Rational Development of Carbon-Based Materials for Adsorption-Enhanced Conversion of Cellulose to Value-Added Chemicals

Paul J. Dornath

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RATIONAL DEVELOPMENT OF CARBON-BASED MATERIALS FOR
ADSORPTION-ENHANCED CONVERSION OF CELLULOSE TO VALUE-ADDED
CHEMICALS

A Dissertation Presented

by

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DEDICATION

This work is dedicated with love to Todd Dornath
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ABSTRACT

RATIONAL DEVELOPMENT OF CARBON-BASED MATERIALS FOR ADSORPTION-ENHANCED CONVERSION OF CELLULOSE TO VALUE-ADDED CHEMICALS

FEBRUARY 2016

PAUL JOHN DORNATH, B.S., OREGON STATE UNIVERSITY Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Wei Fan

The increasing demands for transportation fuels and commodity chemicals as well as concerns over diminishing fossil fuel resources have driven research efforts towards the efficient utilization of renewable feedstocks, such as naturally abundant lignocellulosic biomass. Co-impregnation of microcrystalline cellulose with dilute sulfuric acid and glucose catalyzed the formation of $\alpha(1\rightarrow6)$ branches onto $\beta(1\rightarrow4)$ glucan prior to ball-milling and reduce the time needed for ball-milling 4-fold compared to impregnation with acid alone. A three dimensionally ordered mesoporous (3DOM) carbon-based catalyst was developed that rapidly hydrolyzed the water-soluble glucan oligomers to 91.2 % glucose yield faster than conventional approaches.

A structure-property relationship was developed for adsorption of saccharides on the carbon catalyst. Van ’t Hoff relationships were derived from adsorption isotherms of glucose and cellobiose and revealed that the adsorption enthalpy increased with increasing chain-length due to the increasing number of CH-$\pi$ interaction between the saccharides and the carbon surface. Adsorption entropy increased with increasing chain-length and with increasing surface hydrophobicity due to the release of solvated water molecules. The catalyst was optimized for glucose production by tuning the sulfonic to adsorption site ratio, which was easily tuned by controlling the precursors during the diazonium sulfonate functionalization step.

The structure-property relationship of carbon materials with key reaction intermediates has also be studied in an effort to develop a green approach to furan extraction. Formation of HMF...
from the dehydration of fructose over zeolite catalysts in aqueous phase was studied in a reactive adsorption system using carbon black (BP2000) as an adsorbent. The dehydration of fructose over zeolite beta catalyst in water revealed that selectivity to HMF is largely influenced by the formation of levulinic acid and formic acid as well as humins from HMF. Reactive adsorption with carbon adsorbents was used to increase selectivity by preventing further reaction of HMF. It was found that BP2000 exhibited high selectivity and capacity for the adsorption of HMF from aqueous phase and was similar to that obtained from the reaction system using MIBK as an extraction phase. The unique adsorption performance of BP2000 is likely due to the large surface area, hydrophobic nature and micropore volume.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xix</td>
</tr>
<tr>
<td>CHAPTER 1: INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1: Lignocellulosic biomass: Renewable feedstock for fuels and chemicals</td>
<td>1</td>
</tr>
<tr>
<td>1.2: Production of value-added chemicals from cellulose</td>
<td>4</td>
</tr>
<tr>
<td>1.3: Challenges with cellulose hydrolysis</td>
<td>6</td>
</tr>
<tr>
<td>1.4: Introduction to solid acid catalysts and carbon materials for cellulose conversion</td>
<td>8</td>
</tr>
<tr>
<td>1.5: Production of 5-hydroxymethylfurfural (HMF)</td>
<td>12</td>
</tr>
<tr>
<td>1.6: Project objectives</td>
<td>14</td>
</tr>
<tr>
<td>CHAPTER 2: EFFICIENT MECHANOCATALYTIC DEPOLYMERIZATION OF CELLULOSE</td>
<td>16</td>
</tr>
<tr>
<td>2.1: Abstract</td>
<td>17</td>
</tr>
<tr>
<td>2.2: Introduction</td>
<td>17</td>
</tr>
<tr>
<td>2.3: Experimental section</td>
<td>21</td>
</tr>
<tr>
<td>2.3.1: Materials</td>
<td>21</td>
</tr>
<tr>
<td>2.3.2: Preparation of acidulated ball-milled cellulose</td>
<td>22</td>
</tr>
<tr>
<td>2.3.3: Characterization of acidulated ball-milled cellulose</td>
<td>22</td>
</tr>
<tr>
<td>2.3.4: Catalyst synthesis</td>
<td>23</td>
</tr>
<tr>
<td>2.3.4.1: Synthesis of 3DOM carbon</td>
<td>23</td>
</tr>
<tr>
<td>2.3.4.2: Synthesis of 3DOM carbon catalyst</td>
<td>24</td>
</tr>
</tbody>
</table>
2.3.5: Characterization ................................................................. 25

2.4: Results and discussion .......................................................... 28

2.4.1: Acid and saccharide co-impregnation .................................... 28

2.4.2: Comparison of α(1→6) branched portion for G-ABMC and N-ABMC ................................................................. 32

2.4.3: Physical mixture experiments ............................................... 35

2.4.4: Hydrolysis of soluble glucan oligomers over SO_3H-3DOM carbon catalyst ................................................................. 37

2.4.4.1: SO_3H-carbon characterization ........................................... 37

2.4.4.2: Hydrolysis reaction results ................................................ 39

2.5: Conclusion ......................................................................... 41

2.6: Acknowledgements ............................................................ 41

3. ADSORPTION PROPERTIES OF THREE-DIMENSIONALLY ORDERED MESOPOROUS CARBON CATALYSTS FOR THE SELECTIVE HYDROLYSIS OF GLUCAN OLIGOMERS ........................................... 43

3.1: Abstract ............................................................................. 43

3.2: Introduction ....................................................................... 44

3.3: Experimental section .......................................................... 46

3.3.1: Materials ....................................................................... 46

3.3.2: 3DOM carbon synthesis and functionalization ...................... 46

3.3.3: Carbon characterization .................................................. 47

3.3.4: Chain-length analysis of large oligomers ............................. 49

3.3.5: Saccharide adsorption ..................................................... 50

3.3.6: Excess adsorption calculations ......................................... 52

3.3.7: Chain length distribution before and after adsorption .......... 53

3.3.8: Catalytic reaction ........................................................... 53

3.4: Results and discussion ....................................................... 54

3.4.1: Textural properties ......................................................... 54

xii
LIST OF TABLES

Table 2.1: Yields of glucose and glucan oligomers in the soluble component of different acidulated ball-milled cellulose measured by HPLC ........................................... 32

Table 2.2: Anomeric AGU abundance in different acidulated ball-milled cellulose samples calculated from $^1$H-NMR ................................................................. 34

Table 2.3: Textural properties of SO$_3$H-carbon ........................................ 39

Table 2.4: Langmuir isotherm constants of saccharides adsorption on SO$_3$H-3DOm-carbon at room temperature ............................................................. 39

Table 3.1: Prior model parameters for Bayesian inference peak fitting of Raman spectroscopy ................................................................. 49

Table 3.2: Textural properties of parent-3DOm and SO$_3$H-3DOm carbons ........ 55

Table 3.3: Room temperature Langmuir adsorption constants for glucon of different chain-lengths ................................................................. 61

Table 3.4: Langmuir adsorption constants for glucose and cellobiose on parent and SO$_3$H-3DOm carbon at different temperatures ......................................... 67

Table 3.5: Adsorption enthalpy and entropy of cellobiose and glucose on parent-3DOm and SO$_3$H-3DOm carbon ................................................................. 68

Table 4.1: Soluble portion of samples milled for 1 h using different impregnation solvents and solvent boiling points ................................................................. 79

Table 4.2: Chain-length and branching data obtained from $^1$H-NMR of fractionated oligomers prepared from milling of water and ethanol solvent impregnated samples milled for 1 h ................................................................. 81

Table 5.1: Adsorption isotherm models used to fit the adsorption data ...................... 96

Table 5.2: Textural properties of the carbon materials measured from Nitrogen adsorption/desorption ................................................................. 99

Table 5.3: Adsorption isotherm parameters for chemicals adsorption on carbon materials measured at 298 K ................................................................. 101

Table 5.4: Surface oxygen containing groups on different carbon materials ............ 102

Table 5.5: Adsorption on H-BEA with 10 mg mL$^{-1}$ initial concentration .............. 110
<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1: Biopolymer abundance in lignocellulosic biomass</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1.2: Strategies for production of fuels from lignocellulosic biomass put forth by Huber and Dumesic</td>
<td>3</td>
</tr>
<tr>
<td>Figure 1.3: Renewable chemicals from cellulose: 1: Hydrolysis of cellulose to glucose; 2: Conversion of glucose to 5-hydroxymethyl furfural (HMF); 3: Production of levulinic acid and jet fuel additives; 4: Production of p-xylene and aromatics; 5: Production of Ethoxymethyl furfural; 6: Production of hydrogen; 7: Production of ethanol; 8: Production of mannitol; 9: Production of sorbitol</td>
<td>5</td>
</tr>
<tr>
<td>Figure 1.4: Production of p-xylene from cellulose. Topics in this thesis listed in red</td>
<td>6</td>
</tr>
<tr>
<td>Figure 1.5: Hydrolysis mechanism of cellulose from Rinaldi et al. The glycosidic oxygen is protonated followed by unimolecular scission of the glycosidic bond which occurs with a half chair rotational conformation change. Nucleophilic attack of water reestablishes the hydroxyl group</td>
<td>8</td>
</tr>
<tr>
<td>Figure 1.6: Carbon structure from Hara et al. and Katz et al.</td>
<td>10</td>
</tr>
<tr>
<td>Figure 1.7: Brønsted acid catalyzed reaction of fructose and HMF</td>
<td>13</td>
</tr>
<tr>
<td>Figure 1.8: Extraction solvent systems for HMF production from fructose</td>
<td>13</td>
</tr>
<tr>
<td>Figure 2.1: Cover art for Chapter 2 featured in Green Chemistry</td>
<td>16</td>
</tr>
<tr>
<td>Figure 2.2: HPLC Chromatograms from 2h-G-ABMC, glucose (G1), isomaltose (G2) and the cellodextrins cellobiose (G2), cellotriose (G3), cellotetraose (G4), cellopentaose (G5) and cellohexaose (G6) as well as levoglucosan (LGA) are shown</td>
<td>26</td>
</tr>
<tr>
<td>Figure 2.3: 1H-NMR spectrum of LGA in D2O</td>
<td>27</td>
</tr>
<tr>
<td>Figure 2.4: Mass spectra of A) LGA collected by fractionation of 2h-G-ABMC and B) standard LGA sample</td>
<td>27</td>
</tr>
<tr>
<td>Figure 2.5: Soluble portion percentage from acidulated ball-milled cellulose after 1.0 and 2.0 h of milling determined by HPLC. Error bars present a 95% confidence interval of the average soluble portion</td>
<td>31</td>
</tr>
<tr>
<td>Figure 2.6: 10 wt.% i-G-ABMC in water at different milling times</td>
<td>31</td>
</tr>
<tr>
<td>Figure 2.7: 1H-NMR spectra of 2.0 h ball-milled cellulose co-impregnated with glucose (2h-G-ABMC) and 2.0 h ball-milled cellulose impregnated only with acid (2h-N-ABMC)</td>
<td>33</td>
</tr>
</tbody>
</table>
Figure 2.8: α(1→6) linkages and sample solubility for G-ABMC and N-ABMC. .......................... 34

Figure 2.9: α(1→6) linkages and sample solubility for G-ABMC and PM-ABMC. ....................... 36

Figure 2.10: Nitrogen physisorption isotherms of parent 3DOM carbon and SO₃H 3DOM carbon catalyst at 77 K. ................................................................. 38

Figure 2.11: SAXS of 3DOM carbon and SO₃H 3DOM carbon catalyst. ................................. 38

Figure 2.12: Adsorption isotherms for glucose and water-soluble glucan oligomers from 2.0 h ball-milled cellulose co-impregnated with glucose (2h-G-ABMC) on SO₃H-3DOM carbon at room temperature. Data points are from experiments. Line is a fitted Langmuir model................................................................. 39

Figure 2.13: A) Turnover frequency (TOF) of SO₃H-3DOM carbon and HCl for 2.0 h ball-milled cellulose co-impregnated with glucose (2h-G-ABMC) at 120 °C in water (reaction time: 2.0 h, conversion: < 20 %), and B) Glucose yield from 2h-G-ABMC, non-milled acidulated cellulose (0h-N-ABMC) and microcrystalline cellulose (0h-MCC) over SO₃H-3DOM carbon at 165 °C......... 40

Figure 2.14: Carbon catalyst reproducibility. Cellulose was reacted for 6 h at 120 °C and washed with DIW at 70 °C until all reactants and products were removed (checked by HPLC). ................................................................. 41

Figure 3.1: Textural properties of parent-3DOM and SO₃H-3DOM carbons. A) Nitrogen adsorption/desorption isotherms. B) Pore size distribution calculated from the adsorption branch using QSDFT model. C) SAXS ................................................................. 55

Figure 3.2: Raman scattering spectra of carbon materials. A) Parent and SO₃H-3DOM carbon. B) Peak deconvolution of Raman spectrum of parent-3DOM carbon............. 57

Figure 3.3: Optimization of acid sites and adsorption properties of the 3DOM catalyst.  
(A) Control of the number of acid sites on 3DOM carbon by tailoring the amount of sulfanilic acid precursor in solution. The x-axis is the amount of sulfanilic acid used during synthesis and the y-axis is the number of sulfonic acid groups functionalized on the carbon. (B) Correlation between cellobiose adsorption capacity and sulfonic acid groups on various SO₃H-3DOM carbons. The number of sulfonic groups plus the number of cellobiose adsorption sites is approximately constant. (C) TOF obtained from the hydrolysis of cellobiose over SO₃H-3DOM carbons with different amounts of sulfonic acid sites. ................................................................. 59

Figure 3.4: ¹H-NMR of fractionated oligomers produced from 1 hour milling of cellulose co-impregnated with acid and 12.5 wt.% glucose. Reducing ends (RE) and linkage peaks are labeled. ................................................................. 60

Figure 3.5: Corrected room temperature adsorption of glucose, cellobiose and mixed oligomers on (A) parent-3DOM carbon and (B) SO₃H-3DOM carbon. The points are from experimental measurement. The lines are from Langmuir adsorption fitting. ................................................................. 60
Figure 3.6: Oligomer distribution data. A: Distribution starting from 1 mg ml⁻¹. B: Starting from 10 mg mL⁻¹. C: Starting from 50 mg mL⁻¹.

Figure 3.7: Room temperature maximum capacity of saccharide species on parent-3DOm and SO₂H-3DOm carbon.

Figure 3.8: Real adsorption isotherms for (A) cellobiose on parent-3DOm carbon; (B) cellobiose on SO₂H-3DOm carbon; (C) glucose on parent-3DOm carbon; and (D) glucose on SO₂H-3DOm carbon. Adsorption was measured at 0, 20, 50 and 70 °C. The points are from experimental measurement. The lines are from Langmuir adsorption fitting.

Figure 3.9: Van’t Hoff Diagram of cellobiose and glucose adsorption on parent-3DOm and SO₂H-3DOm carbon.

Figure 4.1: Soluble portion of samples milled for 1 h after using different impregnation solvents.

Figure 4.2: ¹H-NMR of the large oligomer fraction obtained from samples using either water or ethanol as the impregnation solvent milled for 1 hour.

Figure 4.3: Soluble portion yield cellulose impregnated with n-butanol and acid milled for 1 h after different 60 °C aging times.

Figure 4.4: ¹H-NMR of T₀ glucose and acid impregnated samples. Sample GW-24H-CEA-3H had glucose and no acid for 24 h, sample NGW-0H-0EA-24H had acid and no glucose for 24 h, and sample GW-0H-0EA-24H has both acid and glucose for 24 h.

Figure 4.5: Soluble oligomer yield after A) 10 and B) 20 minutes of glucose and acid co-impregnated samples.

Figure 4.6: ¹H-NMR of reported and measured ¹H-NMR of disaccharides and milled glucose: A)¹²⁹, B)¹³⁰ and C)¹²⁹) ¹H-NMR spectra plotted using peak position and peak splitting data reported in literature. Tall and short lines correspond to β and α reducing end isomers in a 62 : 38 ratio; D – E) ¹H-NMR spectra of cellobiose and isomaltose standards; F) ¹H-NMR of milled glucose for comparison.

Figure 5.1: Nitrogen physisorption isotherms for carbon materials.

Figure 5.2: Single component adsorption isotherms at room temperature fitted with the Redlich Peterson model. a) HMF adsorption isotherms on BP2000, 3DOm, OX-BP2000 and Norit Ultra carbons. b) HMF, levulinic acid (LA) and fructose adsorption on BP2000. c) HMF, levulinic acid and fructose adsorption on OX-BP2000.

Figure 5.3: Multicomponent adsorption on BP2000 at room temperature. The data was measured using the solutions with equal masses of HMF, levulinic acid and fructose.
Figure 5.4: Adsorption isotherm of HMF on BP2000 at different temperatures. The dots are from experiments. The lines are from fitting using the Redlich-Peterson adsorption model.

Figure 5.5: Fructose conversion, furan, levulinic and formic acid selectivity from the reaction systems with and without using carbon adsorbent BP2000. Fructose dehydration with H-BEA and 2 wt.% BP2000 at a) 393 K, b) 423 K and c) 438 K. d) Fructose conversion vs. HMF selectivity using H-BEA under different temperatures.

Figure 5.6: Fructose conversion and HMF selectivity for fructose dehydration catalyzed by H-BEA with different amounts of BP2000 loading. (Reaction conditions: 1.2 wt.% fructose, 4 h, 423 K).

Figure 5.S1: Single component isotherms for HMF, levulinic acid and fructose on 3DOM carbon (a) and Norit Ultra activated carbon (b). The dots are from experiments. The lines are from fitting using the Redlich-Peterson adsorption model.
# LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme 2.1: Hydrogen bonding structure of cellulose.</td>
<td>18</td>
</tr>
<tr>
<td>Scheme 2.2: Chemical structure of an α(1→6) branched β(1→4) glucan oligomer</td>
<td>20</td>
</tr>
<tr>
<td>Scheme 2.3: Proposed two-step process to produce glucose from crystalline cellulose</td>
<td>21</td>
</tr>
<tr>
<td>Scheme 2.4: Synthesis of 3DOm carbon (credit Wei Fan and Hong Je Cho)</td>
<td>24</td>
</tr>
<tr>
<td>Scheme 2.5: Synthesis SO₃H-3DOm carbon catalyst</td>
<td>25</td>
</tr>
<tr>
<td>Scheme 3.1: Possible arrangement of adsorbed glucose, cellobiose and oligomers on carbon surface</td>
<td>64</td>
</tr>
<tr>
<td>Scheme 3.2: Adsorption of glucan oligomers on parent-3DOm carbon</td>
<td>65</td>
</tr>
<tr>
<td>Scheme 3.3: Representation of cellobiose and carbon surface desolvation upon adsorption</td>
<td>68</td>
</tr>
<tr>
<td>Scheme 4.1: Hydrolysis mechanism of cellulose from Rinaldi et. al.</td>
<td>75</td>
</tr>
<tr>
<td>Scheme 5.1: Chapter 5 Graphical Abstract</td>
<td>91</td>
</tr>
<tr>
<td>Scheme 5.2: Reaction scheme for fructose dehydration in the presence of Brønsted acid catalysts</td>
<td>94</td>
</tr>
<tr>
<td>Scheme 7.1: Theoretical hydrolysis of two glucan trimmers containing both one α(1→6) and one β(1→4) linkage</td>
<td>116</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION

1.1: Lignocellulosic biomass: Renewable feedstock for fuels and chemicals

Today, fossil fuels such as oil, natural gas, and coal produce over 75% of the world’s energy as well as a large portion of commodity chemicals and plastics.¹ The global demand for energy and chemicals is growing while the reserves of fossil fuels are diminishing. The worldwide reserves of oil are only sufficient for approximately another 40 to 50 years of production, leading to concerns about the inevitable rise in prices and depletion of supplies.² The use of fossil fuels has also led to a dramatic increase in the production of CO₂, affecting the global climate.³ Lignocellulosic, or ‘plant-based’, biomass has the potential to serve as a carbon neutral and sustainable feedstock for the production of fuels and value-added chemicals for industrialized society.⁴

Lignocellulosic biomass is one of the most abundant renewable sources of carbon and can be harvested from fast-growing switchgrass, woodchips and other agricultural waste. Over one billion tons of dry lignocellulosic biomass is available annually in the United States.⁵ The US Department of Energy (DOE) has made it a goal to produce 30% of the nation’s liquid-phase transportation fuels and add 25% of industrial derived chemicals from bio-derived chemicals by 2030.⁶ The role of lignocellulosic biomass in the renewable energy sector will come largely as a source of carbon. A number of other renewable options can produce sustainable electricity such as solar, wind, geomethermal, tidal and hydroelectric power. Lignocellulosic biomass, on the other hand, is currently one of the only renewable resources that can be used directly to produce carbon-based fuels and chemicals. Ethanol and precursors for plastics are some of the most important and potentially viable commodity chemicals to be produced from cellulosic biomass, but a variety of other compounds including phenolic resins, cleaning fluids, adhesives, fatty acids, carbon black, paints and coatings, dyes, pigments, detergents, and hydraulic and lubricating fluids can all be produced synthetically from lignocellulosic biomass.⁷
Lignocellulose is composed of three biopolymers as shown in Figure 1.1. On average, it is composed of roughly 40 to 50 wt.% cellulose, which is a polymer of glucose, 25 to 35 wt.% hemicellulose, which is a heteropolymer composed of C5 sugars such as xylose and arabinose as well as some C6 sugars such as galactose, glucose and mannose, and 15 to 20 wt.% lignin, which is a resin-like material containing a variety of moieties including aromatic, phenolic, lactonic and methoxy functional groups. Lignocellulosic biomass typically also contains 1 to 4 wt.% inorganic ash, which includes minerals such as SiO₂ and CaO.

Figure 1.1: Biopolymer abundance in lignocellulosic biomass

In addition to being a renewable feedstock, lignocellulosic biomass has the potential to be a carbon neutral feedstock for fuels by removing CO₂ from the atmosphere produced from the burning of fuel as the feedstock is regrown. However, this point has been much debated, especially for the first generation of biofuels such as corn grain-based ethanol. The cultivation and conversion of corn grain to ethanol requires the use of traditionally non-renewable energy. A gallon of corn grain ethanol produced using electricity generated by either natural gas or coal produces either 7 % or 40 % more greenhouse gases (GHG), respectively, than a gallon of gasoline when factoring in
energy inputs, fertilization, as well as indirect and direct land use.\textsuperscript{10, 11} However, chemicals produced from lignocellulosic biomass need not use corn grain as a feedstock. Nonfood sources, such as prairie biomass and switchgrass, are less nutrient/fertilizer intensive crops. These crops can be cultivated more easily and in more areas than corn, and can utilize lignin combustion as a heat source. As a result, the greenhouse gas emissions using non-corn lignocellulosic biomass has 4 to 12 fold less GHG emissions compared to gasoline depending on the specific feedstock and land usage.\textsuperscript{11}

Lignocellulose can be converted into fuels through three primary routes as shown in Figure 1.2 from Huber et al.\textsuperscript{4} The first route is gasification to produce syngas, which can be used to produce hydrocarbons such as diesel and gasoline as well as methanol. The second route is pyrolysis to produce bio-oil, which is a heterogeneous mixture of over 200 compounds including hydrocarbons, furans and oxygenated organics. The low selectivity to one particular compound requires bio-oil to be upgraded in order to form specific products. The third method is biomass hydrolysis, which allows for the highly selective conversion of cellulose and hemicellulose to sugar monomer units, which can then be selectively converted to fuels and chemicals. There are still many challenges such as development of selective catalysts and efficient separations.

\textbf{Figure 1.2:} Strategies for production of fuels from lignocellulosic biomass put forth by Huber and Dumesic.\textsuperscript{4}
1.2: Production of value-added chemicals from cellulose

The hydrolysis pathway is one of the most important routes for synthesis of biorenewable chemicals due to the abundance of different compounds that can be derived from reducing sugars such as glucose and xylose. This process is high selective compared to pyrolysis due to the low temperatures and relatively fewer number of side reactions. The six-carbon anhydroglucose units in cellulose are the most abundant repeating units in lignocellulosic biomass. Anhydroglucose units can be hydrolyzed to produce glucose. Therefore, many research efforts have been recently driven towards the study of producing a wide variety of fuels and chemicals from glucose as shown in Figure 1.3.

Cellulose can be utilized as a feedstock for many renewable fuels and chemicals. Production of ethanol via fermentation of glucose through biological pathways is one major process currently realized on an industrial scale. Ethanol currently produced from corn is roughly 40% cheaper to produce compared to cellulosic ethanol due to the greater capital costs needed for cellulosic ethanol plants. However, the high price of corn and advances in cellulosic technology are rapidly making cellulosic ethanol more competitive. While ethanol may be one of the first chemicals to be produced commercially from cellulosic feedstocks, many other value-added chemicals, including those currently produced from petroleum, can be produced from cellulosic biomass conversion as shown in Figure 1.3. Levulinic acid, for example, can be hydrogenated to form gamma valerolactone, which can either be substituted with ethanol in gasoline or upgraded to form alkenes to be hydrogenated to form C9 and larger alkanes that can be used as gasoline and jet fuel.

Although fuels can be produced from biomass, the need for liquid transportation fuels in automobiles may be replaced in the future by other sources. The production of chemicals, on the other hand, are a niche unique to biomass compared to other renewable sources due to the abundance of carbon in biomass. Only five major products dominate chemical production in terms of volume and energy consumption including benzene/toluene/xylenes (BTXs), methanol,
ethylene, ammonia, and propylene. Of these, BTXs lend themselves very well for production from lignocellulose. In general this is true because over 70% of biomass is composed of C5 and C6 sugars which can both be converted into furans such as HMF and furfural. These furans can undergo a hydrogenolysis reaction to form methyl furan and dimethyl furan, followed by cycloaddition with alkenes to produce aromatics. Benzene, toluene, para-xylene (p-xylene) as well as meta-xylene (m-xylene) can be readily and selectively produced using zeolite by combining furans derived from sugars with alkenes via Diels-Alder cycloaddition.

