renewable source for biofuels since it can be grown on marginal land and does not compete with crops in the food chain.[8] Once seeded,

the plant will continue to yield its valuable bio-resource for 10 years without reseeding attaining heights of about 7-10 feet, yielding a maximum of 7 tons per acre and producing around 500 – 1000 gallons per year of ethanol.[9, 10]

Lignocellulosic biomass is primarily composed of three components: cellulose, hemicellulose and lignin. Table 1.1 depicts the composition of these components in various types of biomass. The composition of the biomass is critical and important for the point of view of the type of chemical that can be produced. Biomass type with higher hemicellulose content such as wheat straw and coastal Bermuda grasses can be useful for the production of chemicals such as furfural.

Table 1.1: Composition of lignocellulosic biomass[11]

Lignocellulosic material	cellulose (%)	hemicelluose (%)	lignin (%)
hardwood stems	40-55	24-40	18-25
softwood stems	45-50	25-35	25-35
nut shells	23-30	25-30	30-40
corn cobs	45	35	15
grasses	25-40	35-50	10-30
paper	85-99	0	0-15
wheat straw	30	50	15
sorted refuse	60	20	20
leaves	15-20	80-85	0
cotton seed hairs	80-95	5-20	0
newspaper	40-55	25-40	18-30
waste papers from pulp	60-70	10-20	5-10
primary wastewater solids	8-15	-	-
solid cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
coastal bermuda grass	25	35.7	6
switchgrass	45	31.4	12
swine waste	6	28	na

On the other hand, biomass containing a higher fraction of cellulose can be used to produce a variety of chemicals derived from 6-carbon sugars such as glucose, HMF, and levulinic acid.

Hence, compositional analysis of the biomass provides significant guidance towards the selection and an optimal conversion of any type of biomass to specific chemical products.

1.1.1. Cellulose

Cellulose is the most abundant source of glucose on earth. Lignocellulosic biomass has cellulose content in the range of 30-50% depending upon the type of biomass. Cellulose is a fibrous network of amorphous and crystalline components of C, H & O linkages as shown in Figure 1.2. Glucose is the basic building block for cellulose linked by β-1-4-glycosidic bonds making it a seminal biopolymer produced in many plant sources.
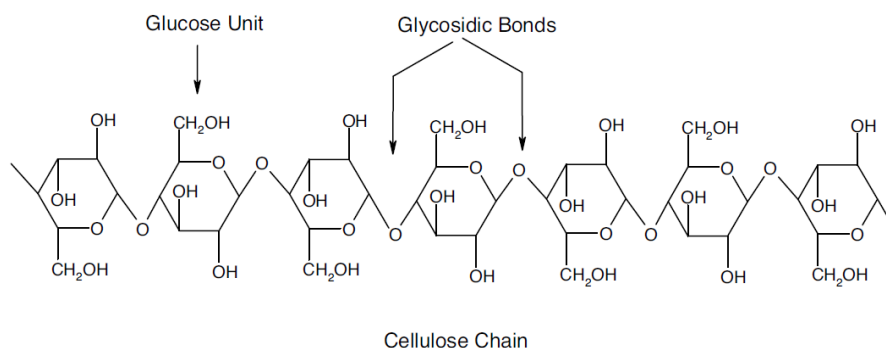
Figure 1.2: Cellulose chain of glucose units connected by glycosidic bonds[12]

Cellulose is embedded in a network lignin-hemicelluloses network which provides the plant stability against chemical or hydrothermal attack. Therefore access to the cellulose requires pretreatment for enhancing its accessibility. This can be achieved via several routes: enzymes, acids and high temperature water. Inherent crystallinity, stability and insolubility in water renders cellulose recalcitrant towards hydrolysis, hence it requires harsh conditions for conversion to sugars, chemicals and fuels by biochemical processes.

Chemical conversion of cellulose into various products requires the release of glucose from the network by cleavage of the glycosidic bonds. Further treatment of glucose results in

dehydration products like HMF which can be further converted towards the formation of dimethylfuran (DMF) and levulinic acid.

1.1.2. Hemicellulose

Hemicellulose is an amorphous polymer composed of pentose sugars primarily arabino-xylan, gluco-mannans, and galactans; with xylan forming this major component in the bio-polymer. Unlike cellulose which is crystalline and homogeneous, hemicellulose is heterogeneous and amorphous and can be hydrolyzed more easily than cellulose producing monomeric sugars such as xylose. Xylan (see Figure 1.3) contains heteropolysaccharides as β-1-4 xylopyranose units attached to the phenyl proponoid component of lignin network by covalent bonds.[13] For an efficient carbon conversion from biomass it is essential to convert the hemicellulosic fraction into value-added product like furfural.
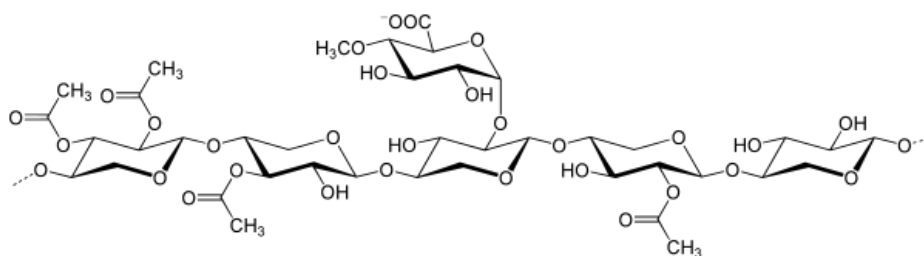
Figure 1.3: Structure of xylan, hemicellulose[14]

1.1.3. Lignin

Lignin consists of phenylpropane oligomers which belonging to model polyphenol-based polymers. It is primarily composed of four monolignols: p-coumaryl, coniferyl, syringol and sinapyl alcohols.[15] Due to the random arrangement in the polymeric structure of lignin the precise structure is difficult to define. A typical hypothetical structure[16] of lignin is shown in Figure 1.4.
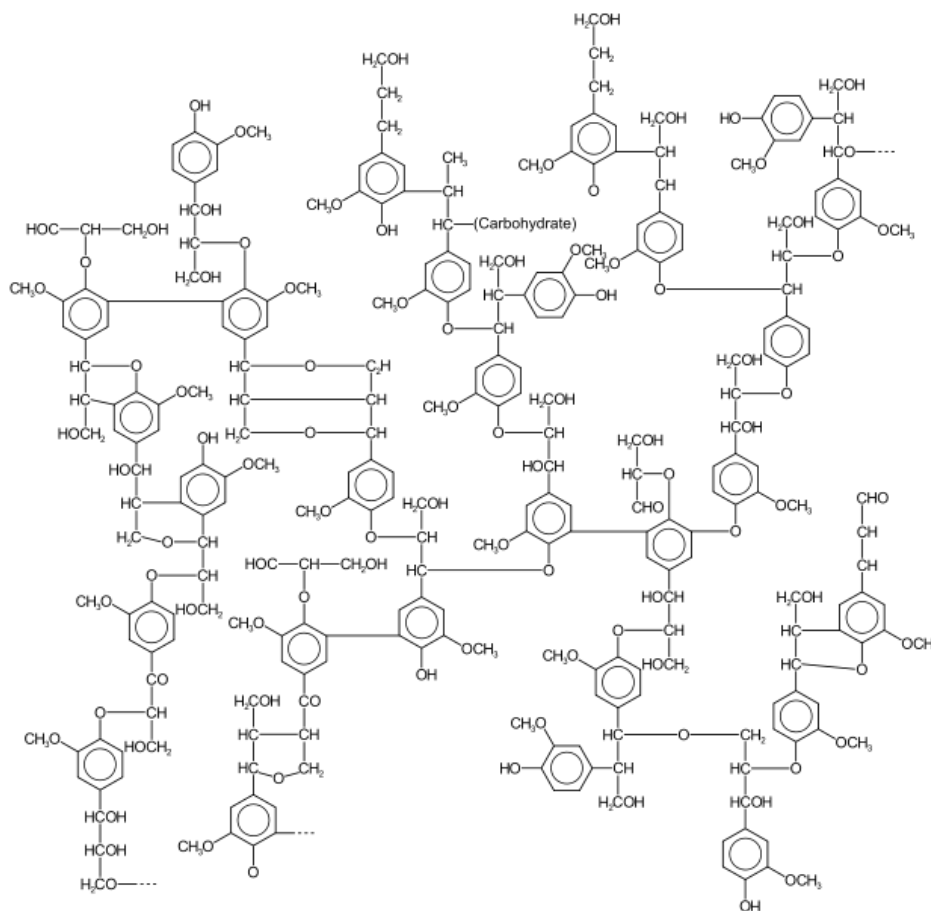
Figure 1.4: Hypothetical structure of lignin[16]

Lignin provides the plant physical structure and protects the plant tissue from chemical or enzymatic attack. It is more hydrophobic than cellulose and hemicellulose. Because of its resistance towards any chemical conversion, lignin removal is the most important step in biomass conversion to sugar. Delignification results in accessibility to the plant cell wall providing more access to cellulose and hemicellulose, resulting in higher yields of sugars via hydrolysis.[17]

1.2. Conversion Technologies for Lignocellulosic Biomass

There are primarily two major platforms (see Figure 1.5) that are traditionally utilized for conversion of biomass to chemical products, the sugar platform and the thermochemical

platform. Over the years research efforts towards the development of both of these platforms has been on-going.
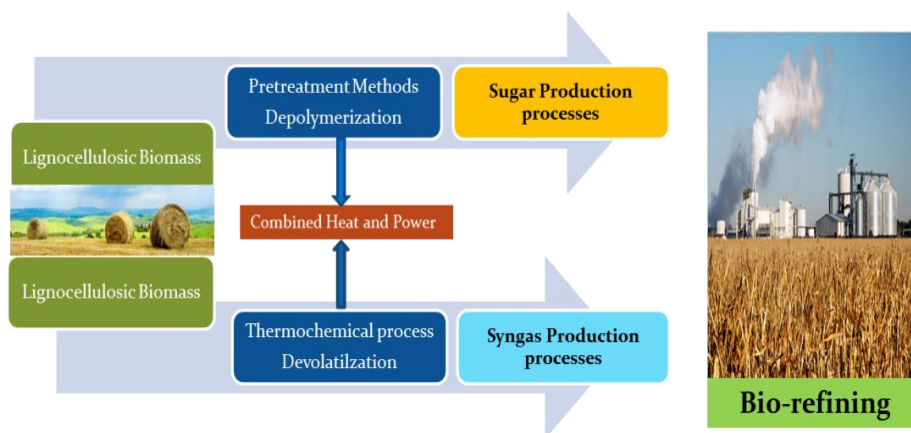
Figure 1.5: Bio-refinery concept – according to NREL[18]

The sugar platform represents a pathway to the production of chemicals such as alcohols, ketones, acids, furfurals, acetone and organic acids.[19] The building blocks for the sugar conversion route are the production of the derivative saccharides produced by a hydrolysis reaction. These conversion pathways from a sugar are shown in the Figure 1.6. Fundamentally, the hydrolysis conversion process results in the formation of monomeric and oligomeric sugars which can be further converted via dehydration, hydrogenation, fermentation, and crystallization into an array of chemicals.

The utilization of biomass requires a hydrolytic pretreatment step. The hydrolysis step is an important process towards selectively converting the bio-polymer constituting the biomass (cellulose, hemicellulose and lignin) towards the above mentioned carbochemicals.
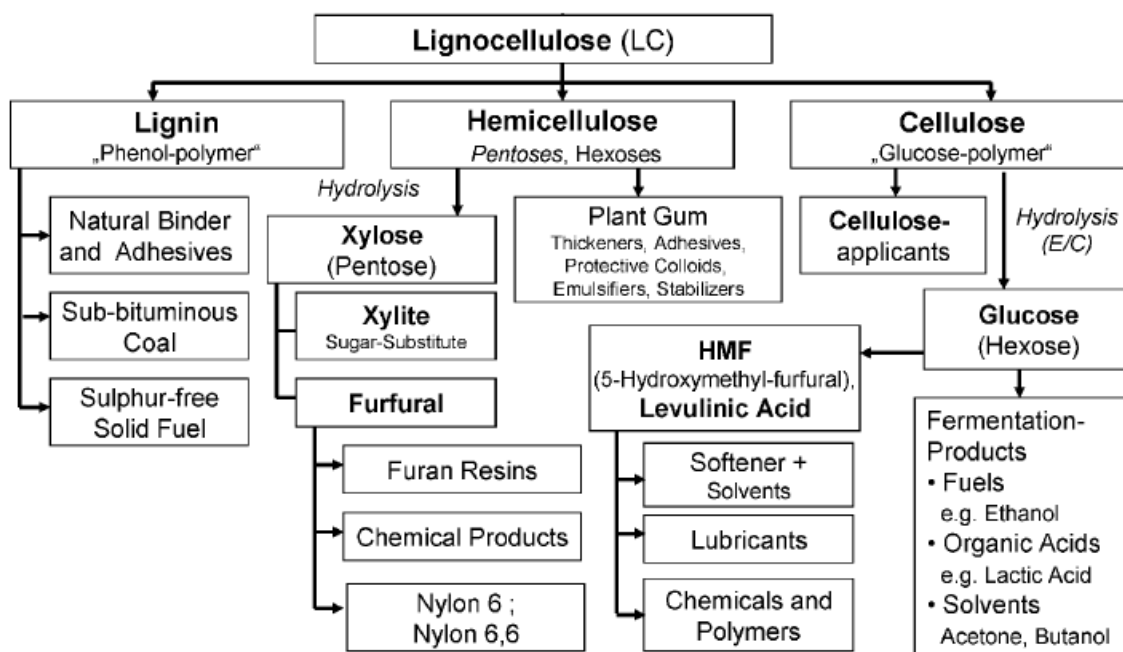
Figure 1.6: Pathways for converting biomass to chemicals using hydrolysis[20]

The thermochemical platform for conversion of biomass utilizes heat as the primary input towards the transformation of biomass chemically i.e. synthesis gas (CO and H_2). Gasification, combustion and pyrolysis are the basic process mechanisms utilized in the thermochemical conversion of biomass. In addition to heat, catalysts are used to form and accelerate conversion towards specific products. Although this process has been investigated for many decades, the mechanism for conversion of lignocellulosic biomass requires additional technological development to enhance the overall carbon conversion efficiency.

Figure 1.7 briefly describes the overall thermochemical conversion routes towards liquid fuels such as gasoline and alcohols. Three major conversion mechanisms are utilized: complete combustion, partial combustion and pyrolysis. Further processes, such as Fisher-Tropsch, utilize syngas which can be converted to liquid fuels and olefinic compounds.
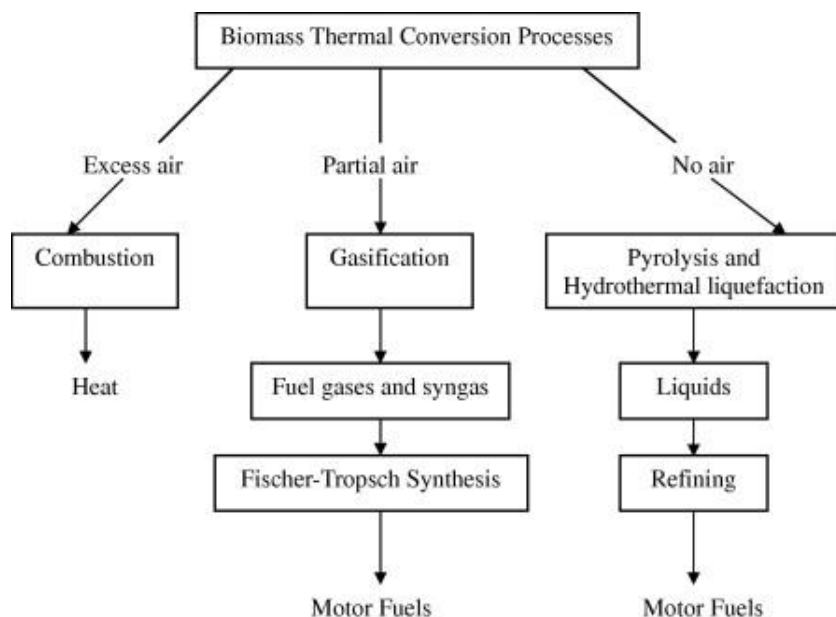
Figure 1.7: Thermochemical route for biomass utilization to fuels[21]

This conversion of biomass to fuels primarily involves the removal of oxygen from the biomass matrix, thereby enhancing the C:H ratio to that of hydrocarbon fuels. The oxygen removal produces CO_2 or H_2O. This step is important because the presence of oxygen reduces the calorific value of a fuel thereby reducing the overall economic efficiency associated with its use.

Integrated petroleum refineries have been the cornerstone for the success of the most developed countries in the 20th century. Various reports have provided evidence that the bio-refinery concept based on lignocellulosic biomass can be an economically-feasible approach towards a more sustainable development of energy and chemical industry. [22-24] Integrated bio-refineries will combine chemical and biological means for the conversion of biomass to value-

added products, resulting in an optimum utilization of the naturally available carbon from lignocellulosic-based resources.

The biorefinery has the potential to approach product chemicals such as succinic acid, glycerol, levulinic acid and others from bio-renewable resources as shown in Figure 1.8. Moreover, it has the potential for substituting chemicals derived traditionally from petroleum using bio-renewable resources. The resultant higher oxygen content in the biomass substrate makes them unacceptable as fuel precursors, but does provide an alternative route to these platform chemicals.
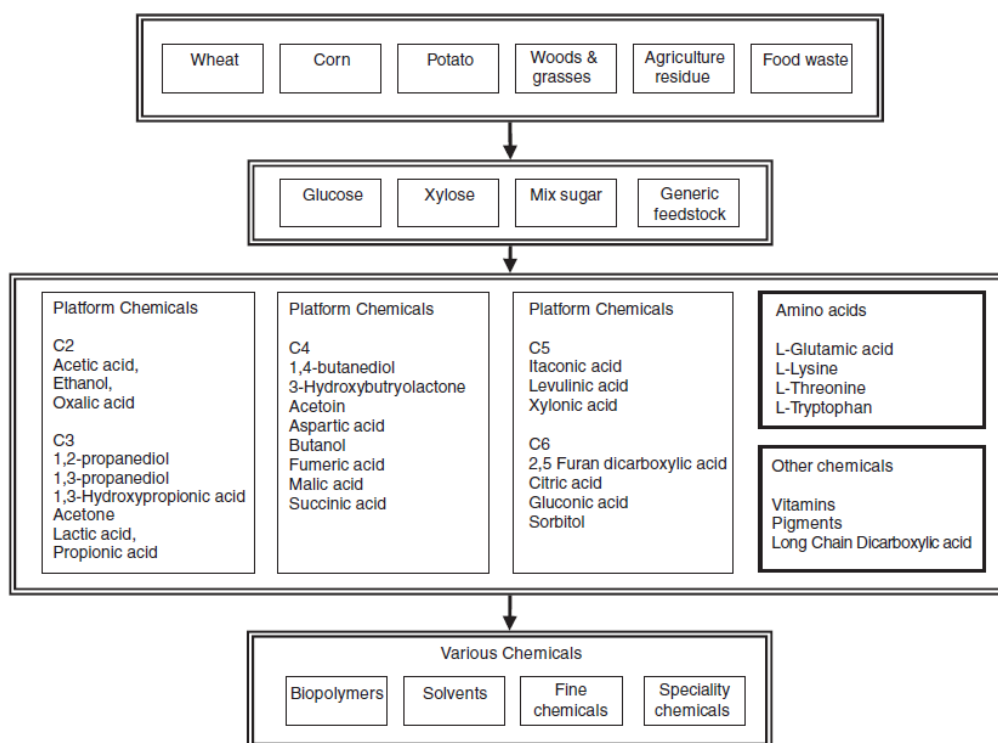
Figure 1.8: Pathways for biomass conversion using carbon platforms[25]

Succinic acid (a dicarboxylic acid) can be obtained by fermentation of sugars. Traditionally, succinic acid is produced by chemical conversion of maleic anhydride obtained from petroleum resources. It can be used as a building block chemical for synthesizing chemicals such as tetrahydrofuran, 1,4 – butanediol (BDO) etc. 1, 3 – hydropropionic acid is derived by fermentation of sugars and can be used in the synthesis of acrylonitrile, malonic acid etc.

Similarly, glucaric acid is produced by oxidizing sugars such as glucose in the presence of an acid. It can be used for the production of various chemicals such as glucaro-γ-lactone, polyhydroxypolyamides, etc (a nylon precursor). Itaconinc acid, a C5 dicarboxylic acid is produced by the fermentation of glucose monomer using the microorganism *aspergillus terreus*. A number of chemicals such as 2-methyl-1,4-BDO, itaconic diamide etc. can be synthesized by hydrogenation. Similarly, 2,5-furandicarboxylic acid (FDCA) produced by conversion of HMF obtained by dehydration of glucose. FDCA can be used for the production of succinic acid, 2, 5 – dimethyl furan and has similar properties as terephthalic acid. Due to its similarity to terephthalic acid it can be used to make a bio-polymer. Finally, all of these platform chemicals can be converted into polymers (from FDCA), as solvents, and specialty chemicals. Hence, considering the potential of the building block chemicals conversion of biomass to some of these valuable chemicals, it is necessary to further develop bio-refineries.[26]

1.3 Incorporating Green Processing into Biomass Conversion

Over the years the society has realized that the generation of waste needs to be minimized and as a consequence government institutions such as EPA (Environmental Protection Agency) have mandated regulations for the generation and disposal of wastes. These have led to added

responsibilities of the chemical engineering profession to mitigate hazardous wastes and to develop alternative processing routes that are environmentally-benign.

Table 1.2: Principles of green chemistry[28, 29]

Twelve Principles of green chemistry
• Waste prevention is better than treatment or clean-up
• Chemical synthesis should maximize the incorporation of all starting materials (atom economy)
• Chemical synthesis ideally should use and generate non-hazardous substances
• Chemical products should be designed to be nontoxic (safer chemicals)
• Catalysts are superior to reagents
• The use of auxiliaries should be minimized, i.e. the use of solvents, separation agents, etc. showed be minimized.
• Energy demands in chemical syntheses should be minimized
• Raw materials increasingly should be renewable
• Derivations (unnecessary derivatization) should be minimized.
• Chemical products should break down into innocuous products.
• Chemical processes require better control - analytical methodologies for real time, in-process monitoring and control prior to the formation of hazardous substances should be developed.
• Inherently safer chemistry for accident prevention.

The principles shown in Table 1.2 focus on generating processes that are designed to minimize wastes. Acid-based used for pretreatment of biomass can require a neutralization step that result in large amount of waste, i.e. gypsum ($Ca(SO_4) \cdot 2(H_2O)$) due to the reaction between H_2SO_4 and $Ca(OH)_2$. Moreover, such inorganic acids are hazardous themselves and corrosive. Avoiding the use of acids in biomass processing will be an important step towards achieving green processing. In this research the use of carbon dioxide provides such a pathway with elimination of acids for pretreatment and conversion of biomass (switchgrass) to carbochemicals. The generation of carbonic acid can provide an alternative route for acid catalyzed reaction involved in the biomass conversion. The use of renewable feedstock such as biomass leads to an inherently greener process.

During the process of biomass conversion, the biomass derived sugars are first extracted using reactive pretreatment methods.[30] Once the sugars are extracted from the biomass matrix they are catalytically converted to specific products such as ethanol, acids and furfurals. Green processing can play a key role in the reactive pretreatment of biomass to sugars wherein environmentally-benign solvents such as water and supercritical carbon dioxide could be used. Use of these green solvents will ensure that minimal hazardous wastes are generated requiring minimal post-processing such as separation of the products, raw materials and wastes from the reaction mixture.

