The Green Conversion of N-Acetyl-*D*-Glucosamine into Platform Chemicals and Biochar

By

Gregory Chipman Thomas Curtis

A Thesis Submitted to the School of Graduate Studies

in Partial Fulfillment of the Requirements for the Degree of

Master of Science

Department of Chemistry

Memorial University of Newfoundland

August 2014

Abstract

The green conversion of N-acetyl-*D*-glucosamine into substituted furans (3-acetamido-5-acetylfuran [3A5AF], 5-hydroxymethylfurfural [5-HMF], 5-acetyl-3-amino-furan [5Ac3NH_2F] and 3-aminofurfural [3NH_2F]) was achieved in subcritical water in the presence of boric acid and sodium chloride. The maximum molar yield for 3A5AF was 75% with a selectivity of > 90% at 180 ^oC in 10 minutes while 5-hydroxylmethylfurfural was obtained with a 69 mol % (>85% selectivity) yield at 220 ^oC in 10 minutes. Biochar was the main by-product of the hydrothermal reaction and thus it was characterized and its potential will be discussed. Reaction conditions were evaluated including substrate concentration, temperature, time, additive concentration and solvent recycling. Based on previous research in our group, the additives with desirable properties (low toxicity) are boric acid and sodium chloride. The synergy observed in this catalytic system shall be discussed along with selectivity and comparison to additive-free experiments.

Dedication

I dedicate this thesis to the green radicals who will prevail in the 21st century over the fossil fuel enthusiasts.

"When all the trees have been cut down, when all the animals have been hunted, when all the waters are polluted, when all the air is unsafe to breathe, only then will you discover you cannot eat money."

~ Cree Prophecy

Acknowledgements

I am thankful for the funding provided by NSERC of Canada, Research & Development Corporation Newfoundland, Canada Foundation for Innovation, Hebron and Memorial University of Newfoundland. I acknowledge the Green Chemistry and Catalysis Group for their support in and out of the lab. I am also thankful for observing the unique culture of Newfoundland while working as a doorman at a bar on George Street and as a cook at Bitters during my M.Sc studies.

Table of Contents

List of Figures

Supplementary Figures

List of Tables

Chapter 1. Introduction

1.1 Motivation for Research

Petroleum derived chemicals dominate our industrial landscape and have been incorporated into numerous facets of our daily lives. Petroleum refineries have developed alongside the chemical manufacturing industry for over a century and this in part has led to numerous negative global impacts on the health of the environment, humans and animals. The greenhouse effect that has moderated the global temperature on Earth (which enabled the evolution of complex life) for millennia has been altered by the anthropogenic release of carbon dioxide, nitrogen dioxide and methane. It is common scientific knowledge that the average global temperature increases with increasing levels of these gases, and more violent storms cause unimaginable destruction so there is a sense of urgency towards ending our industrial dependency on oil and converting to sustainable societies. It is public knowledge that super storms such as hurricanes (Katrina, Sandy), cyclones (Nargis) and typhoons (Haiyan) have in the past decade taken the lives of tens of thousands of people and inflicted tens of billions of damage to infrastructure (1,2). One of the most powerful ways to mitigate this reality is by employing

renewable resources (non-edible biomass, solar/wind/tidal energy) for the production of vital chemicals, fuels and energy (electricity and heat). Corporations and governments will need to fund and develop (carbon negative) technologies that will consume atmospheric carbon dioxide as well as vastly reduce the release of greenhouse gases. These are some of the key pillars of progressive sustainability that puts a carbon-negative future within our grasp. Cleaning the air, water and soil of the world is a generational task that will require monumental commitment leading up to the 22nd century. This change can only be viewed over the course of years but it will require a new type of industrial revolution that is dependent on the mutual cooperation of governments and industry. To accomplish this monumental task it is imperative that the world's leading economies collaborate with the most (green) forward-thinking scientists, engineers and politicians.

The processing of low value or waste biomass will help reduce the need for landfills and the amount of pollutants that end up in our water supplies. As the population of Earth marches toward 10 billion people by the end of the 21st century, we are reminded everyday of the damage done by pollution over the last hundred years. The greenhouse effect has begun to intensify storms/droughts and can simultaneously enhance a polar vortex in North America while prolonging a heatwave in Australia. These examples typify the unpredictable nature of a changing climate and increase the risk of shorter and less productive growing seasons in major traditional agricultural regions. Researching ways to shift our industrial society from emitting large amounts of CO_2 while in tandem utilizing waste we produce will provide us with a more balanced and healthy environment. The cost of storms and other destructive natural phenomena is quickly adding up but this remains only a quick fix. Sea level rise alone will cause urban

flooding globally by the 22nd century and thus uniting to develop a global sustainability strategy is in everybody's best interest.