Figure 1.3: Renewable chemicals from cellulose: 1: Hydrolysis of cellulose to glucose; 2: Conversion of glucose to 5-hydroxymethyl furfural (HMF); 3: Production of levulinic acid and jet fuel additives; 4: Production of p-xylene and aromatics; 5: Production of Ethoxymethyl furfural; 6: Production of hydrogen; 7: Production of ethanol; 8: Production of mannitol; 9: Production of sorbitol.
P-xylene is one of the most commonly produced chemicals globally and is used as a precursor for terephthalic acid, which is used in the manufacture of plastics such as polyethylene terephthalate. The current market price as of July 2015 is $858 per metric ton, but is down from its peak price $1400 per metric ton in August of 2014 due to currently low oil prices. Selective production of p-xylene from dimethyl furan (DMF) has been extensively studied. Chang et al. achieved a p-xylene selectivity of over 90% from dimethyl furan. However, key bottlenecks still exist in other aspects of the production of p-xylene. Figure 1.4 shows the scheme we propose as the five key catalytic steps for production of p-xylene from cellulose. The red text shows the methods developed and discussed for this dissertation: 1: Decrystallization and Brønsted acid catalyzed depolymerization of cellulose to glucose; 2: Lewis acid catalyzed isomerization of glucose to fructose; 3: Brønsted acid catalyzed dehydration of fructose to HMF; 4: Transition metal catalyzed hydrogenolysis of HMF to DMF; 5: Dies-Alder cycloaddition of ethylene to DMF to form p-xylene over zeolite catalysts.

Figure 1.4: Production of p-xylene from cellulose. Topics in this thesis listed in red.

1.3: Challenges with cellulose hydrolysis

One of the key bottlenecks to the production of chemicals from lignocellulose is the selective conversion of cellulose to glucose. Acid catalyzed conversion cellulose conversion to glucose in an aqueous environment, commonly called cellulose hydrolysis, has three major steps
as shown in Figure 1.5. There are two acetal oxygens: the glycosidic oxygen, which is outside ring and branching two adjacent AGUs, and the pyranic oxygen, which is in the ring.\textsuperscript{31} It is believed that the hydrolysis pathway involves the protonation of the glycosidic oxygen as this is the reaction mechanism for many other saccharides, including cellobiose. After protonation of the glycosidic oxygen the neighboring anhydroglucose unit (AGU) connected to the glycosidic oxygen to the C1 position (the anomeric carbon) must undergo a half-chair rotational conformation change. This is considered the rate limiting step in cellulose hydrolysis and is hindered by both intra and interchain hydrogen bonds. Due to the conformational restrictions, the cellulose layers must typically be exfoliated in order to achieve hydrolysis. Exfoliation of the crystalline layers and the second step is hydrolysis of the $\beta(1\rightarrow4)$ glycosidic linkages.\textsuperscript{32} The rotational conformation change allows a unimolecular scission of the glycosidic bond and the subsequent formation of an oxonium and subsequent carbocation intermediates. A nucleophilic attack of water reestablishes the hydroxyl group.

Cellulose hydrolysis typically proceeds by enzymatic conversion to produce glucose with high selectivity.\textsuperscript{33} The enzymes typically have regions for exfoliation and others for hydrolysis. The binding sites can be hydrophobic, such as aromatic groups, or hydrophobic, such as oxygen containing or hydrogen bonding type groups.\textsuperscript{34} While these catalysts are highly selective, they suffer from high cost as well as low hydrothermal stability and are thermolabile above 30 to 40 °C.\textsuperscript{25} The resulting reaction times to fully convert cellulose into glucose are on the order of days. The hydrolysis of cellulose can proceed relatively inexpensive mineral acids such as HCl or $\text{H}_2\text{SO}_4$. These acids, however, are highly corrosive, difficult separate, and are not highly selective to glucose due to further conversion of glucose to humins as well as levulinic acid.\textsuperscript{27,35,36} It is therefore desirable to develop processes that utilize heterogeneous catalyst, which are easier to recover and recycle and also less corrosive than mineral acids. However, a great challenge is posed when trying
to perform a solid/solid reaction, a problem which will be addressed head on in Chapter 2 of this thesis.

Figure 1.5: Hydrolysis mechanism of cellulose from Rinaldi et. al. The glycosidic oxygen is protonated followed by unimolecular scission of the glycosidic bond which occurs with a half chair rotational conformation change. Nucleophilic attack of water reestablishes the hydroxyl group.

1.4: Introduction to solid acid catalysts and carbon materials for cellulose conversion

A new class of solid acid catalysts for the hydrolysis of cellulose has been developed to provide more thermally stable and less costly alternatives to enzymes. The principal design aspect is typically to mimic the action of the enzymes, synthesizing catalysts containing both strong binding and acid sites. Bifunctional polymer-based catalysts have been developed containing sulfonic acid as well as either CH$_2$-Cl, 2-chloro-3-benzosulfonic acid, F$_3$CO$_2$S, and carboxyl groups, which have been predicted to enhance the catalysis of cellulose by adsorption onto the electronegative moieties. Many of the polymer catalysts can efficiently hydrolyze cellobiose but fail to covert crystalline cellulose to glucose with more than 25 % yield in most cases before deactivating. One exception was a chlorinated polystyrene with sulfonic groups developed by Pan.
et. al., which achieved over 90% glucose selectivity in 1 h at 100 °C however the reaction required a very high catalyst to cellulose ratio of 25:1.  

A second and very promising category of solid acid catalyst designed for the conversion of cellulose to glucose are made from amorphous carbon. Unlike the polymer materials, which primarily utilize hydrogen-bonding groups as binding sites, amorphous carbon itself contains graphitic domains of π-bonded carbon atoms that provide a surface for very strong adsorption interaction. The strong adsorption interaction onto carbon materials from water is dominated by enthalpic forces, which consist of van der Waals interactions between the adsorbate and the carbon, as well as entropic forces, which arises from the entropy gained from the release of hydrated water molecules. The entropic contribution increases for larger adsorbates, which can release more moles of water per adsorbed molecule than smaller adsorbates, thus providing a larger entropic driving force.  

In addition to containing graphitic domains capable of entropically driven adsorption of cellulosic material, or ‘glucan’, though CH-π interactions, amorphous carbon can be readily functionalized with a number of oxygen containing as well as sulfonic groups as shown in Figure 1.6. Treatment with nitric acid at different temperature and duration, for example, can functionalize a well-controlled surface concentration of COOH groups. OH groups can be generated by hydrothermal treatment with water above 200 °C and sulfonic groups can be generated either on the edges of domains by mixing with fuming sulfuric acid or on the basal plains by functionalization with diazonium sulfonate. The morphology of amorphous carbon can also be tailored. The introduction of ordered mesopores have been shown to enhance the adsorption strength compared to a flat surface graphite and may also allow for greater mass transport of large glucan molecules. Amorphous carbons have also shown excellent hydrothermal stability compared to resins and enzymes and can be regenerated by washing post reaction. Thus, carbon materials are a tremendously versatile substrate that is hydrothermally stable, have tunable morphologies that
can be used to tailor adsorption or transport of the adsorbate, can have tunable acid site concentrations as well as hydrophobicities.

**Figure 1.6:** Carbon structure from Hara *et. al.* and Katz *et. al.*

One of the major drawbacks to carbon, however, is the heterogeneous surface structure. Graphitic domain edges may contain phenolic, lactonic or carboxylic groups as well as lone methyl groups and aral radicals as shown in the seminal works by Boehm. Some of these features can be controlled by annealing at higher temperatures with H$_2$ atmosphere. However, the main challenge is that it is not easy to control the relative placement of functional groups. For example: It is practically impossible (by conventional techniques) to develop of carbon which possesses a small number of adjacent carbon pairs with one bonded to a COOH group and another bonded to an OH group, a combination which could be used to develop an acid site of intermediate strength between COOH and SO$_3$H due to the electron withdrawing power of the neighboring OH group. Such a system is readily achievable with polymers as the functional groups can be tailored in most cases by the starting monomers. Carbons, however, are typically synthesized from the carbonization of a resin or natural polymer and thus do not maintain the ordered structure of their starting material.

Despite the disadvantage of bearing surface microstructures that are difficult to control, great research efforts and progress have been made towards the development of carbon-based
catalyst for cellulose hydrolysis. Reaction with amorphous ball-milled cellulose has been especially promising. Zhang et al.\textsuperscript{53} and Mao et al.\textsuperscript{54} have shown that up to 75 \% glucose yield in 24 h at 150 °C by reacting carbon-based catalysts over ball-milled cellulose, but once again at an impractically high catalyst to cellulose ratio of 10:1 and long reaction time.

Another class of carbon catalysts are synthesized from lignocellulosic biomass byproducts. The starting materials include glucose, sucrose, cellulose and even lignin.\textsuperscript{55} One of the most interesting classes of carbon-based catalyst for cellulose hydrolysis was developed by Michikazu Hara. Hara’s produced his carbon materials from by partially carbonizing of either glucose, sucrose or cellulose at 300 °C in an inert atmosphere. These carbons contains both a large number of graphitic domains as well as phenolic OH groups that remain due to the incomplete carbonization.\textsuperscript{56-59} Furthermore, these domains are flexible and have been reported to achieve a surface area measured by N\textsubscript{2} adsorption of less than 5 m\textsuperscript{2} g\textsuperscript{-1} but a surface area of over 100 m\textsuperscript{2} g\textsuperscript{-1} when measured by H\textsubscript{2}O adsorption.\textsuperscript{60} This swelling effect in water is attributed to the hydrophilic OH groups on the domains as well as hydrophilic and flexible ether linkages that bridge the domains. Sulfonic acid groups were functionalized by treatment with fuming sulfuric acid. While the flexible ether linkages and hydrophilic phenolic OH groups allow this carbon to swell in water, the overall interaction between glucan and the oxygen containing groups have been touted as capable of enhancing adsorption. However, this claim has yet to be proven. Other reports have suggested that pristine carbon surfaces will adsorb glucan from water with greater strength and capacity, likely due to a competitive adsorption with water that will persist with a hydrophilic carbon.\textsuperscript{61} Hara’s carbons are also very difficult to reproduce. The extent of carbonization will change depending on sample size. Additionally, the fuming sulfuric acid treatment further dehydrates the sample, so great care in sample preparation is needed to obtain a sample that is uniformly carbonized, well-functionalized with sulfonic acid groups, and rich in oxygen containing groups from the native cellulose structure.
Another group who found success in utilizing carbon materials for biomass conversion is that of Atsushi Fukuoka. Fukuoka has investigated many aspects of biomass conversion utilizing the strong adsorption properties of carbon to develop catalysts for cellulose hydrolysis as well as bifunctional transition metal catalysts for cascade reactions of glucose to furans. Fukuoka notably combined DFT and experimental calculations to show that carbon materials adsorb increasingly long glucan chains with increasingly higher entropy. Activated carbon was also co-milled with microcrystalline cellulose, where the carbon was able to more permanently delaminate the cellulose layers compared to ball-milling microcrystalline cellulose alone.

Another successful group who studies the effects of carbon who is very influential to my work is that of Alexander Katz. Katz has studied the how to control the distance between adjacent functional groups and has shown that this functional group gap length-scale is critical when designing a catalyst for the hydrolysis of glucan and xylan. Katz also studied the effect of increasing adsorption strength with increasing chain-length and deduced the benefit of certain carbon morphologies on adsorption as discussed earlier in this section.

1.5: Production of 5-hydroxymethylfurfural (HMF)

Another key intermediate for the production of fuels and value-added chemicals from cellulose is HMF. HMF can be produced directly from the Brønsted acid-catalyzed dehydration of fructose as shown in Figure 1.7. However, HMF can also undergo additional reactions in the presence of Brønsted acid. One reaction is to rehydrate to form levulinic and formic acid. As noted previously, levulinic acid is an important precursor for the formation of alkanes. However, rehydration to levulinic acid is an unwanted side reaction for the production of BTXs and as well as other furan-derived compounds such as EMF. Fructose and HMF can both oligomerize in the presence of Brønsted acid to form compounds called humins, which can be either soluble or insoluble depending on the molecular weight and functionality.
Due to its low stability in the presence of Brønsted acids, processes have been developed to separate HMF \textit{in situ} from the aqueous phase\textsuperscript{31}. One of the most common ways separate HMF \textit{in situ} is to extract it into an organic phase where the HMF can be protected from further reaction.

There are several challenges to \textit{in situ} extraction of HMF as shown Figure 1.8. MIBK is a common extraction solvent due to its low miscibility in water and low reactivity. On the left, a zeolite or other solid Brønsted acid catalyst may be used. However, the partition coefficient for HMF between water and MIBK is approximately 1, so a large volume of MIBK relative to water is required. On the right, saturated salt in the aqueous phase may be used to increase the partition coefficient of HMF in MIBK. However, saturated salt will poison solid acid catalysts and will require the use of corrosive mineral acids. MIBK also has a high boiling point, so separation of HMF from MIBK will be energy intensive.

Figure 1.8: Extraction solvent systems for HMF production from fructose.
1.6: Project objectives

The first objective of this dissertation is to develop a two-step process for the selective aqueous-phase conversion of cellulose to glucose utilizing a rationally designed solid acid catalyst. This objective is split into three studies which are discussed in chapters 2 – 4. The first step in the process is to convert acidulated cellulose to $\alpha(1\rightarrow6)$-branched water-soluble $\beta(1\rightarrow4)$-oligosaccharides via mechanocatalytic depolymerization. The approach is to study the pretreatment condition parameters so that the depolymerization rate can be optimized and also so that the chain-length and extent of branching can be well controlled. The experimental design is based on ideas on how to improve certain key phenomena such as protonation of the glycosidic oxygen and the formation rate of $\alpha(1\rightarrow6)$ branches.

The second step in cellulose conversion process is to selectively convert the $\alpha(1\rightarrow6)$-branched water-soluble oligosaccharides synthesized in the previous step to glucose using a rationally designed carbon-based catalyst. A well-controlled functionalization mechanism will be developed to control the number of acid and adsorption sites on the carbon surface so that they can be optimized for reaction of oligosaccharides. Adsorption isotherms of saccharides with different chain lengths will be collected at different temperatures. The maximum adsorption capacity, the domain size, and the adsorption entropy and enthalpy of the different saccharides will be determined for functionalized and non-functionalized carbon to determine what properties are affected by the functional groups and to gain insights into the parking structure and surface interaction of the adsorbed saccharide species. This knowledge will help to both rationally design this catalyst for oligosaccharide hydrolysis and provide insights into how carbon catalysts and oligosaccharides interact with other compounds in aqueous environments.

The second objective is to develop a more environmentally benign process for fructose conversion to HMF utilizing both solid catalysts and extractants. Fructose will be converted to HMF over zeolite catalysts and the MIBK organic phase will be replaced with a solid carbon extractant which will extract and protect HMF in situ due to strong adsorption of HMF to the
carbon. The approach will first be to find a suitable carbon adsorbent for HMF. The adsorption capacity and affinity for HMF and other key reaction species as well as physical properties, such as surface area, pore size and number of oxygen containing groups, will be determined for different carbon species. Different amounts of carbon will be tested for the selective conversion of fructose to HMF and compared to the performance of MIBK.
CHAPTER 2

EFFICIENT MECHANOCATALYTIC DEPOLYMERIZATION OF CELLULOSE BY FORMATION OF BRANCHED GLUCAN CHAINS

Figure 2.1: Cover art for Chapter 2 featured in Green Chemistry
2.1: Abstract

Selective hydrolysis of cellulose into glucose is a critical step for producing value-added chemicals and materials from lignocellulosic biomass. In this study, we found that co-impregnation of crystalline cellulose with sulfuric acid and glucose can greatly reduce the time needed for ball milling compared with adding acid alone. The enhanced reaction time coincides with the rapid formation of branched $\alpha(1\rightarrow6)$ glycosidic bonds, which have been shown to increase water solubility of $\beta(1\rightarrow4)$ glucan oligomers. Co-impregnation of glucose was crucial for the rapid formation of the $\alpha(1\rightarrow6)$ branches, after which a carbon-based catalyst can rapidly hydrolyze the water-soluble glucan oligomers to 91.2 % glucose yield faster than conventional approaches.

2.2: Introduction

Selective hydrolysis of cellulose into glucose is considered one of the most important chemical reactions for the production of renewable biofuels and platform chemicals from lignocellulosic biomass.\textsuperscript{4, 17, 71-79} Compared with the production of biofuels and platform chemicals by upgrading the complex mixture of compounds from bio-oil produced from pyrolysis, hydrolysis of cellulose into glucose can be coupled with several catalytic reactions to produce value added platform chemicals with high selectivity, which is critical for the efficient utilization of the renewable carbon feedstock.

Despite the potential of cellulose as a sustainable feedstock, utilization via hydrolysis remains a processing challenge. The biopolymer exhibits low reactivity due to its highly hydrogen-bonded semi-crystalline structure, which not only contributes to its low solubility in conventional solvents, but also limits the interaction between the internal cellulose layers and catalysts. Cellulose is a linear, syndiotactic polymer of $\beta$-D-glucose.\textsuperscript{20, 80} Anhydroglucose units (AGUs) are bonded by $\beta(1\rightarrow4)$ glycosidic linkages, and the degree of polymerization (DP) of cellulose and glucan oligomer chains is defined by the number of repeated AGUs. Cellulose has a highly interconnected hydrogen bonding network arising from interactions between hydroxyl groups of neighboring
AGUs as shown in Scheme 2.1. Abundant hydrogen bonds lead to the recalcitrant nature of cellulose, requiring an activation energy for acid catalyzed hydrolysis of 125 to 170 kJ mol\(^{-1}\). However, glucose is relatively reactive in the presence of Brønsted acids, having a similar activation energy for dehydration of about 130 kJ mol\(^{-1}\). The similarity in the reactivity of glucose and crystalline cellulose leads to a challenge in the acid catalyzed hydrolysis of cellulose with a high selectivity to glucose. Accordingly, high throughput methods of biomass conversion (e.g. pyrolysis) produce products with a high degree of heterogeneity in the resulting chemical compositions with almost no selectivity to glucose. Enzymatic hydrolysis can be performed selectively and requires a lower activation energy (3-50 kJ mol\(^{-1}\)). However, the slow reaction rate, high operation cost and catalyst deactivation in the presence of lignin limit the application of the enzymatic process for the large-scale production of glucose from lignocellulosic biomass.

Scheme 2.1: Hydrogen bonding structure of cellulose.

Recently, a two-step strategy has been developed for the selective hydrolysis of crystalline cellulose to increase the efficiency of the acid catalyzed hydrolysis reaction. Namely, crystalline cellulose is first decrystallized into an amorphous phase to reduce the number of hydrogen bonds such that it is more easily hydrolyzed to glucose over acid catalysts. Ionic liquids (ILs) have shown distinct capability for decrystallization of crystalline cellulose; the resulting amorphous cellulose can then be converted into glucose with a high selectivity through enzymatic processes.
However, recovery and manufacturing of these expensive ILs limit their practical applications and requires further research efforts.

Mechanical milling of cellulose is an alternative method to reduce cellulose crystallinity.\textsuperscript{40} Amorphous cellulose prepared by ball milling contains fewer hydrogen bonds compared with crystalline cellulose, which significantly lowers the hydrolysis reaction temperature.\textsuperscript{86} Unfortunately the solubility of amorphous cellulose in water is still low due to a high degree of polymerization, which limits the efficiency of both homogeneous and heterogeneous acid catalysts.

Recently, impregnation of cellulose with catalytic amounts of a strong acid (\textit{e.g.}, $\text{H}_2\text{SO}_4$, HCl) has shown effective for decrystallization and depolymerization of crystalline cellulose to produce water-soluble glucan oligomers.\textsuperscript{87-89} Surprisingly, the glucan oligomers with DP = 6-9 produced by this method exhibit excellent solubility of up to 34 wt.% in water at room temperature,\textsuperscript{88} which is much higher than linear $\beta$-glucan oligomers composed of only $\beta(1\rightarrow4)$ glycosidic linkages. For example, linear $\beta$-glucan oligomers with DP = 5-6 are only 1 wt.% soluble in water.\textsuperscript{90, 91} High solubility of oligomers produced from ball milling of acidulated cellulose has been ascribed to the acid-catalyzed formation of new glycosidic linkages during the milling process. Käldström\textit{ et. al.} concluded that acid and not free radicals play an important role in the synthesis of these glucan oligomers as the reaction will not proceed under acid-free conditions.\textsuperscript{89} Shrotri\textit{ et al.} further elucidated the mechanism and found that milling of cellulose with catalytic amount of strong acid forms $\alpha(1\rightarrow6)$ glycosidically linked branches, which are not present in original cellulose structure.\textsuperscript{88} It is believed that the formation of these branches results from the acid-catalyzed repolymerization of glucose monomers produced during the milling process. A depiction of the branched oligomers that denotes the carbon numbers in the each AGU is shown in Scheme 2.2.
Scheme 2.2: Chemical structure of an $\alpha(1\rightarrow6)$ branched $\beta(1\rightarrow4)$ glucan oligomer.

Although the role of the $\alpha(1\rightarrow6)$ glycosidic linkages in the depolymerization mechanism is not fully understood, it is likely that branches with $\alpha(1\rightarrow6)$ glycosidic linkages on large cellulose chains can inhibit the relamination of exfoliated cellulose chains by increasing the steric hindrance between adjacent layers, thus preventing the stacking and reformation of interchain hydrogen bonds. Once the branches begin to form, the sub-layers in the cellulose structure may be more accessible, and the delamination and subsequent depolymerization of the entire cellulose particle could proceed. The rate of depolymerization during milling could therefore be limited by the rate of $\alpha(1\rightarrow6)$ linkage formation and amount of available glucose.

The goal of this project is to develop a selective and rapid process that utilizes heterogeneous catalyst in solution to produce glucose from cellulose. A two-step approach is taken whereby cellulose is first depolymerized into short, soluble oligomers. To improve the process and to reduce the amount of acid needed we will attempt to increase the depolymerization rate by adding glucose and other low molecular weight saccharides to the solution prior to milling. The second step will be to react the soluble glucan oligomers of a rationally designed carbon-based catalyst. The proposed process is shown in Scheme 2.3. The catalyst synthesis will be introduced in this chapter and studied in much greater detail in Chapter 3.
Scheme 2.3: Proposed two-step process to produce glucose from crystalline cellulose.

2.3: Experimental section

2.3.1: Materials

Microcrystalline cellulose (Avicel, 4 wt.% moisture, DP 215), sulfanilic acid (98 wt.%), sodium nitrite (98 wt.%), hyphphorous acid (H₃PO₂) (50 wt.% in water), tetraethylorthosilicate (TEOS, 98 wt.%) and furfural alcohol (98 wt.%) were purchased from Alfa Aesar. Sulfuric acid (H₂SO₄, both 98 wt.% and 0.005 M), 200 proof ethanol, N,N-dimethylformamide (DMF) (99.8 wt.%), methanol (99.8 wt.%), acetone (99.8 wt.%), and 12.1 M hydrochloric acid (HCl) were purchased from Fisher Scientific. Linear glucan β(1→4) oligomers (cellotriose (95 wt.%), cellotetraose (95 wt.%), cellopentaose (95 wt.%) and cellohexaose (94 wt.%)) were purchased from Megazyme. Oxalic acid (99 wt.%), L-lysine (98 wt.%), levoglucosan (99 wt.%), 4,4-dimethyl-4-
silapentane-1-sulfonic acid (DSS, 97 wt.%) cellulbiose (99 wt.%), maltose monohydrate (99 wt.%), isomaltose (98 wt.%), glucose (99 wt.%) and deuterium oxide (D$_2$O, 99.9 wt.%) were purchased from Sigma Aldrich.

2.3.2: Preparation of acidulated ball-milled cellulose

For the impregnation process, microcrystalline cellulose was first impregnated with 0.25 mmol H$_2$SO$_4$ g$^{-1}$ and LMSs with a LMS:MCC weight ratio of 12.5:87.5 with a total of 10 g of saccharide. Typically, 1.25 g of LMS and 140 μL of 98 wt.% H$_2$SO$_4$ were dissolved in 20 mL of water, and then added to 8.75 g of MCC drop-wisely. In the case of 1h-N-ABMC sample, only H$_2$SO$_4$ was impregnated with 10 g of MCC. After the impregnation, the samples were left in an oven at 50 °C for 2.0 days to remove the water and form acidulated microcrystalline cellulose with co-impregnated LMS. For the ball-milling process, 2.0 g of the acidulated microcrystalline cellulose samples with different LMSs were ball-milled for up to 6.0 h using an SFM-3 high-speed shimmy ball-mill (MTI Corporation). Milling proceeded in 30 minute durations with 15 minute cool down periods to avoid heating above 50 °C. After milling the samples were stored at -18 °C. A control sample was also prepared by physically mixing glucose with the microcrystalline cellulose only impregnated with acid. The sample is named 0h-PM-ABMC. Typically, 0.25 g of D-glucose powder was added to 1.75 g of MCC and mixed with a spatula inside the milling canister followed by the standard milling procedure.

2.3.3: Characterization of acidulated ball-milled cellulose

The amount of soluble material in each sample was determined by dispersing 40 mg of 1h-j-ABMC in 0.80 mL of deionized water by 15 minutes of sonication and 3 minutes of vortexing followed by filtration using a 0.20 μm pore-size filter and analyzed using a high performance liquid chromatography (HPLC) (LC-20AT, Shimadzu) equipped with refractive index (RID-10A) and UV–Vis (SPD-2AV) detectors at oven temperature of 85 °C. An Agilent Hi-Plex-Na HPLC column (7.7 mm (ID), 300 mm (Length), 10 μm (particle size)) with a guard column was used. HPLC grade water (Fisher) was used as a mobile phase with a flow rate of 0.3 mL minute$^{-1}$. 

22
$^1$H-NMR was performed on a Bruker Advance 400 (400 MHz) spectrometer to determine the prevalence of glycosidic linkages and reducing ends. Samples were prepared by dispersing 5.0 wt.% $^i$h-$^j$-ABMC in D$_2$O with 10 mM 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as an internal standard. $^1$H-NMR samples were sonicated for 15 minutes and vortexed for 3 minutes followed by filtration before the measurement. The $^1$H-NMR was performed with 32 scans.

Determination of levoglucosan was performed using gas chromatography/mass spectroscopy (GC/MS) using an Agilent 7890A gas chromatograph (GC) with flame ionization detector (FID), an Agilent DB-5 column (30 m length, 0.320 mm diameter, 1.5 μm film) and Agilent 5975C mass spectrometer (MS). The GC oven was heated from -30 to 260 °C over 71 minutes.

2.3.4: Catalyst synthesis

2.3.4.1: Synthesis of 3DOm carbon

3DOm carbon with 35 nm cage size was prepared according to literature. The synthesis of 3DOm carbon is portrayed in Scheme 2.4. Briefly, 35 nm silica nanoparticles (SNPs) were prepared by mixing 0.198 L-lysine, 13.3 g TEOS and 180 mL of water at 90 °C in a Teflon bottle stirring at 1000 rpm. An additional amount of 26.6 g of TEOS was added after 24 h and 48 h for a total of 66.5 g TEOS. The solution was stirred for an additional 24 h after the adding the last amount of TEOS. The resulting solution was evaporated in a convection oven at 70 °C for 72 h. The precipitated SNPs were calcined for 24 h at 600 °C (with 3 °C min$^{-1}$ heating) to remove L-lysine. To prepare the resin, 0.10 g oxalic acid were dissolved in 20 g of furfural alcohol. The SNPs were impregnated with the furfural alcohol solution by incipient wetness. Excess furfuryl alcohol solution was removed by whipping with filter paper. The sample was then put in a 70 °C oven for 48 h and subsequently carbonized under nitrogen at 200 °C for 3 h followed by 900 °C for 2 h (1 °C min$^{-1}$ heating). The sample was then treated twice under hydrothermal conditions at 150 °C with 6 M KOH for 2 days to remove silica. Finally, the carbon was washed in 1 L of 70 °C water for 3
h repeatedly until the pH of the solution fell below 8. The resulting 3DOm carbon was dried overnight at 70 °C.