1.4 Pretreatment Methods for Biomass Processing

The main purpose of the pretreatment processes applied to biomass to increase the surface area of the biomass fibers, delignification, reduction of crystallinity of the cellulose and increasing the accessibility of cellulose and hemicellulose for hydrolysis. Figure 1.9 gives a

pictorial view of the effects of the pretreatment on the biomass fibers. This process is carried out using various methods some of these methods; are discussed below:
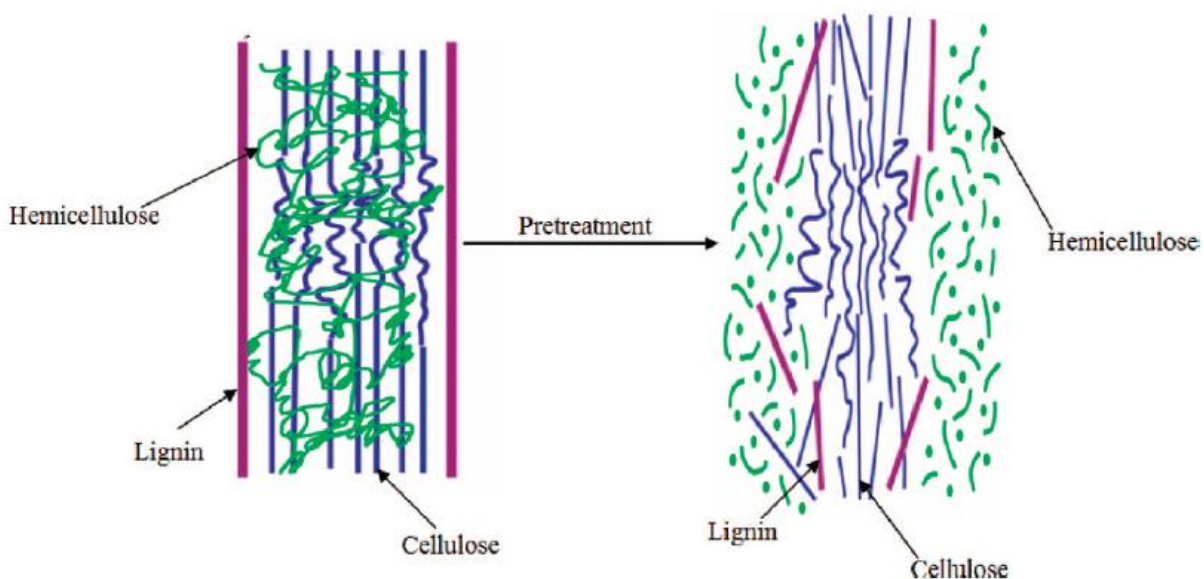
Figure 1.9: Effect of pretreatment on the cellulose, hemicellulose and lignin[31]

1.4.1 Acid Pretreatment

There are two types of acid pretreatment methods that has been applied for the pretreatment of biomass: concentrated acid pretreatment and dilute acid pretreatment. Dilute acid pretreatment is primarily used on the removal of hemicellulose from the biopolymer, whereas concentrated acid processes are applied for the conversion of the cellulose entity. The concentrated acid process, which is carried out at lower temperatures, is highly efficient in releasing the sugars from the bio-polymers, but also results in high degradation of the sugars into dehydration products.[32] On the contrary, dilute acid processes are carried out at relatively high temperatures but are more efficient in the generation of sugars while minimizing degradation

products. Acids such as sulfuric, hydrochloric, phosphoric acid, nitric acids are commonly used for the pretreatment of biomass.[33]

1.4.2 Alkaline Hydrolysis

Pretreatment of biomass can also be carried out using a base such as calcium, sodium or potassium hydroxides and is called alkaline hydrolysis. This method is found to be efficient for the removal of lignin from the biopolymer, thus increasing the accessibility of hemicellulose and cellulose for further conversion to monomeric sugars via hydrolysis. Alkaline hydrolysis is based on the mechanism of saponification of the biomass resulting in the removal of acetyl linkages along with uronic acid linkages releasing the hemicellulose with minimal degradation of the sugars.[34, 35]

1.4.3 Steam Explosion

Steam explosion is a pretreatment method which involves high temperature (160-260°C) and high pressure (0.69-4.83 MPa) steam. In this pretreatment method, steam is injected into a reactor (usually batch) at high temperature and pressure, and is then suddenly released to atmospheric conditions. The purpose of high pressure release is to create an explosive condition, thereby resulting in delignification and opening of the fibers in the bio-polymer. This process was performed by Mason in 1925, and this is known as Masonite process[36]. The pressure applied in this process was 90 atm (9.11 MPa) followed by a sudden release to atmospheric conditions. Thus, steam explosion results in complete removal of lignin and hemicellulose, thereby increasing the accessibility of the cellulose for further conversion to sugars by hydrolysis. [37]

1.4.4 Ammonia Fiber Explosion (AFEX)

The ammonia fiber explosion[38] method for the pretreatment of biomass involves physiochemical treatment of biomass in presence of ammonia. In this method, the biomass samples are pressurized in presence of ammonia usually (1-2 kg/kg of biomass) at 90°C for 30 min. Following pressurization, there is a sudden release of pressure similar to steam explosion, resulting in disruption of the structure of the biomass. The AFEX pretreatment method does not result in the removal of hemicellulose and lignin from the bio-polymer, however, due to the changes in the structural composition as a result of sudden release of pressure, AFEX results in increasing the surface area of the biomass fibers, allowing higher accessibility to the hemicellulose in the biomass. Overall, AFEX is a milder technique compared to acid pretreatment or steam explosion.

1.4.5 Carbon Dioxide Explosion

In this method of pretreatment, supercritical carbon dioxide is injected into a reactor (batch reactor) containing the biomass samples. Supercritical CO_2 injected at high pressure is suddenly released, similar to the steam and ammonia explosion techniques, resulting in a sudden depressurization of the biomass. As a consequence, the biomass is disintegrated, resulting in the swelling of the polymer, thus enhancing the surface area and accessibility to the hemicellulose and cellulose. Supercritical fluids, due to their properties of high density and low viscosity, penetrate easily into the biomass to bring about the disintegration of the structure. The process is carried out at lower temperatures than steam and ammonia explosion. The CO_2 explosion technique results in the removal of the hemicellulose and results in minimal degradation of the hemicellulose as compared to steam explosion pretreatment. [39]

The conversion of biomass to fuels such as ethanol involves the fermentation of sugars using specific microorganisms such as *Saccharomyces cerevisiae* (known as Bakers' yeast), *Escherichia coli* and *Zymomonas mobilis*.[40] The activity of these microorganisms is severely affected by the presence of furfural, HMF and acids generated during the pretreatment process. Pretreatment method based on strong acids such as HCl and H_2SO_4 generate the highest amount of these inhibitory compounds.[41] These inhibitory compounds are classified in three categories namely, organic acids, furan, and phenolic compounds. The higher severity of the reactions results in the formation of higher organic acids and furans compounds such as HMF and furfural. The presence of these compounds in concentrations of higher than 1-2 g/L affects the growth of the microorganism that carry out the fermentation process. The removal of the inhibitory compounds is carried out by processes such as membrane separation, activated charcoal treatment and ion-exchange resins.[42,43] Considering the above possibilities of obtaining value-added chemicals from biomass, such as the furans, furfural and HMF, these materials provide an ideal building blocks for a variety of chemicals and fuels.

1.5 Furfural (2-furaldehyde)

Furfural was first discovered in 1821 by J. Dobereiner and is derived from acid catalytic dehydration of a pentosan i.e. a 5-carbon sugar such as xylose. It consists of a heteroatomic furan ring and an aldehyde group (see Figure 1.10) with the molecular formula $C_5H_4O_2$.[44]
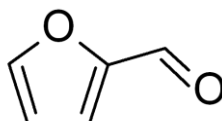
Figure 1.10: Structure of furfural (2-furaldehyde)

Furfural is an almond-scented colorless to yellow, oily, combustible liquid that darkens to red-brown on exposure to light and air as a result of auto-oxidation. Furfural is a hetero-aromatic aldehyde with the physical properties shown in the Table 1.3. Furfural boils at 161.7°C and melts at -36.5°**C**. It is heavier than water with specific gravity of 1.15. The production of furfural began in 1922 and was developed commercially by Quaker Oats Company[45.] Furfural can be a precursor to a number of chemicals and industrial useful resins.

Table 1.3: Physiochemical properties of furfural[46]

General Physical properties of furfural	
Molecular weight	96.08
Boiling point at 101.3 kPa (1 atm), °C	161.7
Freezing Point, °C	-36.5
Refractive index, n_D	
20°C	1.5261
25°C	1.5235
Density at 20°C	1.1598
Vapor density (air = 1)	3.3
Critical Pressure (P_c), MPa	5.502
Critical Temperature, T_c, °C	397
Solubility in, wt%	
Water	8.3
alcohol, ether	∞

Furfural has numerous industrial applications. Biologically, it can be used as a fungicide for seed processing, fumigant for poultry houses, when furfural is mixed with fuel oil like kerosene it can be used as an herbicide.[44] Furfural can be converted to furfuryl alcohol which can be further converted to a chemical intermediate for pharmaceutical industry. Chemically, furfural can be used for manufacture of furan resins and polymeric substances through furfuryl alcohol.

Furan resins have a furfuryl alcohol content in the range of 60-95%. Since the resins are used for the manufacture of highly specialized castings, the amount of furfuryl alcohol that provides strength to the mould is critical. Also, furfuryl alcohol can be used to make high strength fiber reinforced plastics. Furfural finds its biggest application as solvent in the manufacture of lubricating chemicals. 2-MTF (2-methyltetrahydrofuran) can be produced by catalytic hydrogenation of furfural which can be used as a substitute of THF which is produced from nonrenewable sources.

The overall consumption of furfural is shown in the Figure 1.11. It can be seen that China is the largest producer and consumer of furfural with 74% of the world's furfural share. A production capacity of more than 250 000 tons per year is produced worldwide.
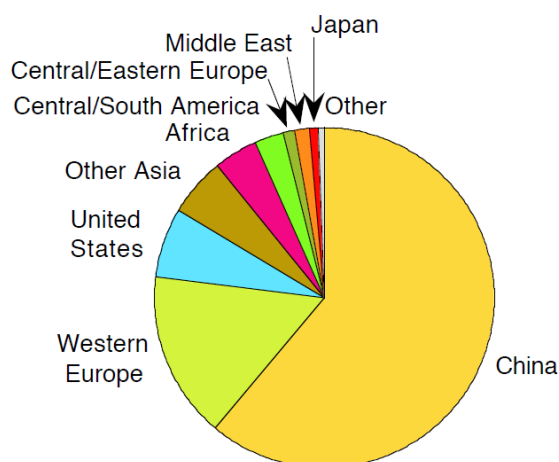
Figure 1.11: Overall consumption of furfural in the world[47]

Furfural can be produced by triple dehydration of xylose, initially which can be formed by hydrolysis of hemicelluloses fraction. Ideally, biomass resources containing the highest

fraction of pentosans (xylans) such as corncobs, bagasse, oat hulls, cottonseeds, almond husks are found to produce high yields of furfural when treated with acids.[48]

The possibility of a bio-refinery based on the utilization of the lignocellulosic biomass optimized towards the production of furfural is highly desired since it can provide a route for the utilization of the C-5 sugars from the bio-polymer. Traditional processes for the production of furfural are based on the conversion of pentosans containing biomass, followed by purification using distillation. Due to the hydrophobic nature of furfural, the use of distillation process for the purification of furfural has been successful. Furfural forms a minimum boiling azeotrope with water at concentrations of 65% water and 35% furfural. Separation of furfural from the hydrolyzate is a difficult due to the presence of by-product acids such as acetic and formic acids. Traditionally, azeotropic distillation is employed for the separation of the furfural/water mixture. As the liquid mixture enters the column, furfural (being the heavier component) is obtained as bottoms, whereas water is obtained at the top. Further, the contents from the bottoms are fed to another distillation column were 99% pure furfural is obtained. Typical yields for furfural from various biomass are corn cobs: 10~12 %, rice hulls: 5.0 ~ 7 %, cotton hulls: 8~11 %, sugar cane bagasse: 8~11 %, wood: 4~8 %. [49] These yields are low because furfural, in the presence of acids, further reacts to form resins, which decreases the furfural yield.

In the process of furfural production developed by Quaker Oats Company (shown in Figure 1.12), raw materials (oat-hulls) are mixed with water and sulfuric acid catalyst and fed to the axially rotating horizontal cylinders through trunnions. High pressure steam is passed into the cylinder to provide the thermal energy for the reaction to take place at 153°C. Following the reaction, lignin is separated in a screw press and the products from the reactor are cooled and fed to an azeotropic distillation column. The separated furfural from the distillation column further

passes through a dehydration step in which traces of water are removed in a dehydrating column, wherein pure furfural is obtained.

In a further development of the Quaker process, the reactors used for the process were brick-lined with acid proof cement. The heating of the raw material was achieved using steam and the products obtained were distilled to produce pure furfural with yields of 40-50%. The overall process flow diagram is shown in the Figure 1.12.
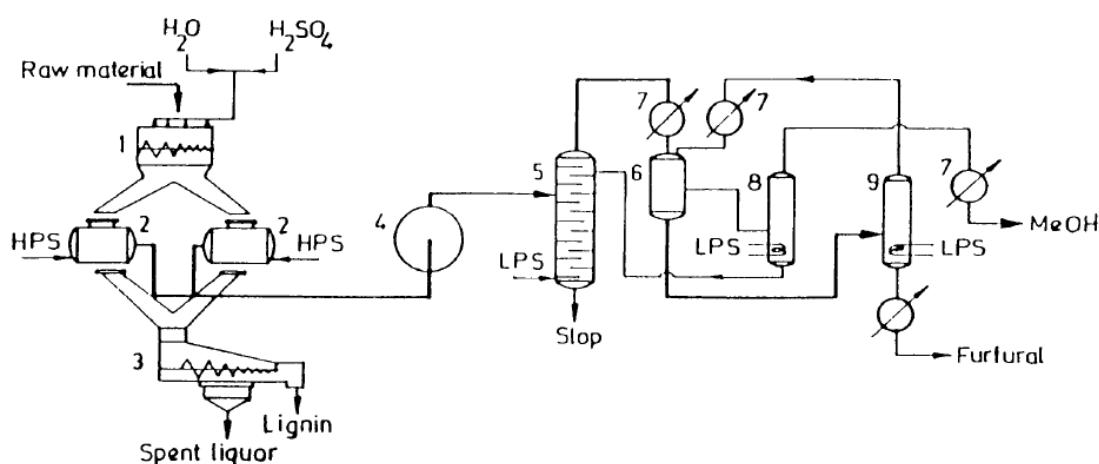
(1) Mixer. (2) Reactors. (3) Screw Press. (4) Secondary Steam Generator. (5) Azeotropic Distillation Column.
(6) Decanter. (7) Condensers. (8) Recovery Column for Low Boilers. (9) Furfural Dehydration Column.
HPS = High Pressure Steam. LPS = Low Pressure Steam.

Figure 1.12: Process flow diagram for Quaker Oats furfural production process[50]

1.6 HMF (5-hydroxymethylfurfural)

HMF (5-hydroxymethylfurfural) is a chemical which can also be derived from cellulose-based sugars. HMF is derived by conversion of 6-carbon sugars such as glucose and fructose by the triple dehydration of these sugars in the presence of strong acids. HMF has been investigated for a number of decades and was first reported in 1964 by Moye et al.[51] During the acid

pretreatment of lignocellulosic biomass, HMF is produced depending on the severity of the reaction and usually increases with temperature and acid concentration.[52] HMF is a furan derivative with the chemical formula, $C_6H_6O_3$ and chemical structure as shown in Figure 1.13.
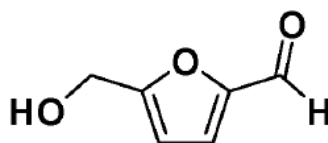
Figure 1.13: Structure of HMF (5-hydroxymethyl furfural)

HMF consists of a furan ring along with two functional groups: an aldehyde and an alcohol group. Despite potentially being an important chemical intermediate, to date no chemical process has been optimized and implemented for an industrial scale production. HMF is a highly unstable compound that can be converted as an intermediate towards the production of levulinic acid and formic acid.[53] The productions of these acids is favored in an aqueous environment and hence a number of solvents that have also been tested for selectively towards extracting HMF such as dimethyl sulfoxide (DMSO) [54], methyl tert-butyl ether (MTBE) [55], ethyl acetate-diethyl ether.[56]

Recent interest in chemicals derived from biomass and the implementation of a bio-refinery has driven many publications and patents for the production of HMF.[57] Other chemicals that can be derived from HMF originating from bio-based resources are shown in the Figure 1.14. Shown in green are the many uses for 5-HMF-derived chemical intermediates many can be used in the synthesis of a number of sustainable chemical platforms.
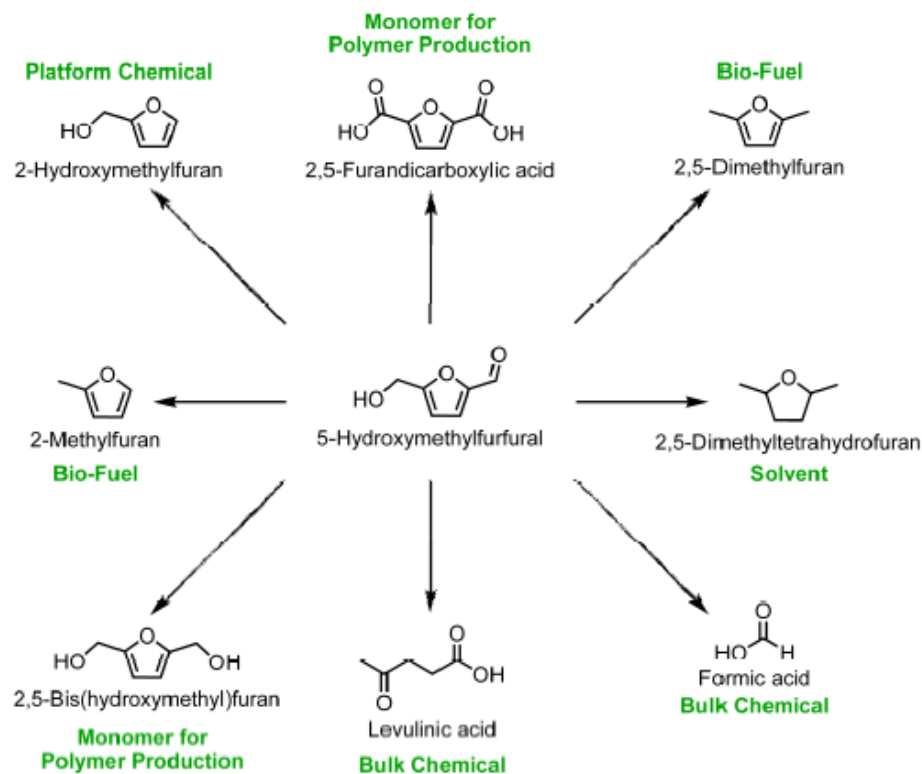
Figure 1.14: Chemical intermediates from HMF.[58]

HMF can be converted to a variety of value added chemicals such as 2,5-furan dicarboxylic acid (FDCA) produced by oxidation of HMF, 2,5-dimethyl furan (DMF) produced by hydrogenation of HMF, levulinic acid by rehydration of HMF, formic acid.[57] Avantium, a Netherlands based chemical manufacturer, is building an industrial scale production plant for HMF.[59]

1.7 Objectives of This Study

The objectives of this research are to develop an environmentally-benign method and a comprehensive technique to convert lignocellulosic biomass (switchgrass) to carbochemicals such as HMF and furfural. These chemicals are produced in the presence of an acid catalyst.

Hence, the production of these chemicals using an alternative catalytic method seems worthy of investigation. The process of pretreatment using acidic media is essential to produce carbochemicals such as HMF and furfural along with the attendant organic acids. Moreover, the use of inorganic acids such as H_2SO_4 and HCl is discouraged because these acids are highly corrosive and requires expensive metallic alloys for the reactors. Hence, the development of a process utilizing a catalyst that is environmentally-benign and inexpensive was the goal of this research.

The development of a semi-continuous process technique has been developed utilizing a biomass source of switchgrass, to produce carbochemicals forms the basis of this research. The following are the specific objectives of this research:

- To explore the possibility of switchgrass as a lignocellulosic biomass substrate towards its eventual conversion and production of carbochemicals.

- To develop a semi-batch flow-through reactor system for conversion of switchgrass to carbochemicals.

- To utilize water as a "green" solvent, i.e. subcritical water, for the conversion process under subcritical conditions.

- To utilize CO_2 in water, i.e. carbonated water, as a "green" catalyst to enhance the formation of the furan derivatives via acid catalyzed reactions

- To optimize the reaction conditions as a function of temperature to achieve optimal production of HMF and furfural.

To better understand the basis of these "green" synthetic methods, we will describe and discuss the proportion and use of subcritical water and supercritical carbon dioxide in the following chapters.

Chapter 2. Background and Literature Review

2.1 High Temperature-Pressure Water as a Reaction Medium

Water has been extensively studied as a media for sustainable chemical processing since it is non-toxic, environmentally-benign, and readily available. It increases the rate of the reaction when utilized at higher temperatures.[60] Water as a function of temperature and pressure at ambient conditions, near critical conditions and supercritical conditions exhibits a variation in its characteristics which are critical for its application in extraction and reaction engineering.[61] Since, the reactive properties of water can be tuned via the control of temperatures from the subcritical condition to supercritical state, it can be applied for the treatment of recalcitrant lignocellulosic biomass. Due to its tunability, even higher temperature water can be used for biomass liquefaction and gasification as shown in the highlighted region of Figure 2.1.
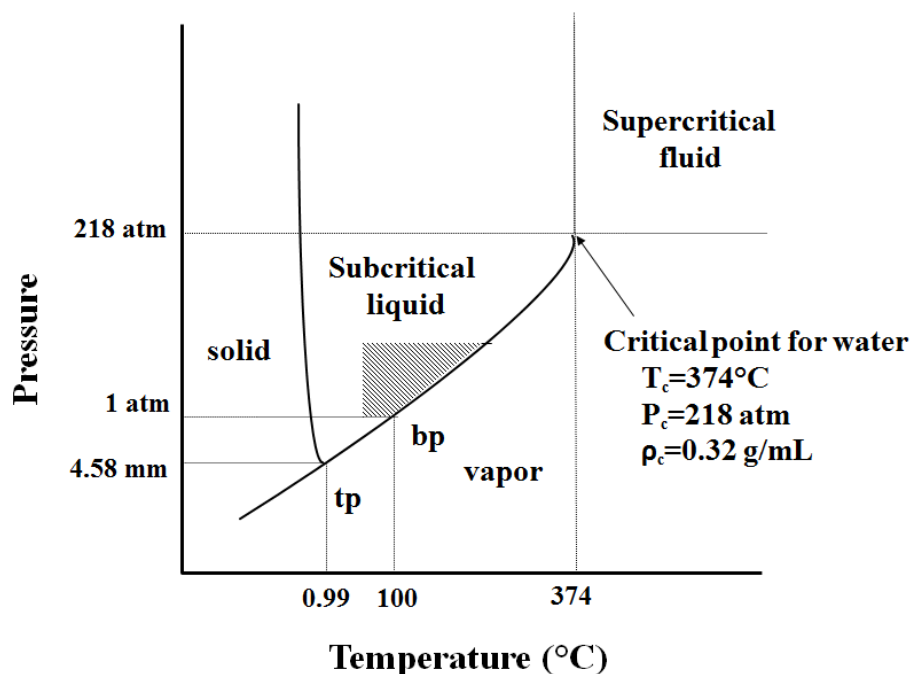
Figure 2.1: Phase diagram of water showing area of application to biomass[62]

Water exhibits a critical point at a temperature of 374°C and pressure of 218 atm (22.08 MPa) as shown in the Figure 2.1. Above this point, as seen from the phase diagram in Figure 2.1, water becomes supercritical. Below this temperature range, and under high pressure, water is called as sub-critical water or hot compressed water.[63]

The major factors involved in changing the reactivity of water are its ionic product, dissociation constant and solvation power as a function of temperature. The polarity of water decreases from that experienced using water at ambient conditions to that at near critical conditions. Its dielectric constant decreases from 80 at ambient temperature to 18 at temperatures of 330°C and even 2 at 450°C (see Figure 2.2).[64, 65] The reason for this decrease in the dielectric constant, as pointed out by Savage[66]; is due to the disruption of the hydrogen bonding network with increasing temperature. The decrease in the dielectric constant results in a higher solubilizing power of water for many polar and non-polar compounds. As an example, hexane is totally miscible at the critical point (T_c, P_c) of water.

King et al.[67] discussed the properties of subcritical water and its application to the depolymerization of the biomass using the solubility parameter concept. According to the authors, subcritical water has the ability to extract components from bio-polymers. Interestingly, they showed that the conditions at which the solubility parameter of both the subcritical water and cello-oligomers were identical, corresponding to the optimum conditions for the depolymerization of the biopolymers. This is the basis for subcritical water being utilized as a green solvent of extraction and conversion of biomass to valuable products.