1.1.1 : The Acceleration of Climate Change by Unsustainable Food Production Practices

It is generally accepted in the scientific community that the atmospheric CO_2 content has increased from 280 ppm from the dawn of the industrial revolution (1700s) to 380 ppm in 2005 and >400 ppm today due to anthropogenic emissions, which has led to an increase in unpredictable storm and drought patterns (3). The higher frequency of severe storms in heavily populated coastal areas in North America, Europe and South Asia are linked to the warming climate and changing jet stream patterns amongst other phenomena. These emissions stem primarily from 1) the burning of fossil fuels, 2) deforestation/desertification, and 3) factory (livestock) farming. These three acts are tied together when it comes to monocropping; which means growing the same crop year after year on the same land without crop rotation. This agricultural technique increases the risk of large portions of a seasonal harvest being wiped out due to new (invasive) insects/weeds or bad weather. The main crops that follow this practice are corn, soybean and wheat. This in turn results in depletion of soil nutrients and an increase of artificial fertilizers and pesticides. Fertile land in South America is being deforested to make room for livestock grazing and/or soybean production to feed animals (4). This is an energy intensive process that even if the crops are used for biofuels provide a negative net result to CO_2 emission. Employing biochar to revitalize soil and emphasizing crop rotation (preferably with a nitrogen-fixing plant) can significantly help mitigate the destructive effect of deforestation/

monocropping. Biochar is one possible product from biomass transformations and will be discussed in more detail later in this thesis.

1.1.2 : Biomass (Food Vs. Fuel) as a Renewable Feedstock

Biomass consists primarily of cellulose, hemicellulose and lignin with the two former being carbohydrate-based polymers while the latter is the oxygen-rich aromatic structure that gives plants their rigidity. Biofuels and biomaterials are produced in biorefineries that focus on renewable feedstocks and are a sustainable replacement for oil refineries. To best utilize biomass it is paramount that industries employ non-edible or waste feedstocks to prevent rapid increases in food (corn, soy, wheat) prices. It is common knowledge that the global food crisis that began in 2007 was ignited in part by the US (the world's largest corn and soy exporter) devoting a large percent of their corn crop towards bioethanol production (5). Another major factor of this crisis was the rising cost of oil that increased the cost of fertilizers, pesticides and transportation. The ethical debate between food vs fuel is focused on the first generation biofuels that relied on edible biomass. Second and third generation biofuels and biomaterials focus on non-edible feedstocks as their source of carbohydrates. The second most abundant biopolymer (behind cellulose) is chitinous biomass and it differs from cellulose by possessing an acetamido functional group instead of one of the hydroxyl group. This presents an opportunity for the green process chemist to utilize this biopolymer that can be obtained as a fishing industry (non-edible/ waste) by-product for platform chemical production. The chemicals obtained from the conversion of chitin and related amino-carbohydrates can be different or identical to those

obtained from cellulose. Biopolymers remain the most renewable carbon source and their utilization will allow for more of the fossil fuels to stay in the ground.

1.1.3 : Biorefineries

In an oceanic, lignocellulosic or waste biorefinery the energy efficiency impacts the economics of the facility and using aqueous processing as well as biocatalysts is certainly in line with green methodology. Green chemistry is viewed as a collection of principles that promote sustainability and reduce toxics; there remain many industries that aim to "green wash" a process, project or product. Terms like "biodegradable/compostable" and "natural" tend to be misleading for products such as plastic containers/bags and processed food (6). Just as clean coal is the ultimate climate change oxymoron, there remains motivation for companies/governments to say one thing but mean another. In my person experience, as the availability of organic food at grocery stores rises, companies have begun to add more of the color green on to non-organic food packaging in an attempt to mislead customers.