2.3.4.2: Synthesis of 3DOm carbon catalyst

The surface functionalization of amorphous carbon by benzenesulfonic acid radicals derived from diazonium salts has been reported previously.93 The synthesis of the 3DOm carbon catalyst is portrayed in Scheme 2.5. 60 mL deionized water were mixed with 4 mL of 12.1 M HCl and 0.6 g of sulfanilic acid. This solution immersed in an ice bath and stirred for 5 minutes. 0.704 g of sodium nitrite were added to the solution and stirred for 10 minutes. A clear solution typically formed after 1 minute. At high concentrations of sodium nitrite and sulfanilic acid a white precipitate (likely the diazonium intermediate) formed after 5-7 minutes. 0.4 g of 3DOm carbon, 60 mL ethanol and 60 mL of 50 wt.% H₃PO₄ were added to the solution and stirred for 30 minutes, followed by the addition of 60 mL more H₃PO₄. The resulting solution was mixed for 8 h at ice bath temperature.

Scheme 2.4: Synthesis of 3DOm carbon (credit Wei Fan and Hong Je Cho).
After functionalization the catalyst was washed by shaking/sonicating 100 mL water, DMF, methanol and acetone, followed by washing with 2.0 L of 70 °C water. The sample was then washed overnight in 1 L of 70 °C water, filtered, then dried overnight at 70 °C. The number of acid sites was controlled by the amount of sulfanilic acid and sodium nitrite formed. It should be noted that the diazoniumsulfonated intermediate will precipitate after 10 minutes at 5 °C in water. Diazoniumsulfonate is not stable when dry and can spontaneously release nitrogen gas. Caution should be taken during filtration. Excess diazoniumsulfonated precipitate can be easily dissolved in DMF for safe separation and storage.

**Scheme 2.5:** Synthesis SO$_3$H-3D0m carbon catalyst.

**2.3.5: Characterization**

The number of acid site and surface area were also measured for the carbon materials. Acid site concentration was measured by ion exchange with 0.050 M NaCl. Typically, 0.020 g of catalyst was placed in 10 mL of NaCl solution and sonicated for three hours. The solution was titrated with 0.010 M HCl with phenolphthalein as the indicator.$^9$ The carbon catalyst synthesized in this manner contained 0.57 mmol SO$_3$H g$^{-1}$. N$_2$ adsorption/desorption isotherms for different carbons were measured on an Autosorb®-iQ system (Quantachrome) at 77 K. Total surface area was
calculated using the Brunauer–Emmett–Teller (BET) method. LGA was confirmed by three techniques: HPLC (Figure 2.2), $^1$H-NMR (Figure 2.3) and GC-MS (Figure 2.4). A standard of LGA has identical retention time to the suspected peak observed in the HPLC at 42.5 minutes for the $^1$h-$^j$-ABMC samples on HPLC as shown in Figure 2.2. The amount of LGA in each sample is shown in Table 2.1. $^1$H-NMR results are shown in Figure 2.8 for 2h-N-ABMC and 2h-G-ABMC show a singlet at 5.439 and a doublet at 4.082 ($J = 7.8 \text{ Hz}$). The $^1$H-NMR LGA standard shown in Figure 2.3 confirms that these peaks are from LGA. Figure 2.4 shows the mass spectra of LGA extracted from 2h-G-ABMC using a sample prepared by HPLC fraction collection of the peak suspected to be LGA and a standard LGA sample. The two spectra are nearly identical, with strong peaks at 60 and 73 m/z. Additionally, both spectra generated positive identification as LGA when searching the NIST spectral library. The search generated an R-match (software matching criteria; max score is 999) for LGA of 876 using the mass spectra obtained from the extracted LGA sample, while the pure LGA standard generated an R-match of 908 for LGA. This data indicates that the unknown sample extracted from 2h-G-ABMC on HPLC fraction collection is indeed LGA.

![Figure 2.2: HPLC Chromatograms from 2h-G-ABMC, glucose (G1), isomaltose (G2) and the cellodextrins cellobiose (G2), cellotriose (G3), cellotetraose (G4), cellopentaose (G5) and cellohexaose (G6) as well as levoglucosan (LGA) are shown.](image-url)
Figure 2.3: $^1$H-NMR spectrum of LGA in D$_2$O.

Figure 2.4: Mass spectra of A) LGA collected by fractionation of 2h-G-ABMC and B) standard LGA sample.

The hydrolysis reactions were performed using 1 wt.% 2h-G-ABMC obtained by ball-milling microcrystalline cellulose co-impregnated with glucose and acid for 2.0 h. 30 mg of 2h-G-ABMC were mixed with 20 mg of catalyst and 3 mL of deionized water, and sealed in a 5.0 mL borosilicate microwave heating vial (Chenglass). The reaction was performed on a Dynabloc aluminum stir plate with 22 (ID) x 35.6 (depth) mm holes (Ace Glass) at 120 °C for 2.0 h and at 165 °C from 10 to 60 minutes. Blank (no additional acid) reactions and reactions with HCl (4.6 mM HCl) were run as control experiments at with 2h-G-ABMC at 120 °C. The turnover frequency
(TOF) was determined by subtracting the moles of glucose produced during the blank reaction after 2.0 h from the moles of glucose produced during the catalyzed reaction after 2.0 h and dividing by the reaction time and number of acid sites added from either HCl or the carbon catalyst. The calculation is shown in Equation 2.1:

\[
TON = \frac{\text{Moles of glucose(sample)} - \text{Moles of glucose (blank)}}{\text{Added Acid} \times \text{time}}
\] (2.1)

Additionally, non-milled microcrystalline cellulose as well as non-milled acidulated cellulose (0h-N-ABMC) and 2h-G-ABMC were reacted for up to 1h at 165 °C over the SO₃H-3DOm carbon catalyst.

2.4: Results and discussion

2.4.1: Acid and saccharide co-impregnation

Cellulose is first co-impregnated with glucose (or other low molecular weight saccharides) and sulfuric acid. The resulting acidulated cellulose is ball-milled to produce branched glucan oligomers, which are subsequently reacted over a sulfonated carbon catalyst to selectively produce glucose.

Given that formation of branches with \(\alpha(1\rightarrow6)\) linkages is critical for the production of water-soluble glucan oligomers, we hypothesize that the addition of low molecular weight saccharides (LMSs) in the acidulated ball milling process can increase the rate of \(\alpha(1\rightarrow6)\) glycosidic linkage formation through acid catalyzed condensation between the C1-OH group of the LMSs and a C6-OH group on an AGU of the oligomer chain. Following this hypothesis, crystalline cellulose was co-impregnated with both LMSs and acid, and then ball-milled to study the effects of co-impregnation on the solubility of the produced glucan oligomers. The results indicate that the co-impregnation of glucose can largely improve the performance of the depolymerization process. In addition, we observed that using carbon-based acid catalysts can break down the water-soluble glucan oligomers more efficiently compared with homogenous acid due to an adsorption-enhanced reaction rate.
Acidulated ball-milled cellulose (ABMC) was formed by co-impregnation of microcrystalline cellulose (MCC) with an aqueous solution of LMSs and sulfuric acid followed by evaporation of water as shown in Scheme 2.3. Impregnation was performed for four different LMSs including glucose, maltose (glucose dimer with $\alpha(1\rightarrow4)$ linkage) and the oligomers made by milling the acid-only impregnated cellulose for 4.0 h. The achieved samples were named $i$h-$j$-ABMC where $i$h represents the milling time (in hours), and $j$ represents the LMS species that are co-impregnated. The samples prepared without LMS species were named $i$h-N-ABMC. MCC was impregnated with glucose to form $i$h-G-ABMC, maltose to form $i$h-M-ABMC, and oligomers from 4h-N-ABMC to form $i$h-O-ABMC. A control sample was also prepared by physically mixing glucose with microcrystalline cellulose impregnated only with acid named 0h-PM-ABMC. The impregnation procedure is further described in the supplementary information.

Typical HPLC chromatograms of 2h-G-ABMC is shown in Figure 2.2. To identify the components in the solution, standards of linear $\beta(1\rightarrow4)$ glucan oligomers including cellohexaose, cellopentaose, cellotetraose, cellotriose and cellobiose as well as isomaltose (glucose dimer with $\alpha(1\rightarrow6)$ linkage), were analyzed on the same column. The data suggests the $\beta(1\rightarrow4)$ glucan oligomers of different chain lengths can be distinctly separated using an Agilent Hi-Plex-Na HPLC column. However, the difference in retention time between oligomers with the same degree of polymerization such as for isomaltose ($\alpha(1\rightarrow6)$ dimer) and cellobiose ($\beta(1\rightarrow6)$ dimer). Furthermore, it was found that the response factors from the refractive index (RI) detector on HPLC for all five linear $\beta(1\rightarrow4)$ glucan oligomers as well as for isomaltose are similar, varying less than 3 %. The amount of glucan oligomers with DP $\leq$ 6 was thus calculated based on these measured response factors. Because oligomers with $\beta(1\rightarrow4)$ and $\alpha(1\rightarrow6)$ linkages with the same length were difficult to separate, the product distribution was denoted as G2, G3, G4, etc.. The largest peak in the chromatogram of milled samples has a shorter retention time compared to the standard linear glucan oligomers with DP $\leq$ 6. The peak was assigned to all glucan oligomers with DP $> 6$.
the similarity in response factor for all five of the glucan oligomers and isomaltose, an average response factor was used to calculate the amount of glucan oligomers with DP > 6. The total glucan oligomers determined by the HPLC measurement was used to calculate the soluble portion of the ball-milled samples. To further confirm this calculation, 2h-G-ABMC was dispersed in deionized water, and the insoluble and large particles were removed by filtration with a 0.20 μm membrane filter. The amount of total soluble glucan oligomers measured by this method after evaporation was found to be 92.3 ± 4.3 wt.%, compared to 92.7 wt.% as measured by HPLC.

The total amount of soluble glucan oligomers in each i_h-j-ABMC sample prepared by milling for 1.0 and 2.0 h are shown in Figure 2.5. The percentage of individual glucan oligomers with the chain lengths DP ≤ 6 as well as total soluble glucan oligomers detected by HPLC are shown in Table 2.1. It was found that co-impregnation with glucose greatly decreases the time needed for milling. 71.2 wt.% of the 1h-G-ABMC sample was soluble in water, which was similar to the soluble portion of 4h-N-ABMC (64.5 wt.%). Increasing the milling time to 2.0 h yielded 2h-G-ABMC with an even higher soluble portion of 92.7 wt.%. The remarkable solubility can be seen in Figure 2.6, which shows 10 wt.% of MCC, 1h, 2h and 3h-G-ABMC. Interestingly, the distribution of glucan oligomers achieved from the co-impregnation of glucose was different from those made without adding glucose. Namely, for the samples with similar soluble portions, 1h-G-ABMC contains 47.5 wt.% of glucan oligomers with DP > 6 while 4h-N-ABMC only contains 29.8 wt.% of glucan oligomers with DP > 6. Levoglucosan (LGA) was also detected in amounts ranging from 0.0 to 6.5 wt.%. Detailed information about LGA determination (characterization section 2.3.5 and Figure 2.2-2.4) is included in supplementary information. In addition to glucan oligomers and LGA, 5-hydroxymethylfurfural (HMF), formic acid and levulinic acid were also observed in the soluble portion. Trace amounts of HMF (0.13-0.20 wt.%), levulinic acid (0.15-0.31 wt.%) and formic acid (0.06 to 0.12 wt.%) were found in most samples milled for longer than 2.0 h. These trace furans and organic acids are not believed to the significantly contribute catalytically in neither the milling nor the aqueous phase reactions.
Figure 2.5: Soluble portion percentage from acidulated ball-milled cellulose after 1.0 and 2.0 h of milling determined by HPLC. Error bars present a 95% confidence interval of the average soluble portion.

Figure 2.6: 10 wt.% i-G-ABMC in water at different milling times.
Table 2.1: Yields of glucose and glucan oligomers in the soluble component of different acidulated ball-milled cellulose measured by HPLC.

<table>
<thead>
<tr>
<th>i-ABMC (Impregnation)</th>
<th>Time (h)</th>
<th>α-RE (%)</th>
<th>α(1→6) (%)</th>
<th>β-RE (%)</th>
<th>β(1→4) (%)</th>
<th>Soluble-Portion (wt. %)</th>
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<tbody>
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<td>N-ABMC</td>
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<td>0.0</td>
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<td>23.7</td>
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<td>79.8</td>
</tr>
</tbody>
</table>

1 Abundance of AGU anomers in the soluble portion, measured by 1H-NMR.
2 Percentage of total material, measured by HPLC.
3 Only acid was impregnated.
4 Glucose and acid were co-impregnated.
5 Maltose and acid were co-impregnated.
6 Acid only impregnated cellulose and physically mixed with glucose.

2.4.2: Comparison of α(1→6) branched portion for G-ABMC and N-ABMC

To understand the structure of the water-soluble glucan oligomers formed by the milling process, 1H-NMR spectra were collected for the i/j-ABMC samples and the relative abundance of each anomic hydrogen is shown in Table 2.2. Representative 1H-NMR spectra normalized using an internal standard are shown in Figure 2.7 for 2h-G-ABMC and 2h-N-ABMC. Peaks from anomic hydrogens appear in the 5.2 to 4.3 ppm δ range. The peak position of the hydrogens on the α and β reducing ends (α-RE and β-RE, respectively), α(1→6), and β(1→4) anomic hydrogens have been reported in literature as indicated in Figure 2.6 Abundance was calculated by a comparison of the integrated individual peak areas (A_{Hi}) in the 1H-NMR spectra:

\[
Abundance = \frac{A_{Hi}}{\sum A_{Hi}} \times 100\%
\]
As shown in Table 2.2, both $\alpha$ and $\beta$ reducing end as well as $\alpha(1 \rightarrow 6)$ hydrogen peaks increase with increasing milling time, indicating a decrease in chain length and an increase in branching, both of which likely contributed to a higher solubility. In addition, Figure 2.8 shows the increase in the $\alpha(1 \rightarrow 6)$ linkages as sample solubility for G-ABMC as well as N-ABMC. It is clear that $1h$-G-ABMC samples have many more $\alpha(1 \rightarrow 6)$ bonds than $1h$-N-ABMC. Namely, 9.7 % of AGUs contain $\alpha(1 \rightarrow 6)$ bonds for $1h$-G-ABMC, while only 2.2 % and 7.3 % of AGUs contain $\alpha(1 \rightarrow 6)$ bonds for $2h$-N-ABMC and $4h$-N-ABMC, respectively. The increased breakdown rate has significant implications for the economic feasibility for mechanical pretreatment of cellulose as demonstrated by the economic analysis of Hick et al.\textsuperscript{28} One interesting note is that only $\alpha(1 \rightarrow 6)$ linkages are detected, although in solution the $\beta$ anomer is more prevalent. We offer two possible explanations. The first is that the glucose crystalizes from solution to the $\alpha$ form. It is known that glucose crystallized from water or cellulose below 150 °C will form primarily crystals containing the $\alpha$ anomer form of glucose.\textsuperscript{95} Another possibility may be that the $\alpha(1 \rightarrow 6)$ branch is more sterically stable than the $\beta(1 \rightarrow 6)$ branch.
Figure 2.8: $\alpha(1 \rightarrow 6)$ linkages and sample solubility for G-ABMC and N-ABMC.

Table 2.2: Anomeric AGU abundance in different acidulated ball-milled cellulose samples calculated from $^1$H-NMR.

<table>
<thead>
<tr>
<th>i-ABMC (Impregnation)</th>
<th>Time (h)</th>
<th>$\alpha$-RE$^1$ (%)</th>
<th>$\alpha(1 \rightarrow 6)$ (%)</th>
<th>$\beta$-RE$^1$ (%)</th>
<th>$\beta(1 \rightarrow 4)$ (%)</th>
<th>Soluble Portion$^2$ (wt.%)</th>
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</thead>
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<tr>
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<td>0</td>
<td>8.1</td>
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</table>

$^1$Abundance of AGU anomers in the soluble portion, measured by $^1$H-NMR.
$^2$Percentage of total material, measured by HPLC.
$^3$Only acid was impregnated.
$^4$Glucose and acid were co-impregnated.
$^5$Maltose and acid were co-impregnated.
$^6$Acid only impregnated cellulose and physically mixed with glucose
2.4.3: Physical mixture experiments

Several control experiments were performed to understand the effects of the co-impregnation. Instead of impregnation with glucose and acid together, microcrystalline cellulose was first impregnated with $\text{H}_2\text{SO}_4$ and water, and dried at 50 °C to form 0h-N-ABMC. Thereafter, 1.75 g of 0h-N-ABMC was physically mixed with 0.25 g of glucose to form 0h-PM-ABMC. Figure 2.9 shows the increase in the $\alpha(1\rightarrow6)$ linkages as sample solubility for G-ABMC as well as PM-ABMC. After 3.0 h of the milling, 37.9 wt.% of the 3h-PM-ABMC sample was soluble compared with 91.5 wt.% for 3h-G-ABMC, indicating that co-impregnation with both glucose and acid is crucial for enhancing the efficiency of the milling process. One explanation for the improvement may be that co-impregnation enhances the transport of glucose and provides feasible interaction for branching to rapidly occur. In addition, it was found that impregnated glucose started reacting with cellulose during the impregnation process. The amount of water-soluble glucan oligomers in the glucose co-impregnated cellulose sample (0h-G-ABMC) detected after 15 minutes of sonication and 3.0 min of vortexing was 10.7 wt.% (Table 2.1). However, only 1.0 wt.% of free glucose were detected in the soluble portion, which is much less than the amount of glucose (12.5 wt.%) added in the beginning of the impregnation process. The $^1\text{H}$-NMR spectra of the soluble portion revealed that 7.0 % of AGUs contain $\alpha(1\rightarrow6)$ bonds, while the soluble portion of the 0h-N-ABMC sample does not show any amount of $\alpha(1\rightarrow6)$ linkages as shown in Table 2.2. These results clearly indicate that glucose can react with cellulose under acidic and static condition even without the milling.
We further investigated the potential of co-impregnation of cellulose with glucan oligomers to enhance the efficiency of the milling process. Co-impregnation with maltose forms 0h-M-ABMC. Co-impregnation of cellulose with 4h-N-ABMC containing both $\alpha(1\rightarrow6)$ linkage and $\beta(1\rightarrow4)$ linkage formed 0h-O-ABMC. The total amount of water-soluble glucan oligomers measured after milling the two samples for 1.0 and 2.0 h are shown in Figure 2.5. The soluble portion of 1h-M-ABMC and 2h-M-ABMC was 44 wt.% and 77 wt.%, respectively. The solubility at identical milling times for maltose impregnated samples was less than that of the samples made by co-impregnating with glucose, but was higher than that of the samples prepared with acid only. The slower increase in soluble portion from co-impregnation with maltose may result from the requirement that maltose first hydrolyze into glucose. This hypothesis is supported by the slower rate of increase in $\alpha(1\rightarrow6)$ linkage as shown in Table 2.2, which is likely directly related to available glucose in the samples. The depolymerization rate was even lower when larger oligomers were impregnated (Figure.2.4).
2.4.4: Hydrolysis of soluble glucan oligomers over SO$_3$H-3DOm carbon catalyst

2.4.4.1: SO$_3$H-carbon characterization

In order to selectively hydrolyze the produced water-soluble glucan oligomers into glucose, three dimensionally ordered mesoporous imprinted carbon (3DOm carbon) with SO$_3$H catalyst groups on the surface were used (SO$_3$H-3DOm carbon). Nitrogen physisorption and small angle X-ray scattering (SAXS) patterns for both parent 3DOm carbon and SO$_3$H-3DOm carbon are shown in Figure 2.10 and Figure 2.11, and the textural properties of the two samples are shown in Table 2.3. The BET surface areas for the parent and SO$_3$H-3DOm carbons are 1445 and 1191 m$^2$ g$^{-1}$, respectively. The number of acid sites on the SO$_3$H-3DOm carbon was found to be 0.57 mmol g$^{-1}$.

Adsorption of glucose and the water-soluble glucan oligomers from 2h-G-ABMC was performed on SO$_3$H-3DOm carbon. Adsorption isotherms plotted against the Langmuir fitting are shown in Figure 2.12 with the adsorption capacity ($Q_m$), Langmuir Constant ($K_L$) and $R^2$ of the fitting shown in Table 2.4. Adsorption of water-soluble glucan oligomers was much stronger than glucose on the SO$_3$H-3DOm carbon; the adsorption capacity for the water-soluble glucan oligomers was 546 mg g$^{-1}$, while the capacity for glucose was only 118 mg g$^{-1}$. The Langmuir constant, $K_L$, was 3.41 L g$^{-1}$ for the water soluble glucan oligomers, which was over 40 fold higher than the Langmuir constant for glucose of 0.082 L g$^{-1}$. This result was consistent with previous results which show that the adsorption affinity of glucan oligomers on the carbon surface increases with increasing the chain length$^{41,42}$. 

37
Figure 2.10: Nitrogen physisorption isotherms of parent 3DOm carbon and SO$_3$H 3DOm carbon catalyst at 77 K.

Figure 2.11: SAXS of 3DOm carbon and SO$_3$H 3DOm carbon catalyst.
**Figure 2.12:** Adsorption isotherms for glucose and water-soluble glucan oligomers from 2.0 h ball-milled cellulose co-impregnated with glucose (2h-G-ABMC) on SO$_3$H-3DOm carbon at room temperature. Data points are from experiments. Line is a fitted Langmuir model.

**Table 2.3:** Textural properties of SO$_3$H-carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ $^{1}$ m$^2$ g$^{-1}$</th>
<th>$V_{total}$ $^{1}$ cm$^3$ g$^{-1}$</th>
<th>Acid Sites$^{2}$ mmol g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$H-3DOm Carbon</td>
<td>1191</td>
<td>3.84</td>
<td>0.57</td>
</tr>
<tr>
<td>Parent-3DOm Carbon</td>
<td>1445</td>
<td>4.58</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$^{1}$Measured by Nitrogen desorption.
$^{2}$Measured by NaCl ion exchange followed by NaOH titration.

**Table 2.4:** Langmuir isotherm constants of saccharides adsorption on SO$_3$H-3DOm-carbon at room temperature.

<table>
<thead>
<tr>
<th>Component</th>
<th>$Q_m$ $^{1}$ mg g$^{-1}$</th>
<th>$K_L$ $^{1}$ L g$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>118</td>
<td>0.082</td>
<td>0.9242</td>
</tr>
<tr>
<td>2h-G-ABMC</td>
<td>546</td>
<td>3.42</td>
<td>0.9423</td>
</tr>
</tbody>
</table>

**2.4.4.2: Hydrolysis reaction results**

The glucose yield and acid site turn over frequency (TOF) for the hydrolysis of 2h-G-ABMC over SO$_3$H-3DOm carbon sample are shown in Figure 2.13A. The TOF of SO$_3$H-3DOm
carbon, measured at 120 °C after 2.0 h with less than 20 % conversion, was nearly 6 fold higher than the one of HCl (1.48 and 0.25 (mol glucose)/(mol H+)^{-1} h^{-1}, respectively), which we propose is due to the synergy between strong adsorption of glucan oligomers and the sulfonic acid sites on the carbon catalyst. 2h-G-ABMC, non-milled acidulated cellulose (0h-N-AMCC) and non-milled microcrystalline cellulose (0h-MCC) were hydrolyzed using SO_{3}H-3DOm carbon at 165 °C. A glucose yield of 91.2 % was achieved in 1.0 h when 2h-G-ABMC was used over SO_{3}H-3DOm carbon, while only 7.0 and 1.7 % glucose yield for the 0h-N-ABMC and 0h-MCC were achieved, respectively (Figure 2.13B). The results indicate that combining the co-impregnation approach with carbon-based acid catalyst is a highly efficient process to selectively depolymerize crystalline cellulose to glucose. The catalyst reproducibility was also measured and is shown in Figure 2.14. The glucose yield after one, two and three runs using the same carbon catalyst was found to be 91.2, 87.2 and 84.5 %, respectively, demonstrating the good hydrothermal stability of the catalyst. The average carbon balance of 92.8 % was likely low due to the adsorption of unreacted glucan oligomers on the 3DOm carbon surface.

Figure 2.13: A) Turnover frequency (TOF) of SO_{3}H-3DOm carbon and HCl for 2.0 h ball-milled cellulose co-impregnated with glucose (2h-G-ABMC) at 120 °C in water (reaction time: 2.0 h, conversion: < 20 %), and B) Glucose yield from 2h-G-ABMC, non-milled acidulated cellulose (0h-N-ABMC) and microcrystalline cellulose (0h-MCC) over SO_{3}H-3DOm carbon at 165 °C.
Figure 2.14 Carbon catalyst reproducibility. Cellobiose was reacted for 6 h at 120 °C and washed with DIW at 70 °C until all reactants and products were removed (checked by HPLC).

2.5: Conclusion

We found that co-impregnation of crystalline cellulose with sulfuric acid and glucose greatly improves the efficiency of ball milling to selectively produce glucose. By co-impregnating with glucose, cellulose fibers that were exfoliated by the sheer force of ball milling can react with glucose to form $\alpha(1\rightarrow6)$ branches, which might prevent re-lamination of the glucan chains, thus allowing for a rapid production of water-soluble glucan oligomers. Co-impregnation with maltose shows improvement as well, but the decrease in milling time was not as substantial as when glucose was used. In addition, carbon-based acid catalysts can rapidly hydrolyze the water-soluble glucan oligomers to glucose with high selectivity due to the enhanced adsorption for glucan oligomers on the carbon surface.