Water at room temperature also has a high solubility for polar solutes. As the temperature and pressure are increased, closer to the critical point, water shows a preferential dissolving power for more non-polar organic compounds. In addition, the density of water decreases

considerably from 800 kg/m^3 at ambient temperature to about 150 kg/m^3 at temperatures of 450°C (see Figure 2.2). As a consequence, the solubilizing power of water can be tuned based on the density as dictated at the specific temperature and pressure. The components of lignocellulosic biomass react and dissolve as a function of temperature in water.[67] Hence, water with its tunable behavior can be used effectively to selectively dissolve these components of biomass, and hence its conversion to sugars and carbochemicals.

The dissociation constant or the ionic product of water at ambient conditions is 10^{-14} and decreases to 10^{-11} at 300°C. Due to these properties, acid-catalyzed or base-catalyzed reactions can be affected in hot compressed water[68] as exhibited by the trend in K_w shown in Figure 2.2.
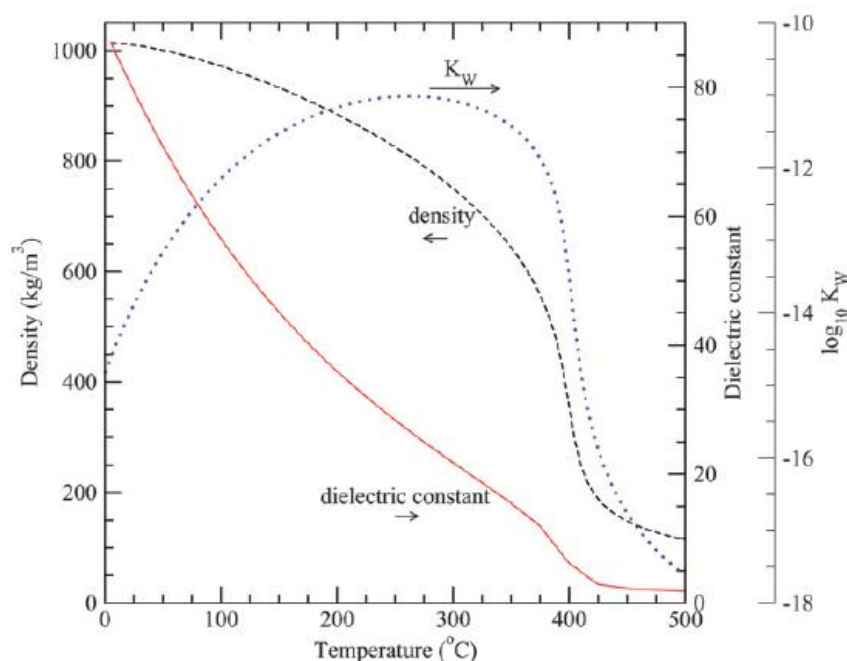
Figure 2.2: Density and dielectric constant variation of water with temperature[64]

The rate of a chemical reaction also affects the rate of diffusion of reactants into the solid matrix of the heterogeneous biomass substrate. High temperature water, due to its low interfacial mass transfer coefficient and lower viscosity, can enhance the rate of a desired reaction towards specific bio-based products.[69] Due to these properties of high temperature water, there has been

an increased interest in the research community to convert recalcitrant biomass to valuable products using water as a green solvent.[70]

2.1.1 Cellulose Conversion in High Temperature Water

Cellulose conversion in subcritical water and supercritical water has been studied by many research groups all over the world.[71-73] Recent interest in biomass conversion and the development of alternative routes for utilizing the highest carbon source has triggered research activities for cellulose conversion. Saka et al.[74] investigated cellulose conversion in batch and flow through reactor systems. Cellulose (Avicel) was used as the model compound, and the temperature ranged from 500ºC for batch to 390ºC for flow-through systems at 40MPa. It was observed that the time required to solubilize cellulose was lower in the flow-through system than in the batch system. Most importantly Saka et al. [74] found that due to higher flexibility with the flow-through reactor system for temperature, residence time and pressure, there was minimal degradation of the products, whereas in the batch based system there were higher concentrations of pyrolysis products. In a similar study by the same research group[75], decomposition of cellulose was studied at 400ºC and 40MPa. Interestingly, they found that the concentrations for HMF and furfural of 11.9 (wt. %) and 1.7 (wt. %), respectively, were higher in subcritical water than in supercritical water confirming the degradation of the sugars to these select carbochemicals.

In another study, Sasaki et al.[76] studied the hydrolysis of cellulose at 290 - 400ºC and 25 MPa. They found that 100% of the cellulose was converted when a 10% (wt.) slurry was used in a reaction time of only 10 seconds. The reaction mechanism resulted in the formation of cello-oligomers and further conversion of sugar monomers to carbochemicals. Furthermore, at lower temperature, the rate of hydrolysis was slower in comparison to the dehydration step, resulting in

higher concentrations of dehydration products. When the experiments were conducted in supercritical
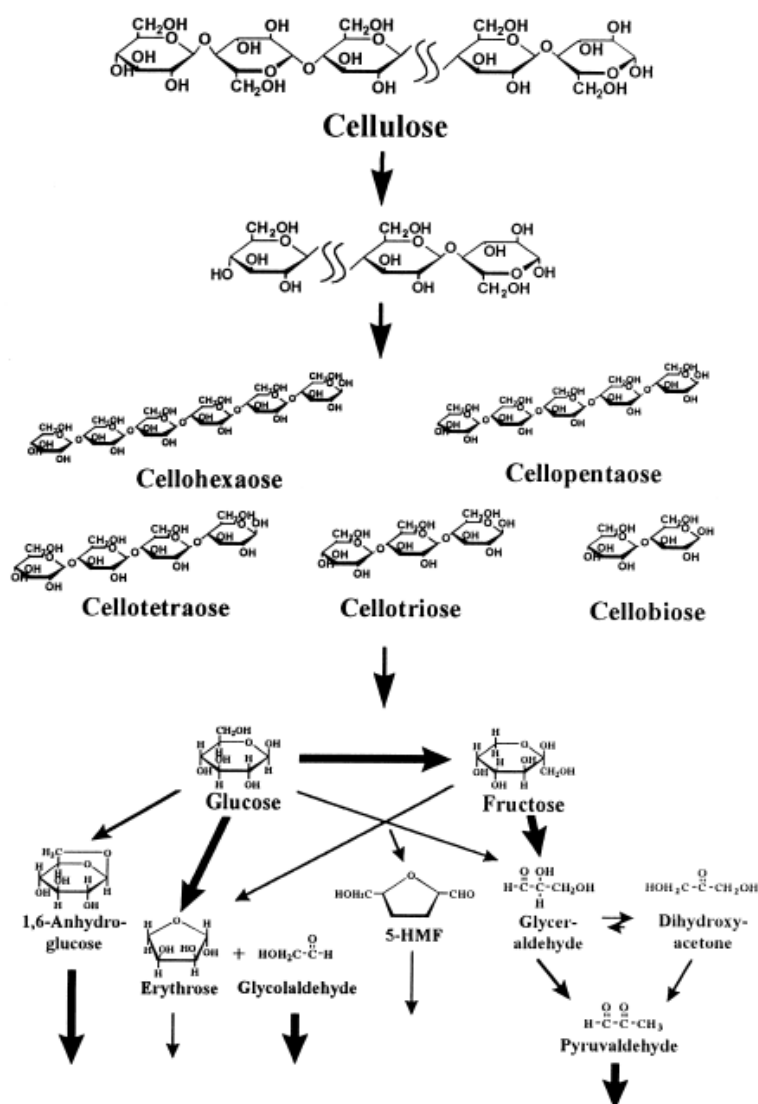
Figure 2.3: Cellulose decomposition pathway in hot compressed water[76]

water, the rate of hydrolysis increased considerably with minimal degradation of hydrolysis products to carbochemicals such as HMF and acids. Hence, based on the experiments under low temperatures and supercritical conditions, it was concluded that reaction in supercritical fluids was better for the optimization of hydrolysis products such as sugars and oligomers.

A reaction mechanism for the conversion of cellulose in hot compressed water is presented in Figure 2.3. The conversion of cellulose occurs through the production of oligomers, that are further converted to monomeric sugars such as glucose and fructose and then further converted to HMF, glycolaldehyde, erythrose etc.

Subcritical and supercritical water have been used extensively for the dehydration of carbohydrates to HMF. Yoshida et al.[77] studied the acid catalyzed dehydration of the model compound D-fructose to 5-HMF in sub-critical water at temperatures in the range of 473-593K and found that, at temperatures greater than 533 K, the yields of HMF decreased due to further degradation to levulinic and acetic acids, indicating the influence of temperature on the dehydration of kinetics of HMF. Yoshida et al.[77] concluded that in presence of acids at higher temperature, HMF being an unstable intermediate compound degrades into acids which result in decreased HMF yields. The reaction mechanism for this work is presented in the Figure 2.4.
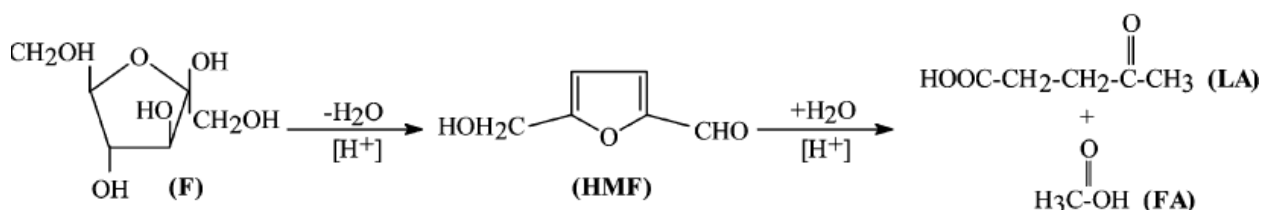
Figure 2.4: Reaction mechanism of fructose to HMF and degradation products.[77]
F= Fructose; LA= Levulinic acid, FA= Formic acid, HMF= 5- hydroxymethylfurfural

Takeuchi et al.[78] studied the acid-catalyzed hydrothermal conversion of carbohydrate (glucose) to HMF in the presence of three acids namely H_2SO_4, HCl, H_3PO_4 with pH varying in the range from 1.5 to 2.5 at 523 K. They concluded that the formation of HMF was highest in the presence of H_3PO_4, followed by H_2SO_4 and HCl. It was also observed that the further degradation of HMF to various acids like levulinic acids was highest in presence of HCl.

Takeuchi et al.[78] found that the formation of degradation products like levulinic and acetic acids was a function of time and the acidity of the reaction mixture. However, the production of HMF from 6-carbon sugars such as glucose and fructose provided varying results. It was observed that glucose, having a more stable ring structure, results in lower concentrations of HMF when compared to fructose that has an open straight chain structure.[79]

Developments in processes that are focused on converting glucose to HMF are of particular significance due to the lower cost of glucose as compared to fructose. The rehydration process for converting HMF into levulinic acid proceeds faster in aqueous medium. Hence, alternative solvents have been tested for the in-situ removal of HMF from the reaction medium, preventing further degradation to acids.

A number of catalyst types have been used for the production of HMF, including organic acids, inorganic acids, salts, Lewis acids and heterogeneous catalysts, as tabulated in the Table 2.1. Catalysts such as zirconium phosphates, sulfated zirconia have been tested for the conversion of sugars such as fructose and glucose into HMF.[80, 81] Dehydration reactions can also be enhanced by implementing the 'H' form of zeolites like H-ZSM-5, H-Y, and H-β types. H-ZSM-5 presents an ideal solid catalyst for selectively converting biomass derived sugars to furan aldehydes due to its high acidity, small pore size and uniformity in the porous network. Various reviews have been presented for zeolite catalyzed dehydration reaction of biomass to HMF and furfural. [82, 83]

Moreau et al.[84] studied the dehydration of fructose to 5-HMF over H-Mordenites zeolite and found that the ratio of Si/Al had an influence on the dehydration of fructose to HMF. It was observed that the optimum Si/Al ratio for the dehydration reaction was 11. Moreau et al.[84] also

observed that the ratio which influences the acidity of the catalyst will also influence the further

rehydration of HMF to the formation of levulinic acids.

Table 2.1: Catalysts used for production of HMF from biomass[85]

Organic acids	Inorganic acid	Salts	Lewis acids	others
Oxalic acid	Phosphoric acid	$(NH4)_2SO_4/SO_3$	$ZnCl_2$	Ion-exchange resins
Levulinic acid	Sulfuric acid	Pyridine $/PO_{4-3}$	$AlCl_3$	Zeolites
Maleic acid	Hydrochloric acid	Pyridine /HCL	BF_3	
p-TsOH	Iodine	Aluminum salts		
	Hydroiodic acid	Th and Zr ions		
	generated in situ	Zirconium phosphate		
		Ions: Cr, Al, Ti, Ca		
		In		
		ZrOCl1		
		$Vo(SO_4)_2,TiO_2$		
		V-porphyrine		
		Zr, Cr, Ti-porphyrine		

2.1.2 Hemicellulose Conversion in High Temperature Water

Contrary to the hydrolysis of crystalline cellulose, hemicellulose hydrolysis occurs at relatively milder conditions i.e. at lower hydrolysis temperature. Bobteler et al.[86] discussed the hydrolysis mechanism applicable to this reaction case and the conditions required when using a hydrothermal-based acid hydrolysis process and concluded that hemicellulose is easily hydrolyzed at temperatures above 180°C.

The relevant conversion mechanism for the formation of furfural from pentose is shown in Figure 2.5. The pentose in presence of a proton (resulting from the acid catalyst) produces xylose by hydrolysis. The reaction mechanism involves conversion through the triple dehydration to furfural. A pentose molecule combines with the proton released from an acid catalyst. The dehydration steps involve the loss of three water molecules in which two molecules are lost from the 1, 2-position and one from the 1, 4-position, resulting in the furfural molecule.
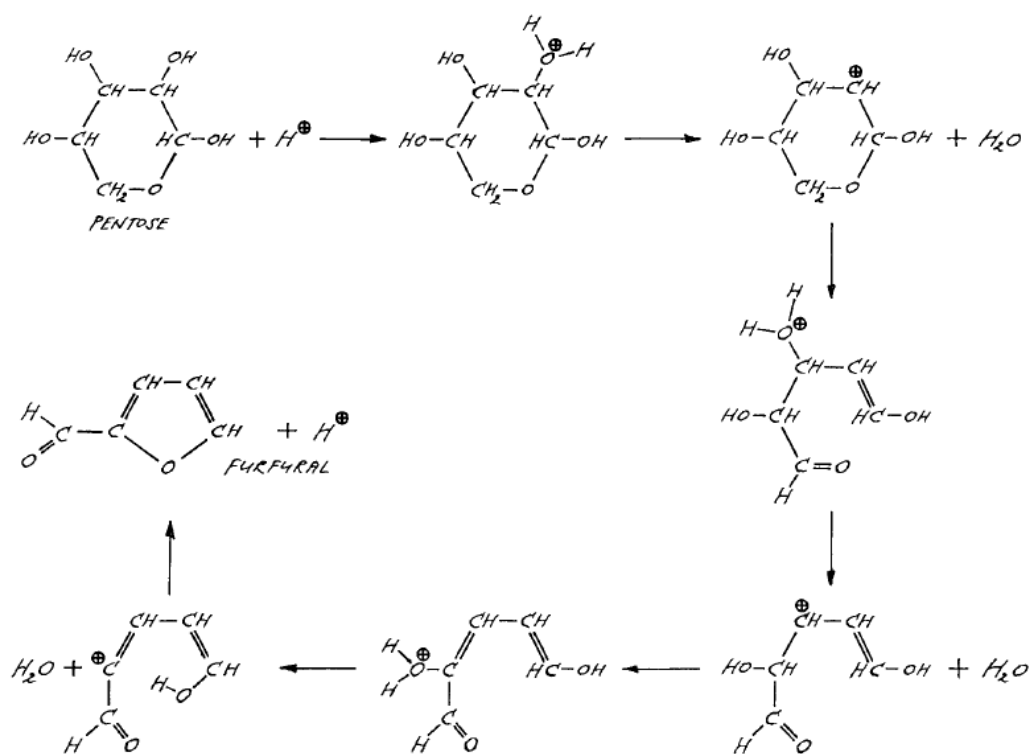
Figure 2.5: Reaction mechanism for conversion of pentose to furfural[50]

Wyman et al. [87] studied the effect of flow rate on the solubilization of xylan when corn stover was treated at 220℃ at 2.1-2.4 MPa. It was found that 90% of the xylan can be solubilized and converted to monomeric and oiligomeric sugar i.e. xylose and xylo-oligomers. They also

concluded that the increase in the yields of xylose-oligosaccharides was due to the use of a flow reactor system that prevented further degradation of monomeric sugars formed in the hydrolysis process. In a related study, Antal et al.[88] studied the effect of a percolation reactor (flow through reactor) system for treating a variety of biomass materials with temperatures ranging from 200 – 230ºC. They found that solubilization increased with an increase in temperature and almost 90% of the hemicellulose was solubilized under the conditions tested.

Kilambi[89] investigated the conversion of xylose/xyloligosaccharides into furfural in high temperature water and in combination with carbon dioxide in a semi-batch reactor system at temperatures ranging from 250-375°C and pressures of about 100-350 bars (10.13-35.46 MPa). Kilambi[89] found that the yields of furfural increased to a maximum of 23 % (original xylose) with an increase in xylose conversion from 50% to 90% as the temperature was increased from 250 to 375°C in the presence of carbon dioxide.

The conversion of rice bran to saccharides and acids was studied by Yoshida et al.[90] in subcritical water and temperatures ranging from 200-360°C. It was observed that the yields of sugars were severely decreased with an increase in reaction temperature. Also, the formation of organic acids was noted with formic acid showing maximum yields at 240°C. Acetic acid increased in concentration until a temperature of 280°C was reached and the levulinic acid yield increased at temperatures up to 320°C, indicating further decomposition of the carbochemicals such as furfural and HMF to organic acids under high temperature and pressure in subcritical water.

2.2. Carbonated Water as a Catalyst for Biomass Conversion

Of all of the processes for the conversion of biomass to bio-chemicals, fermentation is one of the most significant step towards the production of bio-fuels such as ethanol. In the fermentation process, the monomeric sugars obtained during hydrolysis are fermented to ethanol and byproducts such as carbon dioxide, acetone, butanol and acids such as acetic and lactic acid.[91] Further utilization of the carbon dioxide is an important consideration since it is a greenhouse gas.[92] Therefore, the development of a process that will effectively utilize carbon dioxide into the process for the production of various useful products is important.

Carbon dioxide gas is colorless, odorless, nonflammable and non-toxic gas. Due to these benign properties, it has received much interest as a reactant, solvent and as catalyst.[93] Figure 2.6 shows the two dimensional phase diagram for carbon dioxide showing the variation in the phase for the carbon-dioxide with the variation in the temperature and pressure. At very low pressures and temperatures, carbon dioxide exhibits a solid-like behavior, frequently referred to as dry ice. It can also be seen that as the temperature is increased at low pressures, carbon dioxide changes from solid to gas via the process of sublimation (represented by the gas phase). At a temperature of 304.1 K and 72.8 atm (7.37 MPa) pressure, carbon dioxide becomes supercritical, i.e. above the critical parameters. Supercritical carbon dioxide starts to exhibit densities similar to a liquid while maintaining viscosities similar to a gas.
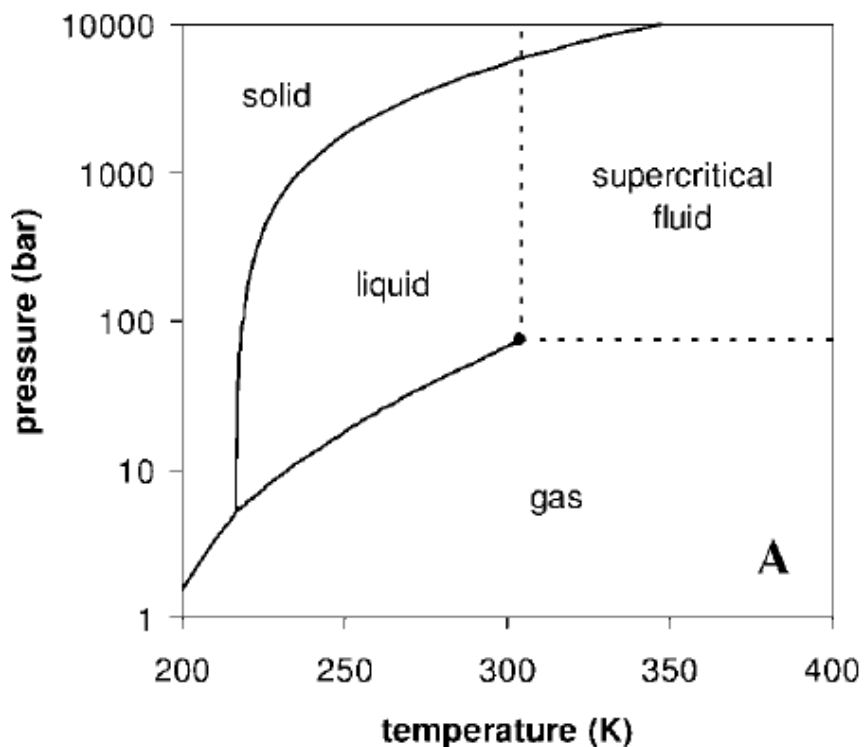
Figure 2.6: Two-dimensional phase diagram for carbon dioxide.[94]

Carbon dioxide, when dissolved in water, results in the formation of carbonic acid which can be potentially used for biomass pretreatment as well to rate enhance the rate of biomass conversion to its constituent sugars and carbochemcials.[95,96] The classic aqueous mechanism reaction for the formation and dissociation of carbonic acid can be represented by the following equation[97]:

$$H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO3^{2-} \tag{2.1}$$
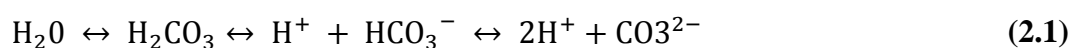
King et al.[67] has discussed the processes involving coupling techniques in which subcritical water can be mixed with supercritical carbon dioxide (SC-CO$_2$) resulting in a considerable pH reduction (as low as 2 – 2.5) of the aqueous medium. This is due to the

increased solubilization of SC-CO$_2$ in water at higher pressures and temperature.[98] This has been exploited by King et al.[30] in the batch hydrolysis of corn stover and switchgrass using carbonated hot water as a reactive pretreatment process. The parameters tested for this conversion process were CO$_2$ pressures ranging from 300-500 bars (30.39-50.66 MPa), temperatures ranging from 150 -180°C and residence times of 60-180 min. In these studies, the carbochemicals were 3.30 (wt. %) furfural, 0.03 (wt. %) HMF, 3.84 (wt. %) acetic acid and 7.7(wt. %) formic acid. They also found a similar composition in carbonated water pretreatment with switchgrass, although the amount of formic acid was higher in case of corn stover.

From Equation 2.1, it is clear that the production of H$^+$ (hydronium) ions in the reaction medium depends on the formation of carbonic acid which is proportional to the amount of carbon dioxide dissolved in water. Carbonic acid at ambient conditions is a weak acid with pKa of 6.38, resulting in a pH at ambient condition of 3.90. The pH can be further lowered over a
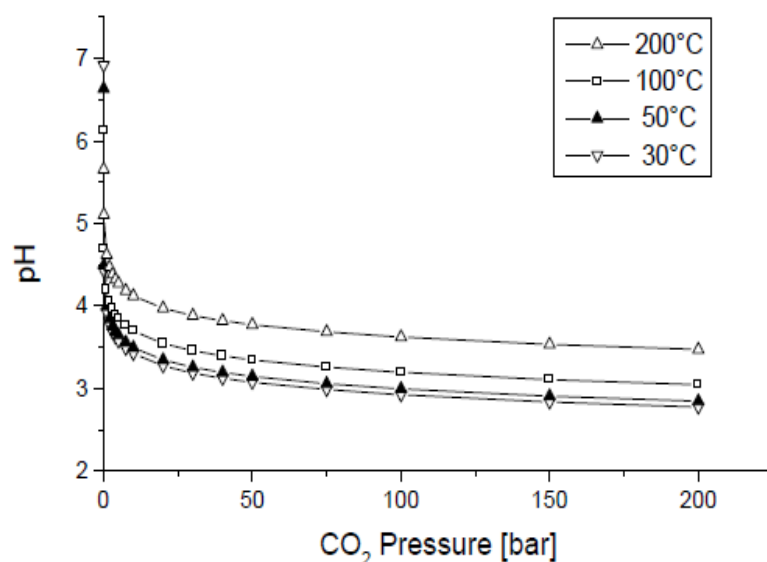
Figure 2.7: Variation in the pH with the variation in temperature and pressure[99]

specific temperature range by dissolving more carbon dioxide in water as indicated in Figure 2.7. It can be seen that the pH is lowest at the lower temperatures and at high carbon dioxide pressures. In our study, the pressure applied for the conversion of switchgrass was 68 bars.