The thermochemical (waste) biorefinery focuses on the pyrolysis/gasification of agricultural/forestry residues for the purpose of bio-oil, synthesis gas and biochar production. This conversion technology can provide the most benefits in the short to medium term by utilization waste biomass for production of high value products. Thus the thermochemical biorefinery is one that focuses also on producing combined heat and power (CHP) as well as carbon capturing. The slash and char approach to charcoal production creates a vast amount (compared to smokeless pyrolysis but less than slash and burn techniques) of soot-black carbon particles/aerosols that can absorb more solar radiation than CO_2 and unfortunately congregates in

the Arctic (7). This could be playing a harmful role in the elevated degree of warming taking place in the Northern Polar Region where the ecosystem is quite fragile to industrial development.

1.1.4 : The Oceanic Biorefinery and Chitin as a Feedstock

Since chitin biomass (chitin and chitosan Figure 1.0) is a by-product of the fishing and aquaculture industries, there will likely always be a surplus and renewable supply. Such opportunities provide the fishing industry with a way to reduce its waste disposal costs while boosting sustainability. The most common methods for the breakdown of chitin biomass are chemical and/or enzymatic treatments. Due to the strong hydrogen bonding group (-NHAc), within chitin it requires ionic liquids or highly polarized organic solvents to dissolve or swell chitin. The price of enzymes has fallen dramatically in the past decade while their effectiveness and robustness has increased. This problem may be approached in a more economically feasible manner from a biotechnological standpoint (or hybrid chemical-enzymatic) for the utilization of this waste stream in the future.

The concept of an oceanic biorefinery has progressed over the recent years to better utilize renewable feedstocks for the production of platform chemicals, polymers, flavor additives and energy (8). Employing waste/low-value material as the feedstock has been deemed essential for the sustainability and cost competitiveness of such a facility. Oceans host a cornucopia of biomass such as algae (micro- & macro-) which can yield lipids, cellulose, agarose, vitamins and invertebrates (e.g. crustaceans, which can yield chitin). By using hot/compressed water as the reaction medium, these conversion processes can become more sustainable and require less post-

treatment (compared to volatile organic solvents). The waste generated in Atlantic Canada fish plants is estimated to be 418, 000 t/yr (9). In this report, it stipulates that Newfoundland alone produces 39,000 t/yr of shellfish waste (Northern Shrimp and Snow Crab) with a chitin content of approximately 20-25 wt% and is typically dumped in the sea. This by-product could be processed by using green techniques and assist in the reduction of waste disposal in the ocean. Enzymatic hydrolysis and fermentation are viewed as flexible and green methodologies for processing this waste (10,11). It has been reported that the hydrolysis of beta-chitin via cellulase (*Tricoderma viride*) can reach monomer yields of N-acetyl-*D*-glucosamine (NAG in Figure 1) up to 75% after 8 days incubation in a mildly acidic solution (12). All shells contain chitin, calcium carbonate and protein in relatively equal portions.

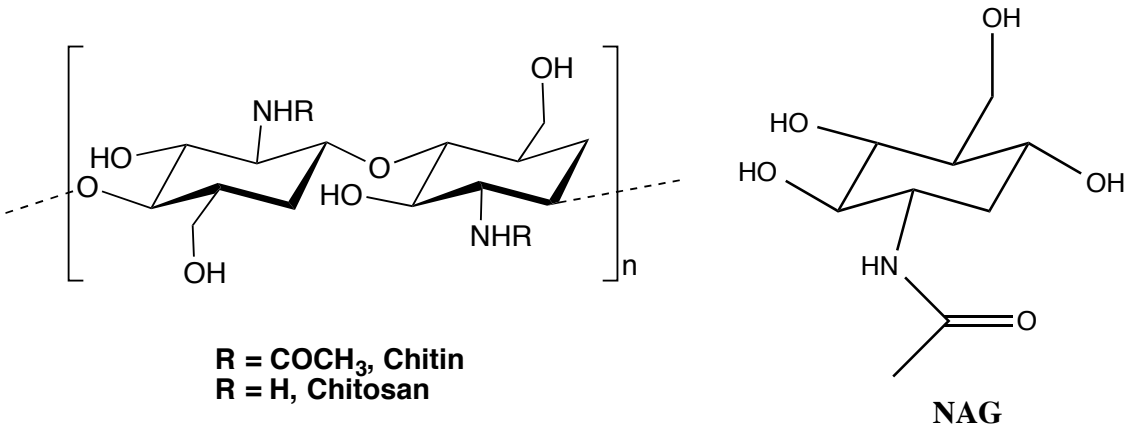


Figure 1.0 : Structures of Chitin, Chitosan and N-Acetyl-*D*-Glucosamine (NAG)

The first step to utilize marine or terrestrial biomass as a chemical feedstock is the fractionation of the main components (cellulose, hemicellulose, lignin, chitin, residue). A physical treatment (eg. milling, steam explosion) is taken to reduce the feedstock particle size then the slurry is treated to separate the fractions. Once the carbohydrates are separated they are

hydrolyzed into sugar molecules that are the starting material for renewable platform chemicals. This hydrolysis can be executed by acid or base treatment as well as enzymes.