2.6: Acknowledgements

This work was supported by the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the US Dept. of Energy, Office of Science, and Office of Basic Energy Sciences under award number DE SC0001004. I would also like to acknowledge my co-authors on this work: Hong Je Cho, Alex Paulsen, Paul Dauenhauer, Wei Fan. This work was
CHAPTER 3

ADSORPTION PROPERTIES OF THREE-DIMENSIONALLY ORDERED
MESOPOROUS CARBON CATALYSTS FOR THE SELECTIVE HYDROLYSIS OF
GLUCAN OLIGOMERS

3.1: Abstract

Hydrolysis of cellulose and β(1→4) oligosaccharides on carbon catalysts is a promising approach for selective production of glucose from cellulose and its derivatives. However, the effects of adsorption and surface properties of carbon catalyst on their catalytic activities are still elusive. In this study, a structure-property relationship was developed for the hydrolysis of water soluble oligosaccharides over three dimensionally ordered mesoporous (3DOm) carbon catalyst. The sulfonic acid group concentration on the 3DOm carbon was finely controlled using an aniline reaction between the carbon surface and diazonium sulfonate. It was found that the number of acid sites on the 3DOm carbon catalysts and their adsorption properties needs to be optimized to maximize the hydrolysis of cellobiose and water soluble oligosaccharides. The adsorption capacity of water soluble oligosaccharides on the 3DOm carbon samples increased with the chain length of the oligosaccharides which is likely due to the following two reasons: a part of oligosaccharides is “dangling” off the carbon surface due to their branched structure; the long oligosaccharides adsorbed on the carbon surface exhibit a dense packing structure compared with relatively small oligosaccharides. Adsorption of glucose and cellobiose on the 3DOm carbon and 3DOm carbon with sulfonic acid group was performed at different temperatures to determine the enthalpy and entropy of the adsorption. It was found that the adsorption enthalpy increased with increasing chain-length which is due to the CH-π interaction between the glucose unit and the carbon surface. Adsorption entropy also increased with increasing chain-length, but the adsorption entropy was higher for cellobiose on 3DOm carbon than that of cellobiose on 3DOm carbon with sulfonic acid groups. This is likely due to an enhanced hydrophobic effect regarding releasing solvated water molecules from cellobiose and carbon surface.
3.2: Introduction

The production of glucose from crystalline cellulose, an abundant biopolymer consisting of anhydroglucose units (AGUs) connected via $\beta(1\rightarrow4)$ glycosidic linkages, is paramount to the efficient utilization of lignocellulosic biomass for production of fuels and value added chemicals.\textsuperscript{4, 22, 71-73} Amorphous carbon materials with functional surface groups have recently received a great deal of interest as catalysts and adsorbents for aqueous phase hydrolysis of cellulose to glucose due to their low cost, hydrothermal stability and unique adsorption properties. Amorphous carbons with high carbon content (>80 wt.%) are composed of polycyclic aromatic domain in irregular arrangements.\textsuperscript{96} The surface of amorphous carbon may also contain a large variety of oxygen containing groups which can tune the carbon surface properties from hydrophobic to hydrophilic.\textsuperscript{50, 51} Recently, Fukuoka et al. and Katz et al. have reported that the interaction between $\beta(1\rightarrow4)$ glucan oligomers and highly carbonaceous amorphous carbon is dominated by the CH-π dispersion forces.\textsuperscript{42, 65, 97} Furthermore, it has been claimed that the adsorption is entropically driven by the release of solvated water molecules from $\beta(1\rightarrow4)$ glucan chains and carbon surface.\textsuperscript{42, 61, 98} This entropically driven adsorption increases with increasing the chain-length of $\beta(1\rightarrow4)$ glucan due to an increase in the number of water molecules being released per glucan molecule, giving rise to strong adsorption for longer glucan chains. Confinement within ordered mesopores is also an important factor for glucan adsorption. Katz et al. showed that a gyroidal ordered mesoporous carbon with pore size of 3 - 4 nm adsorbed 27 fold more glucan oligomers compared to non-mesoporous graphite-like carbon with a similar surface area.\textsuperscript{41}

Enhanced adsorption of long glucan oligomers on carbon materials was also observed in our previous study on the selective conversion of microcrystalline cellulose to glucose.\textsuperscript{99} Cellulose was first co-impregnated with glucose and a small amount of sulfuric acid, then subjected to ball-milling to form water soluble (> 15 wt.% in water) $\beta(1\rightarrow4)$ glucan oligomers with $\alpha(1\rightarrow6)$ branches. These oligomers were then readily converted into glucose over a sulfonated three-dimensionally ordered mesoporous carbon catalyst (SO$_3$H-3DOm carbon) with a glucose yield of
90% under mild reaction conditions. The turn over frequency (TOF) for the hydrolysis of glucan oligomers over the \( \text{SO}_3 \text{H-3DOm} \) carbon catalyst was 10 fold higher than homogeneous acids (e.g. hydrochloric acid). The high activity and selectivity were attributed to the unique adsorption properties of the carbon catalyst. It was observed that the Langmuir constant of the adsorption isotherms increases by over two orders of magnitude from glucose to glucan oligomers, indicating a strong correlation between the chain length of glucan oligomers and the adsorption strength. From a reaction standpoint, the favorable adsorption for long oligomer reactants allows for selective hydrolysis of long glucan oligomers while suppressing the Brønsted acid catalyzed side reactions of glucose to other products such as 5-hydroxymethylfurfural (HMF) and levulinic acid.\(^{76,100}\)

While it has been shown that carbon materials used as adsorbents and catalysts are highly attractive for the hydrolysis of cellulose, the effects of surface properties and polycyclic aromatic domain size on their adsorption and catalytic properties are not well understood. Hara \textit{et al.} studied the activity of partially carbonized cellulose functionalized with sulfonic acid groups and suggested that the OH groups act as adsorption sites for glucan\(^{59}\) while the electron-withdrawing COOH groups adjacent to sulfonic groups stabilize the acid sites by increasing the electron density between the sulfur and surface carbon atoms and thus reducing the electron density associated with the acidic hydrogen.\(^{101}\) Katz \textit{et al.} have shown that mesoporous carbon nanoparticles containing only weak acid sites (OH and COOH groups) can hydrolyze xylan, however the hydrolysis only proceeds on the portions of the nanoparticles with relatively high surface density of phenolic OH groups.\(^{44,65}\) On the other hand, King \textit{et al.} also showed that the heat of adsorption and adsorption capacity of mono- and disaccharides as well as glycols is higher for highly carbonaceous carbons and decreases with increasing phenolic OH concentration, likely due to the competitive adsorption of water with the surface OH groups.\(^{61}\)

The objective of this study is to develop a structure-property relationship for the 3DOm carbon catalyst so that the catalysts can be rationally tailored for the selective hydrolysis of glucan oligomers. 3DOm carbon catalysts with well-controlled mesoporous structures and surface
functional groups were synthesized. In order to understand the adsorption mechanism of $\beta(1\rightarrow4)$ glucan oligomers on the carbon materials, the enthalpy and entropy of adsorption of mono- and disaccharides on the 3DOm carbon were measured and correlated to their surface structures including the domain size and surface functional groups.

3.3: Experimental section

3.3.1: Materials

Glucose (99 wt.%) was purchased from Sigma Aldrich. Microcrystalline cellulose (Avicel, 4 wt.% moisture, DP 215), sulfanilic acid (98 wt.%), sodium nitrite (98 wt.%), hyphophorous acid ($\text{H}_3\text{PO}_2$) (50 wt.% in water), methyl red (99+ wt.%), methyl orange (99+ wt.%), and phenolphthalein (99+ wt.%) were purchased from Alfa Aesar. Sulfuric acid ($\text{H}_2\text{SO}_4$, 98 wt.% and 0.005 M), 200 proof ethanol, N,N-dimethylformamide (DMF) (99.8 wt.%), methanol (99.8 wt.%), acetone (99.8 wt.%), 12.1 M hydrochloric acid (HCl) were purchased from Fisher Scientific.

3.3.2: 3DOm carbon synthesis and functionalization

3DOm carbon with a cage of 35 nm was prepared according to literature. Surface functionalization of the 3DOm carbon with sulfonic acid groups was achieved by reacting with benzenesulfonic acid radicals derived from diazonium salts under mild conditions. 30 mL of deionized water were mixed with 2 mL of 12.1 M HCl and 0.12 to 1.2 g of sulfanilic acid. This solution was immersed in an ice bath and stirred for 5 min. 0.141 to 1.410 g of sodium nitrite (3:1 molar ratio sulfanilic acid to sodium nitrite) were added to the solution and stirred for 10 minutes. Sodium nitrite was completely dissolved in the acid solution after 1 minute. A white precipitate can be observed after 5-7 minutes when the amount of sulfanilic acid was higher than 0.6 g. 0.2 g of 3DOm carbon, 30 mL of ethanol and 30 mL of 50 wt.% H$_3$PO$_2$ were added to the solution and stirred for 30 minutes, followed by the addition of 30 mL of H$_3$PO$_2$. The resulting solution was mixed for 8 hours in an ice bath. After the functionalization, the catalyst was fully washed by shaking and sonicating in 100 mL each of water, DMF, methanol and acetone, respectively, followed by washing with 2 L of 70 °C water. The sample was then washed overnight in 1 L of 70 °C water.
°C water, filtered, then dried overnight at 70 °C. This obtained material is denoted SO$_3$H-3DOm carbon. The number of acid sites can be finely controlled by the amount of sulfanilic acid and sodium nitrite. It should be noted that the diazonium sulfonate precipitated after 10 minutes in an ice bath. Dry diazonium sulfonate is not stable and can spontaneously release nitrogen gas at room temperature. Caution should be taken during the filtration step. Since excess diazonium sulfonate can be easily dissolved in DMF, in order to achieve safe drying and storage washing the formed sample with DMF is highly recommended.

### 3.3.3: Carbon characterization

N$_2$ adsorption/desorption isotherms were measured on an Autosorb®-iQ system (Quantachrome) at -196 °C. 0.01 g of carbon samples was degassed under vacuum for 24 hours at 200 °C. Total surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Pore size distributions were calculated from the adsorption branch using a QSDFT model for carbon materials with slit/cylindrical/spherical pore structures developed by Quantachrome in VersaWin version 1.0. The model is appropriate for carbon materials synthesized using colloidal crystals as templates with heterogeneous surfaces and cage-like structures between 5 and 50 nm.$^{102}$ Small angle X-ray scattering (SAXS) was performed on a Molecular Metrology SAXS line using Cu K$_\alpha$ radiation with a sample-to-detector distance of 148.1 cm. The d-spacing was calculated using Bragg’s law using the first (111) reflection peak of the FCC lattice as shown in Equation 3.1:

$$n\lambda = 2d \sin(\theta) \quad (3.1)$$

Where $\lambda$ is the wavelength (1.54 Å), $n$ is the whole number of wavelengths (using first reflection $n = 1$), $d$ is the d-spacing and $2\theta$ is the reflection angle. For the (111) plane, the center-center distance was calculated from the d-spacing using Equation 3.2:

$$\text{Center – center distance} = \frac{d\sqrt{6}}{2} \quad (3.2)$$

The concentrations of oxygen containing groups on the 3DOm carbon surface were measured by a titration method developed by Boehm. For the parent-3DOm carbon, the total
oxygen containing groups (carboxylic, lactonic and phenolic groups) were estimated by titration with 0.05 M NaOH. The concentration of carboxylic groups (COOH) was estimated by titration with 0.05 M NaHCO₃. For the SO₃H-3DOM carbon, titration with 0.05 M NaCl was used to measure the concentration of SO₃H groups. Titration with 0.05 M NaOH was also performed, which measured the total concentrations of oxygen containing groups and SO₃H groups. The concentrations of oxygen containing groups on the SO₃H-3DOM carbon were calculated by subtracting the NaCl titration result from the NaOH titration result. Typically, 0.020 g of catalyst was placed in 10 mL of 0.05 M NaCl, 0.05 M NaHCO₃ or 0.05 M NaOH solution and sonicated for 3 hours. For NaOH titrations, 0.010 M HCl was used to titrate with methyl red as an indicator. For NaHCO₃ titrations, 0.010 M HCl was used to titrate with methyl orange as an indicator. For 0.05 M NaCl, 0.01 M NaOH was used to titrate using phenolphthalein as an indicator.

Raman spectroscopy was performed using a DXR Raman Spectro-microscope (Thermo Scientific, Madison, WI) with the following conditions: a 10 × confocal microscope objective (3 mm spot diameter and 5 cm⁻¹ spectral resolution), 633 nm excitation wavelength, 4 mW laser power and 50 µm slit width for 1 s integration time. OMNIC™ software version 9.1 was used to control the Raman instrument. Eight spots were selected randomly for each sample, and measured within the range of 100-3300 cm⁻¹. Further details of the Raman measurement are available in the literature by Pang et al. G, D1, D2, D3 and D4 band intensities were estimated by peak fitting analysis. We fit the Raman peaks using an algorithm based on the Bayesian scheme described by Hummer. Each of the five peaks has three defining parameters which are position, width and intensity, for a total of 15 parameters. The peaks were assumed to be Lorenzian in shape. Bayesian inference is a statistical inference technique which is able to incorporate information about the underlying physical model into the fitting via a so called prior distribution by defining a probability distribution governing the values of the 15 model parameters. The peak placement variation was pinned to a Gaussian distribution with standard deviation of 5 cm⁻¹ with an average value of the initial peak position. The initial guess of peak positions were determined by literature. The parameter of peak
width is defined as one quarter of the peak width at one half intensity. The peaks are assumed to be Lorenzian in shape. The initial guesses of parameters used in the prior distribution are shown in Table 3.1. The negative-log likelihood (the negative log of the probability) is minimized with respect to the model parameters by Monte Carlo. This technique is similar to the application of Monte Carlo schemes to minimize the configurational energy of an assembly of Lenard Jones atoms. In this case, the negative-log likelihood is treated as an effective energy function and the values of the 15 parameters are the effective configuration (i.e. x,y,z coordinates). Monte Carlo optimization of the model parameters was carried out in a custom written simulation program using numpy/scipy python packages.

Table 3.1: Prior model parameters for Bayesian inference peak fitting of Raman spectroscopy

<table>
<thead>
<tr>
<th>Peak</th>
<th>Peak placement (cm(^{-1}))</th>
<th>(\frac{1}{4}) peak width at (\frac{1}{2}) intensity (cm(^{-1}))</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>1580</td>
<td>1</td>
<td>100 % average intensity</td>
</tr>
<tr>
<td>D1</td>
<td>1350</td>
<td>1</td>
<td>100 % average intensity</td>
</tr>
<tr>
<td>D2</td>
<td>1620</td>
<td>1</td>
<td>100 % average intensity</td>
</tr>
<tr>
<td>D3</td>
<td>1500</td>
<td>1</td>
<td>10 % average intensity</td>
</tr>
<tr>
<td>D4</td>
<td>1200</td>
<td>1</td>
<td>10 % average intensity</td>
</tr>
</tbody>
</table>

3.3.4: Chain-length analysis of large oligomers

The mixture of soluble oligomers produced from the ball-milling of cellulose co-impregnated with glucose and acid. The Large oligomer portion (chain length > 7 AGUs) was fraction collected over HPLC. The oligomers were purified by drying on 50 °C hotplate with airflow over the liquid surface over a period of 3 hours. Samples for NMR were prepared by dispersing 5.0 wt.% dried oligomers in D\(_2\)O with 10 mM 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as an internal standard. \(^1\)H-NMR was performed on a Bruker Advance 400 (400 MHz) spectrometer to determine the prevalence of glycosidic linkages and reducing ends. \(^1\)H-NMR samples were sonicated for 15 minutes and vortexed for 3 minutes followed by filtration before the measurement. The \(^1\)H-NMR was performed with 32 scans.
3.3.5: Saccharide adsorption

Aqueous phase adsorption of glucose and cellobiose on the carbon samples was performed at 0, 20, 50 and 70 °C with saccharide concentrations from 1 to 50 mg mL\(^{-1}\). 3 to 20 mg of carbon samples was added to 1 mL saccharide solution and equalized for up to 24 h. Isotherms of mixed oligomers as well as fractionated trimers and tetramers were measured at room temperature. Mixed oligomer solutions were prepared from 1 to 50 mg mL\(^{-1}\) while fractionated trimers and tetramers were prepared from 0.5 to 10 mg mL\(^{-1}\). For the adsorption measurements at high temperatures (50 and 70 °C), sample weights were recorded before and after the adsorption measurements to ensure no evaporation of water during the measurement. Additionally, the syringes and filters used in the measurement were heated or cooled to adsorption temperature prior to filtration to ensure no effects from temperature changes during the filtration step. All adsorption solutions were analyzed using high performance liquid chromatography (HPLC) (LC-20AT, Shimadzu) equipped with refractive index (RID-10A) and UV–Vis (SPD-2AV) detectors at oven temperature of 85 °C. An Agilent Hi-Plex-Na HPLC column (7.7 mm (ID), 300 mm (Length), 10 µm (particle size)) with a guard column was used. HPLC grade water (Fisher) was used as a mobile phase with a flow rate of 0.3 mL minute\(^{-1}\).

Adsorption data was fitted to the Langmuir model as shown in equation 3.3. The Langmuir model is shown in Equation 3.3:

\[
Q_e = \frac{Q_m K_L C_{te}}{1 + K_L C_{te}}
\]  

(3.3)

Where \(Q_e\) is the equilibrium loading of the adsorbate on the adsorbent, \(Q_m\) is the maximum loading, \(K_L\) is the Langmuir constant proportional to the ratio of adsorption/desorption rate constants, and \(C_{te}\) is the equilibrium concentration. As discussed in the manuscript, isotherms used for the calculation were corrected for real adsorption. The parameters were calculated by the least squares method.
The adsorption capacity of porous materials in an aqueous phase is usually estimated by the “excess” adsorption, as defined in the Equation 3.4:

\[ Q_{e}^{Ex} = \frac{V_s(C_{Ai} - C_{ Ae})}{m} \]  

(3.4)

Where \( Q_{e}^{Ex} \) is the excess adsorption of adsorbate per mass of adsorbent, \( V_s \) is the initial volume of solution used, \( C_{Ai} \) and \( C_{Ae} \) are the initial and equilibrium concentration of the adsorbate in solution and \( m \) is the mass of adsorbent. As reported by Léon et al., in an aqueous phase the density and volume of solution may change over the course of the adsorption process. Using the changes in the equilibrium concentration may not correctly describe the adsorption properties of the materials. 

Therefore, the method derived by Léon et al. shown in Equation 3.5 was used to achieve the adsorption isotherms of glucan oligomers on the 3DOm carbon samples.

\[ Q_{e}^{R} = \frac{C_{Ai} - \left( \frac{d_i}{d_e} - \frac{\bar{V}_p}{\bar{V}_w} \frac{m}{V_e d_e} \right) C_{Ae}}{m \left[ 1 + \left( \frac{\bar{V}_A}{\bar{V}_w} - 1 \right) \frac{C_{Ae}}{d_e} \right]} \]  

(3.5)

The variables in Equation 3.5 are defined as follows: \( Q_{e}^{R} \) is the real adsorption of adsorbate per mass of adsorbent. \( d_i \) is the initial solution density, and \( d_e \) is the equilibrium solution density. The density of the solutions depends on both adsorbate concentration and experiment temperature. Glucose and cellobiose solution densities were obtained from literature and were used to interpolate the solution densities at the given concentrations and adsorption temperatures used in this study. Trimer solution density was estimated by interpolating cellotriose solution density reported in literature. It was found that the difference in solution density in g cm\(^{-3}\) between cellotriose and cellobiose was less than 0.16 % at identical saccharide weight fraction. We therefore used cellobiose density data to approximate the solution density for the tetramer and mixed oligomer adsorption isotherm adjustments due to relatively small change in density as a function of chain-length. \( \bar{V}_p \) is the pore volume per gram of catalyst, which is equal to the BET surface area multiplied by 7 Å, which we assumed to be the thickness of a monolayer of glucose or...
cellulbiose adsorbed on the surface of carbon samples. $V_w^r$ is the specific molar volume of water, which was found in Perry’s Chemical Engineering Handbook.\(^{110}\) $V_i$ is the initial volume of solution, which was calculated by dividing the measured initial solution mass by $d_i$. $V_A^r$ is the specific molar volume of the adsorbate at the adsorption temperature. The specific molar volume can be calculated by a combination of Schroeder’s method and Gain’s method.\(^{111}\) Schroeder’s method (Equation 3.6) was used to estimate the specific molar volume at the normal boiling point. Gain’s method was used to calculate the specific molar volume at different temperatures based on the value at the normal boiling point (Equation 3.7). The specific molar volumes of glucose, cellulbiose, cellotriose and cellotetraose at their normal boiling point were estimated using the ChemSpider database.\(^{112}\) These calculations are shown in the following paragraph. Cellotetraose specific molar volume data was used to correct the mixed oligomer isotherm.

### 3.3.6: Excess adsorption calculations

The specific molar volume of the adsorbent at the experimental temperature, $V_A^r$, were estimated using a combination of Schroeder’s and Gain’s method for glucose and cellulbiose. Schroeder’s method is shown in equation 3.6:

$$V_b^r = \sum_i n_i \cdot v_{b,i} \quad (3.6)$$

Where $V_b^r$ = molar volume at normal boiling point in cm\(^3\) mol\(^{-1}\), $n_i$ = the number of features $i$ in the molecule, and $v_{b,i}$ = contribution of feature $i$ molar volume in cm\(^3\) mol\(^{-1}\). In the case of glucose and cellulbiose, $v_{b,i}$ of C, H and O = 7 and $v_{b,i}$ of a ring = -7. For example: The molecular formula of cellulbiose is C\(_{12}\)H\(_{22}\)O\(_{11}\). The molar volume at normal boiling point of cellulbiose is:

$$V_b^r = [(12 \times 7) + (22 \times 7) + (11 \times 7) - (2 \times 7)] = 301 \text{ cm}^3 \text{ mol}^{-1}$$

The molar volume at normal boiling point is used to calculate the molar volume at a given temperature using Gain’s method as shown in equation 3.7:

$$\rho_A = \frac{M}{V_b^r} \left[3 - 2 \left(\frac{T}{T_b}\right)\right] \quad (3.7)$$
Where \( \rho_A \) is the density of the adsorbate at temperature \( T \) in g cm\(^{-3} \), \( M \) is the molecular mass in g mol\(^{-1} \), \( T_b \) is the boiling point temperature in K. The molar volume \( V_A \) in cm\(^3\) mol\(^{-1} \) is calculated by dividing \( \rho \) by the molecular mass. \( T_b \) for glucose, cellobiose, cellotriose and cellotetraose were estimated by Chemspider to be 527 K, 941 K, 1138 K and 1268 K respectively. The molar volume of cellobiose at 20 °C is calculated as follows:

\[
\rho_A = \frac{342 \text{ g mol}^{-1}}{301 \text{ cm}^3 \text{ mol}^{-1}} \left[ 3 - 2 \left( \frac{298 \text{ K}}{941 \text{ K}} \right) \right] = 1.485 \text{ g cm}^{-3}
\]

\[
V_A = \frac{342 \text{ g mol}^{-1}}{1.485 \text{ g cm}^{-3}} = 230.5 \text{ cm}^3 \text{ mol}^{-1}
\]

3.3.7: Chain length distribution before and after adsorption:

Saccharide distributions before and after adsorption for parent carbon starting from initial concentrations of 1, 10 and 50 mg mL\(^{-1} \) were prepared to show a comparison between the adsorption affinities of large and short oligomers. The concentrations were measured by referencing HPLC peak area integration of the solutions before and after adsorption and to a standard curve. Chains up to 7 AGUs long were able to be separated. The large oligomer fraction (\( L-OF \)) was the remaining peak containing the oligomer too large to separate.

3.3.8: Catalytic reaction

Hydrolysis reactions were performed using 1 wt.% cellobiose. 30 mg of saccharide were mixed with 20 mg of SO\(_3\)H-3DOM carbon catalyst and 3 mL of deionized water, and sealed in a 5.0 mL borosilicate microwave heating vial (Chemglass). The reaction was performed on a Dynabloc aluminum stir plate with 22 (ID) × 35.6 (depth) mm holes (Ace Glass) at 120 °C for up to 2.0 h. Hydrolysis reactions of cellobiose without additional catalyst (blank reaction) at 120 °C were also performed. The TOF for hydrolysis determined by subtracting the moles of glucose produced during the blank reaction from the moles of glucose produced from the carbon catalyst reaction at identical reaction time. The TOF calculation is shown in Equation 3.8 when the conversion of glucan oligomers was less than 20%:
3.4: Results and discussion

3.4.1: Textural properties

3DOm carbon samples used in this study are highly ordered mesoporous materials with interconnected mesoporous cages of 35 nm. The high surface area and large interconnected mesopores facilitate the transport of large glucan oligomers within the porous catalysts during the hydrolysis reaction. They also allow for access to the active sites on the carbon surface. The morphologies and surface properties of the 3DOm carbon catalysts before and after the addition of sulfonic acid groups were characterized. The sulfonated 3DOm carbon after surface functionalization contains 0.5 mmol SO$_3$H g$^{-1}$. The textural properties of the two carbon samples were characterized using a nitrogen physisorption at -196 °C and SAXS as shown in Figure 3.1. The BET surface area and average pore size were calculated from the nitrogen physisorption isotherms, and center to center distance between the cages was calculated from the Bragg’s law using the (111) reflection peak in the SAXS patterns as shown in the SI. The N$_2$ sorption isotherms as well as the SAXS patterns of the SO$_3$H-3DOm carbon are nearly identical to the parent-3DOm carbon, suggesting that the ordered porous structures of 3DOm carbon remain intact after the functionalization by the diazomium salts. The center to center distance of the 3DOm carbon did not change after the functionalization as shown in Table 3.2, indicating that the change of the ordered structures is not significant. The BET specific surface area decreased by 18 %, which is likely due to the increases in specific mass from the addition of the sulfonic acid groups. The average pore width of the SO$_3$H-3DOm carbon is slightly smaller than the parent-3DOm carbon.
Figure 3.1: Textural properties of parent-3DOm and SO₃H-3DOm carbons. A) Nitrogen adsorption/desorption isotherms. B) Pore size distribution calculated from the adsorption branch using QSDFT model. C) SAXS.

Table 3.2: Textural properties of parent-3DOm and SO₃H-3DOm carbons.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area¹ (m² g⁻¹)</th>
<th>Pore size² (nm)</th>
<th>Center-center distance³ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent-3DOm Carbon</td>
<td>1445</td>
<td>29.0</td>
<td>29.4</td>
</tr>
<tr>
<td>SO₃H-3DOm Carbon</td>
<td>1191</td>
<td>28.1</td>
<td>29.1</td>
</tr>
</tbody>
</table>

¹The BET surface area is calculated from Nitrogen adsorption/desorption isotherms with a relative pressure from 0.05-0.2 P/P.
²The pore size is calculated from the QSDFT model.
³The center-center distance is calculated from the Bragg’s law using the (111) reflection peak.

3.4.2: Oxygen containing groups

In order to evaluate the effects of the surface functional groups on the adsorption properties of the 3DOm carbon materials, the concentrations of oxygen containing groups on the carbon surface were measured by a titration method developed by Boehm⁵⁰. The results showed that the parent-3DOm carbon contains 0.67 mmol g⁻¹ oxygen containing groups including carboxylic, lactonic and phenolic groups, which is higher than conventional activated carbon and carbon black (0.22 - 0.33 mmol g⁻¹)⁵ø,⁵¹,⁷⁶. The result indicates that the 3DOm carbon samples are relatively more hydrophilic in nature compared to conventional carbon black and activated carbon. The titration results on the SO₃H-3DOm carbon suggested that the carbon sample contains around 0.5 mmol SO₃H g⁻¹ and 0.80 mmol g⁻¹ oxygen containing groups. The number of oxygen containing groups increased by 0.13 mmol g⁻¹ compared to the parent-3DOm carbon. Liu et. al. showed similar
results, increasing the number of oxygen containing groups by 0.07 mmol g \(^{-1}\) on activated carbon functionalized with diazonium sulfonated with hypophosphorous acid as a reducing agent.\textsuperscript{46} This change in surface oxygen containing groups is relatively small, which is likely due to the mild functionalization process.