The formation of carbonic acid from the dissolution of carbon dioxide into water is a transient step. Due to carbonate equilibria, the formation of H_2CO_3 occurs at slower pace than its decomposition. As the pressure increases, the pH is found to decrease. The lowering of the pH in carbonated water can be utilized also towards the conversion of recalcitrant biomass to valuable chemicals. Since, HMF and furfural are products of acid-catalyzed reactions, the lowering of the pH can play a significant role in catalyzing the yields of these carbochemicals. The equilibrium constant for a CO_2 enriched water (carbonated water) can be expresses as:

$$K_H = \frac{[H_2CO_3{}^*]}{P_{CO_2}} \tag{2.2}$$

Here $H_2CO_3^*$ represents the sum of aqueous CO_2 and undissociated carbonic acids species.[92] Carbonic acid is a diprotic acid, consisting of two protons. Hence, there are two dissociation constants for carbonic acids. The first dissociation constant variation with temperature can be observed from in Figure 2.8
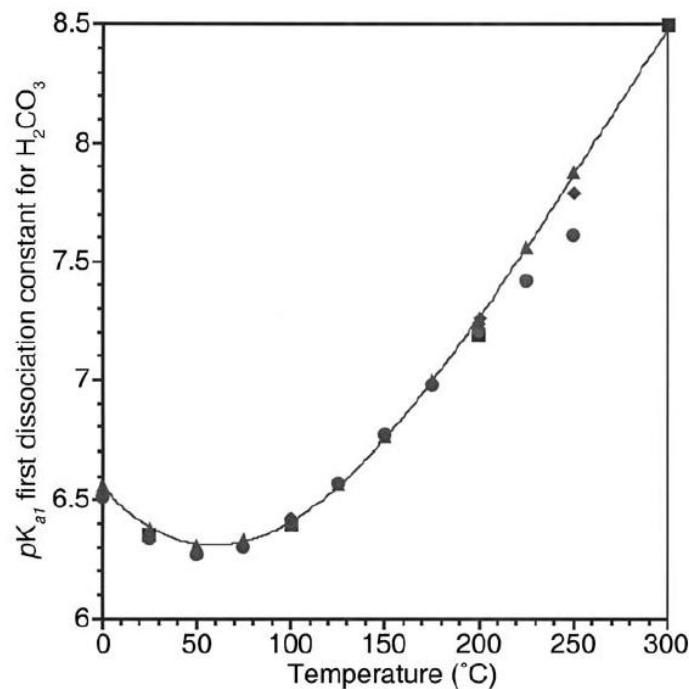
Figure 2.8: The variation in the first dissociation constant with temperature for of carbonic acid[100]

A summary of the solubility of carbon dioxide in water at different pressures and temperatures is given in Figure 2.9 from King and Srinivas [67]. It can be seen that the solubility of carbon dioxide varies with temperature and pressure. Interestingly, all of the curves show that the solubility increases with pressure. Moreover, the solubility of CO_2 is found to decrease with an increase in the temperature, which indicates that the use of lower temperatures and high pressure can result in higher dissolution of carbon dioxide. These phenomena have been used and applied for the hydrolysis of biomass as well as production of carbochemicals. For example, van Walsum
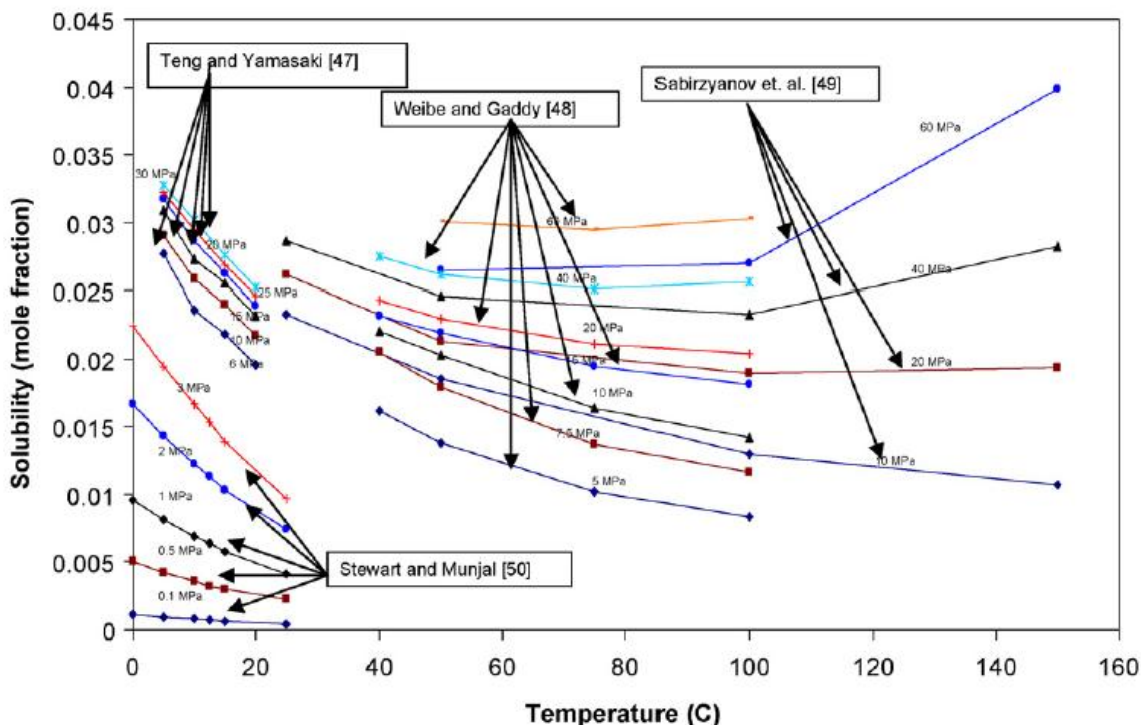
Figure 2.9: Mole fraction solubility of CO_2 in water as a function of temperature and pressure[67]

et al.[101] found that carbonic acid significantly increased the formation of xylose and furan aldehydes when corn stover was used as a starting material, while when aspen wood was used a raw material, carbonic acid seemed to have no effect on the sugar sachharification and dehydration mechanisms. [100, 102]

Brunner et al.[103] studied hydrolysis of rye straw and silage in a continuous flow reactor system. The reaction conditions were maintained at 100 bars (10.13 MPa) pressure and a maximum temperature of 310°C. It was found that the addition of CO_2 in water did not affect the overall hydrolysis yield of sugars. Since the objective of the research was to minimize the production of degradation products (carbochemicals) such as HMF, furfural and acids they

concluded that complete solubilization of the biomass substrate was not essential for optimization of the biomass hydrolysis process.

In another study by Spycher et al.[98], the hydrolysis of cellulose was carried out at temperatures ranging from 210-310°C. When carbon dioxide was added to the water, there was a significant increase in the cellulose liquefaction at 240°C. In addition, the rate constants for cellulose hydrolysis increased with temperatures to 260°C. Beyond 260°C, no significant rate enhancement was observed, and this phenomenon was attributed to the increase in the pH of the reaction mixture due to lower solubility of carbon dioxide in water.

As further evidence of the utility of carbonated water, Huisheng et al.[104] investigated the conversion of pure cellulose to 5-HMF in sub-critical water with the addition of CO_2. They found that cellulose decomposed through dehydration to give 5-HMF. The maximum yield for 5-HMF were found to be at 250°C when using 5 mole % CO_2 in water over a 30 min time period.

In another study involving the pretreatment of biomass, Lee et al.[105] studied the effect of carbon dioxide in water for the separation of the cellulose and hemicellulose from yellow poplar substrate. The process was carried out in using a stainless steel reaction cell packed with biomass substrate (yellow poplar). The reaction was carried out at temperatures of 150 and 190°C. It was observed that, when carbon dioxide was mixed with water in a stirred reactor (400 ml stainless steel autoclave vessel), the pH of the mixture remained constant at 3.7 for 24 hrs. It was also observed that when the pretreatment was carried out by applying a back pressure of 350 psi (2.41 MPa) and temperature of 180°C for 20 minutes, there was no effect of carbonic acid on the conversion of hemicellulose. On the contrary, when a CO_2 pressure of 450 psi (3.10 MPa) was applied, 100% removal of the hemicellulose from the hydrolyzate was achieved. Interestingly,

the hemicellulose removal was only 87% when using sulfuric acid at a 0.025 wt. % concentration.

Traditional processes for biomass conversion are focused on the determining the optimum conditions for the production of sugars and its oligomers. During the process of conversion of biomass to sugars, carbochemicals such as HMF and furfural are formed. These are inhibitors in maintaining the activity of the microorganisms to ferment sugars to various chemicals such as ethanol. Hence, the focus has been on the reduction and separation of the concentrations of these above mentioned carbochemicals moities.

In this research, we have focused on utilizing carbonated water as a catalytic medium towards the production of the acid-catalyzed products from biomass (switchgrass) such as HMF and furfural. Using a semi-continuous laboratory scale process, we have ascertained the effect of carbonated water on the production of these carbochemicals. The chapter which follows presents the methods and materials which were utilized to carbonate the water and analyze the hydrolyzate for concentrations and yields.

Chapter 3. Materials and Experimental Methods

3.1. Materials

Alamo switchgrass (*Panicum Virgatum L.),* harvested at University of Arkansas Agricultural Research and Extension Station in Fayetteville, Arkansas, was generously supplied by Dr. Chuck West. The switchgrass was comminuted using a cyclone mill (UDY Corporation, CO). After grinding, the ground switchgrass was sieved for a particle size range of 180-250 µm using US standard testing sieve (Arthur H. Thomas Company, PA).

The compositional analysis of the switchgrass was obtained from Microbac Laboratories (Boulder, CO) utilizing National Renewable Energy Laboratory (NREL) developed Laboratory Analytical Procedure (LAP) for carbohydrate and compositional analysis.[106] In this analysis (using NREL LAP), the biomass samples are first prepared for analysis using "Preparation of Samples for Compositional Analysis"[107] wherein the biomass samples are dried, ground to a uniform particle size and fractionated based on particle sizes. The samples are further used for the analysis of ash, extractives and carbohydrates content. The "Determination of Ash in Biomass" [108] procedure provides a method for determination of the inorganic content that is bound to the biomass sample. In this analysis, the biomass samples are heated to a constant weight in a muffle furnace at 575 ± 25 °C. The weight by difference of the samples in the crucible represents the ash content.

Extractives are inorganic materials present in biomass that are soluble in water or ethanol that can be extracted. For the "Determination of Extractives in Biomass"[109] analysis, the samples were extracted using Soxhlet extraction or an automatic extraction method using a Dionex Accelerated Solvent Extractor, model 200. This procedure is essential for the carbohydrate

composition analysis on an extractive free basis for the quantification of the biomass cellulose, hemicellulose and lignin components. The Soxhlet apparatus consisted of 85ml glass tube, 500ml boiler flask, accompanied by 250 ml glass rotary evaporator. A solvent reflux of 6-24 hrs was applied for water extractives, whereas reflux with ethanol for 16-24 hrs was applied for ethanol soluble extractives. The removal of solvents was achieved using a rotary evaporator with a water bath at $40\pm5°C$ accompanied by a vacuum source.

An analysis of carbohydrates was performed using samples that were extractives-free to avoid interferences of the inorganic compounds in the determination of the carbohydrates. The procedure involved a two-step process in which the biomass samples were first treated with 72 % sulfuric acid concentration at 30°C for 60 minutes. Following the 60 minutes treatment, the contents were further treated with 4% concentration of this acid at 121°C. The quantification of the structural carbohydrates was performed using ion-chromatography consisting of an ion exchange column. For this purpose, an HPLC (High performance liquid chromatography) system consisting of a sugar analysis column HPX-87P (lead based) for 35 minutes was used to quantify the carbohydrates. HPLC grade degassed water was used as a mobile phase and the temperature of the column was maintained at 85°C.

Table 3.1: Composition of switchgrass (*Panicum Virgatum L.)* biomass (wt. % dry basis)

Glucan	Xylan	Galactan	Arabinan	Manan	Lignin	Acetyl	Ash	Extractives
36.98	22.41	2.44	3.67	1.57	21.28	2.63	2.56	11.86

The composition of Alamo switchgrass used for this study is shown in Table 3.1. It can be observed from the table that the concentration of glucan (polymer of glucose) was 36.98%, whereas the concentration of xylan (polymer of xylose) was 22.41%. Moreover, the

concentration of lignin was 21.28%. This composition analysis is critical to ascertain the type of the chemicals that can be produced from the biomass substrate.

Figure 3.1 shows a flow schematic of the experimental apparatus used in this research. The apparatus consisted of three high precision Isco syringe pumps (Teledyne Isco, Lincoln NE) and a Hewlett-Packard Model 5890 gas chromatographic (GC) oven primarily used at constant air bath to regulate the temperature for the hydrolysis reaction. For the experiments, ultrapure deionized water was obtained from Milli-Q Synthesis Model A10 unit (18.2 MΩcm; Millipore, Bellerica, MA) water purification unit. Pure xylose, glucose, arabinose, galactose and mannose standards were obtained from Sigma (St. Louis, MO). Siphon tube CO_2 with a purity of 99.0% was supplied by Air Gas (Radnor, PA) for carbonating the continuously flowing water stream p. Deionized water was used for the HPLC analysis of sugars samples.
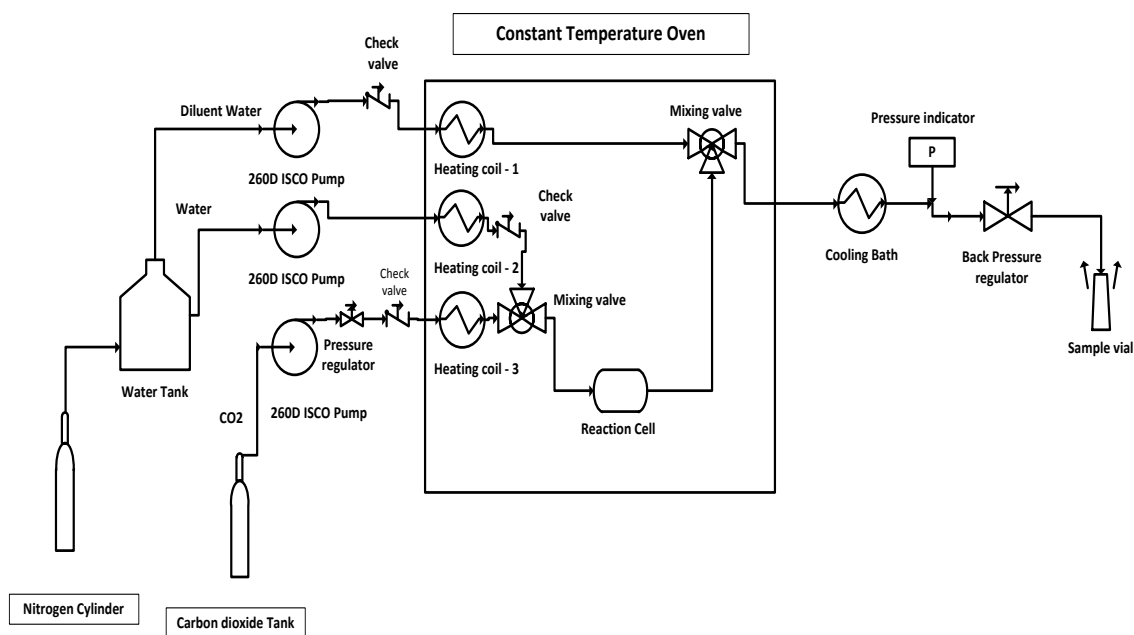
Figure 3.1: Flow diagram for the batch semi-continuous processing unit

The apparatus consisted of three Teledyne Isco Model 260D syringe pumps for supplying water and carbon dioxide to the system. In addition, the apparatus consisted of a constant temperature oven for heating the contents such as water, carbon dioxide and packed biomass in the stainless steel reaction cell to the reaction temperatures. Check valves were used to prevent the back flow of the contents into the pumps through the 1/16" tubing. The operation of check valves is critical since considerable back pressure is generated during the start of the reaction procedure due to the resistance to flow generated by the solid biomass samples along with the pressure generated due to the heating of water. Three heating coils 1/16" tubing were placed before the reaction cell to preheat the water and carbon dioxide prior to entering in the reaction cell. Preheating was necessary to ensure that both carbon dioxide and water entered the reaction cell at the same conditions. A mixing valve mixed the diluent water with the hydrolyzate exiting the reactor. A cooling bath was used for cooling the hydrolyzate before passing through the back pressure regulator which maintained the pressure in the system.

Figure 3.2: Photograph of lab-scale semi-continuous flow process unit
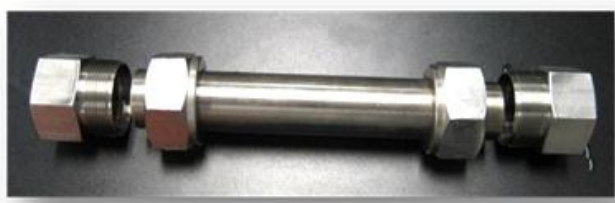
Figure 3.3: Reaction cell used for the experiments

A photograph of the laboratory setup is shown in the Figure 3.2. The components shown in the Figure 3.2 are: two Teledyne Isco Model 260D syringe pumps (left of the oven), of which one was used for pumping reaction water and other for pumping carbon dioxide at a constant flow rate; a constant temperature oven (center); a cooling batch placed on the top of the oven enclosed in polystyrene insulation; a diluent pump; a back pressure regulator and sample collection (extreme right side of the oven). A stainless steel (SS 316) reaction cell (see Figure 3.3) of dimensions: 3" x 0.29" (76.2 mm x 7.3 mm) (L x I.D) having a volume of 12.75 ml was used for the semi-continuous flow experiments. The reaction cell was completely filled with approximately 0.9 g of the ground switchgrass samples. The contents from the reaction cell (biomass) were prevented from flowing out of the cell by using a 5 μm stainless steel frit placed at both ends of the reaction cell.

Figure 3.4 shows the sample vials that were collected during the experiments. It can be seen that the color of the samples varied from left to right. Starting from the left, the first four samples were collected during the preheating stage. Following the preheating stage, sample 1 represents the samples collected at the end of first 5 minutes. The darker color in the samples represents the higher concentration of phenolic compounds as a result of the degradation of lignin and the formation of the carbochemicals such as furfural and HMF at high temperatures. As the residence time was increased, the samples become clearer.

Figure 3.4: Sample vials containing the collected hydrolyzate

The subcritical carbonated water experiments were conducted using the conditions shown in the Table 3.2. Four temperatures were chosen for the study: 220, 250, 280, 310°C. Since the research focused on the generation of carbochemicals such as furfural and HMF, a wider range of temperatures was essential for the conversion of hemicellulose and the cellulose in a single step process. As discussed in the Chapter 2, hemicellulose requires lower temperatures for solubilization and conversion as compared to the cellulose, therefore a lower limit of 220°C was chosen. Moreover, cellulose is solubilized at temperatures higher than 250°C; thus, a temperature in excess of 250°C was chosen. Three replicates for each experimental condition were conducted and the data were compared to analyze the effects of carbonation of water on the production of carbochemicals. Initial experiments were conducted with lower particle sizes such as 106-180 µm but, due to lower particle sizes and high temperature coupled with high pressure, we observed frequent plugging by the solids in the tubing. Hence, to avoid instant solubilization and flushing out of the solid biomass from the reaction cell, a larger particle size in the range of 180-250 µm was chosen. Carbon dioxide at high pressure in water was essential for carbonating the water. Hence, a pressure of 1000 psi (6.89 MPa) was chosen for this study. For the conversion of biomass in a flow reactor system, 60 minutes was chosen as the

residence time; considering lower residence times of less than 60 minutes will not effectively convert the biomass at lower temperatures.

Table 3.2: Experimental parameter matrix for carbonated and subcritical water experiments

Experimental Parameters	Conditions
Particle Size (Switch grass) (µm)	180 - 250
Reaction Water flow rate (mL/min)	3
Diluent flow rate (mL/min)	2
Temperatures (°C)	220, 250, 280, 310
Pressure (psi)	0 and 1000
Reaction time (min)	60

3.2. Experimental Procedure

Comminuted switchgrass was packed into a stainless steel (SS 316) cell. The cell was packed with 0.9 g of switchgrass and placed in the constant temperature Hewlett-Packard Model 5890 gas chromatographic (GC) oven. Deionized water at a flow rate of 3 mL/min commenced to flow using a Teledyne Isco Model 260D syringe pump through a preheating coil 4 m in length (1/16" SS tubing) into the reaction cell to flush air from the system. In addition, preheating coils provided the residence time for the fluids to reach the reaction conditions before they entered the reaction cell. After flow stabilization, i.e. when no air bubbles were seen at the collection vial end, dilution water at a flow rate of 2 mL/min was added using another Teledyne Isco Model 260D syringe pump, as this hydrolyzate exited the reaction cell. The addition of the diluent water was to prevent precipitation of the solubilized solids at ambient conditions, thus preventing the

clogging of the tubing. Once the flows from both water pumps were stabilized, the temperature of the oven was set to the desired reaction temperature. The average time required for the temperature to reach the set reaction temperature was between 4-7 minutes based on the final desired temperature. After the reaction temperature was reached, the process was continued for 60 min.

For the experiments involving carbonated water, the carbon dioxide flowing at a constant flow rate of 0.1 mL/min was supplied using a Teledyne Isco Model 260D syringe pump. Carbon dioxide was pumped in the liquid form, which was maintained by sufficiently cooling the carbon dioxide. A mixture of 50% ethylene glycol – 50% water was used as the refrigerant. Control of the flow of the respective pumps in the system was maintained using an Isco Model SFX 200 controller module. A cooling bath was placed after the process stream exited the oven in order to cool the hydrolyzate. The pressure in the system was maintained using a back pressure regulator, a GO Model BP66-1A11QEN151 (GO, Inc., Spartanburg, SC, 0-4000 psi). The back pressure regulator is a critical component in the system since water and the carbon dioxide were contacted at high pressure. Carbon dioxide was found to flush out of the system unrestricted if the system pressure was not maintained at the set pressure (1000 psi or 6.89 MPa). The pH levels of the collected samples were measured using a Mettler Toledo Seven-Easy pH meter system (Columbus, OH).

During experimentation at the higher temperatures such as 250, 280 and 310°C, the solubility of the solids (biomass) changed considerably in the subcritical water. When the reaction solutions were cooled to ambient conditions precipitation of the solids in the sample vials at room temperature (ambient) condition occured. The precipitated solid-liquid mixture were then centrifuged using Thermo Scientific Speed-Vac system (Model SC210A), and then the

supernatant was re-filtered using a 5µm nylon membrane before the samples were analyzed by high performance liquid chromatography (HPLC).

3.3. SEM Analysis of the Post-treated Switchgrass Samples

To prepare for the SEM analysis of the post-treated switchgrass samples, the filtrate was dried at 105°C. Following drying, the morphology of the samples was analyzed using environmental scanning electron microscopy (ESEM) under the microscope (Philips FEI XL-30 Environmental SEM). The ESEM was operated under high vacuum and with the beam energy of 10 keV. High resolution images of the samples were captured at magnification of 500x. The samples were analyzed at a distance of 27.2 mm from the beam and were gold sputtered for 10-15 minutes.