1.1.5 : The Relationship between Biorefineries and Food Processing Facilities

Research that is directed to the chemistry of cooking and flavors is important and provides insight into nutrition and health care. Food processing facilities operate in a similar fashion to a refinery in the sense they process various feedstocks to produce a variety of products. In the future it would be reasonable to predict that they will exist alongside biorefineries that will produce chemicals and energy in addition to food. In the Canadian province of Prince Edward Island there is a relatively new company called Solarvest (www.solarvest.ca). Their focus is on the production of omega fatty acids directed towards the health food market while simultaneously producing hydrogen gas from the oil-rich microalgae. This type of tandem production brings down the cost and reduces the risks associated with focusing on one industry (food or fuel). The underlying theme is the role of entanglement between green methodology, energy production, novel materials, and organic food and hence a holistic approach should be expressed to unite these issues.

1.2.0 : Green Chemistry and Waste Utilization

This review covers the conversion of carbohydrates and amino-carbohydrates into platform chemicals in a variety of systems with different catalysts. However, none of these reactions are 100% selective and a main by-product is biochar, which can play a pivotal role in a more sustainable food supply system. Relevant literature in the areas of waste utilization,

aqueous dehydration of carbohydrates and biochar applications forms the basis of the current research project. This project employs aqueous catalytic system of boric acid and sodium chloride due to their catalytic synergy and relatively environmentally benign nature.

1.2.1 : Water as a Solvent for Green Reactions

Reactions performed in subcritical water are unique because it behaves more like an organic solvent due to the reduced polarity (as a result of elevated temperature and pressure). Water in this sense can act like a reagent, catalyst and solvent in reactions such as hydrolysis, transformations (e.g oxidation) and cleaning. In an aqueous reaction with carbohydrates they are readily dissolved at low concentrations and as temperature increases there is an increase in diffusivity and the sugars become activated by hydronium ions and organic or inorganic acids, which translates into fast reactions under dilute conditions. The critical pressure of water is 21.7 MPa with a critical temperature of 374 ^{o}C and when operating below these conditions the energy is easier to recover from heat/steam exchangers. When conducting a reaction in supercritical water, a special alloy (e.g Hastelloy from Haynes International Inc) must be used to withstand the corrosive nature of water under these harsh conditions.

1.2.2 : Degradation and Conversion of Amino-Carbohydrates in Water

Historically, as amino-carbohydrates are used as nutraceutical supplements while also being present in food, much of the early research in its conversion was performed by food chemists. Degradation studies were performed on aqueous solutions of glucosamine hydrochloride at a temperature of 150 ^{o}C for 5 minutes, with furfurals being the main product in

the pH range of 4-7 (13). In this study, flavor compounds were generated under alkaline conditions (pH > 8.5) including: methylpyrazines, 3-hydroxypyridine, furans and acetol. In the late 1990s, there were researchers studying the thermal degradation of glucosamine for the purpose of enriching their understanding of the role of Maillard reactions in flavor chemistry. Chitin had been employed as a tobacco extender and as food additives because its derivatives possess roasty, smoky and acidic flavors (14). One such study was conducted at 200 ^{o}C for 30 minutes in a dry atmosphere, yielding furyl derivatives, pyrazines and polyhydroxypyrazines from the dimerization of glucosamine.

N-acetyl-*D*-glucosamine can be obtained by either chemical or enzymatic hydrolysis of chitin. Quite recently researchers in the M. Osada group in Japan performed autocatalytic reactions of N-acetyl-*D*-glucosamine in high temperature water at high pressure for the production of food additives and biologically active compounds (15). If the desired fields of application are the food and medicinal industries then processing amino-carbohydrates under green conditions is essential to prevent contamination. The logical solvent is water for processing carbohydrates for food/medical applications because of its universal nature and biocompatibility. In this area of research it is imperative that these versatile compounds be produced in a cost effective manner from N-acetyl-*D*-glucosamine; this will provide researchers a cost-competitive building block for a varitiy of industries that extend beyond food and medical (e.g. energy and materials).