### 3.4.3: Raman spectroscopy and domain size

The sizes of the polycyclic aromatic domains for the 3DOm carbon samples before and after surface functionalization were estimated by Raman spectroscopy. The domain size is defined as the diameter of the polycyclic aromatic basal planes. It has been known that the first order sp\(^2\) vibration bands of carbon materials occur in the region of 1100 to 1800 cm\(^{-1}\).\textsuperscript{96, 113, 114} An undisturbed graphitic lattice exhibits one first order band at around 1580 cm\(^{-1}\). This band is known as the G or “graphitic” band, and it corresponds to a lattice vibration mode with E\(_{2g}\) symmetry. The spectrum of a graphitic lamella exhibits an additional first order band at around of 1360 cm\(^{-1}\).This band is known as the D1 or “defect” band, which corresponds to the atoms on the edge of graphitic lattice with vibration modes of A\(_{1g}\) symmetry. The D1/G ratio can be used to determine the domain size using the Equation 3.9:\textsuperscript{114}

\[
L_a = \frac{C(\lambda)}{I_{D1}/I_G} \quad (3.9)
\]

where \(L_a\) is the domain diameter, \(I_{D1}\) and \(I_G\) are the peaks areas of the D1 and G peaks, respectively, and \(C(\lambda)\) represents a wavelength dependent factor of \(C(\lambda) = C_0 + C_1\lambda\), \(C_0 = -12.6\) nm and \(C_1 = 0.033\), valid for 400 nm < \(\lambda\) < 700 nm.\textsuperscript{114, 115}

The Raman spectrum of amorphous carbon is more complex than that of pure graphene substrates. There are several other types of defect carbon vibrations (called D2, D3 and D4). As suggested in literature,\textsuperscript{96} the D2, D3 and D4 peaks for amorphous carbon are located at 1559 - 1628, 1489 - 1545, and 1127 - 1208 cm\(^{-1}\), respectively as shown in Table 3.1. In order to determine the domain size, the Raman spectra were fitted using an algorithm based on the Bayesian scheme described by Hummer \textit{et. al.}\textsuperscript{104} This algorithm finds the most likely set of model parameters, which
in this case are peak position, width, and intensity of the G and D1-4 bands combined with instrument noise. The likelihood maximization is carried out by applying a Monte Carlo based scheme which treats the negative likelihood as an effective energy functional and minimizes it with respect to the model parameters. Figure 3.2A shows the Raman spectra of the parent and SO$_3$H-3DOm carbon samples. The two spectra are nearly identical, which is reasonable since the number of sulfonic acid groups on the carbon surface is roughly two orders of magnitude fewer in surface concentration than C atoms in the 3DOm carbon samples. Figure 3.2B shows the deconvoluted peaks of the parent-3DOm carbon Raman spectrum. Using the G and D1 values obtained from the peak deconvolution, the domain size was calculated to be around 1.55 nm. The resulting domain size is similar to that of chars produced from cellulose pyrolyzed at similar temperatures (less than 1000 °C), which bear domain sizes of less than 2 nm.\textsuperscript{114}

![Figure 3.2: Raman scattering spectra of carbon materials. A) Parent and SO$_3$H-3DOm carbon. B) Peak deconvolution of Raman spectrum of parent-3DOm carbon.](image)

3.4.4: Tuning surface acid site and adsorption site concentrations

SO$_3$H-3DOm carbon catalysts with different quantities of sulfonic acid groups were prepared in order to understand the effects of acid sites on the adsorption properties of the carbon catalysts. It was observed that the number of sulfonic acid sites on the carbon catalysts can be easily controlled by varying the amount of diazonium sulfonate generated from sulfanilic acid and sodium nitrite used in the synthesis solution. The results suggest that the number of sulfonic acid sites on
the carbon catalyst can be varied from 0.14 to 1.31 mmol SO$_3$H g$^{-1}$ as shown in Figure 3.3A. The adsorption sites were estimated by the maximum adsorption capacity of cellobiose at 0 °C. Figure 3.3B shows the total number of adsorption and acid sites for the 3DOm carbon samples with different quantities of sulfonic acid groups. It was observed that the total number of sulfonic acid and adsorption sites is approximately constant for each sample, with each acid site annihilating one adsorption site. The linear reduction in adsorption sites with the addition of acid sites is likely due to the reaction between the carbon surface and diazonium sulfonate, which annihilates the basal-plane π-bonds responsible for the adsorption of saccharides. Additionally, the sulfonic acid group may reduce electron density from the surrounding carbon surface, an effect which is proportional to the number of acid sites. This electron-poor region may not be able to adsorb saccharides strongly. The SO$_3$H-3DOm carbon catalysts were optimized by testing the TOF for hydrolysis of cellobiose at low conversion (< 20 %) as shown in Figure 3.3C. The TOF for the hydrolysis of cellobiose over SO$_3$H-3DOm carbon is highest for the sample containing 0.50 mmol SO$_3$H g$^{-1}$, indicating that an optimized adsorption and reaction sites is critical for the carbon catalysts. Based on this result the SO$_3$H-3DOm carbon sample with 0.50 mmol SO$_3$H g$^{-1}$ was used for all of the remaining experiments.
Figure 3.3: Optimization of acid sites and adsorption properties of the 3DOm catalyst. (A) Control of the number of acid sites on 3DOm carbon by tailoring the amount of sulfanilic acid precursor in solution. The x-axis is the amount of sulfanilic acid used during synthesis and the y-axis is the number of sulfonic acid groups functionalized on the carbon. (B) Correlation between cellobiose adsorption capacity and sulfonic acid groups on various SO$_3$H-3DOm carbons. The number of sulfonic groups plus the number of cellobiose adsorption sites is approximately constant. (C) TOF obtained from the hydrolysis of cellobiose over SO$_3$H-3DOm carbons with different amounts of sulfonic acid sites.

3.4.5: Langmuir adsorption isotherms

To compare the adsorption strength and capacity of glucan oligomers on the 3DOm carbon samples, adsorption isotherms of glucose, cellobiose and mixed glucan oligomers produced from the milling of co-impregnated cellulose were measured at room temperature. The composition of the mixed oligomers produced from milling of cellulose co-impregnated with glucose using our previous method$^{99}$ is as follows: 3 wt.% levoglucosan, 6.3 wt.% glucose, 7.0 wt.% dimers, 4.3 wt.% trimers, 4.3 wt.% tetramers, 3.8 wt.% pentamers, 4.1 wt.% hexamers, 3.9 wt.% heptamers, and 63.2 wt.% of the large glucan oligomers with chain length greater than 7 AGUs. The resulting $^1$H-NMR spectra is shown in Figure 3.4. The peak of the reducing ends as well as the $\alpha$(1→6) and $\beta$(1→4) glycosidic linkages were integrated. It was found from standards of glucose and cellobiose that the area of peaks in $^1$H-NMR are proportional to the number of hydrogens present. It was found that the average oligomer contained 14.5 AGUs per chain with an average of 1.65 branches per chain.
The 63.2 wt.% portion of oligomers which contains an average chain-lengths of 14.5 AGUs will be referred to as the large oligomer fraction \((L-OF)\) while the remaining fraction contain G1-G7 species will be referred to as the small oligomer fraction \((S-OF)\).

**Figure 3.4:** \(^1\text{H}-\text{NMR of fractionated oligomers produced from 1 hour milling of cellulose co-impregnated with acid and 12.5 wt.% glucose. Reducing ends (RE) and linkage peaks are labeled.**

**Figure 3.5:** Corrected room temperature adsorption of glucose, cellobiose and mixed oligomers on (A) parent-3DOm carbon and (B) \(\text{SO}_3\text{H}-3\text{DOm carbon. The points are from experimental measurement. The lines are from Langmuir adsorption fitting.**
Table 3.3: Room temperature Langmuir adsorption constants for glucan of different chain-lengths.

<table>
<thead>
<tr>
<th>Saccharide</th>
<th>Parent-3DOm carbon</th>
<th>SO$_3$H-3DOm carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_m$ (mg g$^{-1}$)</td>
<td>$Q_m$ (mmol g$^{-1}$)</td>
</tr>
<tr>
<td>Mixed oligomers</td>
<td>834</td>
<td>0.35</td>
</tr>
<tr>
<td>Cellobiose</td>
<td>357</td>
<td>1.04</td>
</tr>
<tr>
<td>Glucose</td>
<td>285</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Adsorption isotherms on parent-3DOm and SO$_3$H-3DOm carbon are shown in Figure 3.5A and Figure 3.5B, respectively. The adsorption isotherms were fitted using the Langmuir adsorption model. The adsorption capacities, $Q_m$, and Langmuir adsorption constants, $K_L$, for cellobiose and glucose are shown in Table 3.3. Figure 3.6 shows the chain-length distribution of the solutions of mixed oligomers before and after adsorption onto parent-3DOm carbon at three initial oligomer concentrations (1, 10 and 50 mg mL$^{-1}$). The result clearly demonstrates that large oligomers preferentially adsorb on the carbon compared to the smaller species. At high concentration (50 mg mL$^{-1}$) the adsorption surface coverage is dominated by large oligomers, with 90.2 % L-OF and 9.8 % S-OF adsorbed on the surface. Thus the $Q_m$ of the mixed oligomer sample estimated in Table 3.3 is based on the assumption that oligomers with chains averaging 14.5 AGUs were adsorbed at high concentration. However, the $K_L$ of the mixed oligomer sample is not calculatable using the current set of experiments as more significant adsorption of the S-OF took place at lower concentrations. For example: 79 wt.% of the L-OF and 18 wt.% of the S-OF are adsorbed at 10 mg mL$^{-1}$ while 93 wt.% of the L-OF and 78 wt.% of the S-OF are adsorbed at 1 mg mL$^{-1}$. The result is easy to understand since the surface coverage on the carbon catalysts from the S-OF is not sufficiently high under the low concentration of the mixed oligomers so that the S-OF can be adsorbed on the surface. However, under the high concentration of the mixed oligomers, the surface of the carbon catalyst is mainly covered by the L-OF due to the preferred adsorption.
The number of saccharides adsorbed on the 3DOM carbon samples compared to their domain size was evaluated in order to understand the adsorption properties of the carbon samples. It was observed that the adsorption capacity for cellobiose on the parent-3DOM carbon was 1.04 mmol g\(^{-1}\) while adsorption capacity for glucose was 1.58 mmol g\(^{-1}\). Additionally, the domain size calculated from Raman spectroscopy is approximately 1.55 nm, which is close to the length of a cellobiose molecule with dimensions of 1.1 x 0.7 x 0.4 nm.\(^{42}\) The adsorption capacity for cellobiose and glucose on the parent-3DOM carbon has a 2:3 ratio. However, given that cellobiose is about twice as large as glucose, the expected adsorption ratio should be close to 2:4. We hypothesize that the relatively low adsorption of glucose may be due to limitations in the coverage of the domains or the different adsorption equilibrium between the adsorption on the carbon surface and in the aqueous phase. The measured BET surface area of the parent carbon was 1445 m\(^3\) g\(^{-1}\). The bulk density of the carbon was assumed to be the same as furfural alcohol resin carbonized at 900 °C of 1.50 g cm\(^{-3}\).\(^{116}\) The density of carbon atoms per nm\(^2\) was estimated to be the same as graphene, which is 36 atoms nm\(^{-2}\).\(^{117}\) Additionally, the domains were assumed to be circular with a diameter of 1.55 nm (from Raman), or an area of 1.89 nm\(^2\). Based on the surface area and the domain size, there are 0.68 mmol domain per gram. Based on the 0 °C adsorption capacity of cellobiose and glucose, the number of cellobiose and glucose molecules per domain are 2.6 and 1.8 molecules nm\(^2\). These calculations based on the specific surface area, density and the adsorption capacity of

---

**Figure 3.6:** Oligomer distribution data. A: Distribution starting from 1 mg mL\(^{-1}\). B: Starting from 10 mg mL\(^{-1}\). C: Starting from 50 mg mL\(^{-1}\).
the carbon materials indicated that the number of glucose and cellobiose per domain is 2.6 and 1.8, respectively.\textsuperscript{116, 117} This is consistent with the 2:3 ratio obtained from the adsorption capacity.

The small domain size compared with cellobiose implies that the interaction between cellobiose and the domain are less than ideal, and it may be possible that some functional groups can ‘dangle’ off of the ends of the domain. The interaction between the cellobiose molecule and the carbon surface may therefore be less than the maximum number of possible CH-π interactions. The adsorption capacity, $Q_m$, increase with increasing chain-length from 285 mg g$^{-1}$ for glucose, 357 mg g$^{-1}$ for cellobiose to 834 mg g$^{-1}$ for mixed oligomers on the parent carbon. Trimers and tetrarmers were fractionated from mixed oligomers using HPLC, dried and used to collect room temperature adsorption isotherms. The maximum capacity in mg g$^{-1}$ as a function of the number of AGUs per molecule for parent-3DOm and SO3H-3DOm carbon is shown in Figure 3.7. The maximum capacity of saccharides on carbon increases monotonically with increasing chain-length. The increase in adsorption capacity may be explained by two possible phenomena. First, it is likely that the packing fraction of saccharides on the carbon surface increases with increasing chain length. It has been shown with Monte Carlo simulations that the solid state density of alkanes will increase with increasing chain-length due to increasing overlap between the central molecule and the neighboring molecules.\textsuperscript{118} The same phenomenon could occur on a larger scale for the surface packing of saccharide species on the carbon surface, with the AGUs in cellobiose dimers being able to pack more closely than two glucose molecules, and the AGUS in long oligomers being able to pack more closely than those in cellobiose. Second, longer saccharides may have a higher adsorption capacity as they may be less affected by domain boundaries compared to the smaller saccharide species. Glucose and cellobiose may not be able to easily adsorb on areas of the surface containing domain edges, while longer oligomer chains may be able to adsorb across multiple domains. For the very long saccharides, it may be possible that not all AGUs are closely interacted with the carbon surface, and a few AGUs are able to ‘dangle’ off of carbon surface as shown in Scheme 3.1 and 3.2.
**Figure 3.7**: Room temperature maximum capacity of saccharide species on parent-3DOm and SO$_3$H-3DOm carbon.

**Scheme 3.1.** Possible arrangement of adsorbed glucose, cellobiose and oligomers on carbon surface.
Scheme 3.2: Adsorption of glucan oligomers on parent-3DOm carbon.

Cellobiose and glucose adsorption isotherms at different temperatures were measured on parent-3DOm and SO₃H-3DOm carbon to further understand the adsorption mechanism. Corrected adsorption isotherms of glucose and cellobiose at 0, 20, 50 and 70 °C on parent and SO₃H-3DOm carbon with curves fitted from the Langmuir adsorption model are shown in Figure 3.8. The adsorption capacities, $Q_m$, and Langmuir adsorption constants, $K_L$, for glucose and cellobiose at different temperatures are shown in Table 3.4. Detailed fitting information is available in section 3.3.6. For the adsorption of cellobiose on parent-3DOm and SO₃H-3DOm carbons, the difference in $Q_m$ is approximately equal to the number of acid sites due to the annihilation of adsorption site with increasing acid site as discussed previously and shown in Figure 3.3B.

3.4.6: Adsorption enthalpy and entropy

Van ’t Hoff dependencies were utilized to further study the interaction between glucose and cellobiose on the carbon surface. The Langmuir adsorption constant, $K_L$, is related to the Gibbs free energy of adsorption as shown in Equation 3.10:

$$\Delta G^{\circ}_{ads} = -RT\ln(K_L) \quad (3.10)$$

where $\Delta G_{ads}$ is the Gibbs free energy of adsorption, $R$ is the ideal gas constant and $T$ is temperature. The classical linear van’t Hoff equation can be used to calculate the thermodynamic properties when adsorption experiments are performed at a narrow temperature range where enthalpy, entropy
and heat capacity are assumed to be constant. The enthalpy and entropy of adsorption can be expressed in terms of \( K_L \) as shown in Equation 3.11:

\[
\ln(K_L) = -\frac{\Delta H^\circ_{ads}}{RT} + \frac{\Delta S^\circ_{ads}}{R}
\]  

(3.11)

Plotting \( \ln(K_L) \) (L mol\(^{-1}\)) vs. \( T^{-1} \) (K\(^{-1}\)) produces a van’t Hoff diagram, which can be used to determine \( \Delta H^\circ_{ads} \) and \( \Delta S^\circ_{ads} \) experimentally. The van’t Hoff diagram of adsorption of glucose and cellobiose on parent 3DOm and SO\(_3\)H-3DOm carbon is shown in Figure 3.9. The slope of this line can be multiplied by \( R \) to determine the adsorption enthalpy as shown in Equation 3.12:

\[
\frac{d\ln(K_L)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ_{ads}}{R}
\]  

(3.12)

The adsorption entropy can be calculated by multiplying the intercept of the van’t Hoff diagram by \( R \). \( \Delta H^\circ_{ads} \) and \( \Delta S^\circ_{ads} \) for cellobiose and glucose on parent-3DOm and SO\(_3\)H-3DOm carbons are shown in Table 3.5.

It should also be emphasized that \( \Delta H^\circ_{ads} \) and \( \Delta S^\circ_{ads} \) determined by the van’t Hoff method are thermodynamic properties of the overall adsorption process. \( \Delta H^\circ_{ads} \), for example, does not only reflect the enthalpy released by the formation of CH-\( \pi \) dispersion bonds between the saccharides and the carbon surface. In fact, adsorption can be classified into five sequential processes, namely, (a) the desolvation of the saccharide, (b) the desolvation of the carbon surface, (c) the interaction between the saccharide and the carbon surface, (d) structural rearrangement of saccharide upon adsorption, and (e) structural rearrangement of the excluded water molecules or ions in the bulk solution. A visualization of the desolvation is shown in Scheme 3.3.
Figure 3.8: Real adsorption isotherms for (A) cellobiose on parent-3DOm carbon; (B) cellobiose on SO_3H-3DOm carbon; (C) glucose on parent-3DOm carbon; and (D) glucose on SO_3H-3DOm carbon. Adsorption was measured at 0, 20, 50 and 70 °C. The points are from experimental measurement. The lines are from Langmuir adsorption fitting.

Table 3.4: Langmuir adsorption constants for glucose and cellobiose on parent and SO_3H-3DOm carbon at different temperatures.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Cellulose Parent-3DOm</th>
<th>Cellulose SO_3H-3DOm</th>
<th>Glucose Parent-3DOm</th>
<th>Glucose SO_3H-3DOm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q_m</td>
<td>Q_a</td>
<td>K_L</td>
<td>R^2</td>
</tr>
<tr>
<td>0</td>
<td>378</td>
<td>1.13</td>
<td>844</td>
<td>0.9361</td>
</tr>
<tr>
<td>20</td>
<td>357</td>
<td>1.04</td>
<td>658</td>
<td>0.8958</td>
</tr>
<tr>
<td>50</td>
<td>341</td>
<td>1.00</td>
<td>407</td>
<td>0.9088</td>
</tr>
<tr>
<td>70</td>
<td>350</td>
<td>1.02</td>
<td>284</td>
<td>0.9364</td>
</tr>
</tbody>
</table>
Figure 3.9: Van’t Hoff Diagram of cellobiose and glucose adsorption on parent-3DOm and SO$_3$H-3DOm carbon.

Table 3.5: Adsorption enthalpy and entropy of cellobiose and glucose on parent-3DOm and SO$_3$H-3DOm carbon.

<table>
<thead>
<tr>
<th>Carbon Material</th>
<th>Saccharide</th>
<th>$\Delta H_{\text{ads}}^\circ$ kJ mol$^{-1}$</th>
<th>$\Delta S_{\text{ads}}^\circ$ J mol$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent-3DOm</td>
<td>Cellobiose</td>
<td>-12.14</td>
<td>12.06</td>
</tr>
<tr>
<td>SO$_3$H-3DOm</td>
<td>Cellobiose</td>
<td>-11.94</td>
<td>7.24</td>
</tr>
<tr>
<td>Parent-3DOm</td>
<td>Glucose</td>
<td>-8.55</td>
<td>-7.48</td>
</tr>
<tr>
<td>SO$_3$H-3DOm</td>
<td>Glucose</td>
<td>-8.58</td>
<td>-7.46</td>
</tr>
</tbody>
</table>

Scheme 3.3: Representation of cellobiose and carbon surface desolvation upon adsorption upon adsorption.

The thermodynamic properties of adsorption on parent and SO$_3$H-3DOm carbon are shown in Table 3.5. The adsorption enthalpy and entropy for glucose on both carbons are nearly identical, with adsorption enthalpies of -8.55 and -8.58 kJ mol$^{-1}$, respectively, and adsorption entropies of -7.48 and -7.46 J mol$^{-1}$ K$^{-1}$, respectively. The main difference for the adsorption of
glucose is the adsorption capacity, which is higher for the parent-3DOm carbon. However, the
analysis of adsorption thermodynamic data suggests that the adsorption processes are identical for
glucose on each carbon, and not affected by the presence of sulfonic acid group. The results
suggested that the introduction of sulfonic acid groups on the 3DOm carbon surface only reduces
the surface area for the adsorption of glucose, but not changes the interactions between glucose and
carbon surface. It was noticed that the entropy for the adsorption of glucose on both 3DOm carbon
samples was negative, indicating the adsorption is not entropically favorable compared to that of
cellobiose as shown later.

The adsorption enthalpies of cellobiose on parent and SO$_3$H-3DOm carbon are also
similar to each other, with values of -12.14 and -11.94 kJ mol$^{-1}$, respectively. The adsorption
entropy of cellobiose on both carbon samples is positive, indicating an entropically favorable
adsorption process compared to glucose. Interestingly, the adsorption entropy of cellobiose on the
parent-3DOm carbon (12.06 J mol$^{-1}$ K$^{-1}$) is higher than the entropy of adsorption measured for
cellobiose on SO$_3$H-3DOm carbon 7.24 J mol$^{-1}$ K$^{-1}$. The higher entropy for the parent-3DOm
carbon is likely due to higher hydrophobicity which causes the release of more solvated water
molecules from cellobiose and the carbon surface compared to the more hydrophilic SO$_3$H-3DOm
carbon. The entropy difference in the glucose adsorption on the two carbon samples is not obvious,
which might to due to the relatively small glucose molecules mainly interacting with the carbon
surface where not covered by sulfonic acid groups.

It has been known that the thermodynamic properties for the adsorption of saccharides
highly depends on the physical properties of the carbon materials. Fukuoka et al. reported that the
adsorption enthalpy and entropy of glucose on activated carbon, K28, is -8.4 kJ mol$^{-1}$ and +16.5 J
mol$^{-1}$ K$^{-1}$, respectively, and adsorption enthalpy and entropy of cellobiose on the carbon is -14.1 kJ
mol$^{-1}$ and +23.5 J mol$^{-1}$ K$^{-1}$, respectively. The 3DOm carbon samples studied in the work exhibited
similar adsorption enthalpy for the glucose adsorption, but slightly lower adsorption enthalpy for
cellobiose. The adsorption entropy, however, is much higher for K28. Since the two carbons have
similar numbers of oxygen containing groups (about 1.0 mmol g\(^{-1}\)), and the difference in adsorption properties is likely not due to the surface hydrophobicity, but the different surface structures. One possibility is that presence of micropores can affect the adsorption entropy through the confinement effects as more water molecules will be released when the adsorbate is limited in a confined space. It was reported that K28 activated carbon has micropores of 0.7 nm and an internal surface area of 2200 m\(^2\) g\(^{-1}\) associated with the micropores. However, the internal surface area associated with micropore smaller than 2 nm in the parent 3DOm carbon is only 46 m\(^2\) g\(^{-1}\) based a t-plot analysis compared to an external surface area of 1399 m\(^2\) g\(^{-1}\). In the case of 3DOm carbon, therefore, the confinement in the large 35 nm mesopores is apparently less effective for saccharide adsorption compared to the small micropores. Additionally, McCay et. al. recently examined the effects of micropore volume on the adsorption of phenol on carbon and found that the Langmuir adsorption, \(K_L\), increased with increasing micropore volume, indicating that the micropores are capable of interacting more strongly with the probe molecules and high adsorption enthalpy. The phenomena is also consistent with the report from Katz et. al.. They have observed that that adsorption of glucan oligomers onto a flat, non-porous graphite exhibited 27-fold less adsorption capacity than mesoporous carbon nanoparticles with 3.2 nm pores.

The results of this study show that the catalytic properties of 3DOm carbon for the hydrolysis of water soluble oligosaccharides can be controlled by tuning the adsorption properties and sulfonic acid sites. The adsorption properties are critical for the selectively hydrolysis of the large glucan oligomers into glucose. With regard to thermodynamics, the adsorption enthalpy and entropy are determined by several parameters including the hydrophobicity, mesopore/micropore size, surface functional group (sulfonic acid group in this study) and adsorbed molecules. Large domains and a hydrophobic surface might lead to strong adsorption for glucan oligomers with regard to both enthalpy and entropy aspects. The decrease in adsorption entropy after surface modification of the carbon catalysts is likely caused by the introduction of the acid sites on the surface, which enhances hydrophilicity. The maximum reaction rate at 0.50 mmol SO\(_3\)H g\(^{-1}\) is likely
achieved by balancing the number of adsorption sites, the adsorption strength and acid site concentration. Decreasing the number of acid sites and increasing the number of adsorption sites should increase the TOF for the production of glucose on acid sites as there are more glucan oligomers adsorbed on the carbon surface available to rapidly diffuse onto the acidic catalytic site. However, further increase in the adsorption strength is not necessarily preferred for the hydrolysis of glucan oligomers because of the difficulty in desorption of the formed product. An optimized hydrophobic surface should be ideal for designing the carbon catalyst for the hydrolysis of glucan oligomers. It is also interesting that the large glucan oligomers are preferentially adsorbed on the carbon surface compared with small oligomers and adsorb at much greater capacity. This is likely because of the small domain size of the carbon materials which leads to a part of the oligomer chain’s AGUs or functional groups to ‘dangle’ off of the domain and a dense packing structure. The unique adsorption properties are preferred for the selective hydrolysis of large glucan oligomers. Furthermore, compared with other carbon materials, we noticed that the presence of microporosity in the carbon materials favors the adsorption of glucan oligomers without changing the surface hydrophobicity, which might be another approach for further improvement of the carbon catalysts.