3.4. Analysis of the Liquid Sample

3.4.1 Analysis of Sugars in the Hydrolyzate

An HPLC system consisting of a Dionex pump (Model P-580) and a Dionex autosampler (Dionex Corporation, Bannockburn, IL, USA), along with a Shodex RI-101 detector was used for the analysis of samples. A Bio-Rad Aminex HPX-87P (lead based) ion-exchange column 300 x 7.8 mm, lead form, 9 µm particle size, 8% cross linkage, (Bio-Rad, Hercules, CA) was used in this analysis. The column was held at a constant temperature of 85°C during the analysis. Correspondingly, the refractive index detector was maintained at a temperature of 85°C. The mobile phase consisted of deionized water at a flowrate of 0.6 ml/min, and the injection volumes utilized were 20µL. All samples were filtered through a Nylon 5 micron membrane before injection into the HPLC. Chromatographic data were processed using Chromeleon software - 6.2 (Version 2.0). Table 3.3 provides the retention times of the constituent pure standard sugar

standard samples. Based on the retention times (min), the sugar peaks were identified and further quantified for the concentration of the sugars in the hydrolyzate.

Table 3.3: Retention time for the sugar standards.

Sugars	Retention time (min)
Cellobiose	10.3
Glucose	12.7
Xylose	13.7
Galactose	14.4
Arabinose	15.5
Mannose	16.1

3.4.2 HPLC Analysis of Carbochemicals (HMF, furfural, organic acids)

HPLC analysis for carbochemicals was performed using a Waters Alliance 2650 and Aminex ion exclusion HPX-87H cation exchange column with the dimensions of 300 x 7.8 mm, hydrogen form, 9 μm particle size, 8% cross linkage (Bio-Rad, Hercules, CA) at 60ºC and a mobile phase of 0.006M H_2SO_4 at a flowrate of 0.6ml/min for 60 min. The carbochemicals solutes were detected using a photodiode detector–array detector (Waters PDA 2998). The PDA 2998 photodiode array detector operated within the wavelength of 200-800 nm. A polychromatic beam was projected on the sample; wherein a polychromator dispersed the beam on a diode array. The diode array converted light to wavelengths and allowed high precision detection of samples simultaneously over a wide range of wavelengths. During the analysis, it was found that acetic acid and formic acid could be detected at lower wavelengths such as 210 nm. This was due to the sigma-type conjugation of the σ-bonds in the organic acids that permitted the detection at much lower wavelengths. On the other hand, HMF and furfural consists of the π-type

conjugation due to the presence of alternating double bonds and hence were detected at wavelengths greater than 250 nm.

For the analysis of carbochemicals, Table 3.4 shows the optimum wavelengths for the analysis of specific carbochemicals. The chromatographic system was powered by Empower software which provided the analysis and quantification of the separated components chromatographic peaks. The separation of the components present in the hydrolyzate was carried out using the ion-exchange (cation exchange) system discussed previously. Figure 3.5 shows a typical chromatogram for carbochemicals. It can be seen that HMF and furfural were eluted before the organic acids, showing weak interaction between the column and the furfural species.

Table 3.4: Retention times of carbochemicals and associated wavelengths for their detection

Carbochemicals	λ(max) (nm)	Retention time (min)
Furfural	280	42-43
HMF	280	28-29
Formic Acid	210	13-14
Acetic Acid	210	14-15

A typical chromatogram profile, shown in Figure 3.5 which was established using wavelengths in the range of 210 – 280 nm showed profiles for acids and carbochemicals at the following retention times:
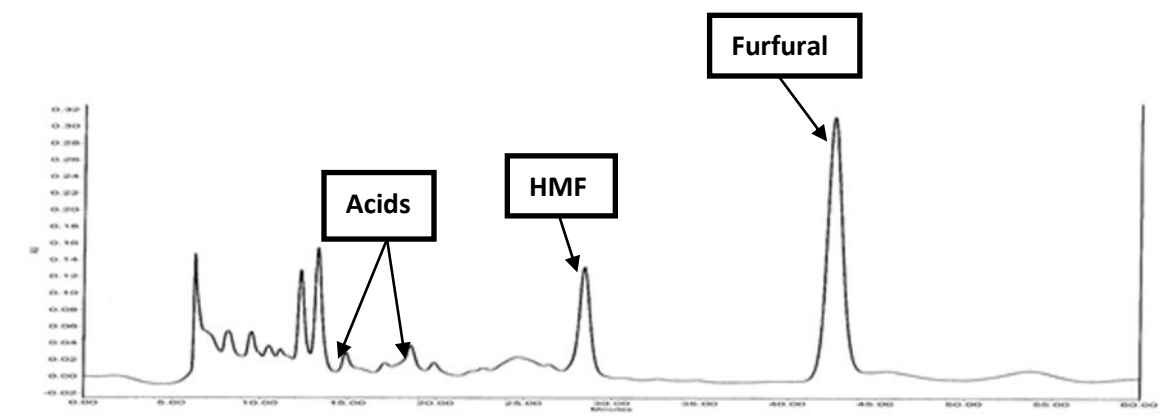
Figure 3. 5:Typical chromatogram for acids and carbochemicals in subcritical water-treated switch grass samples

3.5 Calculations

3.5.1 Yield calculations for Sugars and Carbochemicals

The yields of carbochemicals, acids and sugars from switchgrass was calculated based on the equation:

$$\text{yield(wt. \%)} = \frac{\text{concentration}\left(\frac{\text{g}}{\text{L}}\right) * \text{F(ml)} * 100}{\text{W(g)} * 1000} \qquad \textbf{(3.1)}$$

where:

F= Flowrate of reacting solvent (Water and Carbonated water) in to the cell (ml).

W= Weight of biomass substrate packed in the cell (g).

Weight % yield calculations for HMF and furfural were based on the total hexosan (C-6 sugars) and pentosan (C-5 sugars) loading per gram of raw biomass. From the composition

analysis for biomass as stated previously in the Table 3.1, the amount of glucan is representative of the hexosans. Similarly, the amount of xylan is representative of the pentosans present in the solids.

3.5.2 Solid Loss from the Reaction Cell

$$\text{Solid Loss (\%)} = \frac{W_0 - W}{W_0} \, x \, 100 \qquad (3.2)$$

W – Weight of the biomass substrate in the reaction cell

W_0 – Weight of the solids packed in the cell = 0.9 g

The % solid loss represents the amount of solids solubilized and converted during the reaction from the reaction cell. In this study, the reaction cell was packed with 0.9 g of raw comminuted switchgrass. The loss of solids is expected due to higher temperatures at which the experiments are conducted.

3.5.3 Severity Factor of the Reaction Medium

The conversion of biomass using hydrolysis can be expressed as a function of the severity of the reaction conditions, which is a function of temperature and time of the reaction process applied to specific biomass substrate.[110] The mathematical expression for severity of a biomass pretreatment process is as follows:

$$\text{Severity (Ro)} = t \, x \, \exp[\frac{T - 100}{14.75}] \qquad (3.3)$$

where:

Ro – Severity of the reaction

T – Temperature (°C)

t – Time of the reaction (min)

The severity function is usually represented as log (R_0). In this research, the total time of the reaction was 60 min and the temperatures were varied from 220, 250, 280, 310ºC. Hence, a range of values of log (R_0) can be calculated. The severity factor has been used as an empirical equation to model the conversion processes for lignocellulosic biomass. Being an empirical relationship, it has been used for mathematically quantifying the extent of xylan, lignin and cellulose removal from the bio-polymers using various pretreatment processes.

Chapter 4. Results and Discussion

4.1 Effect of Temperature on Furfural Yields in Neat Subcritical Water and Carbonated Water

As discussed earlier, furfural is a product of dehydration of xylose. During the process of hydrolysis, the water molecule is added to the ether and ester linkages in the hemicellulose. It can be seen in Figure 4.1 that the furfural yield increased with an increase in the temperature in both carbonated water and subcritical water. The yield of furfural at 220^oC in carbonated water was 0.19 g/100g biomass, whereas in subcritical water the furfural yield was 0.15 g/100g biomass. Also, the yields at 310^oC were constant at 1.24 g/100g biomass in both carbonated and subcritical water. This increase can be attributed to the high solubility of hemicellulose in water above 220^oC. In addition to the high hemicellulose solubility in subcritical water as a result of its low dielectric constant and high K_w, it acts as a catalyst for the conversion of hemicellulose to its constituent sugars.[61] Moreover, the generation of carbonic acid due to carbon dioxide dissolving in water increased the yield of furfural at 220^oC. As discussed earlier, carbonated water lowers the pH at lower temperatures due to high solubility of carbon dioxide in water. At 310^oC, the effectiveness of carbonated water decreases due to the reduction of the pH effect as a result of low solubility of carbon dioxide to form carbonic acid.

Hydrothermal processing of hemicellulose results in the formation of the acetic acid due to the cleaving of the acetyl linkages in the hemicellulose biopolymer network. The formation of acetic acid from acetyl bonds further acts as a catalyst towards the hydrolysis of the unconverted xylans and the hydrolyzed xylose, and this process is referred to as auto-hydrolysis. Hence, due to the amorphous nature and the presence of acids, hemicellulose is completely hydrolyzed at temperature of 250^oC. [88]
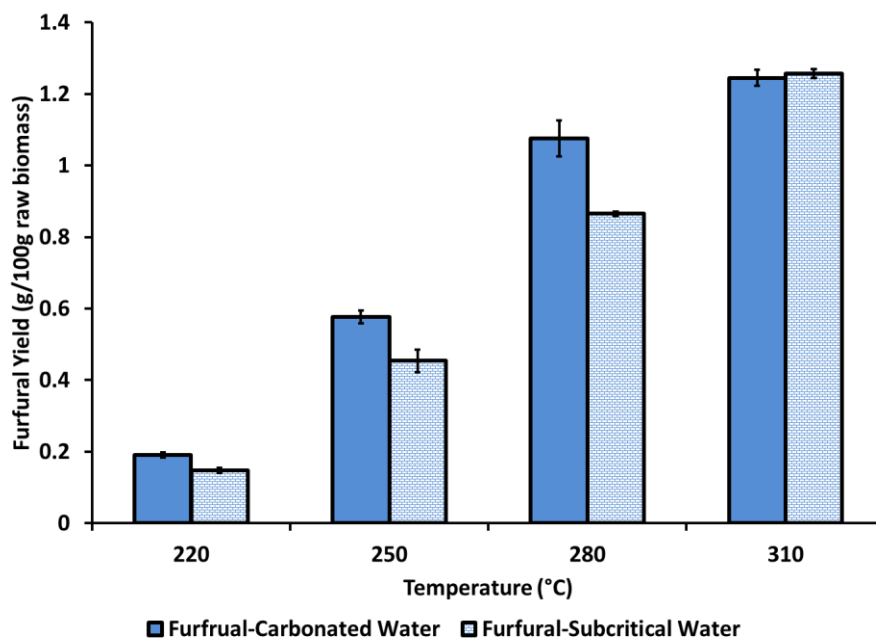
Figure 4.1: Variation in furfural yields in neat vs. carbonated water as a function of temperature

Lee et al.[111] found that when corn stover was treated with dilute acid in a flow-through reactor that, 91% of the xylan present in corn stover was converted, of which 85% was collected as xylose monomers and oligomers. Similar results were observed in this study, wherein high concentrations of oligomers were found in the hydrolyzate. Due to the limitations of the current HPLC analysis system, we were unable to separate the oligomers.

The effect of using carbonated water on the formation of furfural can be observed in Figure 4.1. The catalytic effect of carbonated water in terms of accelerating the formation of larger amounts of furfural at various temperatures from 220°C to 280°C is clearly evident. Similar results were reported by van Walsum et al.[101] who found that carbonic acid enhanced the hydrolysis of xylan to form xylose and xylo-oligomers. The effect was also attributed to the effect of combined severity. Combined severity is the cumulative effect of the severity factors

due to carbonated water and the temperature. Moreover, when studies by the same research group were conducted on the hydrolysis and conversion of aspen wood in presence of carbonic acid, no effect on the conversion of aspen wood to hydrolysis products was observed.[102]

In this study, xylose was observed only in trace amounts indicating that the xylose was instantaneously converted to furfural under the temperature range utilized. Also, at 310°C the difference in the yields of furfural in carbonated water when compared to the yields of furfural in subcritical water were minimal, indicating that there was apparently no catalytic activity due to the presence of carbonated water. This effect can be attributed to the lower solubility of carbon dioxide in water to form carbonic acid and catalyze the reactions at a temperature in excess of 300°C.

4.2 Effect of Time on Furfural Yields in Neat Subcritical Water and Carbonated Water

The effect of time on the total yields of furfural from raw biomass for a period of 60 minutes is shown in Figure 4.2 (a-c) for the four studied reaction temperatures. It can be observed that the yields of furfural at 220°C (a) and 250°C (b) increased over the period of 60 minutes. This is due to the effect of lower severity of the reaction conditions to depolymerize and convert lignin, cellulose and hemicellulose. Also, due to lower solubility of the biomass (switchgrass) in the reaction medium at 220°C and 250°C, the delignification step is slower and therefore the formation of xylose and furfural proceeds over the period of 60 minutes.

Bobleter et al.[112] performed hydrolysis of various substrates such as wheat straw, poplar, birch wood as well as rice straw in a flow-through experiment and found that the hemicellulose solubilization varied from 30% (solids removed) at 190°C to 60% (% solids removed) at 250°C.

In this study, the cumulative yields of furfural at 280°C and 310°C (see Figure 4.2 (c) and (d)) were found constant after 30 minutes. This effect can be explained due to the further degradation

(a)
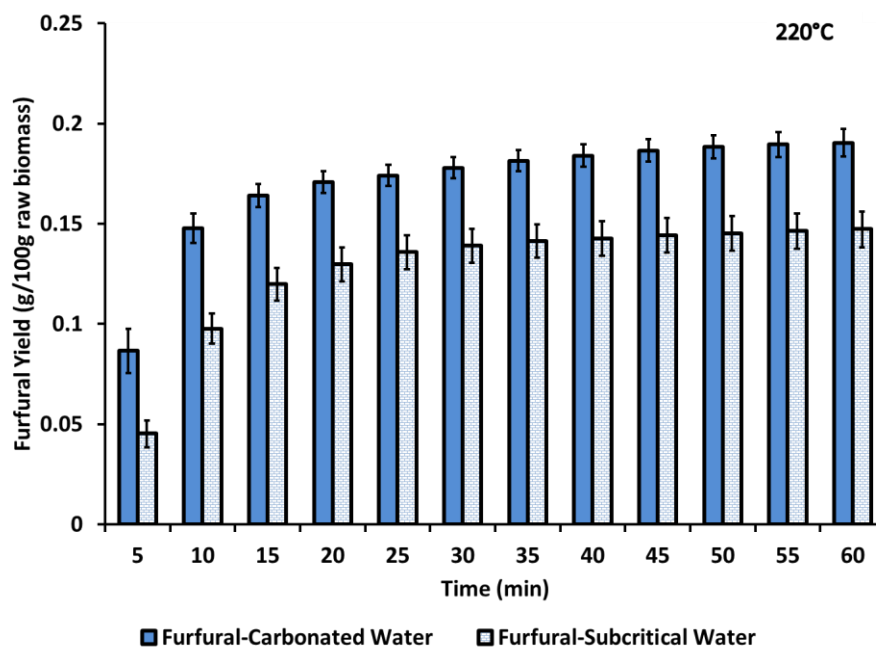
(b)
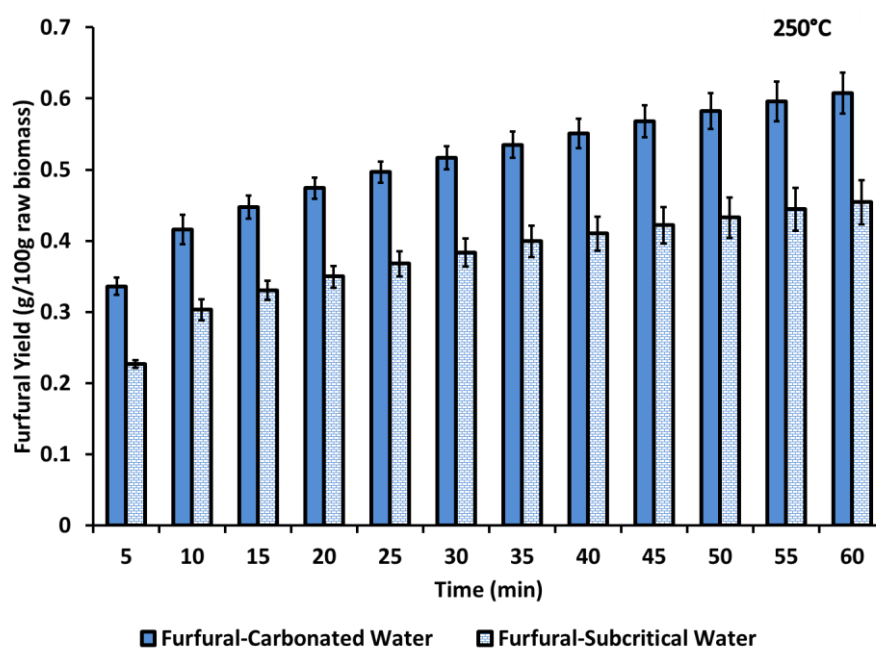
(c)

(d)

Figure 4. 2: Variation in the yields of furfural in carbonated water and subcritical water at (a) 220°C, (b) 250°C, (c) 280°C, (d) 310°C

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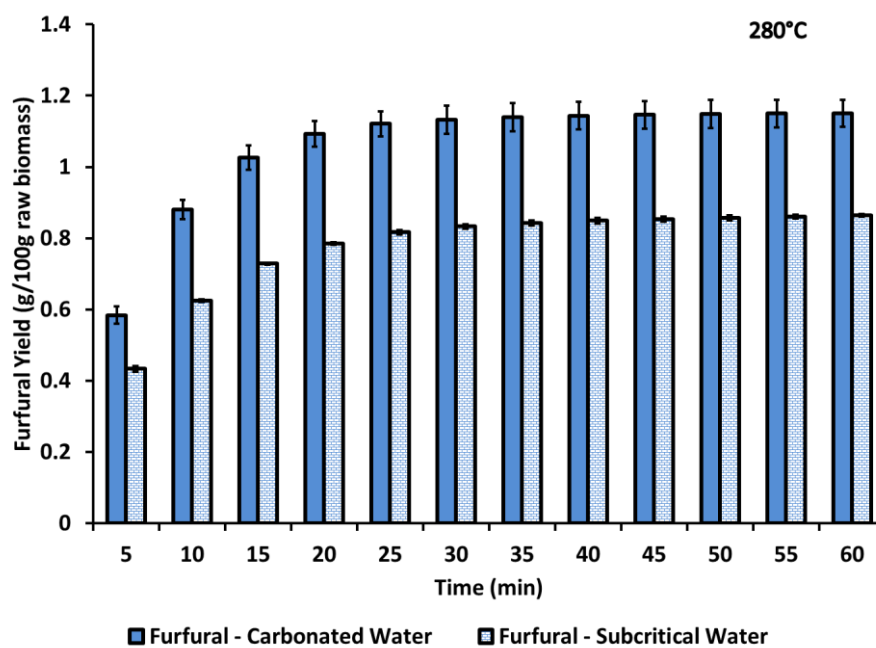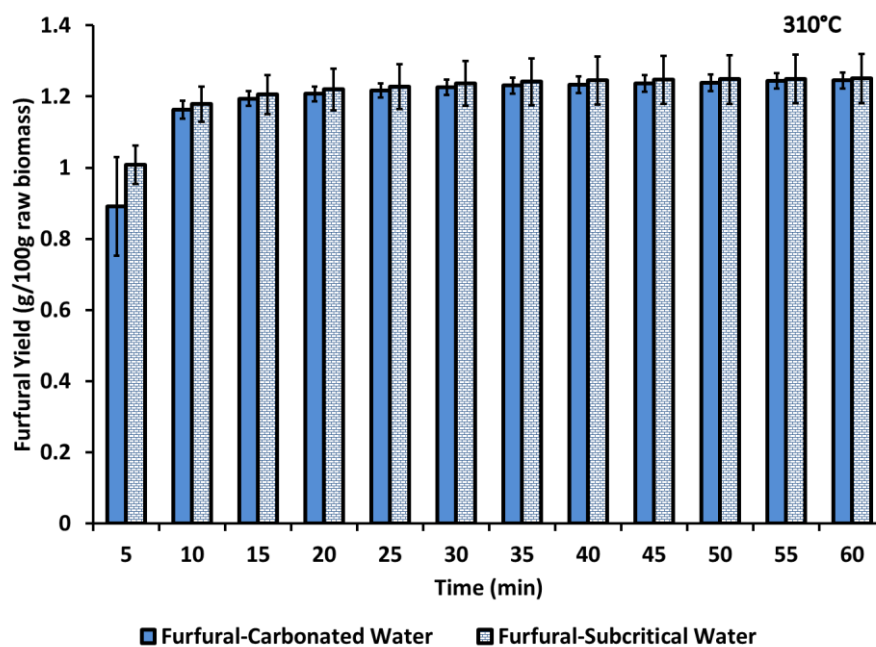of the furfural formed during the process. The asymptotic trends for the yields of furfural also show that the reaction can be carried out at a residence time of 30 minutes to optimize the yields of furfural in carbonated as well as in neat subcritical water. The production of furfural is slower at temperatures of 220°C and 250°C due to its dependence on the continuous production of xylose. Hence, the cumulative yield of furfural increased continuously over period of 60 minutes.

As commented previously, carbonated water showed a larger catalytic effect for the formation of furfural at lower reaction temperature. From Figures 4.2 (a-d) it is clear that carbonated water can catalytically convert higher amounts of xylose/xylan into furfural.
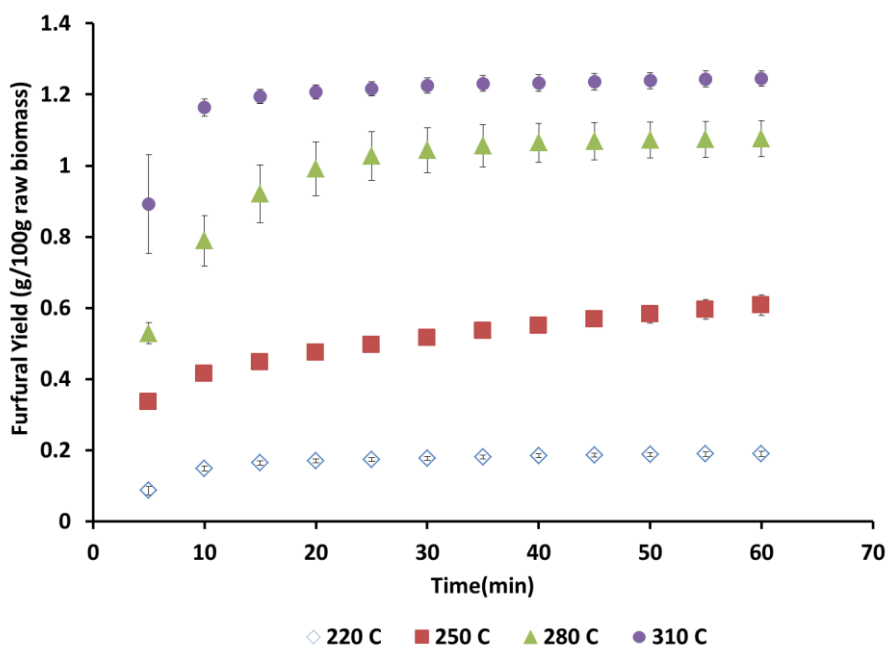

Figure 4.3: Variation in the production of furfural directly from switchgrass biomass in hot carbonated water with reaction time

Furthermore, in Figure 4.3 it was observed that the maximum cumulative yields of furfural at temperatures of 280°C and 310°C were achieved in 30 minutes as indicated by the

asymptotic trend in furfural production (cumulative yield) with respect to residence time. This trend can also be attributed to the optimization of the yields at lower residence times and further degradation of furfural to degradation products as the residence time is increased.

Gupta et. al [113] studied the decomposition and solubilization of switchgrass to produce bio-crude oil containing oxygenated hydrocarbons that can be used for energy purposes. In this study, water and K_2CO_3 were pumped through the reaction cell packed with biomass. It was found that 82 % of the switchgrass was solubilized in subcritical water (T = 260°C) and K_2CO_3. From the Figure 4.4, it can be seen that 70% of the switchgrass at 220°C and 75% of the switchgrass at 250°C in this study were solubilized in carbonated water. Moreover, it was found that 99% of the biomass was solubilized at 280°C and 310°C temperatures (see Figure 4.4).
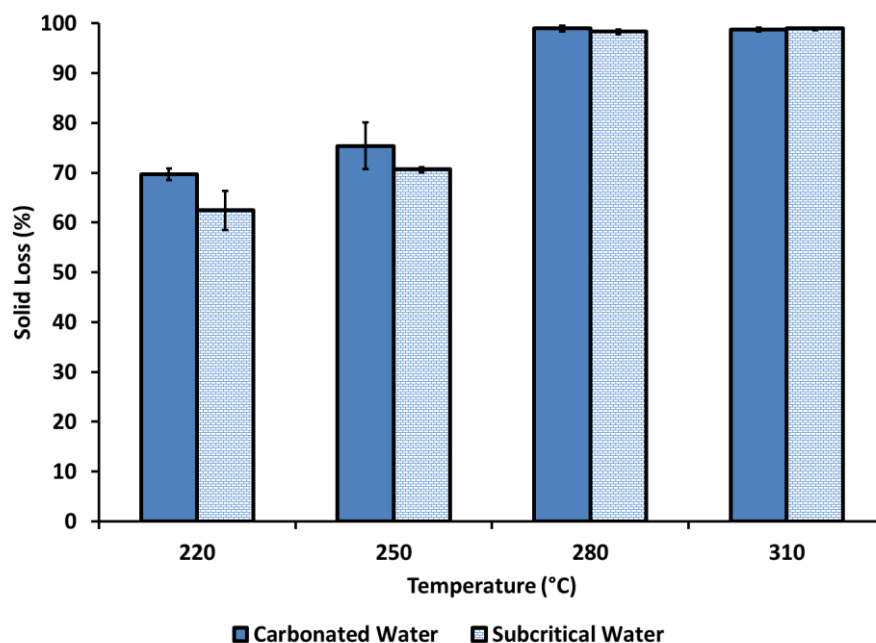

Figure 4. 4: Solid loss (%) in the reaction cell at various temperatures.

Gupta et al. found that the yield of carbochemicals were HMF (4%), furfural (6%), organic acids (17%) at a 85 % confidence level. They also observed a catalytic effect of K_2CO_3 in accelerating the conversion of biomass to sugars as well as carbochemicals in the temperature range of 235 -260°C, with carbochemicals formation dominating at 260°C.

In another study using a flow reactor,[114] the decomposition of various biomass such as bamboo, hardwood and Japanese cedar in a flow type reactor at temperatures ranging from 235ºC to 285ºC were studied. Here, it was observed that the degradation of cellulose started at temperatures above 235ºC. Interestingly, it was observed that 95% of all the biomass solids charged to the reactor was removed from the reaction cell in a residence time of 60 mins and this observation was similar to our results shown in Figure 4.4.

4.3 Effect of Temperature on the Production of Sugars and Oligomers in Carbonated and Neat Subcritical Water

Figure 4.5 shows the effect of carbonated water as a function of time on the production of sugars (monomers and oligomers). It was observed that the liquid hydrolyzate exiting the reactor had the highest concentration of the carbochemicals in the first few samples. Lee et al.[115] observed similar trends in the concentration profiles of the liquid hydrolyzate exiting the reactor when corn stover was packed in a tubular reactor and water-acid mixture was passed through the reaction cell. It was also observed that the hydrolyzate had a higher concentration of oligomers than monomeric sugar in addition to the degradation products such as HMF and furfural.
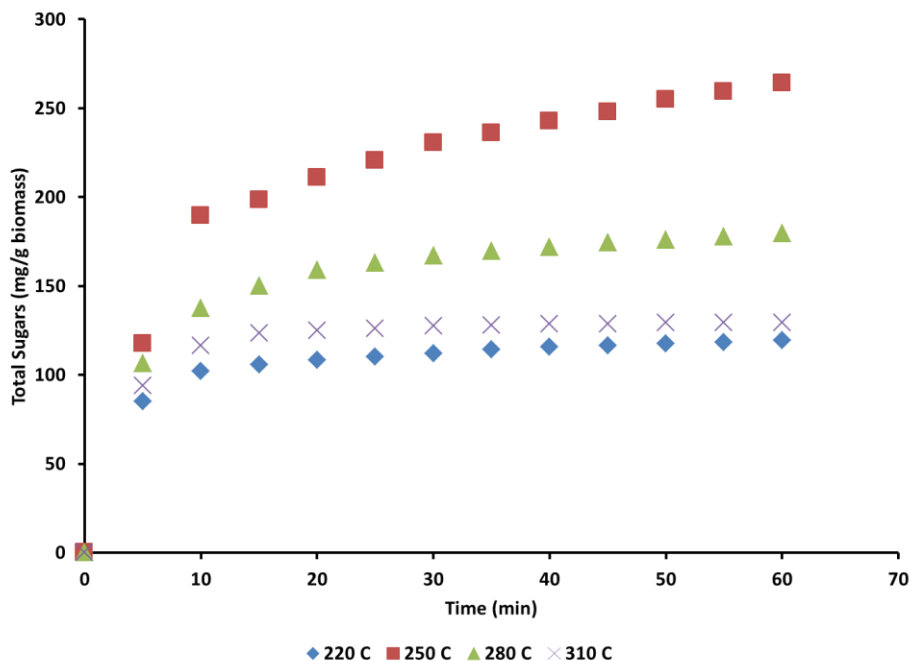
Figure 4.5: Variation in total sugars in carbonated water as a function of hydrolysis time

Due to the continuous inflow of fresh stream of water through the reaction cell, the oligomers formed were instantaneously removed from the system and were collected in the vials. Due to the instantaneous removal, the concentrations of the monomers were found to be lower than the oligomeric sugars. In contrast to the batch reactor in which the oligomers formed are rapidly converted to monomeric sugars, semi-batch systems produce higher concentrations of oligomeric compounds. A semi-batch flow-through reactor limits the residence time of the components involved in the reaction by a continuous flushing of the products out of the reaction system. One modification to the current system would be to decrease the flow rate of the reaction water which will allow higher residence time for the components to be converted to monomeric sugars as observed in a batch reactor system. Another modification to decrease the oligomeric concentrations is to involve a recycle stream of unconverted hydrolyzate in the process, thereby resulting in higher conversion of oligomeric sugars to monomers.

Figure 4.5 shows the total amount of sugars and oligomers that were found in the hydrolyzate in carbonated water as a function of time. It was observed that at 250°C that the concentration of the total sugars was a maximum, indicating the degradation of the sugars and oligomers was lower at 250°C when compared to 280°C and 310°C. It was also observed that the cumulative yields of the total sugars at 220°C were similar to that at 310°C. Since switchgrass is a highly recalcitrant bio-polymer, due to lower severity hydrolysis reaction at 220°C removal of lignin was limited and hence the conversion of hemicellulose and cellulose. Hence, the yields of sugars were lower at 220°C and 310°C. It should be noted that, at temperatures beyond 280°C results in complete solubilization of the switchgrass.[113] Due to high degree of solubilization of the biomass higher amount of sugars and oligomers were formed that consequently could be converted to products such as HMF, furfural and organic acids. Lower yields in the amounts of sugars and oligomers at 310°C indicate the further conversion of these oligomers and sugars to HMF, furfural and acids.

Figure 4.6 represents the yields of total sugars that were formed in the semi-continuous process as a function of time in subcritical water. Interestingly, the yields of sugars (monomer and oligomers) were highest at 250°C in carbonated as well as in subcritical water. The rate of production of sugars in carbonated water (Figure 4.5) was higher as compared to that in subcritical water (see Figure 4.6). Although the trends in the total yields of the sugars were similar for both carbonated water and subcritical water, the overall yields were highest in the carbonated water medium. The maximum yields of total sugars in carbonated water were 264 mg/g biomass, whereas in neat subcritical water the maximum total sugar yield was 223 mg/g biomass.
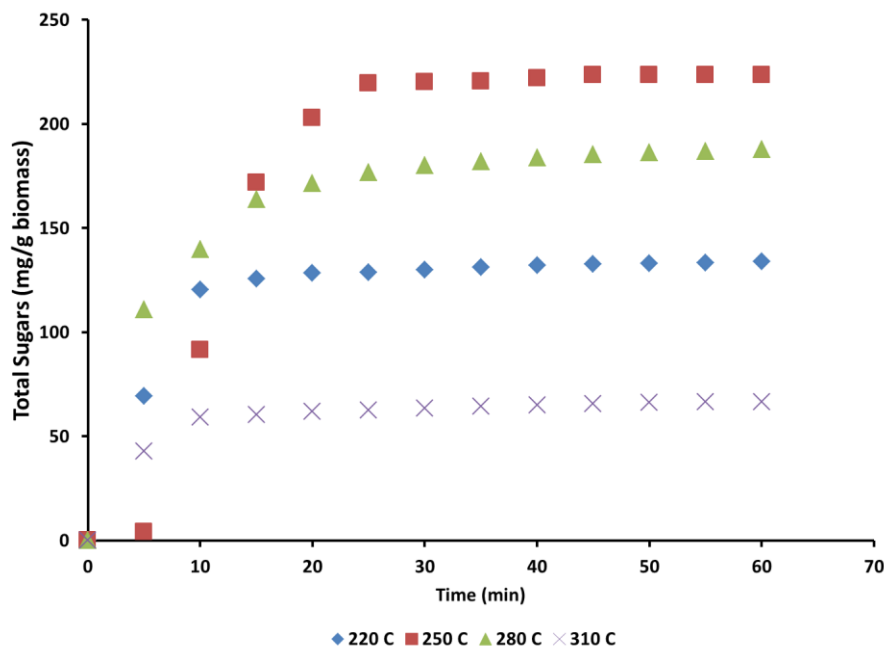
Figure 4.6: Variation in total sugars in subcritical water as a function of hydrolysis time.

4.4 Effect of Temperature on HMF Yields in Neat Subcritical Water and Carbonated Water

Figure 4.7 shows that the cumulative yield of HMF in presence of carbonated water is enhanced when compared to neat subcritical water. In the processing of biomass, cellulose is hydrolyzed to glucose and higher oligomeric sugars and further converted by acid-catalyzed reaction in to HMF.[117] The concentration of oligomers was found to be higher in case of flow reactor systems as compared to batch reactor process.[118] This is due to the instant removal of the formed oligomers by the fresh stream of water in a semi-batch system. On the contrary, when the reactions are carried out in a batch reactor, the formed oligomers are further degraded to monomeric sugars and carbochemicals under conditions of high severity.

Sasaki et al.[76] studied the hydrolysis of cellulose at temperatures of 290-400ºC and 25MPa and found that the decomposition of cellulose occurs via the formation of cello-oligomers such as cellobiose, cello-triose etc. in the process. Glucose, being unstable at such

severe reaction conditions is then further dehydrated in presence of acids such as carbonic acid. Kamio et al.[119] have proposed steps for cellulose decomposition as hydrolysis of cellulose to oligosaccharides, the decomposition of oligosaccharides and further degradation to carbochemicals and finally formation of char.

In this research we found that the cumulative yield of HMF in carbonated water at 280ºC was similar to that at 310ºC. On the contrary, it was observed that the cumulative yields at 280ºC in subcritical water were lower than at 310ºC. This observation for lower yield of HMF at high temperature such as 310ºC can be based on the decomposition of the HMF into degradation products. Substantial amount of solid residue was found at higher temperatures which could indicate the potential for the formation of char-like substance.

Carbochemicals such as HMF, formic and acetic acids are formed by discrete degradation steps. Due to the formation of acids the pH of the reaction medium was found to be in the range of 3–3.5 (see Figure 4.7) providing a further catalytic effect for the conversion of the sugars and oligomers. As can be observed from the Figure 4.8, the pH of the hydrolyzate was lowest during the first ten minutes and increased with time for the reaction process. Generally, it was observed that the pH of the hydrolyzate varied between 3 and 5 with initial samples showing lowest pH values due to high concentration of organic acids. The final pH of the carbonated water hydrolyzate after 60 min of reaction time is shown in the Figure 4.7. The actual pH of the carbonated water hydrolyzate is difficult to ascertain due to the escape of carbon dioxide from the aqueous medium after the hydrolyzate is collected under atmospheric pressure.
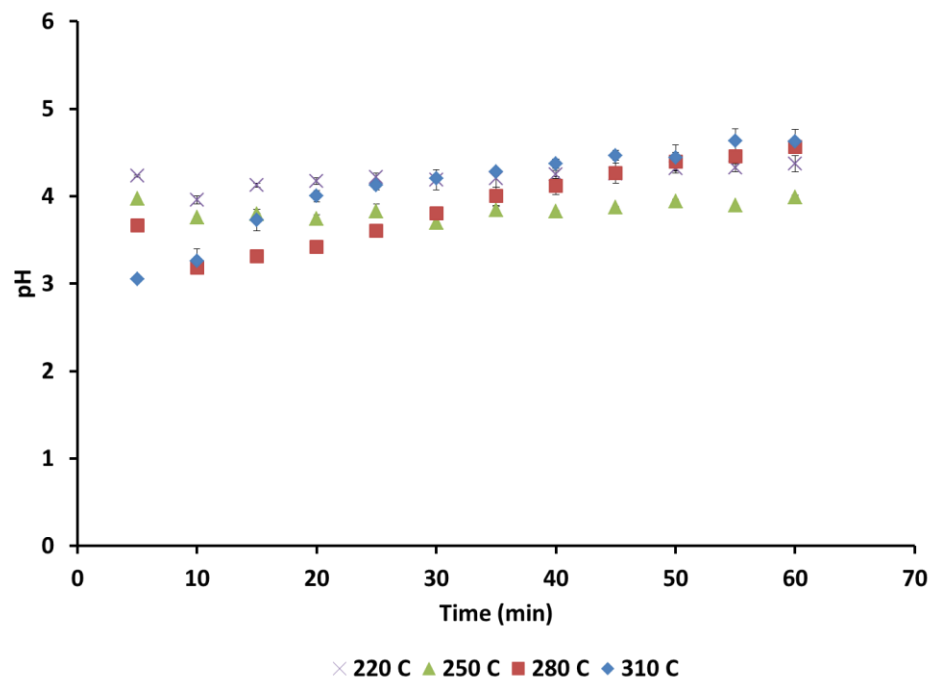
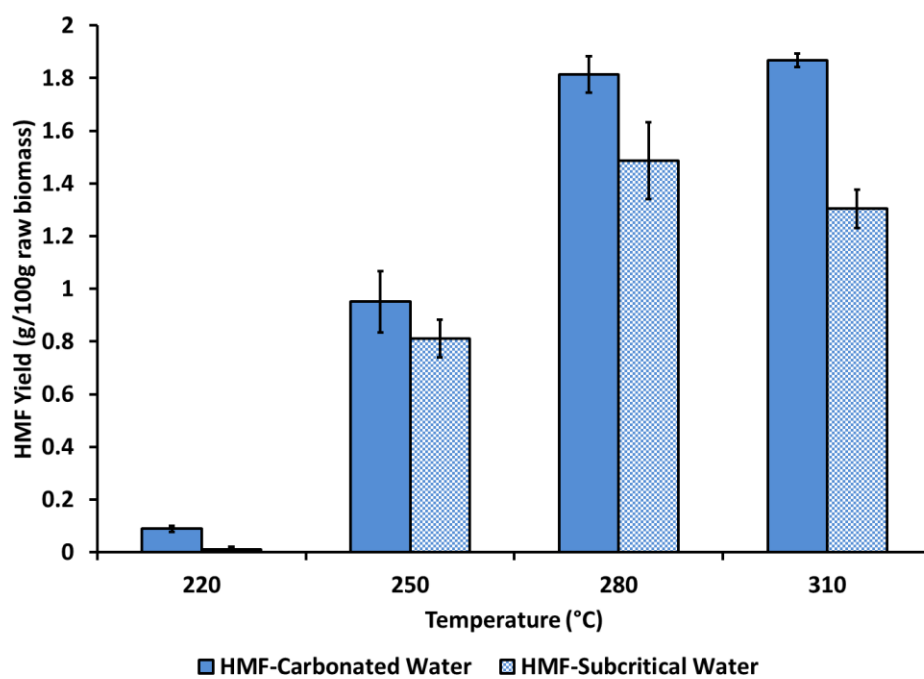**Figure 4.7: Variation in the pH of the hydrolyzate during treatment in carbonated water**

Figure 4.8: Variation in the total HMF produced in neat vs carbonated subcritical water as a function of temperature

King et al.[67] discussed and rationalized the effect of solubility parameter and its influence

on the solubilization of the cellulose. They found that the point at which the solubility parameter

equalled the solubility parameter of the cello-oligomers and those conditions were optimum for

the solubilization of cellulose in subcritical water. Figure 4.9 shows the variation in the solublity

parameter for cello-oligomers in subcritical water at various degree of polymerization.
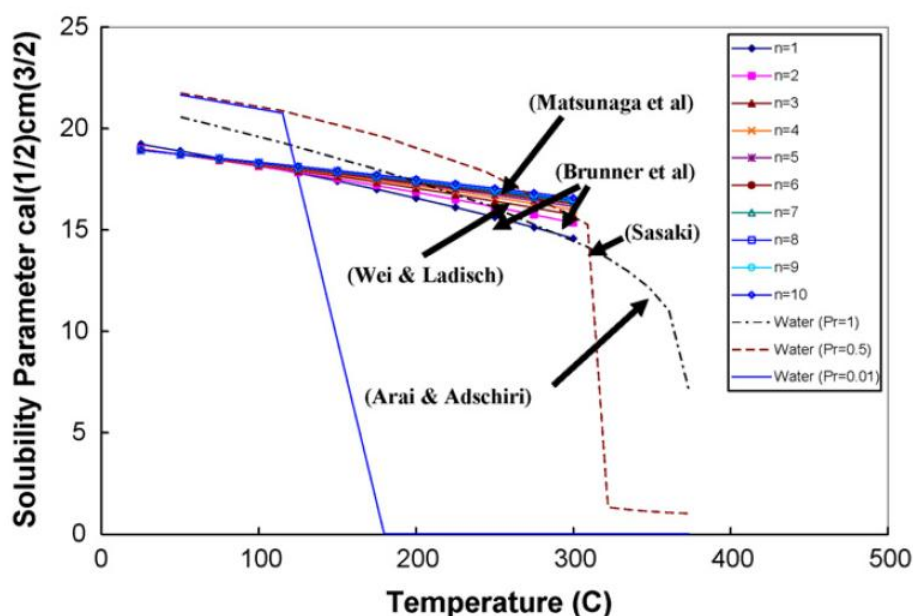
Figure 4. 9: Variation in the solubility parameter in subcritical water at various reduced pressure and cello-oligomers with temperatures[67]

The conditions that indicated the interception of the solubility parameters were above

300ºC and below the critical point of water. Similar conditions were applied in this study and it

was observed that complete solubilization of the biomass (switchgrass) was observed for

temperatures of 280 ºC and 310ºC. Moreover, Figure 4.4 shows that the % solid removed from

the cell at 280 ºC and 310 ºC were 99%. This observation is consistent with the solubility parameter theory discussed in Figure 4.9.

Since, HMF is an intermediate product towards the formation of acids; it is instructive to study the mechanism of acid formation. Since, levulinic acid formation occurs via rehydration of HMF, the formation of levulinic acid is highly favored in an acidic-aqueous medium. This trend can be observed from the Figure 4.8, the yields of HMF remained unchanged when the reaction temperature was increased from 250°C to 280°C. This can be due to the degradation of carbochemicals into acids at higher temperatures.

Due to the limitations of our current HPLC analysis systems, we were not able to separate peaks for acetic acid and levulinic acid. However, the total organic acids variation in carbonated water with temperature can be seen in the Figure 4.10. The cumulative yields of total organic acids in this study were found to be highest at 280°C. Moreover, the highest yields were 9 g/100g raw biomass followed by 6.5 g/100g raw biomass at 310°C. The lower yields at 310°C can be attributed to their degradation under more severe subcritical conditions. It has been observed that substantial degradation of the carbochemicals to acids occurs at higher temperatures in carbonated subcritical water.[94]

Due to the formation of carbonic acid, the cellulose is hydrolyzed and further dehydrated at a higher rate relative to that experienced with neat subcritical water. This is consistent with the reaction rate trend observed by Brunner et al.[97] using carbonated water, where they found that the rate of the reaction increased until 260°C. This increase in the reaction rate was attributed to the
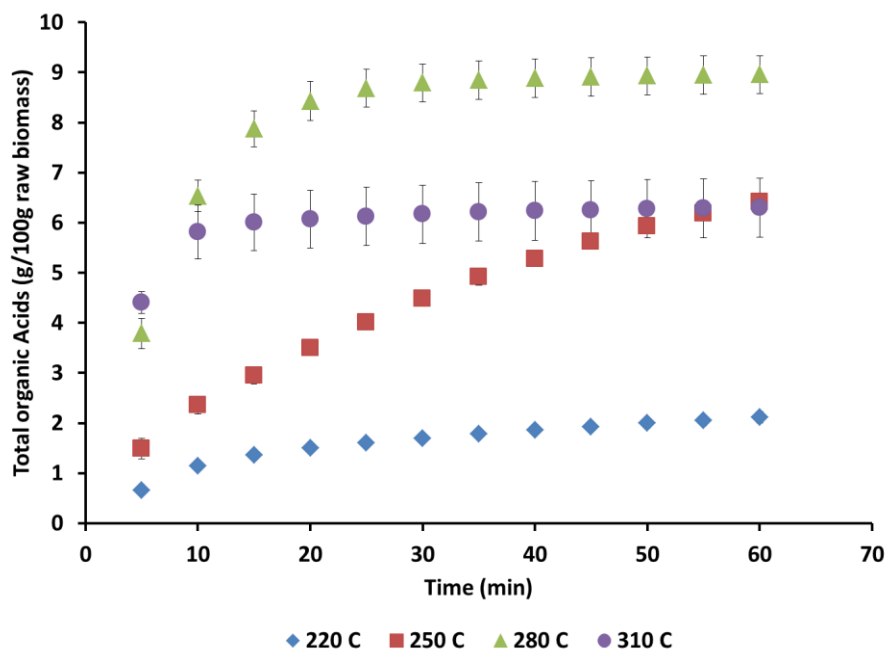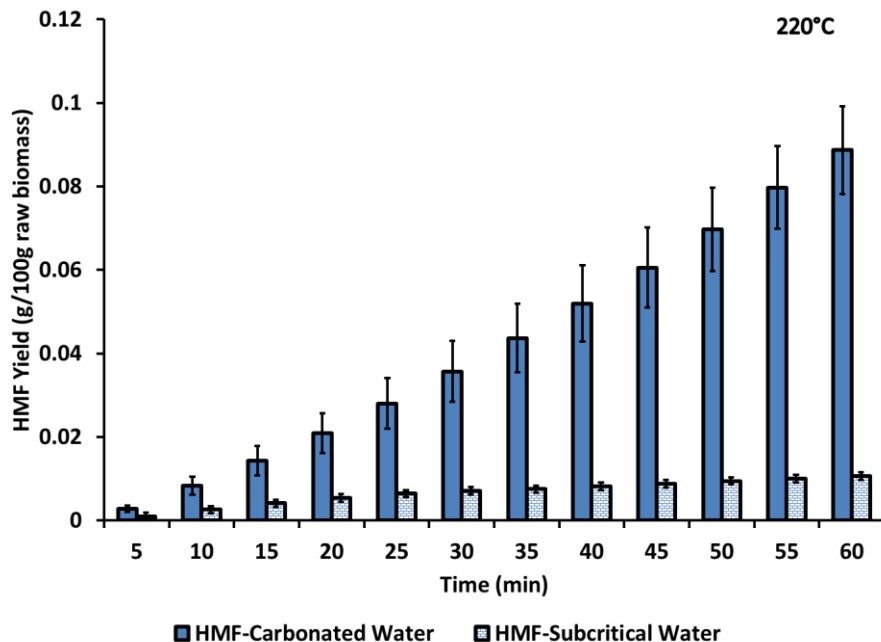
Figure 4.10: Variation in the yields of total organic acids in carbonated water as a function of time and temperature

increased cellulose liquefaction due to the addition of carbon dioxide to the hot water. This observation is also significant for the formation of carbochemicals. It was postulated that CO_2 addition to subcritical water increases the H^+ ions required for an acid catalyzed reaction resulting in an increase in the yield of sugars and carbochemicals.[120] In a similar study by the same research group[100], it was found that when rye straw was hydrolyzed in presence of carbon dioxide in water, no enhancement of the reaction rates was observed. Hence, carbonated water has shown varying results on different biomass substrates.
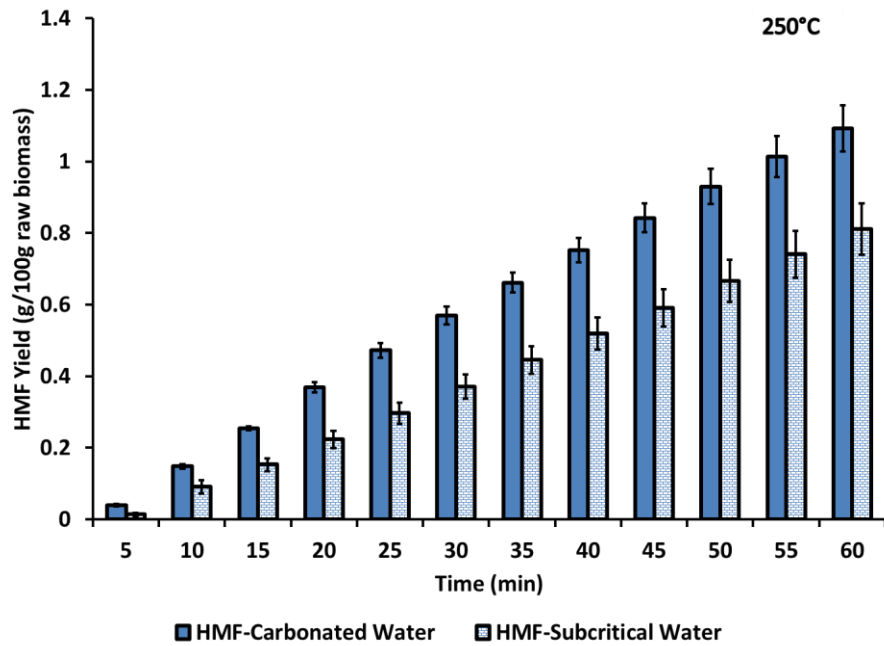
King et. al [33]studied the conversion of switchgrass and corn stover in carbonated water using batch rector and found considerable increases in the yields of carbochemicals in carbonated water. From Figure 4.11, it can be seen that the yield of HMF was higher in carbonated water at all of the experimental temperatures (220, 250, 280 and 310°C). The

increase in the yields demonstrates that the catalytic effect of carbonated water is more pronounced at lower temperatures, attributed to the reduction of pH with increasing temperature. The yields at 220°C in carbonated water were found to be 0.08 g/100g biomass and in neat subcritical water was found to be 0.01 (g/100g biomass). This is a significant increase considering, cellulose is not hydrolyzed at 220°C. Based on the increase, it can be postulated that carbonic acid does influence the hydrolysis of cellulose, utilizing in further conversion to HMF resulting in nine- fold increase in the yield. It was also found that the yields of HMF at 310°C were very similar to those at 280°C indicating the optimal formation of HMF occurs at 280°C. Moreover, reaction temperatures above 300°C have been found to form various degradation products from HMF such as 1, 2, 4-benzenetriol, pyruvaldehyde, glyceraldehyde etc.[121, 122]