3.5: Conclusion

3DOm carbon was functionalized with benzenesulfonic acid groups using a well-controlled aniline reaction on the carbon surface. Raman spectroscopy of the parent carbon surface was used to determine that the carbon has domain sizes around 1.55 nm in diameter. Adsorption of glucose, cellobiose, extracted trimers and tetramers as well as mixed oligomers on the parent and SO$_3$H-3DOm carbons were performed at room temperature to determine adsorption capacity and its relationship to domain size. It was found that the adsorption capacity increased with increasing oligomer chain-length. The mixed oligomers, which contained a large oligomer fraction with an average chain-length of 14.5, adsorbed 3.2 and 3.9 times more mass of oligomers than glucose for
the parent-3DOm and SO3H-3DOm carbons, respectively. The adsorption capacity and domain size measurements indicated that two cellobiose molecules or three glucose molecules could fit on each domain of the parent material. The increased adsorption mass was attributed to more efficient packing of large oligomers on the surface as well as to the likelihood that large oligomers could adsorb across multiple domains, thus allowing them more area to adsorb compared to glucose and other small oligomers that may not be able to adsorb on areas of domain edges. Glucose and cellobiose adsorption isotherms were collected at different temperatures to determine entropy and enthalpy of adsorption. The adsorption enthalpy increased with increasing chain-length but did not change with the surface properties of the carbon samples. Adsorption entropy also increased with increasing chain-length, but the adsorption entropy was higher for cellobiose on parent-3DOm carbon than that of cellobiose on SO3H-3DOm carbon. The relatively exoentropic adsorption of cellobiose on parent-3DOm carbon is likely due to the low solubility of cellobiose in water, which may lead to an enhanced hydrophobic effect and release of a large portion of solvated water molecules from the cellobiose molecules. The number of acid sites was optimized by cellobiose hydrolysis TOF and it was found that carbon containing 0.50 mmol g⁻¹ sulfonic groups to be the most efficient catalyst activity, resulting from balancing adsorption strength, number of adsorption sites and acid sites.

3.6: Acknowledgements

This work was supported by the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the US Dept. of Energy, Office of Science, and Office of Basic Energy Sciences under award number DE SC0001004. I would like to acknowledge Ray Sehgal for his assistance with Raman peak deconvolution and Bayesian inference and Professor Peter Monson for advising us through helpful discussions on adsorption interactions. I would also like to acknowledge my co-authors on this work: Stephen Ruzycky, Shintaro Pang, Lili He, Paul Dauenhauer and Wei Fan. Manuscript under preparation.
CHAPTER 4
EFFECTS OF SOLVENT AND IMPREGNATION TIME ON ACIDULATED CELLULOSE MECHANOCATALYTIC DEPOLYMERIZATION RATE

4.1: Abstract

A parameter study was performed on the synthesis of soluble glucan oligomers by mechanocatalytic depolymerization of acidulated cellulose in order to maximize the formation rate. The effects of solvent type, heat treatment during acid impregnation, and heat treatment duration during glucose and acid co-impregnation on the depolymerization rate were investigated. Samples were prepared by impregnation with acid dissolved in either water, ethanol, n-butanol, or cyclohexanol, followed by removal of excess solvent via drying in a vacuum oven. After 1 h of milling, soluble-portion yields from cellulose impregnated with alcohols all exceeded 82 wt.% compared to under 21 wt.% from cellulose impregnated with water. The superior performance of alcohols as impregnation solvents is likely due to the difficulty of removing water via drying as excess water will likely both scavenge protons to prevent protonation of glycosidic oxygen as well as buffer the mechanical milling force. Aging with acid and n-butanol solvent 60 °C was tested for different durations. The soluble portion after 1 h was found to increase sharply for up to 3 h of treatment and increased only slightly more after 48 h. The 3 h treatment time is likely required for sufficient diffusion of H\(^+\) to the interior glycosidic oxygens. It was discovered that co-impregnated glucose reacts with cellulose to form \(\alpha(1\rightarrow6)\) via an acid catalyzed reaction during the heat treatment, which requires a longer duration than with acid alone to fully utilize the impregnated glucose. It was found that the impregnated glucose will react with cellulose during the milling process and that at least two different types of linkages form from free impregnated glucose, one of which is \(\alpha(1\rightarrow6)\) and the other may be either \(\beta(1\rightarrow6)\) or \(\beta(1\rightarrow4)\). Cellulose impregnated with glucose and acid for 24 h had superior performance after short milling durations, producing 34.6 wt.% soluble oligomers after 20 minutes compared to 25.2 wt.% for acid alone treated for 24 h and
12.7 wt.% for glucose and acid treated for 3 h. Overall, it was found that solvent type and heat treatment time with both glucose and acid together had a significant effect on soluble product yield.

4.2: Introduction

The novelty of our previous work demonstrated that co-impregnation of cellulose with glucose and a relatively small amount of acid in water greatly reduced the milling time compared to impregnation with acid alone. This result showed a great improvement in milling time compared to a similar study using the same amount of acid (0.14 mmol g\(^{-1}\))\(^{88}\) and achieved similar milling times to studies using over 6 fold more acid (0.88 mmol H\(_2\)SO\(_4\) g\(^{-1}\)).\(^{119}\) However, the structure and formation mechanism of the water soluble oligomers is still being investigated. Also, it is greatly desired to control he chain-length and extent of branching to tailor the oligomer properties to specific applications.

Two key steps are required to hydrolyze the β(1→4) glycosidic bond. The first is that the glycosidic oxygen must be protonated, which can be hindered by the proton scavenging action of the other hydroxyl groups.\(^{120}\) Transfer of a proton from H\(_3\)O\(^+\) is also difficult due to the higher proton affinity of water.\(^ {121}\) It has been reported by DFT calculations that protonation of the glycosidic oxygen accounts for 90 % of the activation energy for cellobiose hydrolysis.\(^ {122}\) The second step is the scission of the glycosidic bond, which requires a chair to half-chair conformational change to induce the electronic effects that weaken the glycosidic bond. This rotational change is illustrated Scheme 4.1 from Rinaldi \textit{et. al.}. This conformational change accounts for about 10 % of the activation energy of cellobiose, but can be assumed to be much higher for cellulose due to the constraints of the inter and intra-chain hydrogen bonding network.\(^ {123}\)
Scheme 4.1: Hydrolysis mechanism of cellulose from Rinaldi et. al.\textsuperscript{31} The glycosidic oxygen is protonated followed by unimolecular scission of the glycosidic bond which occurs with a half chair rotational conformation change. Nucleophilic attack of water reestablishes the hydroxyl group.\textsuperscript{20}

Considering the protonation and rotational configuration requirements for hydrolysis will give insight into designing and optimized process for mechanocatalytic depolymerization. Dry conditions are likely critical for the depolymerization. It has been reported by Meine et. al. that an increase in humidity from 6 to 20 wt.\% causes a decrease in soluble product yield from 100 to 22 wt.\%.\textsuperscript{123} It was proposed that the water may act as a buffer to the mechanical forces through the substrate particles. Excess water may also scavenge protons required for protonation of the glycosidic oxygen. The protonation of the glycosidic oxygen during the solvent/glucose/acid impregnation treatment and during the dry milling conditions have been considered but not thoroughly studied. Schüth has reported that after sufficient aging at high temperature during acid impregnation that the glycosidic bond will enter a ‘latent state’ of protonation which can be stable for months and readily milled to form soluble oligomers.\textsuperscript{123} This idea is very intriguing, but effects of solvent, temperature and duration of aging treatment during impregnation have not been well documented at this point in time.
The roll of the mechanical force is likely to aid in the activation of the ‘latent state’ of acid-impregnated cellulose by bringing the environment of the glycosidic linkage to the necessary conformation. Prolonged storage of acidulated cellulose at room temperature and at 100 °C only carbonizes the cellulose, resulting in an insoluble greyish powder. The thermoliable nature of acidulated cellulose indicates that the depolymerization is not driven by hot-spots created by friction of the ball-ball and ball-wall collisions.

Formation of the α(1→6) branches is thought to be crucial for the depolymerization reaction. We hypothesize that the branched AGUs serve two key functions to enhance the cellulose particle depolymerization: 1: Allow permanent disruption of interchain hydrogen-bonding between layers by steric hindrance. 2: Lower the stability of the adjacent β(1→4) bonds by disrupting the intrachain hydrogen-bonds associated with the now removed C6 hydroxyl. Both abilities should allow the glucose units in the β(1→4) backbone to more easily undergo the half-chair rotational conformation required for hydrolysis.

The purpose of this chapter is to study the effects of solvent on the production rate of cellulose impregnated with acid and the effects of aging time on both acid impregnated and glucose-acid coimpregnated cellulose. We propose that impregnation with more volatile solvents that can be more easily removed from the substrate to study the effects of solvent boiling point on the soluble portion. Solvents other than water may also interact more weakly with H⁺, allowing for a stronger protonation. We will also study the effect of different 60 °C aging during impregnation times on soluble portion.

4.3: Experimental section

4.3.1: Materials

Microcrystalline cellulose (MCC, Avicel, 4 wt.% moisture, DP 215) was purchased from Alfa Aesar. Sulfuric acid (98 wt.%) 200 proof ethanol, and methanol (99.8 wt.%) were purchased from Fisher Scientific. Cellobiose (99 wt.%), isomaltose (98 wt.%), glucose (99 wt.%) and deuterium oxide (D₂O, 99.9 wt.%), n-butanol cyclohexanol, and 4,4-dimethyl-4-silapentane-1-
sulfonic acid (DSS, 97 wt.%) were purchased from Sigma Aldrich. Labeled $^{13}$C1 glucose was purchased from Cambridge Isotopes.

4.3.2: Impregnation with alcohol and water procedure

MCC was impregnated using 0.140 mmol H$_2$SO$_4$ g$^{-1}$ using four different solvents: Water, ethanol, n-butanol and cyclohexanol (50/50 mixture of cis/trans). The acid and a small amount of solvent (1.25 mL) was added to 4.5 g of microcrystalline cellulose and treated in an auto-pressurized bomb at 60 °C for three hours followed by drying in a vacuum oven at 80 °C. The sample was dried until at least 95 % solvent removal. Solvent removal was checked by measuring the weight before and after drying. Excess organic solvent was also checked by HPLC for ethanol, n-butanol and cyclohexanol samples. All milling experiments were conducted using the following procedure unless stated otherwise: 2.0 g of the acidulated microcrystalline cellulose samples ball-milled for 1.0 h using an SFM-3 high-speed shimmy ball-mill (MTI Corporation). Milling proceeded in 30 minute durations with 15 minute cool down periods to avoid heating above 50 °C. After milling the samples were stored at -18 °C.

4.3.3: Aging during impregnation

Aging with n-butanol and sulfuric acid at 60 °C was tested at different times. 72 μL of 98 wt.% H$_2$SO$_4$ were added to 1.25 mL of n-butanol and sealed in an auto-pressurized bomb. The bomb was placed in a 60 °C oven for 1, 3 and 48h. The samples were then dried for up to 20 minutes in a vacuum oven at 80 °C until 95+% of the n-butanol was removed (confirmed by HPLC). The samples were milled using the same conditions as described in section 4.4.2.

4.3.4: Glucose and acid co-impregnation heat treatment duration testing.

Five samples were prepared: Samples 1 and 2 were both two-step impregnations identical to those in section 4.3.4 with 0 and 12.5 wt.% glucose, respectively. The first sample, NGW-0H-CEA-3H, was impregnated with water without glucose followed by drying, then impregnated with acid in ethanol and heat treated for 3 h at 60 °C in a closed container followed by drying in a vacuum
oven. The second sample, GW-0H-CEA-3H, was identical to the first sample except that glucose was added to the aqueous solution used in the first step. The third sample, GW-24H-CEA-3H, contained 12.5 wt.% glucose and was prepared by adding glucose dissolved in water and dried for 24 h in a 60 °C convection oven followed by impregnation with acid dissolved in ethanol and heat treated for 3 h at 60 °C in a closed container flowed by drying in a vacuum oven. The fourth sample, NGW-0H-OEA-24H, was impregnated with pure water and immediately dried in a vacuum oven followed by addition of acid dissolved in ethanol followed by vacuum drying and placed in an open beaker in a convection oven at 60 °C for 24 h. The Fifth sample, GW-0H-OEA-24H, was similar to the fourth sample except that glucose was added during the water impregnation. In all cases, the amount of cellulose used was 4.5 g, the amount of water was 2 mL, the amount of H$_2$SO$_4$ was 72 μL, and for the glucose samples the amount of glucose was 0.643 g.

$^1$H-NMR was performed on a Bruker Advance 400 (400 MHz) spectrometer to determine the chain-length and extent of branching of the L-OF samples by analyzing the peak areas of the reducing end as well as the $\alpha$(1→6), and $\beta$(1→4) anomeric hydrogen peaks. Samples were prepared by dispersing the dried L-OF in D$_2$O with 10 mM 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as an internal standard. $^1$H-NMR samples were sonicated for 15 minutes and vortexed for 3 minutes followed by filtration before the measurement. The $^1$H-NMR was performed with 16 scans.

4.3.5: Pure glucose impregnated with acid experimental procedure

4.5 g of pure glucose was impregnated using 1.25 mL ethanol and 72 μL of H$_2$SO$_4$. The sample was immediately vacuum dried to 95 % removal of ethanol (checked by weight). The Glucose sample was milled for 0.5, 1 and 2 hours using the procedure described in section 4.3.2.
4.4: Results and discussion

4.4.1: Water vs. alcohol solvents on soluble portion yield

Impregnation with organic solvents has been reported previously Schüth where acid was dissolved in ether to impregnate real biomass.\textsuperscript{124} It would be useful to test a comparison between using water vs. organic solvents for acid impregnation. The yields of soluble portion are shown in Figure 4.1 and the yields as well as the boiling point and latent heats of vaporization of each solvent are shown in Table 4.1. The samples prepared using water as the solvent had low soluble-portion yield compared to the samples impregnated with different alcohols. In our previous study, the water was evaporated over two days in a convection oven at 60 °C and atmospheric pressure. The soluble portion found from vacuum dried (20.9 wt.%) sample is similar to the soluble portion from the convection oven dried sample (18.1 wt.%) reported in Chapter 2.

**Figure 4.1:** Soluble portion of samples milled for 1 h after using different impregnation solvents.

**Table 4.1:** Soluble portion of samples milled for 1 h using different impregnation solvents and solvent boiling points.

<table>
<thead>
<tr>
<th>Material</th>
<th>Soluble portion yield (%)</th>
<th>Boiling point (°C)</th>
<th>$\Delta H_{\text{vap}}$ (kJ kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20.9</td>
<td>100</td>
<td>2255</td>
</tr>
<tr>
<td>Ethanol</td>
<td>96.9</td>
<td>78.4</td>
<td>838</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>87.0</td>
<td>117.4</td>
<td>592</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>82.7</td>
<td>161</td>
<td>539</td>
</tr>
</tbody>
</table>
The large oligomer fraction (L-OF) of water and ethanol solvent samples ball-milled for one hour were purified by HPLC fractionation and observed by $^1$H-NMR to determine the average chain-length and average number of branches per oligomer. The $^1$H-NMR spectra are shown in Figure 4.2 and the chain-length results are shown in Table 4.2. The $^1$H-NMR spectra exhibit four peaks associated with the C1 anomeric carbons including the $\alpha$ and $\beta$ reducing ends (5.22 and 4.63 ppm, respectively) as well as the linkage peaks from the $\beta(1\rightarrow4)$ (4.52 ppm) and $\alpha(1\rightarrow6)$ (4.98 ppm) glycosidic linkages. The peak at 4.8 ppm is due to H$_2$O and HDO impurities produced from deuterium exchange with the cellulose hydroxyls. The different in chemical shift for the H$_2$O and HDO depends on the concentration. The chemical shift is likely different because the water-impregnated sample had much less solid sample collected by fractionation due to the difficulty of preparing a high concentration from the sample with a low soluble portion.

![Figure 4.2: $^1$H-NMR of the large oligomer fraction obtained from samples using either water or ethanol as the impregnation solvent milled for 1 hour.](image-url)
Table 4.2: Chain-length and branching data obtained from $^1$H-NMR of fractionated oligomers prepared from milling of water and ethanol solvent impregnated samples milled for 1 h.

<table>
<thead>
<tr>
<th>Property</th>
<th>Water-impregnated</th>
<th>Ethanol-impregnated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta(1\rightarrow4)$ linkages molecules$^{-1}$</td>
<td>7.69</td>
<td>14.20</td>
</tr>
<tr>
<td>Length of $\beta(1\rightarrow4)$ backbone</td>
<td>8.69</td>
<td>15.20</td>
</tr>
<tr>
<td>$\alpha(1\rightarrow6)$ molecule$^{-1}$</td>
<td>0.63</td>
<td>1.59</td>
</tr>
<tr>
<td>AGUs molecule$^{-1}$</td>
<td>9.31</td>
<td>16.79</td>
</tr>
<tr>
<td>% branching</td>
<td>6.7 %</td>
<td>10.0 %</td>
</tr>
</tbody>
</table>

There is one reducing end per chain and one per monomer and $\alpha$ and $\beta$ reducing ends exist in a 36:64 ratio. The ratio of reducing ends to the number of $\beta(1\rightarrow4)$ linkages can be determined by directly comparing the areas of the $^1$H-NMR peaks and can be used to determine the number of $\beta(1\rightarrow4)$ linkages per molecule and the length of the $\beta(1\rightarrow4)$ backbone (equal to the number of linkages plus one to account for the reducing end). The number of $\alpha(1\rightarrow6)$ linkages can be determined in a similar fashion.

We first hypothesized that the $L-OF$ of the water-impregnated sample would have longer chains than that of the ethanol-impregnated sample as we assumed that the chain-length would decrease with extent of reaction due to a larger number of $\beta(1\rightarrow4)$ glycosidic linkages hydrolyzing. However, the $L-OF$ chains of the water-impregnated sample are shorter those of the ethanol-impregnated sample. The short chains may be due to the low extent of branching as there are less than 1 branch per chain. Cellodextrins 6 AGUs and longer have solubilities of less than 1 wt.% in water. Thus longer oligomers may exist in the sample but, due to their low solubility, were not measured in the 5 wt.% solid that was prepared in Figure 4.1 nor the 20 wt.% solid that was prepared for fractionation. The branching rate is dependent on the formation rate of glucose units produced from hydrolysis of the bulk cellulose. Therefore the water impregnation sample seems to suffer from an apparently low hydrolysis reaction rate.
We hypothesize two phenomena occurring that result in the water-impregnated sample to exhibit a slower formation rate of soluble glucan oligomers compared to the alcohol-impregnated samples. Both phenomena may be, at least partially, related to incomplete removal of water. Although the boiling point of water is lower than n-butanol and cyclohexanol, water has a relatively high latent heat of vaporization compared to the organic alcohols. This high heat of vaporization may cool the sample away from the container walls and pose a practical challenge for drying. Additionally, water can readily form two hydrogen bonds with cellulose, which may make it more difficult to remove compared to the organic alcohols.

The first phenomenon is proton scavenging by water during either heat treatment or during milling if excess water remains after drying. By scavenging available $H^+$, water may interfere with the protonation of the glycosidic oxygen. Liang et. al. showed that the proton affinity for water is intrinsically higher than that of the glycosidic oxygen.\textsuperscript{121} The activation barrier for the glycosidic oxygen protonation in water is 35 kCal mol\textsuperscript{-1} and that the bulk of the free energy barrier is due to the transport of the proton to the vicinity of the glycosidic oxygen due to the high proton affinity of water.

As explained by Rinaldi et. al., the oxygens in cellulose fall into either the acetal and hydroxyl type. The acetal oxygens are considerably less basic than the hydroxyl oxygens.\textsuperscript{120} The basicities can be compared by comparing the difference in the pKa of the conjugate protonated acid. A moiety with a higher (less negative) protonated-form pKa will be more basic. The pKa value of the protonated acetal oxygens was estimated from those of monoprotonated formaldehyde acetics, R-O-CH2-O-R, where R is methyl-, ethyl-, and isopropyl, showing pKa values -4.57, -4.13, -3.70, respectively.\textsuperscript{127} The pKa values of the protonated cellulose hydroxyls was estimated to be between that of methanol (-2.4) and isopropanol (-3.2). The hydroxyl oxygens of cellulose are expected to be 10 to 100 times more basic than acetal oxygens. Therefore, even in the absence of other species, the protonation of the glycosidic oxygen will be favored by high acid concentration due to intramolecular proton scavenging. $H_3O^+$ has a pKa of -1.7. Water is therefore even more
basic than the cellulose hydroxyl groups. This highly favorable protonation of water is known to cause interference with other reactions requiring an initial protonation step. In alcohol solution, a number of acid-catalyzed reactions are known to be strongly retarded by traces of water. Newall and Eastham determined that relative basicity of water is 120 fold greater than methanol and 210 fold greater than ethanol by experimentally determining the $\frac{[\text{H}_3\text{O}^+][\text{ROH}][\text{H}_2\text{O}]^+}{[\text{ROH}_2^+]}$ ratio. It is expected that the other alcohols used in this study will have basicities similar to ethanol. Therefore, the enhancement with alcohol could be due to a weaker basicity compared to water. The lower $pK_a$ of the organic alcohols compared to water greatly reduces the negative impact from proton scavenging due to excess solvent as the protonation favorability of the alcohols is likely to be very similar to at least the protonation favorability of the cellulosic hydroxyl groups, which may allow for a decrease in the activation energy barrier needed for $\text{H}^+$ to diffuse to the cellulose surface. A higher surface concentration of $\text{H}^+$ will imply that the diffusion of $\text{H}^+$ to the interior layers will also be enhanced during high temperature aging.

The second inhibiting phenomenon is buffering of mechanical force caused by incomplete removal of water. As shown by Meine et al., increasing the humidity of acidulated cellulose from 6 to 16 wt.% the soluble portion yield 100 wt.% to 22 wt.% for the same milling duration and attributed this to water having a plasticizing effect. Excess solvent remaining in the sample after drying may buffer mechanical force and retard the depolymerization rate as the mechanical force is needed to both delaminate the cellulose layers and assist in the rotational conformation of the AGUs needed for hydrolysis. This mechanical buffering effect would likely occur with any excess solvent. However, 3 to 5 wt.% organic solvent remained after drying as determined by HPLC. The key difference with water may be that it is more likely to remain in the sample after drying. However, the amount of excess water was more difficult to confirm, and for a future experiment we will check TGA data to determine excess solvent. The potential challenge in water removal from cellulose highlights a potential drawback to using it as an impregnation solvent.
4.4.2: Effect of aging time on soluble portion yield

To test the importance of 60 °C aging time, cellulose was impregnated with n-butanol and acid and heated in an autopressurized bomb reactor for 0, 1, 3 and 48 h followed by drying for 30 minutes in a vacuum oven at 80 °C. The results are shown in Figure 4.3. Surprisingly, the non-aged (0 h) sample showed 61 wt.% soluble-portion yield. The soluble portion yield did increase with increasing aging time, to 80 wt.% for 1.5 h, 87 wt.% for 3 h and 95 wt.% for 48 h, revealing that protonation does not occur instantly but instead likely requires time for H+ to diffuse into the cellulose structure. The time it took to evaporate the solvent (30 minutes) likely contributed to the aging step as well. Overall, it was decided that 3 h aging time was sufficient for our standard procedure.

![Figure 4.3: Soluble portion yield cellulose impregnated with n-butanol and acid milled for 1 h after different 60 °C aging times.](image)

4.4.3: Glucose and acid co-impregnation study

Five samples were prepared and are described in detail in section 4.3.4 in order to test the effects of acid and glucose co-impregnation time. HPLC analysis of the non-milled (T0) powder mixed with water GW-0H-CEA-3H, GW-24H-CEA-3H and GW-0H-OEA-24H was performed, and the samples were found to contain 9.1, 8.0 and 2.1 wt.% free glucose. Sample GW-24h-CEA-3H did not show any glucose reaction without the presence of acid during the heat treatment.
Sample GW-0H-OEA-24H, however, showed significantly less free glucose than was added, indicating a reaction has taken place due to the presence of acid and the 24 h duration of heat treatment. Samples NGW-0H-CEA-3H and NGW-0H-OEA contained 0.09 and 0.64 wt.% free glucose, respectively. The $^1$H-NMR of the soluble-portion of the $T_0$ samples of samples GW-0H-CEA-3H, NGW-0H-OEA-24H and GW-0H-OEA-24H are shown in Figure 4.4. The spectrum from sample GW-0H-OEA-24H clearly shows the $\alpha(1\rightarrow6)$ peak at 4.98 ppm. Sample NGW-0H-OEA-24H shows a very slight shoulder at 4.98 ppm indicating the presence of a trace amount of $\alpha(1\rightarrow6)$ linkages. Sample 3 shows no peak at all, indicating that without acid the $\alpha(1\rightarrow6)$ branches are not likely to occur.

![Figure 4.4](image_url)

**Figure 4.4:** $^1$H-NMR of $T_0$ glucose and acid impregnated samples. Sample GW-24H-CEA-3H had glucose and no acid for 24 h, sample NGW-0H-OEA-24H had acid and no glucose for 24 h, and sample GW-0H-OEA-24H has both acid and glucose for 24 h.

The soluble-oligomer yields for samples GW-0H-CEA-3H, NGW-0H-OEA-24H and GW-0H-OEA-24H after 10 minutes are shown in Figure 4.5A and for all samples after 20 min are shown in Figure 4.5B. Sample GW-0H-OEA-24H, the glucose plus acid 24 h sample, showed the fastest depolymerization rate compared to all of the other samples. At minutes the formation soluble glucan oligomer is almost double compared to that of the acid 24 h and more than double the glucose 24 h sample. After 20 minutes the soluble glucan yield is 34.6 wt.% for sample GW-0H-OEA-24H, compared to 25.2 wt.% for sample NGW-0H-OEA-24H, indicating that the increase in
reaction rate is not simply due to longer heat treatment in the presence of acid. Very likely the reaction is enhanced by the prior formation of $\alpha(1\rightarrow6)$, which are produced by an acid catalyzed reaction between glucose and cellulose during the 24 h aging at 60 °C. Sample GW-24H-CEA-3H, by comparison, has similar oligomer yield to samples GW-0H-CEA-3H and NGW-0H-CEA-3H. All three of these samples are aged for 3 h at 60 °C. The removal of solvent may or may not have an important impact. The presence of excess water or ethanol during aging may play a role in the formation if $\alpha(1\rightarrow6)$ linkages. This will be a parameter for future study.

![Figure 4.5: Soluble oligomer yield after A) 10 and B) 20 minutes of glucose and acid co-impregnated samples.](image)

**Figure 4.5:** Soluble oligomer yield after A) 10 and B) 20 minutes of glucose and acid co-impregnated samples.

### 4.4.4: Pure glucose impregnated with acid studies

Pure glucose was impregnated with H$_2$SO$_4$ and milled to study what linkages will result from the mechanocatalytic reaction starting only from monomers. Upon milling, however, the morphology of the milled glucose changed dramatically. The initial powder turned to a brittle, white, shard-like substance which covered the ceramic grinding media after 30 minutes. We are unsure how this morphology could form and survive the harsh milling conditions. This substance was scraped off and placed back in the canister. After another 30 minutes (1 hour total), the brittle shards had been ground to a fine powder. However, after another 1 hour of milling (2 hours total) the substance became hard, sticky and sponge-like. The milling balls were completely suck inside
the canister. The substance was scraped off of the grinding media and returned to the canister for further milling. However, the milling balls immediately became stuck to the walls of the canister. Therefore it was not possible to continue mechanocatalytic reactions of this substance.

Several unknown peaks were discovered in the $^1$H-NMR spectra for the 2 hour milled glucose sample shown in Figure 4.6F. There exists a set of peaks centered at around 4.2 ppm which did not appear in the acidulated microcrystalline cellulose samples. To elucidate the meaning of the peak, several other reference $^1$H-NMR spectra are shown for comparison. Figure 4.6 $^1$H-NMR spectra of standards of cellobiose, isomaltose and gentiobiose (the $\beta(1\rightarrow6)$ dimer) from literature (Figure 4.6A, B and C),\textsuperscript{129, 130} standards measured by our group of isomaltose and cellobiose(Figure 4.6D and E), and the spectrum of milled acidulated glucose (Figure 4.6F).
Figure 4.6: $^1$H-NMR of reported and measured $^1$H-NMR of disaccharides and milled glucose: A$^{129}$, B$^{130}$ and C$^{129}$ $^1$H-NMR spectra plotted using peak position and peak splitting data reported in literature. Tall and short lines correspond to $\beta$ and $\alpha$ reducing end isomers in a 62 : 38 ratio; D – E) $^1$H-NMR spectra of cellobiose and isomaltose standards; F) $^1$H-NMR of milled glucose for comparison.
This spectrum of milled glucose has two strong peaks at 4.63 ppm and 5.22 ppm, corresponding to the reducing ends of glucose as well as the reducing end of the dimers as can be seen in Figure 4.6A-C. There also exists a peak at 4.98 ppm corresponding to the α(1→6) linkage as shown in Figure 4.10B and E. The peaks at 4.2 ppm could be due to the presence of β(1→6) as shown in the spectrum of gentiobiose (Figure 4.6C). These peaks correspond not to the anomeric H1 or H1' hydrogens, but to the H6a hydrogen in the β(1→6) glycosidic bond. This set of peaks only corresponds to one of the CH₂ hydrogens on C6 as they are not chemically nor magnetically equivalent due to the diastereomeric effect. There also exists a peak at 4.52 ppm, which could correspond to either β(1→6) or β(1→4) as shown in Figure 4.6A and C. 2D-NMR techniques are needed to elucidate the answer to which linkage is present or in which abundance. One interesting experiment to try to control the amount of β(1→6) linkages would be to dissolve the glucose in water for up to 3 days at room temperature and then use that solution to impregnate cellulose. Crystalline cellulose is typically α-glucose and can take up to 3 days at room temperature to equalize into the β-dominant ratio. Purchasing crystalline β-glucose may to impregnate with a small amount of acid may also yield a larger portion of β(1→6) linkages.

4.5: Conclusion

Several parameters for soluble oligomer synthesis by mechanocatalytic depolymerization were tested. Most notably, the solvent used for acid impregnation was found to be very important. Soluble yields when using ethanol, n-butanol and cyclohexanol exceeded 82 wt.% compared to under 21 wt.% for water as the solvent after 1 h of milling. The superior performance of the alcohols as impregnation solvents is likely due to strong proton scavenging of water both during impregnation and by excess water during milling. Water may be especially difficult to remove from cellulose upon drying due to its high latent heat and strong interaction with cellulose. Larger amounts of free water may be present compared to the alcohols, which may contribute to buffering of mechanical force.
Aging with acid at and n-butanol solvent 60 °C was tested for different durations. The soluble portion after 1 h was found to increase sharply up to 3 h of treatment and increased only slightly more after 48 h. 3 h treatment time was chosen to infiltrate the remaining samples.

It was discovered that co-impregnated glucose reacts with cellulose to form α(1→6) via an acid catalyzed reaction during the heat treatment, which requires a longer duration than with acid alone to fully utilize the impregnated glucose. It was found that the impregnated glucose will react with cellulose during the milling process and that at least two different types of linkages form from free impregnated glucose, one of which is α(1→6) and the other may be either β(1→6) or β(1→4). Cellulose impregnated with glucose and acid for 24 h had superior performance after short milling durations, producing 34.6 wt.% soluble oligomers after 20 minutes compared to 25.2 wt.% for acid alone treated for 24 h and 12.7 wt.% for glucose and acid treated for 3 h. Overall, it was found that solvent type and heat treatment time with both glucose and acid together had a significant effect on soluble product yield.

4.6: Acknowledgements

This work was supported by the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the US Dept. of Energy, Office of Science, and Office of Basic Energy Sciences under award number DE SC0001004. I would also like to acknowledge Wei Fan for co-authoring this work. Manuscript is under preparation.
CHAPTER 5
CONVERSION OF FRUCTOSE TO 5-HYDROXYMETHYL FURFURAL (HMF) OVER ZEOLITES USING CARBON BLACK AS AN ADSORBENT

Scheme 5.1: Chapter 5 Graphical Abstract

5.1: Abstract

Formation of 5-hydroxymethylfurfural (HMF) from the dehydration of fructose over zeolite catalysts in aqueous phase was studied in a reactive adsorption system using carbon black (BP2000) as an adsorbent. The dehydration of fructose over zeolite beta catalyst in water revealed that selectivity to HMF is largely influenced by the formation of levulinic acid and formic acid from the rehydration of produced HMF as well as subsequent condensation reactions. In order to increase selectivity to HMF, reactive adsorption with carbon adsorbents was used to prevent the further reactions of the produced HMF. It was found that BP2000 carbon black exhibited high selectivity and capacity for the adsorption of HMF and furfural from aqueous phase. The unique adsorption performance of BP2000 is likely due to the large surface area, hydrophobic nature and micropore structure. With using the carbon adsorbent, furan selectivity (selectivity of HMF and furfural) over zeolite beta was improved from 27 % to 44 % with a furan yield of 41 %. The furan selectivity and yield obtained in the presence of the carbon adsorbent were similar to those obtained from the reaction system using methyl isobutyl ketone (MIBK) as an extraction phase.
5.2: Introduction

The increasing demands for transportation fuels and commodity chemicals as well as environmental and political concerns associated with diminishing fossil fuel resources have driven research efforts towards the efficient utilization of renewable feedstock, such as naturally abundant lignocellulosic biomass.\(^4\)\(^,\)\(^72\) Development of economically viable processes for the syntheses of chemical intermediates from biomass-derived carbohydrates has been considered as an important challenge for research in this area. One major pathway for converting lignocellulosic biomass into fuels and chemicals involves the production of furans, such as 5-hydroxymethylfurfural (HMF) and furfural, from the dehydration of hexose and pentose sugars.\(^131\) In particular, the production of HMF from hexose sugars has received considerable attentions because hexose sugars are the most abundant monosaccharide from lignocellulosic biomass, and the formed furans are important intermediates for the synthesis of a wide variety of non-petroleum derived polymeric materials and alternative fuels.\(^100,\)\(^132,\)\(^133\)

HMF can be produced from the dehydration of glucose or fructose in aqueous phase. Much of the previous research in this field has focused on the dehydration of fructose to HMF because of the higher reaction rate and selectivity compared to using glucose as a starting compound.\(^134,\)\(^135\) Yuri Raman-Leskov and coworkers have demonstrated that a high yield of HMF (>75 %) could be achieved from the dehydration of fructose in aqueous/organic biphasic reaction system. However, much lower yield of HMF from glucose (around 25 %) was achieved under the same conditions due to the low reaction rate and by-product formation.\(^69-71\) With abundant availability of glucose produced by saccharification of cellulose, recent efforts have been driven towards using glucose as a starting material for producing HMF. Combination of Lewis acid catalyzed glucose isomerization and the dehydration of produced fructose has led one-pot synthesis of HMF from glucose.\(^78,\)\(^136-141\) For clarity, in this work we focus on producing HMF from the dehydration of fructose because fructose can be readily formed by isomerizing glucose.
For the acid catalyzed dehydration of fructose to HMF in aqueous phase, both homogeneous and heterogeneous acid catalysts have been extensively studied. Organic and inorganic homogeneous acids (e.g. oxalic acid and HCl) show high activity for the reaction. However, heterogeneous acid catalysts (e.g. zeolites, ion-exchange resins) receive much more attention because of the ease of separation and the lack of corrosion to reactors. In particular, zeolites are being considered as a superior candidate because of their excellent hydrothermal stability and ease of regeneration. Moreau and co-workers have shown that zeolite mordenite can selectively produce HMF and furfural from the dehydration of fructose and xylose, respectively.

Ordomsky and co-workers further studied fructose dehydration using zeolite catalysts and concluded that high selectivity to HMF can be achieved from zeolites with strong acid sites. Deactivating the acid sites on external surface and selectively removing extra framework Al from zeolite catalysts can also increase selectivity to HMF by preventing side reactions of fructose.

In addition to catalyst development, undesired rehydration and condensation reactions of HMF in the aqueous phase must be selectively prohibited because these reactions can be also catalyzed by the acid catalysts (Scheme 5.2). Reaction systems have been developed for the production of HMF with using an immiscible organic phase (e.g. methyl isobutyl ketone) to extract HMF from aqueous phase, protecting it from subsequent condensation and rehydration. Selectivity to HMF can be further increased by adding salts (e.g. NaCl) into the aqueous phase to increase the partition coefficient of HMF in the organic phase. Although the aqueous/organic reaction systems have shown promising results on recovering the produced furans, the use of salts - could rule out the possibility of using solid acid catalysts, and non-volatile organic solvents (e.g. MIBK, n-pentanol) would require an energy-intensive separation for obtaining furans from the organic solvents. Economic analysis carried out by Torres et al. on the aqueous/organic reaction system has also shown that HMF produced from this process is still more expensive than petroleum-based polymer precursors, suggesting that alternative processes are needed to improve fructose utilization. One alternative approach to solve the issues is to use reactive adsorption in
the reaction system. Solid adsorbents can be used to adsorb the produced furans from aqueous phase and protect them from further reactions. In this scenario, the solid adsorbents can reduce the effort required for the separation of HMF because the adsorbed HMF can be eluted easily from the adsorbents using volatile solvents (e.g. ethanol). HMF in the volatile solvents can be separated by distillation or further reacted with the solvents, such as ethanol, to form 5-(ethoxymethyl)furfural (EMF) as a potential biofuel alternative. Vinke and co-workers have shown that activated carbon can selectively adsorb HMF from aqueous phase during fructose dehydration operated in a batch reactor or a continuous stirred-tank reactor (CSTR) with effluent continuously flowing over a packed bed of the adsorbent. Both homogeneous acid catalyst (mineral acid) and heterogeneous catalyst (ion-exchange resin) have been studied in the reactive adsorption system. However, due to low stability of ion-exchange resin catalysts, the dehydration reaction can be only performed at a relatively low temperature (363 K), which could limit product selectivity to HMF. Regeneration of the resin catalyst is also an issue because of the formation of humins on the catalyst surface.

Scheme 5.2: Reaction scheme for fructose dehydration in the presence of Brønsted acid catalysts.

In this study, we propose to employ zeolite catalysts together with solid adsorbents to develop an environmentally benign process for fructose dehydration and furan capture. Using zeolites as heterogeneous catalysts for the dehydration of fructose will allow the dehydration reaction to occur at higher temperatures (393 K - 438 K), thereby increasing the reaction rate and favoring high selectivity to HMF. Carbon black BP2000 was chosen as the adsorbent in the
reactive adsorption system because of its outstanding adsorption properties for selectively adsorbing HMF from fructose dehydration reaction media in a wide range of reaction temperatures.

5.3: Experimental Section

5.3.1: Materials

Zeolite beta (BEA, CP814C (Si/Al = 19), ammonium form) was purchased from Zeolyst. Ammonium-type BEA was converted to H-type by calcination at 823 K for 12 h with a ramping rate of 1 K min\(^{-1}\) under dry air. D-fructose (99+ wt.%), 5-hydroxymethyl furfural (98 wt.%), furfural (99 wt.%), levulinic acid (99 wt.%) and formic acid (99 wt.%) were obtained from Acros Organics. Methyl isobutyl ketone (MIBK) (99+ wt.%, HPLC grade) was obtained from Alfa Aesar. Nitric acid (65 wt.%) and hydrochloric acid (37 wt.%) were obtained from Fisher Scientific. BP2000 carbon black and Norit SX Ultra activated carbon (Norit Ultra) were obtained from Cabot Corporation and Sigma Aldrich, respectively. Oxidized BP2000 (OX-BP2000) carbon black was prepared by adding 1 g of BP2000 in 10 mL of nitric acid and reacting at room temperature for 12 h in a closed Teflon® lined stainless steel autoclave. After the reaction, the sample was washed multiple times at 343 K with deionized water until the washing water reached a pH of 4. Three dimensionally ordered mesoporous (3DOM) carbon with a pore size of 35 nm was synthesized using the method reported in previous literature.\(^{92}\)

5.3.2: Adsorption measurements

Adsorption of HMF, levulinic acid and fructose on BP2000, OX-BP2000, 3DOM and Norit Ultra carbon was carried out at room temperature with adsorbate concentrations ranging from 0.5 to 100 mg mL\(^{-1}\). 20 mg of carbon were added into 1 mL solution for each adsorption measurement. Multicomponent adsorption isotherms of HMF, levulinic acid and fructose on BP2000 were measured with a weight ratio of 1 : 1 : 1 and adsorbate concentrations ranging from 0.3 to 100 mg mL\(^{-1}\) at room temperature. HMF adsorption on BP2000 was also collected at higher temperatures, 328 K, 363 K and 423 K, using the method reported in previous literature.\(^{158}\) Detailed information can be found in supplementary information. HMF, furfural, levulinic acid and fructose adsorption
was also measured on H-BEA at room temperature. 1 mL of adsorbate solution with a fixed concentration of 10 mg mL\(^{-1}\) was used for adsorption with 20 mg of H-BEA. The adsorption results are shown in the supporting information Table 5.S1.

The Langmuir, Freundlich and Redlich-Peterson adsorption models, as shown in Table 5.1, were used to fit the adsorption data. The Langmuir model can be used to study the adsorption properties of adsorbents, providing maximum capacity and adsorption equilibrium constant. However, the Langmuir model cannot adequately fit the adsorption profile of HMF on the carbon materials used in this study. Therefore, the empirical models, Freundlich and Redlich-Peterson, were used to obtain a more accurate fit of the data and predict adsorption capacity.\(^{159,160}\) Parameters for these models were determined by the least squares method.

Table 5.1: Adsorption isotherm models used to fit the adsorption data.

<table>
<thead>
<tr>
<th>Adsorption Isotherm Model</th>
<th>Mathematical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>[ Q = \frac{Q_{ML}K_LC_e}{1 + K_LC_e} ]</td>
</tr>
<tr>
<td>Freundlich</td>
<td>[ Q = K_FC_e^{n_F} ]</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>[ Q = \frac{K_{RP}C_e}{1 + b_{RP}C_e^{n_{RP}}} ]</td>
</tr>
</tbody>
</table>

5.3.3: Catalytic reactions

Dehydration reactions were performed in a Parr 4564 reactor with a volume of 160 mL. A 1.2 wt.% (66.4 mM) fructose solution was used for all reactions. Typically, 0.625 g of fructose were added to 52.4 g of deionized water with 1.0 g of solution removed for HPLC measurement as a reference. 0.620 g of H-BEA was added into the fructose solution. The reactor was sealed and pressurized with nitrogen to 500 psi for 5 min to test pressure seals and achieve a nitrogen atmosphere. After nitrogen was purged, the reactor was heated to reaction temperature (393 K, 423 K, and 438 K) which typically took 10 min. The reaction was allowed to operate at an autogenous
pressure with a stirring rate of 600 rpm. Time zero, $t_0$, was taken when the reactor reached to 423 K. Once the reaction was finished, the reactor was quickly cooled down to room temperature in an ice bath.

For the reaction with BP2000, 1.00 g to 4.00 g of carbon corresponding to 2 wt.% to 8 wt.% of the total reaction solution were added into 52 g of 66.4 mM fructose solution containing zeolite catalysts. An extraction procedure was performed after the reaction. The wet carbon was separated from the reaction media by centrifugation. The HMF remaining in the aqueous solution was measured by HPLC. The HMF adsorbed on the carbon was extracted by ethanol using the procedure developed by Vinke et al. Approximately 100 g of ethanol were mixed with the carbon and stirred for 1 h at room temperature. The carbon was centrifuged and re-washed with fresh ethanol 4 times by a Soxhlet extraction device. More than 80 % furans were extracted in ethanol solvent during the first extraction. The fourth extraction was carried out overnight (16 h). The zeolite and carbon material remained physically mixed during the extraction.

The reactions using MIBK as the organic extraction phase were performed using the same fructose and zeolite concentrations described previously. The MIBK to water volume ratio was 5 to 1. Typically, 17.5 g of aqueous solution was mixed with 69.8 g of MIBK and 0.620 g of zeolite.

Selectivity and yield are calculated using Equation 5.1 and Equation 5.2, respectively:

$$Selectivity = \frac{\text{moles of product}}{\text{moles of fructose reacted}} \times 100\% \quad (5.1)$$

$$Yield = \frac{\text{moles of product} \cdot C_p}{\text{initial moles of fructose} \cdot 6} \times 100\% \quad (5.2)$$

where $C_p$ is the number of carbon atoms in the product compounds.

5.3.4: Characterization

The reaction samples were analyzed using HPLC (LC-20AT, Shimadzu) equipped with refractive index (RID-10A) and UV–Vis (SPD-2AV) detectors. A Bio-rad Aminex HPX-87H column was used in the measurement with an oven temperature of 303 K. 0.005 M H$_2$SO$_4$ was used
as a mobile phase with a flow rate of 0.600 mL min⁻¹. Sugars were detected by the refractive index detector. Furans and organic acids were detected by the UV-Vis detector with a wavelength of 210 nm and 254 nm, respectively. N₂ adsorption/desorption isotherms for different carbons were measured on an Autosorb®-iQ system (Quantachrome) at 77 K. Total surface area was calculated using the Brunauer–Emmett–Teller (BET) method. Micropore volume and surface area were calculated using the t-plot method. Oxygen containing groups on the carbons were measured by the Boehm titration method.⁵⁰ 40 mg of carbon were added in 4 mL of either 0.05 M sodium hydroxide or 0.05 M sodium bicarbonate solution and sonicated for 3 h. The titrations were performed with 0.01 M hydrochloric acid using methyl red or methyl orange as the indicator.

5.4: Results and discussion

5.4.1: Selective adsorption of HMF on carbon materials

Previous studies have shown that HMF can be preferentially adsorbed on various adsorbents including zeolites, polymers and carbon materials. In particular, carbon materials such as activated carbon and carbon black, exhibit high selectivity and capacity for the adsorption of HMF over sugars from aqueous solution.¹⁵⁷ The superior adsorption performance of BP2000 carbon black for HMF in dimethyl sulfoxide (DMSO) has been also reported.¹⁶¹ In order to identify a proper adsorbent for the reactive adsorption of HMF produced from sugar dehydration reaction, four representative carbon materials were investigated: BP2000 carbon black, oxidized BP2000 (OX-BP2000), 35 nm 3DOm carbon and Norit SX Ultra activated carbon (Norit Ultra) were chosen in this study. Nitrogen physisorption isotherms of the carbon samples are shown in Figure 5.1. Textual properties calculated from the isotherms, including BET surface area, micropore surface area and micropore volume, are shown in Table 5.2. Interestingly, the micropore volume of BP2000, Norit Ultra and OX-BP2000 is approximately 0.2 mL g⁻¹, while the micropore volume for 3DOm carbon is only 0.067 mL g⁻¹. The difference in the micropore volume affects their adsorption properties for HMF and other chemicals used in the study as shown later.
Figure 5.1: Nitrogen physisorption isotherms for carbon materials.

Table 5.2: Textural properties of the carbon materials measured from Nitrogen adsorption/desorption.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Surface Area (m² g⁻¹)</th>
<th>Pore Size (nm)</th>
<th>Total OX (mmol g⁻¹)</th>
<th>Qₘ (g g⁻¹)</th>
<th>Kₗ (mL mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP2000</td>
<td>1365</td>
<td>1.6</td>
<td>0.22</td>
<td>0.48</td>
<td>10.27</td>
</tr>
<tr>
<td>3DOm</td>
<td>1445</td>
<td>35</td>
<td>0.68</td>
<td>0.51</td>
<td>0.64</td>
</tr>
<tr>
<td>OX-BP2000</td>
<td>1264</td>
<td>1.6</td>
<td>1.64</td>
<td>0.40</td>
<td>1.65</td>
</tr>
<tr>
<td>Norit Ultra</td>
<td>868</td>
<td>1.0</td>
<td>0.16</td>
<td>0.31</td>
<td>9.00</td>
</tr>
</tbody>
</table>

a Surface area (S_{BET}) was calculated by the Brunauer-Emmett-Teller (BET) isotherm method. b Micropore surface area (S_{micro}), external surface area (S_{external}) and micropore volume (V_{micro}) were calculated according to the t-plot method.

The adsorption of HMF, levulinic acid and fructose on the four carbon materials was carried out at concentrations ranging from 0.5 mg mL⁻¹ to 100 mg mL⁻¹ at room temperature. Adsorption isotherms are shown in Figure 5.2. The Langmuir, Freundlich and Redlich-Peterson (RP) models were used to fit the data. Of the three isotherms, the three-parameter RP model provided the best fitting as shown in Table 5.3. Therefore, the RP model was used to predict the adsorption capacity and plotted with the experimental data in Figure 5.2. Table 5.3 also shows the experimental adsorption capacity of the adsorbate measured at an initial concentration of 10 mg
100 mL$^{-1}$, which is approximately the concentration of fructose used in the reaction. BP2000 exhibits the highest adsorption capacity ($Q_e = 0.365$ g g$^{-1}$) for HMF at this low concentration. As shown in Figure 5.2 and Table 2, the adsorption capacity at high concentration (100 mg mL$^{-1}$) of HMF on BP2000, Norit Ultra and 3DOm carbon increases with the BET surface area. While 3DOm carbon has the highest adsorption capacity at high concentration, BP2000 has superior adsorption at the low concentrations close to the reaction conditions. The 1.2 nm slit-shaped micropores in BP2000 as observed in the textural analysis shown before might be partially responsible for the high affinity to HMF.$^{162,163}$ This high affinity to HMF is of critical importance for the reactive adsorption since the low equilibrium concentration of HMF can minimize the amount of HMF remaining in the aqueous phase. The lower adsorption capacity of HMF on 3DOm carbon at 10 mg mL$^{-1}$ of HMF might be due to the absence of the microporosity in comparison to BP2000, although the BET specific area of 3DOm carbon is higher.

![Figure 5.2: Single component adsorption isotherms at room temperature fitted with the Redlich Peterson model. a) HMF adsorption isotherms on BP2000, 3DOm, OX-BP2000 and Norit Ultra carbons. b) HMF, levulinic acid (LA) and fructose adsorption on BP2000. c) HMF, levulinic acid and fructose adsorption on OX-BP2000.](image-url)
Table 5.3: Adsorption isotherm parameters for chemicals adsorption on carbon materials measured at 298 K.

<table>
<thead>
<tr>
<th>Component</th>
<th>Carbon</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
<th>Redlich-Peterson model</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Q_m$ (g g$^{-1}$)</td>
<td>$K_L$</td>
<td>$R^2$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>HMF BP2000</td>
<td>0.481</td>
<td>10.272</td>
<td>0.9176</td>
<td>0.293</td>
<td>0.155</td>
</tr>
<tr>
<td>HMF 3DOM</td>
<td>0.509</td>
<td>0.639</td>
<td>0.8836</td>
<td>0.219</td>
<td>0.224</td>
</tr>
<tr>
<td>HMF OX-BP2000</td>
<td>0.403</td>
<td>1.652</td>
<td>0.9159</td>
<td>0.208</td>
<td>0.187</td>
</tr>
<tr>
<td>HMF Norit Ultra</td>
<td>0.307</td>
<td>8.999</td>
<td>0.8857</td>
<td>0.200</td>
<td>0.134</td>
</tr>
<tr>
<td>LA BP2000</td>
<td>0.378</td>
<td>1.016</td>
<td>0.9243</td>
<td>0.167</td>
<td>0.220</td>
</tr>
<tr>
<td>LA OX-BP2000</td>
<td>0.256</td>
<td>1.084</td>
<td>0.8736</td>
<td>0.124</td>
<td>0.198</td>
</tr>
<tr>
<td>Furfural BP2000</td>
<td>0.483</td>
<td>2.960</td>
<td>0.9264</td>
<td>0.300</td>
<td>0.257</td>
</tr>
<tr>
<td>Fructose BP2000</td>
<td>0.275</td>
<td>0.123</td>
<td>0.9901</td>
<td>0.056</td>
<td>0.357</td>
</tr>
</tbody>
</table>

$Q_e^*$, experimental data at 10 mg mL$^{-1}$ initial concentration

The adsorption isotherms for levulinic acid, HMF and fructose on BP2000 are shown in Figure 5.2b. The adsorption isotherm model fitting parameters are shown in Table 5.3. The adsorption capacity for fructose on BP2000 is relatively low, indicating a weak affinity between fructose and BP2000. The low adsorption capacity of fructose on BP2000 could be caused by the hydrophilic nature and hydrated state of fructose. Levulinic acid shows a higher adsorption capacity and affinity on BP2000 than fructose, which may be due to the interaction of the carboxylic acid group with the basic groups at the surface of BP2000.$^{50,164}$ The outstanding adsorption properties of BP2000 ensure that the carbon black can be used to selectively adsorb HMF from the reaction media of fructose dehydration. Additional single component isotherms for HMF, levulinic acid and fructose on other carbon materials are available in the supporting information.

Since it is likely that the adsorption of levulinic acid on the carbon black is induced by the interaction of the carboxylic acid group with the basic groups on the surface of the adsorbent, it was hypothesized that the adsorption capacity for levulinic acid can be decreased by introducing acid groups on the surface of BP2000. Therefore, oxidation of BP2000 with nitric acid was carried out to increase surface acid groups. The textural properties of BP2000 did not change significantly after the oxidation as shown in Table 5.2. For the adsorption properties, as expected, the $Q_e$ for levulinic acid adsorbed on BP2000 decreased by 29 % after the oxidation (Figure 5.2c and Table

101
5.3). However, the $Q_e$ for HMF also decreased by 22%. The concentrations of oxygen containing groups were measured by the titration method developed by Boehm. The total oxygen containing groups (OH + lactone + COOH) were estimated by titration with 0.05 M NaOH, while COOH groups were estimated by titration with 0.05 M NaHCO$_3$. The total number of OH + lactone sites was calculated by subtracting the titration amount of 0.05 M NaHCO$_3$ neutralized from the amount of 0.05 M NaOH. The number of carboxylic acid groups was estimated by the titration result from 0.05 M NaHCO$_3$ alone. BP2000, Norit Ultra and 3DoM carbon all have relatively few oxygen containing groups on their surfaces with 0.22, 0.16 and 0.67 mmol g$^{-1}$, respectively, while the value for OX-BP2000 is 1.64 mmol g$^{-1}$ (Table 5.4). The result is consistent with previous studies on other carbon materials, indicating the oxidation treatment can reduce the adsorption of levulinic acid. However, adsorption capacity for HMF is also reduced by the oxidation treatment probably because of the reduced hydrophobicity, which is detrimental to the reactive adsorption of HMF in fructose dehydration reaction.