(a)

(b)

(c)

Figure 4.12: Variation in the total HMF yield as a function of temperature and time in carbonated subcritical water

This increase in the yields is also residence time dependent, in which the formation of HMF is favored at higher residence times. Although the final yields at the end of 60 min were the same at 280°C and 310°C, it can be observed that the rate of HMF formation was higher at 310°C. The high rate of HMF formation can be attributed to the initial higher conversion of cellulose to glucose and further dehydration to HMF. The formation of the yielded glucose and xylose was very transient due to the instantaneous degradation of the sugars. Moreover, the yields of HMF at 280°C and 310°C become stabilized after 30 minute. This can be due to high rate of hydrolysis for the step producing higher sugars and their instantaneous conversion to carbochemicals. As time proceeded, the concentration of the available sugars decreases and the

decomposition of HMF dominated among the various reaction steps resulting in a lower concentration of HMF.

4.5 Effect of Temperature on Formic Acid Yields in Neat Subcritical Water and Carbonated Water

It can be seen from the Figure 4.13 that the formation of formic acid in carbonated water and recorded yields depend on the reaction temperature. The yields of formic acid were optimal at 250°C followed by decreasing yields upto 310°C. This decrease in the yield of formic acid at 310°C can be attributed to the further decomposition of formic acid. Also, since it is known that formic acid is a product of the decomposition of furfural and furfural decomposition is higher at temperatures such as 280°C and 310°C, this could lead to lower yields of formic acid. At 310°C, the yields of formic acid in carbonated water were lower than in neat subcritical water. This can be due to the enhanced conversion rates obtained due to the presence of carbonic acid.

Figure 4.13: Variation in the yields of formic acid in carbonated water and neat subcritical water at various temperatures

(a)

(b)
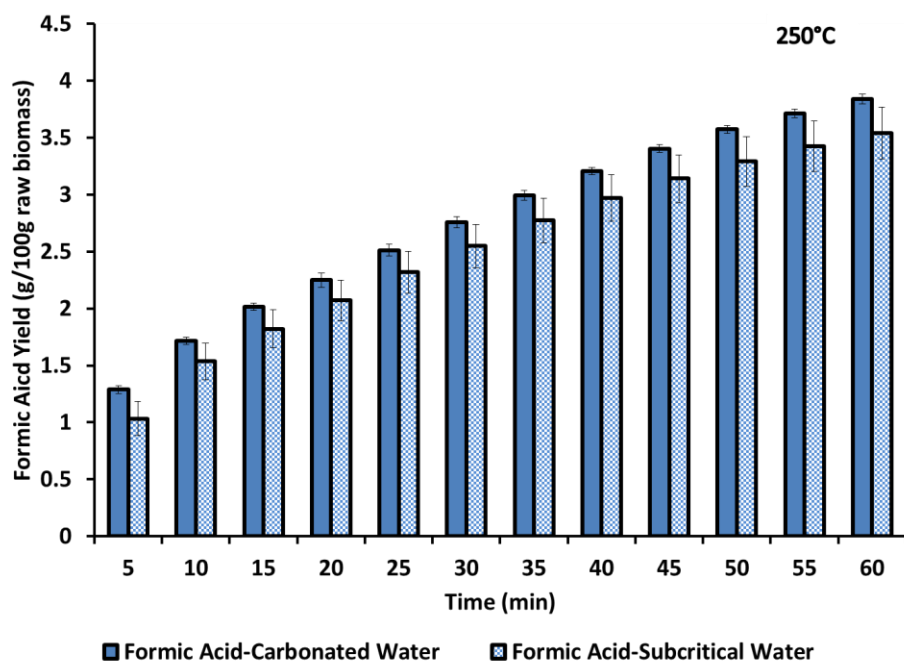
(c)
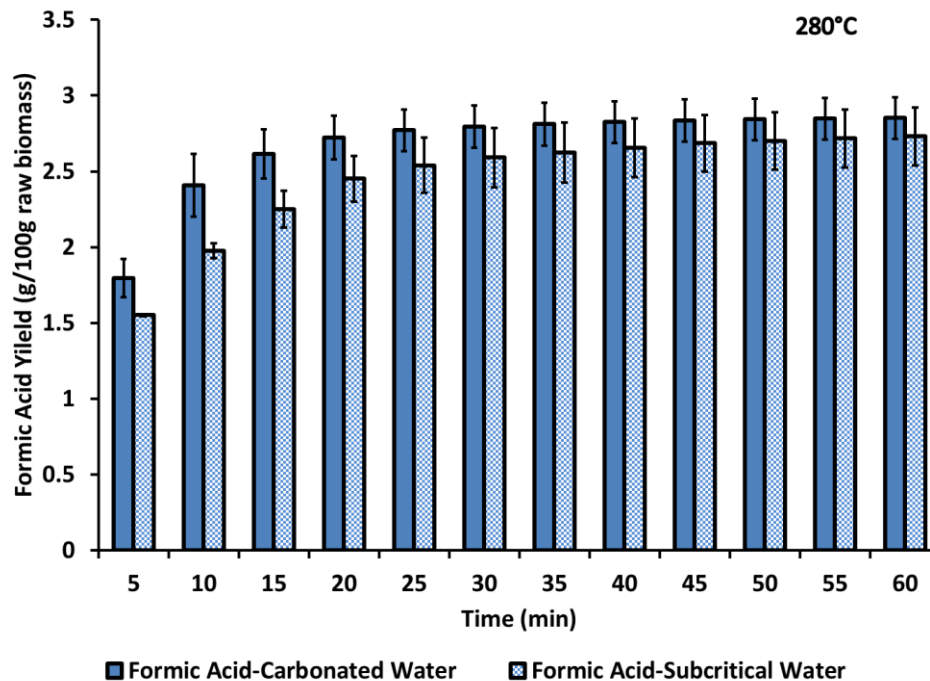
(d)
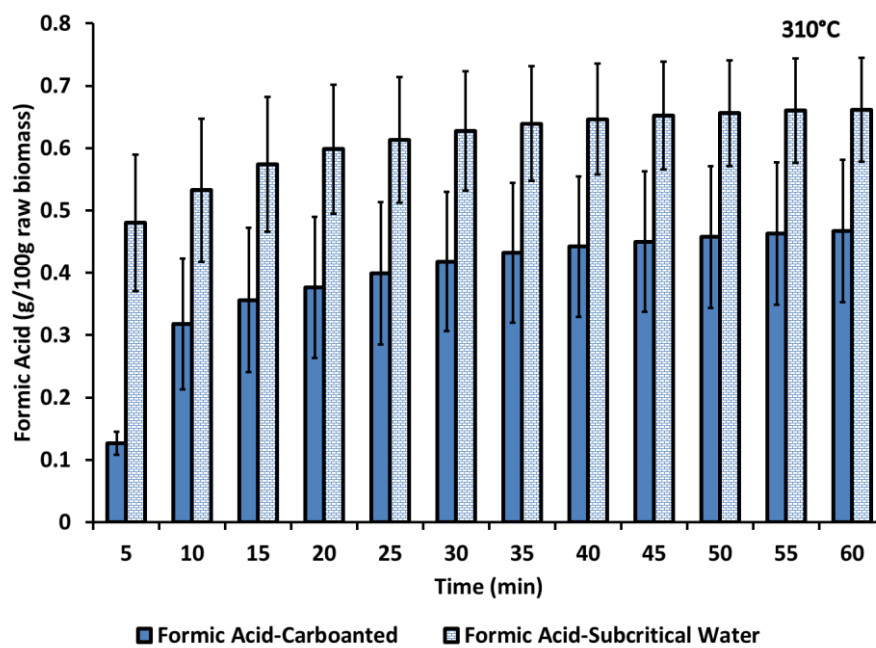
Figure 4.14: Variation in the yields of formic acid with residence time at temperatures of (a) 220° C, (b) 250° C, (c) 280° C, (d) 310° C
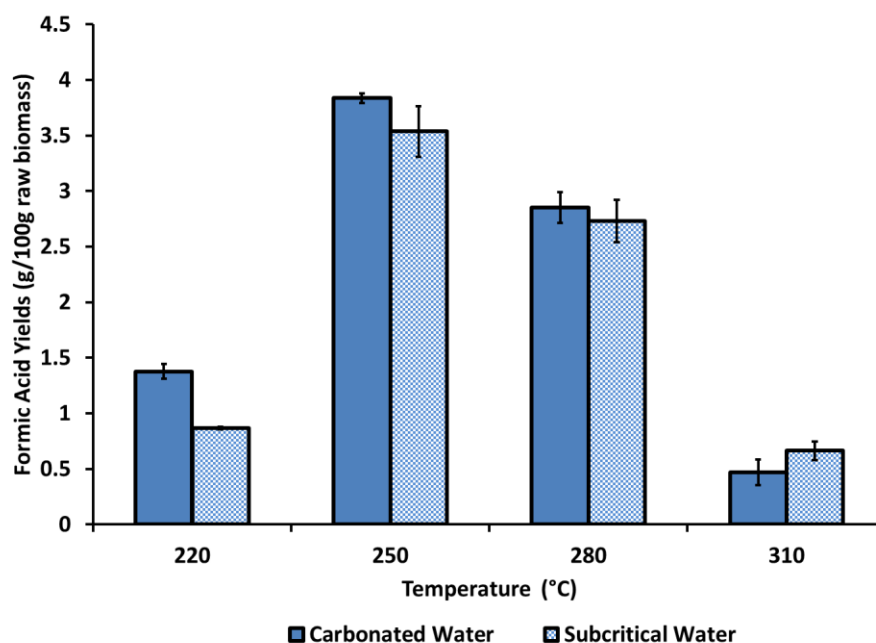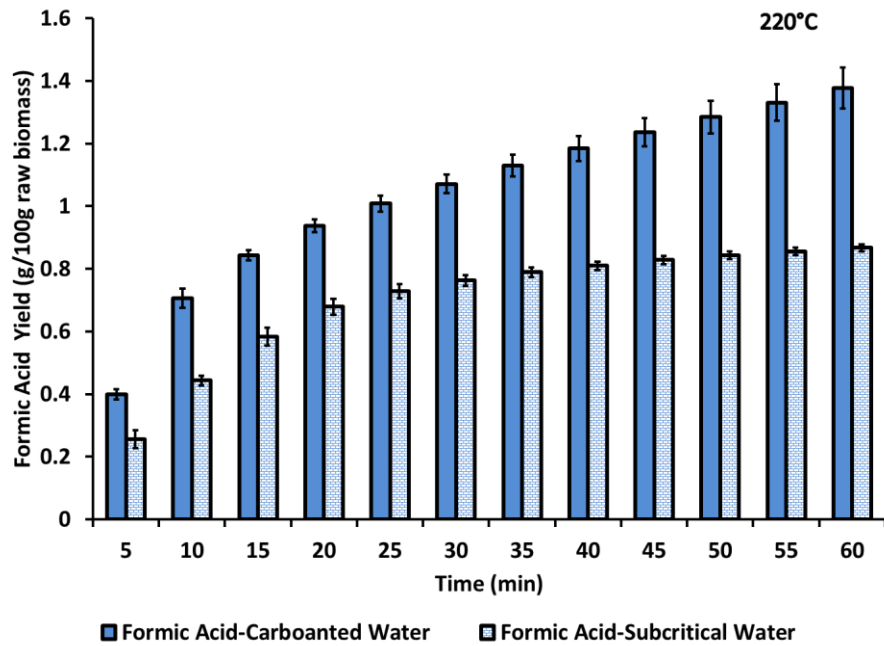
It can also be seen from the Figure 4.14 (a-d) that formic acid was detected in the first sample taken after commencement of the reaction, indicating that furfural decomposed almost immediately as it was formed. Carbonated water had a catalytic effect on the formation of formic acid; this was expected considering carbonated water was effective in increasing the yields of furfural. The yields of formic acid at 220°C and 250°C were found to increase with residence time. It can also be observed that the presence of carbonated water resulted in an increase in the formation of formic acid. Interestingly, at 310°C the yields of formic acid in carbonated water were considerably lower than in neat subcritical water. Furthermore, the small error bars indicate a high degree of consistency in the data obtained from three replicates on the experiments. However, at 310°C, there was a considerable more standard deviation associated in the recorded data for the yield trend with time for formic acid. The reason for the high error bars can be due to the variation in the further degradation of furfural and formic acid to degradation products.

4.6 Effect of Severity on the Yields of Carbochemicals and Solid Loss

Figure 4.15 represents the effect of reaction severity as defined in Chapter 3, on the formation of carbochemicals such as HMF, furfural and acids in carbonated water. It can be seen that logarithmic severity factor log (R_o) as discussed in Section 3.5.3 represents the combined effect of temperature and time on the biomass substrate. It can be observed that the yields of carbochemicals are a strong function of the logarithmic severity factor. The yields of organic acid are highest at log (R_o) of 7. At highest severity conditions (310°C) the yields of the carbochemicals are decreased. This confirms our previous discussions on the effect of higher temperature and time on the biomass substrate and the degradation of carbochemicals. Hence, it can be concluded that the yields of carbochemicals and the acids from switchgrass as a substrate

in a semi-continuous flow reactor system can be optimized at an intermediate level of severity among the factors tested in this study.

Figure 4.15 also displays the percentage of the solid loss from the reaction cell. The solid loss is highest at the higher severity conditions, thus explaining the previously discussed effects of high temperature on the solubilization of the biomass substrate. The solubilization effect is temperature based and severity factor correlates the effect of temperature and the solubilization of the switchgrass substrate.
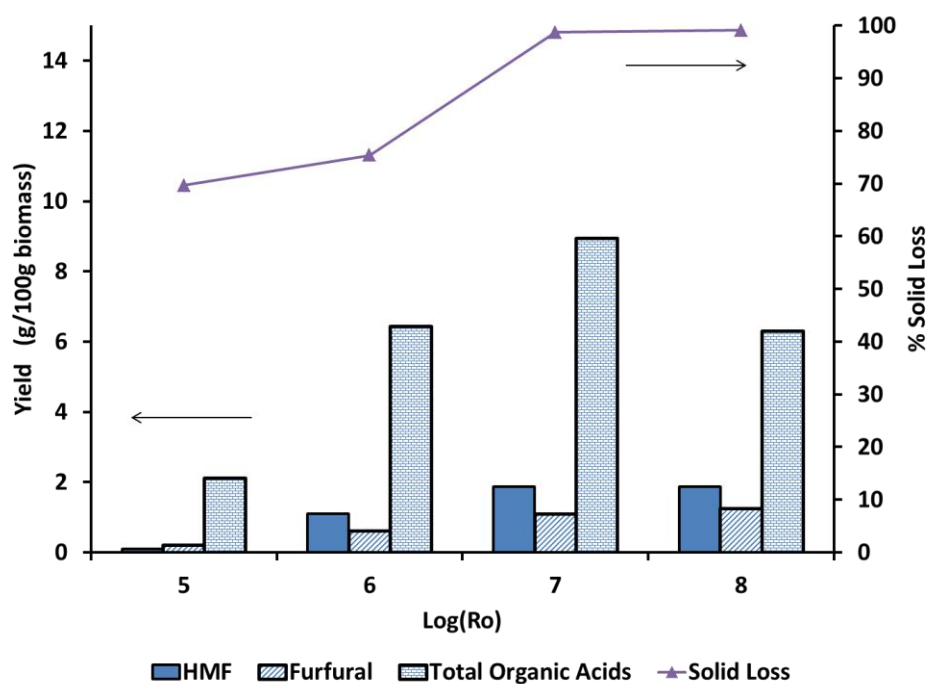
Figure 4.15: Effect of severity factor on the yields of carbochemicals

4.7 SEM (Scanning Electron Microscopy) Analysis of Hot Carbonated Water treated Samples.

Switchgrass samples after treatment at various temperatures were analyzed for their morphology using E-SEM. From SEM photomicrographs (Figures 4.16 (a-d)) it can be seen that the biomass (switchgrass) showed variations in the morphology for the treated vs. untreated samples. The untreated sample (Figure 4.14-a) showed a uniform surface and a compact but well intact structure.
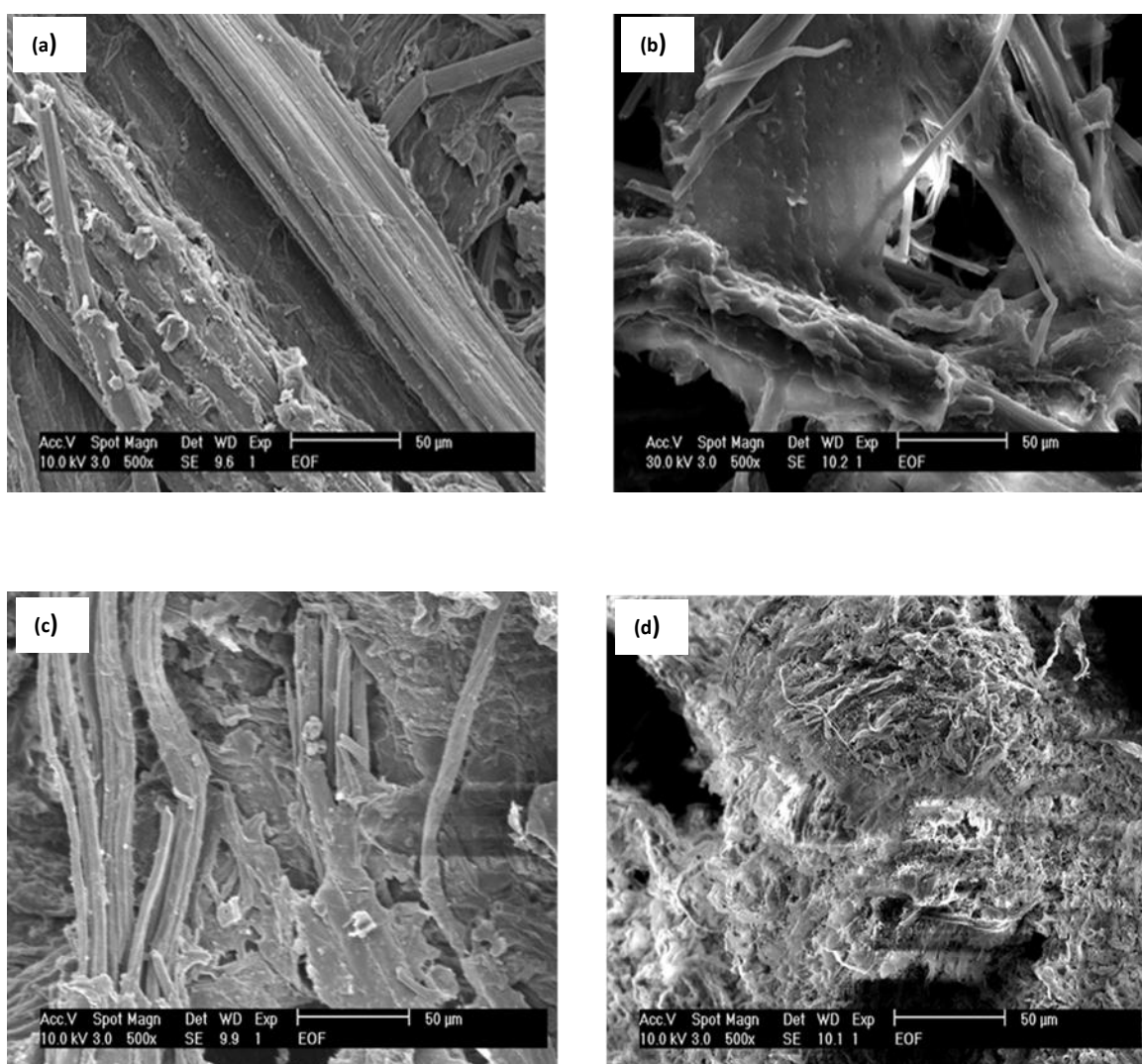
Figure 4. 16: SEM Analysis of hot carbonated water treated samples: (a) Untreated, (b) 220°C, (c) 250°C, (d) 280°C

At 220°C the surface characteristics showed slight disintegration of the surface but the overall structure still seemed to be intact. Furthermore, as the temperatures are increased from 250°C to 280°C, the surface showed considerable particulate disintegration due to increasing severity of the reaction medium. Hydrothermal processing of biomass using subcritical water is an effective method that can significantly expose the internal structures and components in the biomass. This effect results in better access to the cellulose, which forms the inner most recalcitrant portion of lignocellulose vulnerable towards conversion to carbochemicals, such as HMF and furfural. In fact, due to extreme severity at temperatures above 250°C, considerable degradation of the carbochemicals to acids occurs resulting in lower yields of HMF and furfural. This is confirmed by the SEM photomicrographs which confirm the severity of the reaction medium towards switchgrass for the conversion of switchgrass to carbochemicals.

4.8 Reaction Kinetics for HMF and Furfural Formation

The conversion of biomass to carbochemicals such as HMF, furfural and acids proceeds via the formation of monomeric and oligomeric sugars. A number of research groups have applied reaction engineering fundamentals towards the modeling the biomass conversion reaction mechanisms [123,124]. The reaction kinetics of the biomass conversion are generally based on first order conversion process. In this section, the data for the formation and subsequent degradation of the carbochemicals will be discussed. The reaction kinetics parameters such as rate constants will be calculated and activation energy for the HMF formation step will be presented.