Table 5.4: Surface oxygen containing groups on different carbon materials.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>0.05M NaOH$^a$ mmol g$^{-1}$</th>
<th>0.05M NaHCO$_3$$^a$ mmol g$^{-1}$</th>
<th>OH + Lactone$^b$ mmol g$^{-1}$</th>
<th>COOH$^c$ mmol g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP2000</td>
<td>0.218</td>
<td>0.004</td>
<td>0.215</td>
<td>0.004</td>
</tr>
<tr>
<td>3DoM</td>
<td>0.673</td>
<td>0.289</td>
<td>0.384</td>
<td>0.289</td>
</tr>
<tr>
<td>Norit Ultra</td>
<td>0.159</td>
<td>0.003</td>
<td>0.157</td>
<td>0.003</td>
</tr>
<tr>
<td>OX-BP2000</td>
<td>1.644</td>
<td>1.327</td>
<td>0.318</td>
<td>1.327</td>
</tr>
</tbody>
</table>

$^a$40 mg carbon and 4 ml of 0.05M base solution and titrated with 0.01M HCl.
$^b$OH+Lactone (mmol g$^{-1}$) = [0.05M NaOH]$_{neutralized}$ g$^{-1}$ - [0.05M NaHCO$_3$]$_{neutralized}$ g$^{-1}$
$^c$COOH (mmol g$^{-1}$) = [0.05M NaHCO$_3$]$_{neutralized}$ g$^{-1}$

Multicomponent adsorption of HMF, levulinic acid and fructose on BP2000 was measured at room temperature (Figure 5.3). Each point for the multicomponent adsorption began with equal masses of all three components. Compared to levulinic acid and fructose, HMF was found to preferentially adsorb on the carbon black, consistent with the single component adsorption data. More importantly, the adsorption of fructose was approximately zero even at high concentration in the presence of HMF, indicating that BP2000 has very high selectivity to adsorb HMF from the...
multicomponent solution. Adsorption capacity of BP2000 for HMF in aqueous phase at reaction temperatures (298 K to 423 K) has been studied in our previous work.\textsuperscript{158} Adsorption isotherms at different temperatures are shown in Figure 5.4. The HMF adsorption capacity on BP2000 is 0.25 g g\textsuperscript{-1} at 423 K which is sufficient for adsorbing HMF produced under the dehydration conditions used in the study.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5_3.png}
\caption{Multicomponent adsorption on BP2000 at room temperature. The data was measured using the solutions with equal masses of HMF, levulinic acid and fructose.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5_4.png}
\caption{Adsorption isotherm of HMF on BP2000 at different temperatures. The dots are from experiments. The lines are from fitting using the Redlich-Peterson adsorption model.}
\end{figure}

In summary, carbon materials that have high hydrophobicity, large micropore volume and high surface area are best suited for the applications in the reactive adsorption of HMF because of
the strong affinity of HMF to hydrophobic carbon surfaces, the enhanced adsorption through confinement effects in micropores and the high adsorption capacity based on large surface area. BP2000 carbon black was, thus, chosen for this study to demonstrate the advantage of using reactive adsorption for the production of furans from fructose dehydration in the presence of zeolite catalysts.

5.4.2: Dehydration of fructose with reactive adsorption of furan on BP2000 carbon black

Dehydration of fructose was first performed over H-BEA catalyst in aqueous phase. The main products detected in the solution were HMF, levulinic acid and formic acid as expected. In addition, furfural was also observed. A systematic study was performed to evaluate the effects of the carbon adsorbent on the production of HMF from fructose dehydration over the zeolite catalyst. The results collected at three temperatures, 393 K, 423 K and 438 K, with 2 wt.% BP2000 are shown in Figure 5.5, and compared to the ones obtained from the reaction without adding carbon adsorbents. After the reactions, it was found that more than 98 % of HMF and furfural were adsorbed on the carbon adsorbent, and only very limited amount of HMF and furfural was detected in the aqueous phase, indicating an effective adsorption of the components on the carbon black. The furans adsorbed on the carbon black were extracted by washing with ethanol. The total furan selectivity was determined by adding the amount of HMF and furfural detected in the aqueous phase and ethanol solvent. Due to the low adsorption capacity of BP2000 for levulinic and formic acids, the components are mainly detected in the aqueous phase. The selectivity to HMF in the reactive adsorption system is compared to the reaction without carbon adsorbents, and summarized in Figure 5.5d. It is clear that adding BP2000 into the reaction system can effectively improve the selectivity to HMF at all temperatures, especially at low to medium fructose conversion. At 438 K and fructose conversion of 50 %, selectivity to HMF improves from 20 % to 38 %, and total furan selectivity including HMF and furfural improves from 31 % to 54 %. Only limited amount of levulinic and formic acids was produced at low to medium fructose conversion, indicating the carbon black can effectively prevent further hydration of the formed HMF. Selectivity to HMF
drops significantly at high conversion of fructose with the appearance of levulinic and formic acids, which could be because the amount of carbon adsorbent (2 wt.%) is insufficient to protect all of the produced HMF. In addition, we observed the total carbon balance achieved from the HPLC analysis is not close to 100% as shown in Figure 5.4. The remaining products could be insoluble humins formed from the oligomerization HMF and fructose, which has been shown in several previous studies. Using carbon adsorbent and organic extracting solvent, such as MIBK, can certainly improve the selectivity to HMF by preventing the oligomerization of HMF, while humins are still formed under the reaction conditions.

**Figure 5.5:** Fructose conversion, furan, levulinic and formic acid selectivity from the reaction systems with and without using carbon adsorbent BP2000. Fructose dehydration with H-BEA and 2 wt.% BP2000 at a) 393 K, b) 423 K and c) 438 K. d) Fructose conversion vs. HMF selectivity using H-BEA under different temperatures.
Conversion of fructose and selectivity to HMF in the reaction system with different amounts of carbon adsorbent are shown in Figure 5.6. Reaction using MIBK as an organic extracting solvent with H-BEA catalyst was also performed for a comparison. By increasing the amount of carbon black from 2 wt.% to 4 wt.% at 423 K, selectivity to HMF increased from 24 % (34 % for HMF and furfural ) to 33 % (43 % for HMF and furfural) at a high fructose conversion (> 80 %) (Figure 5.6). The formation of levulinic and formic acids was significantly suppressed even at high conversion. This selectivity to HMF is comparable to the selectivity in the reaction system using MIBK as the extracting phase (30 % for HMF, 43 % for HMF and furfural) as shown in Figure 5.6. The results are similar to those reported by Ordomsky where HMF selectivity of approximately 40 % was achieved at 80 % fructose conversion using MIBK as the extracting solvent and H-BEA as the catalyst. Increasing the BP2000 amount to 8 wt.% with H-BEA does not further improve selectivity to HMF. It is worth noting that BP2000 itself can also catalyze the dehydration of fructose, but with a very low activity and selectivity to HMF (selectivity 22 % at conversion of 59 %, 423 K, Figure 5.6) which could be due to the weak acidity from the oxygen-containing groups on the surface of the carbon black. The decreased HMF selectivity with 8 wt.% of BP2000 is most likely because of the high carbon to zeolite catalyst ratio and non-selective side-reactions occurring on the carbon surface forming humins and other by-products. The performance of the reactive adsorption system, thus, cannot be further improved by increasing the amount of carbon adsorbent under the reaction conditions used. Additionally, the physical properties of BP2000, including relatively small particle size and low specific gravity, could lead to difficulties in utilizing BP2000 carbon black in the current reaction system. In particular, when the concentration of the carbon black is higher than 4 wt.%, the solution forms a paste and became noticeably more viscous. One possible solution for further improving the performance of the system is to use a CSTR with effluent running over the carbon adsorbent. This reactor design would allow HMF to be adsorbed on the carbon adsorbent with high capacity at room temperature and inhibit non-selective reactions between the carbon adsorbent and fructose.
Interestingly, it was found that selectivity to furfural was also increased from 8 % to 11 % at 423 K and 11 % to 15 % at 438 K over H-BEA catalyst. The reaction pathway for furfural from fructose is still under discussion. It has been reported that furfural can be produced from an open chain pathway where the aldose form of glucose is tautomerized to 3-ketose. 3-ketose subsequently undergoes retro-aldol reaction to form formaldehyde and arabinose, which is subsequently dehydrated to form furfural. In addition to the retro-aldol reaction pathway, the cleavage of C-6 on fructose by the double bond rule under hydrothermal conditions has been also proposed. The formation of furfural from fructose dehydration was also observed with niobic acid catalysts, but not for ion-exchange resin, clearly indicating the acidity and structure of catalysts might affect fructose reaction pathways. It is noteworthy that, under the reaction conditions used in this study, furfural was formed at 11 % selectivity when H-BEA was used as the catalyst and at only 1 % when using BP2000 alone. It is likely the formation of furfural in the reaction system is related to the catalytic activity or micropore structure of H-BEA catalysts. Further study on the formation pathway of furfural is undergoing in our group.
Compared to aqueous/organic reactive extraction system, the advantages of the use of carbon adsorbent based reaction system include the following three aspects. (1) The amount of solvent used for extracting the adsorbed HMF from carbon adsorbent is much less than the organic solvent used in biphasic reactive extraction system. (2) A CSTR can be developed for the reaction system with effluent running over the carbon adsorbent. This reactor design would allow HMF to be adsorbed on the carbon adsorbent with a higher capacity at room temperature and inhibit non-selective reactions between the carbon adsorbent and fructose. (3) HMF can react directly with ethanol to form 5-(ethoxymethyl)furan-2-carbaldehyde (EMF), an excellent additive to diesel with high energy density. The performance of the reactive adsorption system developed in the study depends on several factors including adsorption properties of the carbon adsorbents, catalytic activities of the zeolite catalysts, mass transfer of the reactants and products within zeolite catalysts, carbon adsorbent and the kinetic of the involved reactions. In this study, we have investigated some critical factors, such as the types of the carbon adsorbent, reaction temperature and loading of carbon adsorbent. Modeling the reactive adsorption system by considering three necessary principles, adsorption, reaction kinetics and fluid mechanics, could further improve the performances as reported in our previous study.

5.5: Conclusion

Using carbon black (BP2000) as a solid adsorbent for reactive adsorption of furans (HMF and furfural) during fructose dehydration in the presence of zeolite catalysts can effectively improve furan selectivity. BP2000 can selectively adsorb furans (HMF and furfural) at greater loadings than levulinic acid and fructose. The adsorption capacity of BP2000 for HMF decreased by 50% when increasing the adsorption temperature from 298 K to 423 K, but still be sufficient for protecting HMF from further hydration. The reactive adsorption system shows similar furan selectivity with a biphasic reactive extraction system using MIBK as the extracting solvent. Furan yields greater than 40% were achieved with BP2000 and H-BEA at 438 K. It was found that the
type and amount of carbon adsorbents as well as reaction temperatures are critical for the reactive adsorption system.

5.6: Acknowledgements

This work was supported as part of the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award no. DE-SC0001004. I would also like to acknowledge Wei Fan for co-authoring this work. This work was published in Microporous and Mesoporous Materials in a journal article titled: Dehydration of Fructose into Furans over Zeolite Catalysts using Carbon Black as Adsorbent, 2014, 191, 10-17 (DOI 10.1016/j.micromeso.2014.02.031) (IF = 3.453)

5.7: Appendix

5.7.1: Adsorption measurements of reactive species on carbon materials

For the measurements at 363 K and below, 32 mg of BP2000 were added to 1.6 g of adsorbate solution in a 2 mL septum-sealed vial. For the room temperature (298 K) adsorption, the vials were placed on a stirring plate at 1000 rpm for 6 h. Adsorption measurements at 328 K and 363 K were performed in oil baths placed on a hotplate at 1000 rpm for 6 h. The solutions were filtered as they were taken out from the vials with syringe filters preheated to 373 K to prevent the samples from cooling. Adsorption measurements at 423 K were performed in a Parr 4564 160 mL reactor. 1.00 g of BP2000 was added to 50 g of HMF solution. The solution was given 1 h for equilibrium at 423 K with a stirring rate of 600 rpm. The solution sample was taken with a two-stage sampling system. The first stage used glass wool and 420 mesh membrane (McMaster) to filter carbon black BP2000 from the solution. The effluent moved to a second stage where it was cooled down with ice water. This effluent was not exposed to atmosphere until it was cooled. Two control experiments were run to confirm that there is minimal reaction of HMF under the measurement conditions. First, 50 g of 2.00 mg mL\(^{-1}\) HMF solution with 1.00 g carbon was reacted at 423 K for 1 h. After the reaction, the wet carbon was separated from the solution by centrifugation. The HMF left in the solution was measured by HPLC. HMF adsorbed on the carbon
was extracted by ethanol using the procedure developed by Vinke et al.\textsuperscript{157} Approximately 100 g of ethanol were added to the carbon and stirred for 1 h. The carbon was centrifuged and re-washed with fresh ethanol for a total of 4 washings with the fourth washing going overnight (16 h) by a Soxhlet extraction device. In total, 91.3\% of the initial HMF was recovered at the end. Considering the HMF extraction efficiency from activated carbon using ethanol is around 90\% as reported by Vinke et al.\textsuperscript{157}, it can be concluded that there is limited reaction of HMF occurred under the measurement conditions. Another test was carried out using a 2.00 mg mL\textsuperscript{-1} HMF solution at 423 K for 1 h. HMF conversion of 1.6\% was observed for this test. It should be noted that there are certain degrees of reactions taking place for the measurement at 423 K, but it is not substantial since more than 90\% of the HMF added in the adsorption measurement were recovered from the aqueous phase and the carbon adsorbent after the equilibrium, and no rehydrated product, levulinic acid, was observed.

5.7.2: Adsorption measurements of reactive species on H-BEA

HMF, furfural, levulinic acid and fructose adsorptions were measured on H-BEA and shown in Table 5.S1. 1 mL of solution with an adsorbate concentration of 10 mg mL\textsuperscript{-1} was mixed with 20 mg of H-BEA and stirred at room temperature for 6 h followed by filtration and analysis with HPLC. The adsorption capacity for HMF on H-BEA is 0.12 g g\textsuperscript{-1}. In comparison, the adsorption capacity of HMF on BP2000 is 0.365 g g\textsuperscript{-1} under the conditions. In the reaction system, 1 g or 2 g of carbon black and 0.62 g of H-BEA are used. Therefore the contribution of HMF adsorption on the zeolite is much less than that of the carbon materials.

Table 5.S1: Adsorption on H-BEA with 10 mg mL\textsuperscript{-1} initial concentration

<table>
<thead>
<tr>
<th>Component</th>
<th>$Q_e$ (10 mg mL\textsuperscript{-1}) g g\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMF</td>
<td>0.120</td>
</tr>
<tr>
<td>Levulinic Acid</td>
<td>0.106</td>
</tr>
<tr>
<td>Fructose</td>
<td>0.006</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.238</td>
</tr>
</tbody>
</table>
**Figure 5.S1**: Single component isotherms for HMF, levulinic acid and fructose on 3DOm carbon (a) and Norit Ultra activated carbon (b). The dots are from experiments. The lines are from fitting using the Redlich-Peterson adsorption model.
CHAPTER 6
CONCLUSION

This body of work has explored the use of carbon materials as catalysts and extractants for biomass conversion to value added chemicals as well as the development of novel mechanocatalytic pretreatment techniques. A great improvement in understanding was gained from the parameter study of acid and glucose/acid co-impregnated cellulose. It was found that impregnating cellulose glucose and acid for 24 or 48 h will produce $\alpha(1\rightarrow6)$ linkages in the static phase, which can promote rapid depolymerization compared to adding acid alone. Formation of the $\alpha(1\rightarrow6)$ branches is thought to be crucial for the depolymerization reaction. We hypothesize that the branched AGUs serve two key functions to enhance the cellulose particle depolymerization: 1: Allow permanent disruption of interchain hydrogen-bonding between layers by steric hindrance. 2: Lower the stability of the adjacent $\beta(1\rightarrow4)$ bonds by disrupting the intrachain hydrogen-bonds associated with the now removed C6 hydroxyl. Both abilities should allow the glucose units in the $\beta(1\rightarrow4)$ backbone to more easily undergo the half-chair rotational conformation required for hydrolysis.

The enhanced milling time coincides with the abundance of $\alpha(1\rightarrow6)$ glycosidic bonds, which increase the water solubility of $\beta(1\rightarrow4)$ glucan oligomers. It was found that the chain-length and degree of branching could be controlled by tuning the milling time and impregnation solvent. The milling-time needed for hydrolysis was improved by four fold using glucose and acid co-impregnation solvent compared to using acid alone. It was also found that impregnation solvent was very important, with alcohol solvent showing over a 4-fold increase in depolymerization rate compared to water. The poor performance of the water impregnated samples may be caused by excess water, which is difficult to remove due to its high latent heat and strong potential for hydrogen bonding with cellulose. Excess water present in the sample may buffer mechanical force scavenge protons strongly to prevent protonation of the glycosidic oxygen.
A sulfonated three dimensionally ordered mesoporous (3DOM) carbon-based catalyst was developed that rapidly hydrolyzed the water-soluble glucan oligomers to 91.2% glucose in 1 h at 165 °C with a catalyst to cellulose ratio of 2:3, which is one of the most efficient processes for conversion of oligosaccharides to glucose on record. A structure-property relationship was developed for adsorption of saccharides on the carbon catalyst. For Van ’t Hoff relationships were derived from adsorption isotherms of glucose and cellobiose and revealed that the adsorption enthalpy increased with increasing chain-length due to the increasing number of CH-π interaction between the saccharides and the carbon surface. Adsorption entropy increased with increasing chain-length and with increasing surface hydrophobicity due to the release of solvated water molecules. Furthermore, Langmuir adsorption isotherm analysis revealed Langmuir adsorption constants ($K_L$) increasing by one or more order of magnitude going from glucose to cellobiose to extracted trimers to glucan oligomers. The high selectivity and excellent conversion likely occurs because the long-chained reactants adsorb much more strongly than the short-chain products, ensuring that surface is fully covered by reactants, even as the reaction proceeds to moderately high conversion. The catalyst was optimized for glucose production by tuning the sulfonic to adsorption site ratio, which was easily tuned by controlling the precursors during the diazonium sulfonate functionalization step.

Formation of HMF from the dehydration of fructose over zeolite catalysts in aqueous phase was studied in a reactive adsorption system using carbon black (BP2000) as an adsorbent. The dehydration of fructose over zeolite beta catalyst in water revealed that selectivity to HMF is largely influenced by the formation of levulinic acid and formic acid as well as humins from HMF. Reactive adsorption with carbon adsorbents was used to increase selectivity by preventing further reaction of HMF. It was found that BP2000 carbon black exhibited high selectivity and capacity for the adsorption of HMF from aqueous phase. The unique adsorption performance of BP2000 is likely due to the large surface area, hydrophobic nature and micropore volume. The furan
selectivity obtained in the presence of the carbon adsorbent was similar to that obtained from the reaction system using methyl isobutyl ketone (MIBK) as an extraction phase.
CHAPTER 7

FUTURE DIRECTIONS AND RECOMMENDATIONS

The insights gained into the mechanocatalytic depolymerization of acidulated and glucose-acid co-impregnated cellulose enhance the fundamental understanding of the hydrolysis and branching mechanisms and offer for new perspectives towards controlling the chain-length and extent of branching as well increasing the depolymerization rate. However, substantial work remains in advancing the fundamental understanding of these mechanisms as well as realizing the full potential of this novel technology. On the fundamental level, several key aspects have been hypothesized but not fully explored including: the types of linkages formed, the placement of the linkage with respect to the non-reducing end of the chain, the effects of the α(1→6) branch on the stability of an adjacent β(1→4) linkage, the role that organic alcohols play in enhancing the depolymerization rate, and the effects of glucose and acid interaction during the pretreatment. A study emphasizing the branch location and its effect on hydrolysis rate of an adjacent β(1→4) linkage would be especially useful as it will provide solid evidence for how the presence of the branches enhance depolymerization and hydrolysis. Specifically, this could be done by studying the effects of hydrolysis rate of a pair of trimers each containing one α(1→6) and one β(1→4) glycosidic linkage as shown in Scheme 7.1. The CH₂-OH group is changed to CH₂-O-Gluc after the formation of the α(1→6) glycosidic linkage. The removal of the CH₂-OH group may eliminate one of the two intrachain hydrogen bonds, thus potentially reducing the conformation barrier about the β(1→4) glycosidic oxygen needed for hydrolysis of the β(1→4) glycosidic bond. It is this unstabilization may be responsible for the apparent limit in chain-length of 15 AGUs. The reaction would be ideally studied using the mechanical catalytic system as ball-milling can impart force that enhances the conformational change. However, the process may be prohibitively expensive due to the large amount of solid sample required for milling (1 - 2 grams) and information gained on the hydrolysis rate in the aqueous phase, which would require only a few mg per sample, would also be very useful.
Scheme 7.1: Theoretical hydrolysis of two glucan trimmers containing both one α(1→6) and one β(1→4) linkage.

Ball-milling of acidulated cellulose has the potential to be a new frontier in biorefining. From a scale-up perspective, many challenges still remain including development of the acid-impregnation and potentially drying techniques as well as determining the optimal grinding media. However, initial scale-up experiments are promising and have already shown that the energy input per ton decrease by a factor of 20 when scaling up from 1 gram to 1 kilogram.\textsuperscript{124}

Control of the chain-length and extent of branching is one area that has yet to be well studied. Table 4.2 shows some preliminary results that suggest that different impregnation conditions can achieve different chain-lengths and extent of branching. My work showed that high-temperature co-impregnation of cellulose with acid and glucose is needed to pre-branch the impregnated cellulose. A research project which studies the amounts of glucose (0, 5, 12.5, 25 wt.%) and different milling times (0.5, 1, 2, 5, 10, 24 h) would be very valuable for determining if the chain-length and extent of branching can be further controlled. Impregnation with $^{13}$C1-labeled glucose and acid for up to 24 h at 60 °C followed by fraction collection of the large oligomer
fraction and $^{13}$CNMR on the non-milled and 1 h milled samples could help reveal both what percentage of the initial glucose is forming branches and what percentage of the branches in the milled sample are from the impregnated glucose. This information would help to optimize the amount of glucose that should be added during the impregnation step and further the understanding of the branching mechanism.

Mechanocatalysis have enormous potential to synthesize rare and difficult to manufacture oligosaccharides with a variety of branched sugars containing different functional moieties. The high solubility, biocompatibility, ease of functionalization and low cost make oligosaccharides synthesized from mechanocatalytic processes highly attractive as substrates for an array of applications including includes biomaterials, drug delivery, biosensors and nutritional supplements. For example: Milling cellulose with impregnated glucose amine or N-acetylglucosamine could yield a material with similar properties to chitosan, a common polysaccharide used in wound dressing. The nitrogen functional groups allow for delivery of drugs and other nutrients. However, chitosan suffers degradation by self-crosslinking due to the high abundance of reactive nitrogen-containing moieties. A hybrid material of composed of glucose and glucose amine units could conceivably yield a more stable material. The ratio of glucose to glucose amine could be easily controlled by the initial substrate ratio. Many potential glucose units with specialized functional groups may also be selected including such as methyl-glucose and glucuronic acid. The technology may not be limited to β(1→4) glucan. There are numerous other polysaccharides used in the food, cosmetic and medical industries. Many of these polysaccharides could potentially be modified by mechanocatalysis.

The work on development of structure property relationships between biomass adsorbates and carbon materials gained many insights into how the morphology and hydrophobicity could be used to control the adsorption properties of carbons. These adsorption properties can be tailored to enhance reaction and separation efficiency of reactive species. The hydrophobic desolvation effects were identified as crucial to the adsorption mechanism. However, their entropic and enthalpic
contributions could not be decoupled experimentally from the adsorption interactions between the substrate and the adsorbate. Moving forward, simulation work that incorporates the interactions between the adsorbate-solvent, the substrate moiety-solvent and the substrate moiety-adsorbent interactions would be very useful. Simulations taking into account solvent effects on the adsorption of sugars onto hydrophilic, oxygen rich carbon surfaces would help to elucidate the answer to the question of whether or not oxygen containing groups promote sugar adsorption through hydrogen bonding or inhibit sugar adsorption by competitive adsorption of water. Simulation would also allow exploration and fast iterations over substrates difficult to synthesize such as having functional groups a certain spacing or in clusters of a certain size and density, which have been reported to both strengthen acid sites and promote favorable adsorption in certain configurations.\textsuperscript{44, 169}

The methods developed in Chapter 3 could be used to characterize the adsorption properties and catalytic performance of other catalysts. Synthesis of carbon catalysts with different mesoporous structures and different surface groups could be compared. The results in Chapter 3 suggest that an optimal ratio between adsorption and active sites exists and it would be interesting to confirm if there is an optimal adsorption strength for different morphologies. For example, it would be beneficial to compare the adsorption properties of parent and sulfonated carbon black and CMK-3 (gyroidal carbon). If one carbon shows intrinsically stronger adsorption, the optimal number of acid sites may be able to be increased, leading to a more active catalyst. Additionally, we have preliminary results that show 3DOm carbon annealed in H$_2$ at 950 °C shows very high adsorption capacity for cellobiose. We attempted to measure the adsorption isotherms of glucose and cellobiose at different temperatures but were not able to collect reproducible isotherms. We suspect the reason is due to poor wetting of the material which appears to be highly hydrophobic and is very difficult to disperse in solution. However, if the materials could be functionalized by diazonium sulfonate, the optimal number of acid sites may be able to be largely increased due to the high hydrophobicity of the parent material surface.
REFERENCES


13. R. Fitzpatrick, Cellulosic Ethanol is Getting a Big Boost from Corn, for Now, DOI: http://www.thirdway.org/report/cellulosic-ethanol-is-getting-a-big-boost-from-corn-for-now


15. , U.S. Energy Information Administration, 2013,


119
38. Great Brittan Pat., 2004


49. Y.-B. Huang and Y. Fu, Green Chem., 2013, 15, 1095-1111

50. H. P. Boehm, Carbon, 1994, 32, 759-769


80. D. Klemm, B. Heublein, H. P. Fink and A. Bohn, Angew. Chem.-Int. Edit., 2005, 44, 3358-3393
81. H. Krassig, Papier, 1990, 44, 617-623

123


102. http://www.quantachrome.com/technical/dft.html,


106. E. A. Guggenheim and N. K. Adam, *The Thermodynamics of Adsorption at the Surface of Solutions*, 1933


129. National Institute of Advanced Industrial Science and Technology, http://sdbs.db.aist.go.jp,
146. V. V. Ordomsky, J. van der Schaaf, J. C. Schouten and T. A. Nijhuis, *J. Catal.*, 2012, 287, 68-75