4.8.1. HMF Reaction Kinetics

The reaction rate constant k_1 and k_2 were determined using solver function in Microsoft Excel. These constants were found by minimizing the sum of squares of the error between the

calculated concentration and the experimental values. During the analysis of the hydrolyzate samples, it was found that HMF and furfural was produced instantaneously. Moreover, the concentration of the oligomeric sugars was found to be higher than the monomeric sugars. Due to marginal yields of monomeric sugars (glucose), modeling of such low concentration was found to be difficult. Hence, a conversion mechanism that assumed direct conversion of switchgrass (containing cellulose) to HMF was developed as shown in Equation 4.1.

The following series reaction for the formation and degradation of HMF from raw biomass containing cellulose and hemicellulose was used to model the experimental data for the conversion of switchgrass to carbochemicals in carbonated water. The rate constant k_1 represents the HMF and furfural formation step and k_2 represents the further conversions of the carbochemicals to degradation products such as organic acids.

The reaction mechanism for the formation of furfural and the degradation is shown in the following equation:

$$\textbf{Cellulose} \xrightarrow{k_1} \textbf{HMF} \xrightarrow{k_2} \textbf{degradation products} \tag{4.1}$$

Table 4.1. Rate constants for HMF formation and degradation (refer to equation 4.1)

Temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})	k_1/k_2
250	1.18E-03	3.32E-04	3.55
280	7.48E-02	1.38E+00	0.05
310	1.70E-01	1.30E+00	0.13

From Table 4.1, it can be seen that the rate constants for the HMF formation step is higher indicating at lower temperature the formation of HMF is favored over the degradation. On the other hand, the rate constant for the degradation reaction was found to be dominating at

temperatures of 280°C and 310°C. The results are consistent to that discussed in the previous sections wherein the further degradation of the HMF was one of the considerations for the reduced yields of HMF at higher temperatures.

Figure 4.17 (a-c) shows the model for HMF using the best fit by estimating the values k_1 and k_2 for the HMF formation and the degradation step respectively. The model is based on the first order series reaction for the formation of HMF and its subsequent degradation.

(a)
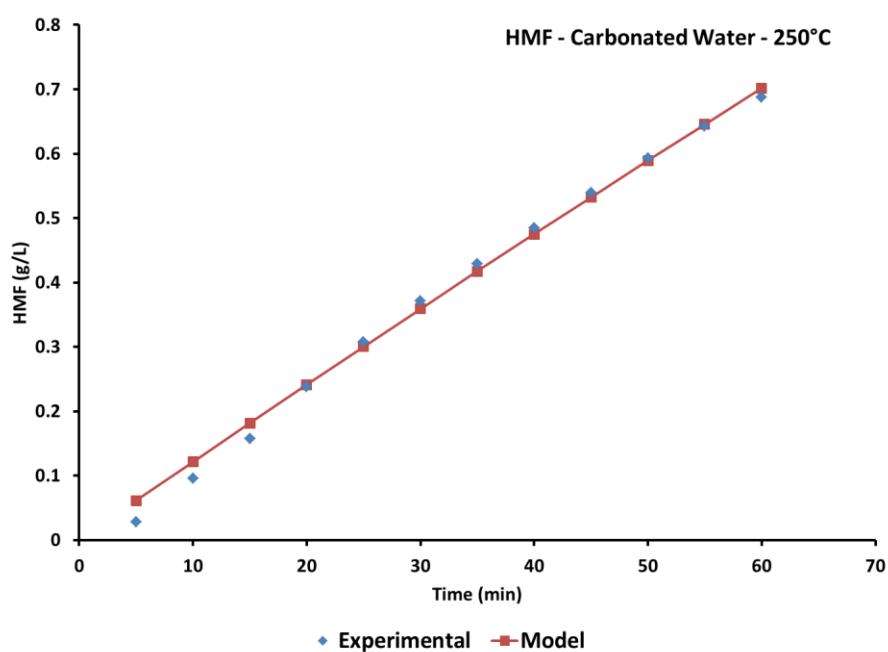
(b)
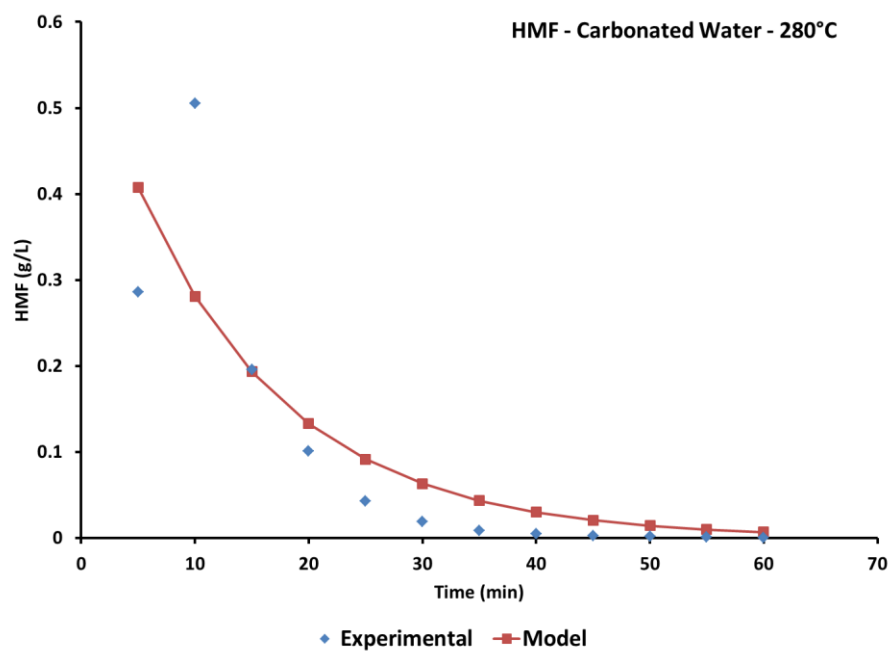
(c)
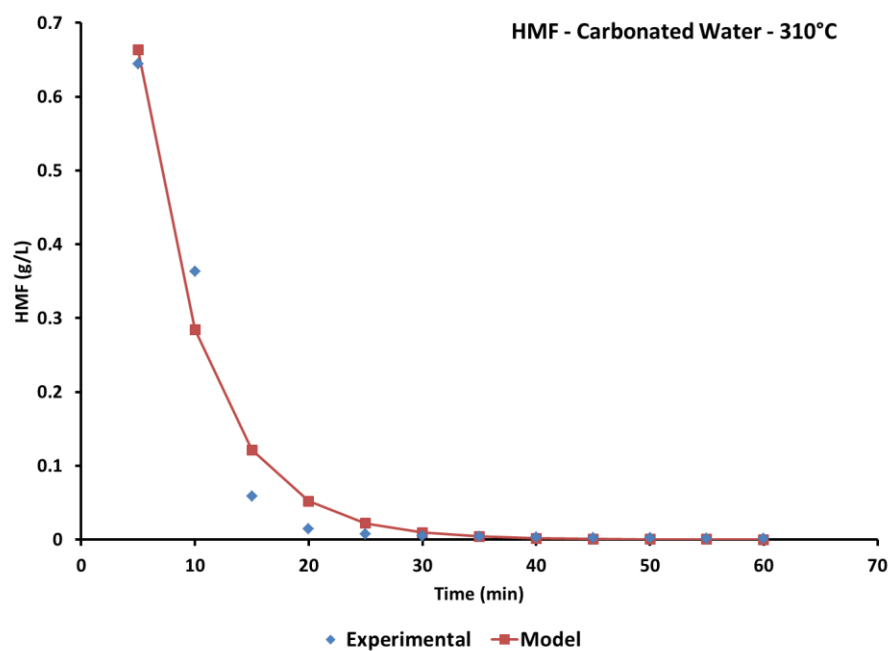
Figure 4.17: Concentration profile for HMF in carbonated water. (a) 250°C, (b) 280°C, (c) 310°C

Figure 4.18 provides the relationship between the rate constant for the formation of HMF and the temperature. Figure 4.18 is plotted using the Arrhenius relationship between the rate constants and the temperature.

$$k = k_0 \exp(\frac{E}{RT})$$
<div align="right">(4.2)</div>

where k = rate constant

k_0 = pre-exponential factor

E = activation energy (kJ/mol)

R = gas constant

T = temperature (K)

The above equation can be solved in the following logarithmic form:

$$\ln(k) = -\frac{E}{RT} - \ln(k_0)$$
<div align="right">(4.3)</div>

The solution to the above equation can be obtained using the linearized form y = mx+c form. From the Figure 4.18, it can be seen that, the slope can be used to calculate the activation energy of the reaction. The activation energy for the formation of HMF was found to be 212.4kJ/mol. The straight line fit of ln(k) vs 1/T shown in Figure 4.18 has an r^2 value of 0.89

Figure 4.18: Relationship between the rate constants and the temperature.

4.8.2 Furfural Reaction Kinetics

Similar to the kinetics for the HMF formation and subsequent degradation as shown in the Equation 4.1, the kinetic study for furfural formation and degradation was conducted. It was observed that, only marginal concentration of xylose (monomer) was found in the hydrolyzate. Hence, a similar mechanism is postulated in which biomass (containing hemicellulose) was converted to furfural was developed as shown in Equation 4.2 below.

$$\textbf{Hemicellulose} \overset{\textbf{k}_1}{\rightarrow} \textbf{furfural} \overset{\textbf{k}_2}{\rightarrow} \textbf{degradation products} \tag{4.4}$$

Table 4.2 represents the rate constants that are calculated using solver function in Microsoft excel. It can be seen from the ratio of the rate constants that the furfural formation step was higher for 250°C and 310°C. It can be observed that the rate of formation of furfural was lower on all the three conditions studied for the kinetics of furfural formation. This can be due to

the high severity of the reaction resulting in further degradation of furfural. The high rate of the rate constant k_2 indicates that the furfural degradation step dominates the overall reaction mechanism.

This is an interesting observation considering the overall yields for furfural were lower as compared to that reported in the literature. This decrease in the yields of furfural can be due to a number of factors such as high degradation rates, self-polymerization of furfural and formation of degradation products.

Table 4.2 Rate constants for furfural formation and degradation (refer to equation 4.12)

Temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})	k_1/k_2
250	4.44E-01	2.64E+00	0.16
280	1.41E-01	1.86E+00	0.07
310	2.67E-01	1.15E+00	0.23

(a)
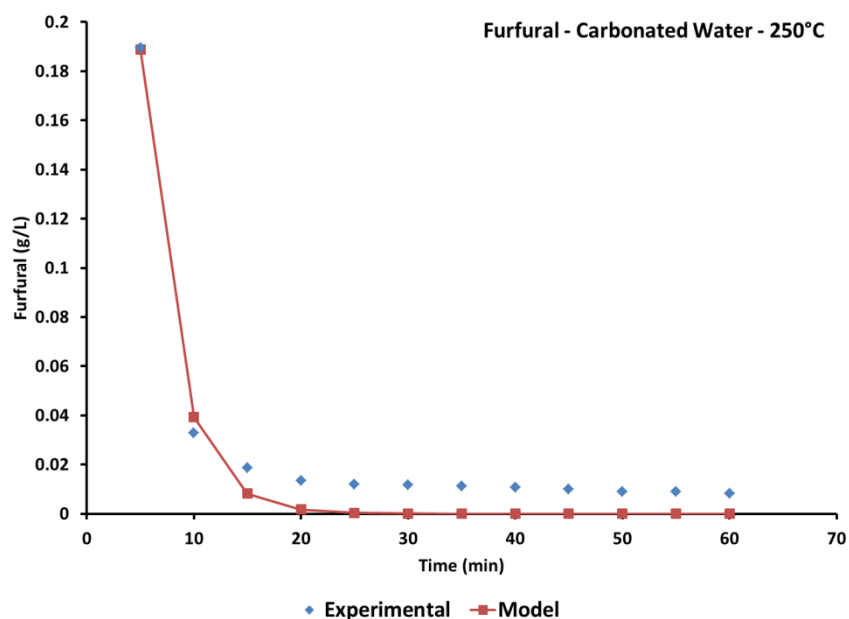
(b)
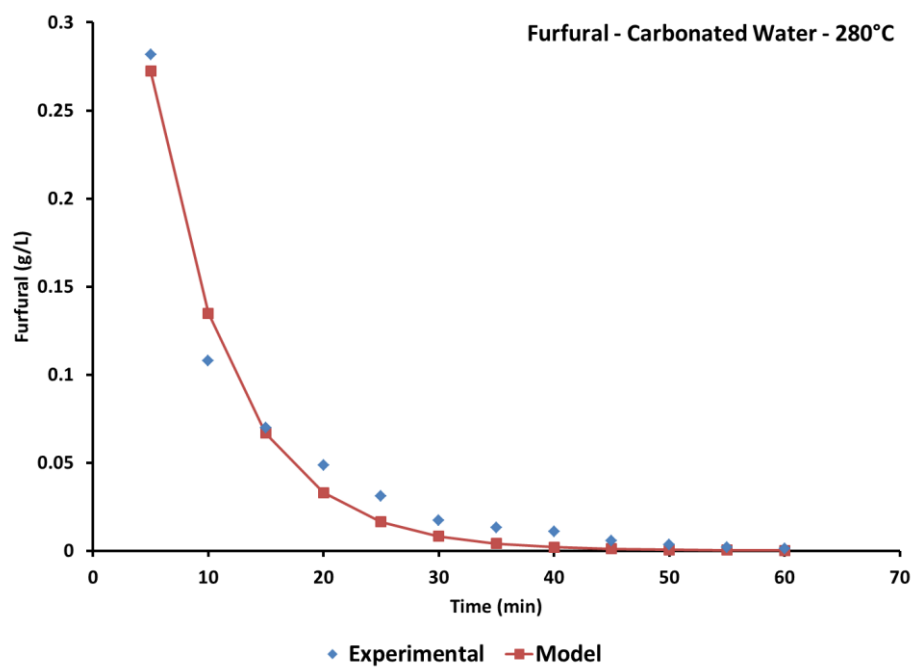
(c)
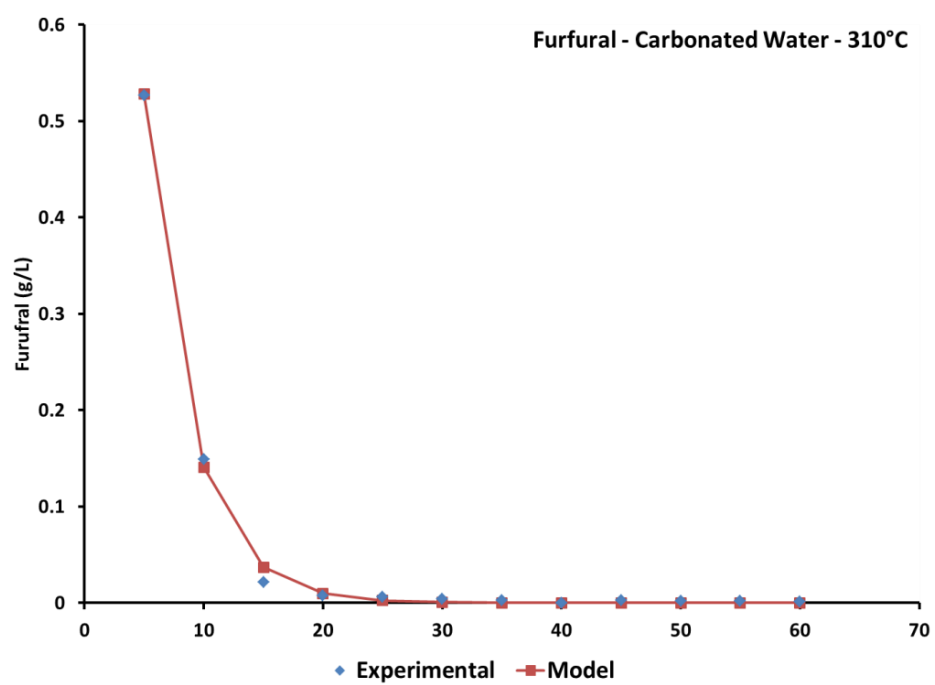
Figure 4.19: Concentration profile for furfural in carbonated water. (a) 250°C, (b) 280°C, (c) 310°C

Figure 4.19 (a-c) shows the concentration of furfural in carbonated water as a function of temperature at 250, 280, and 310°C. The model curves were obtained by using the best fit curve for the experimental values and the values predicted by the furfural formation and degradation model. The rate constants obtained for each model are shown in the Table 4.2.

Figure 4.20 provides the relationship between the rate constant for the formation of furfural and the reaction temperature. Figure 4.20 is plotted using the Arrhenius relationship as shown in the Equation 4.5 between the rate constants and the temperature.

$$k = k_0 \exp(\frac{E}{RT})$$

(4.5)

where: k = rate constant

k_0 = pre-exponential factor

E = activation energy (kJ/mol)

R = gas constant

T = temperature (K)

The above equation can be solved in the following logarithmic form:

$$\ln(k) = -\frac{E}{RT} - \ln(k_0)$$

(4.6)

The solution to the above equation can be obtained using the linearized form y = mx+c form. From Figure 4.20, it can be seen that the slope can be used to calculate the activation energy of the reaction. The activation energy for the formation of furfural was found to be 22.92kJ/mol. The straight line fit of ln(k) vs 1/T shown in Figure 4.20 has an r^2 value of 0.22.
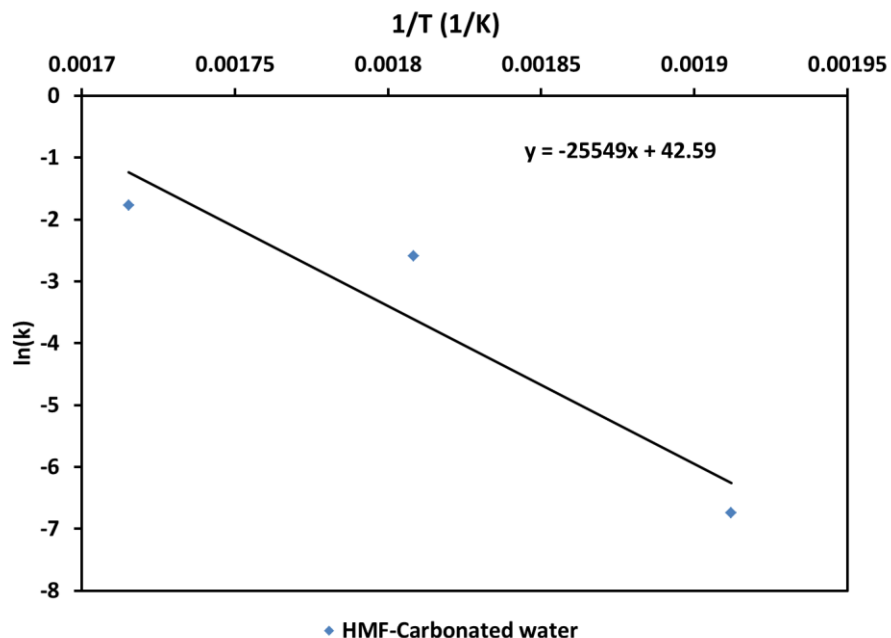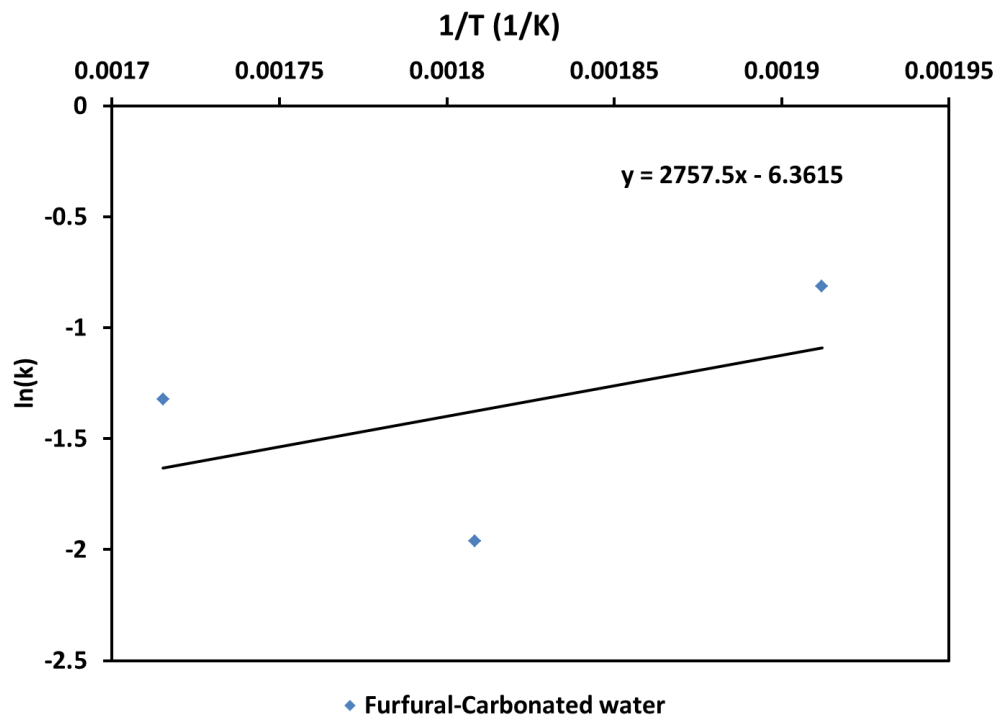
Figure 4.20: Relationship between the rate constants and the temperature.

The r^2 values for the temperature dependence of furfural formation under the conditions tested cannot be established. The lack of fit for the data for furfural formation can be due to further degradation and inconsistencies due to the escaping tendency for furfural from the aqueous phase. Moreover, factors such as furfural polymerizing under the conditions of high severity can also be attributed to the lack of consistent data for the kinetic study of furfural formation.

Kinetic analysis for the formation and degradation of HMF and furfural in carbonated water are discussed in Sections 4.8.1 and 4.8.2. A similar calculation was performed for HMF and furfural formation and degradation in subcritical water. Due to the inconsistency in the kinetic data and lack of fit for the subcritical water for the HMF and furfural, a clear comparison on the effect of carbonated water and subcritical water towards the formation of HMF and furfural based on the kinetic parameters is not discussed and requires additional investigation.

Chapter 5. Conclusions and Recommendations for Future Work

In this study a semi-continuous flow reactor system was used to convert biomass (switchgrass) into carbochemicals such as HMF, furfural and organic acids using water as a green solvent and carbonated water as a green catalyst. A range of temperatures were studied such (220, 250, 280, 310°C). It was found that carbonated water showed catalytic activity in converting biomass to carbochemicals. The cumulative yield of HMF and furfural and organic acids were found to be higher in carbonated water than in subcritical water. Moreover, it was found that the activity of carbonated water to catalyze the conversion decreased with the increase in the temperature. The cumulative yields for HMF and furfural were found to be highest at 310°C. Moreover, the cumulative yields for total organic acids were found to be even higher at 280°C. The total sugars content in the resultant hydrolyzates were found to be highest at 250°C in carbonated water as well as in subcritical water.

The reaction mechanism for the formation and degradation of HMF and furfural were modeled using a hypothetical series reaction with k_1 and k_2 being the rate constants for the formation and degradation respectively for HMF and furfural. It was observed that HMF formation reaction showed Arrhenius dependence, whereas the temperature dependence for furfural formation was unclear.

The further development of the system will be a critical consideration for the future since a semi-continuous system can be considered as a step towards a full-scale industrial continuous process. Hence, further test on the effectiveness of the system towards conversion of biomass would be welcomed. Future studies can be based on the use of model compounds such as pure cellulose, xylose or glucose for the development of the kinetics of conversion to carbochemicals in subcritical water and carbonated water. Moreover, a more extensive study can be performed

on the parameters such as effect of pressure, flowrate and the particle size of the biomass, particularly at lower flowrates for the reaction water.

The development of more sophisticated HPLC analysis systems which will enable us to study the production of oligomers as part of the biopolymer depolymerization process. Since, it was observed that the concentration of the oligomers is higher than the monomers in a semi-continuous reactor system, it will be critical to utilize an analysis system that will enable us to quantify oligomeric concentrations of the components involved. This will ensure a better analysis and mass balance of the components involved. Moreover, an analysis system that can separate the chromatographic peaks for levulinic and acetic acid needs to be implemented.

Several solid acids such as zeolites such as ZSM-5, H-Y, and H-mordenite have found catalyze reaction towards the formation of the carbochemicals. Hence, implementation of the flow reactor system utilizing a packed catalyst bed will be considered. Investigations can be based on determining optimal process conditions for temperature and flowrates for conversion of raw biomass in aqueous media to carbochemicals in presence of heterogeneous solid catalyst.

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