In 2010, NAG dehydration was performed in a borate solution at 100 ^{o}C for 2 hours and gave a 50 % yield of Chromogen I (2-acetamido-2,3-dideoxy-D-erythro-hex-2-enofuranose) it was detected along with 10% 2-acetamido-3,6-anhydro-2-deoxy-*D*-glucofuranose (3,6-anhydro-

GNF) and 10% 2-acetamido-3,6-anhydro-2-deoxy-*D*-mannofuranose (3,6-anhydro-MNF) (Figure 1.1) (16). In the 1950s a research group was able to obtain a 40% yield of Chromogen III (3-acetamido-5-(1,2-dihydroxyethyl)furan) from NAG via an alkali treatment (17). The previous research conducted on NAG has employed relatively long reaction times (hours) and alkaline or borate catalysts that require neutralization. Hence research built on these revelations are likely to focus on shorter reaction times and less harmful catalytic systems that are easily worked up. Recently a study has shown that NAG can be converted into Chromogen I and III (Figure 1.1) in moderate yields (23%, 23.1%) at 190 ^{o}C and 220 ^{o}C respectively (18). The reaction conditions evaluated in this study included a temperature range of 120-220 ^{o}C, reaction time of 7-39 seconds and a pressure of 25 MPa. The amount of sugar in water varied between 0.1 and 5% and the researchers concluded that 3 wt% was optimal.

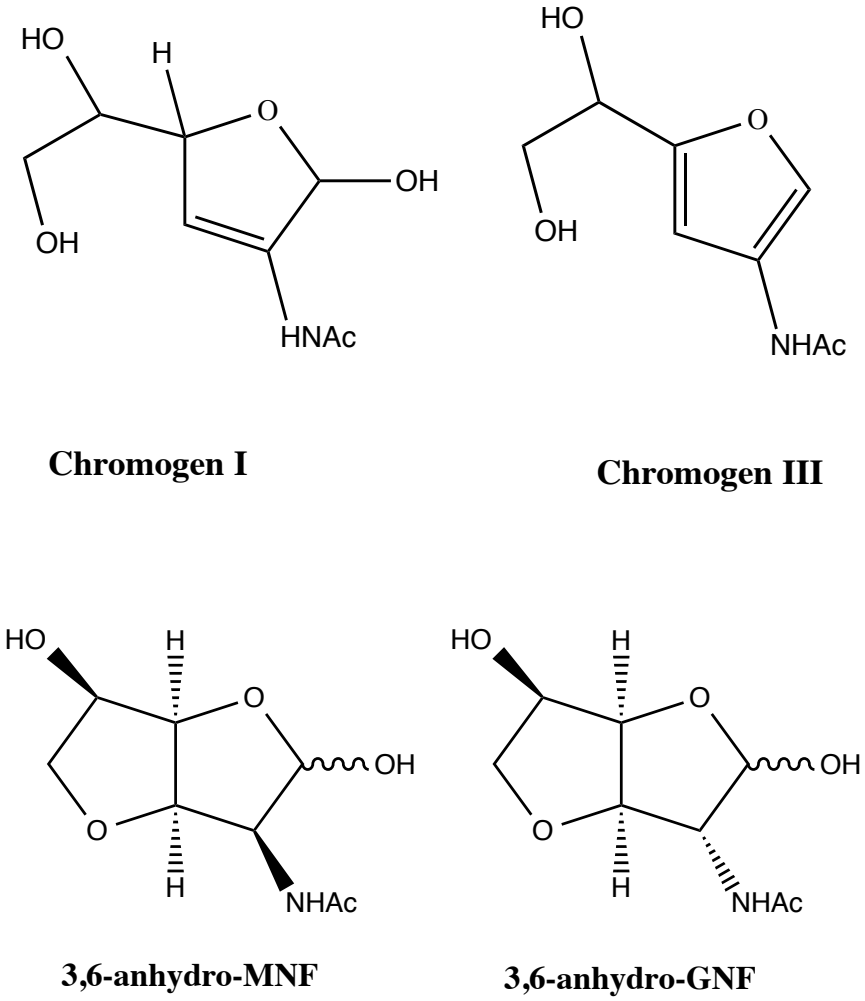


Figure 1.1 : Structures of Chromogen I and III as well as 3,6-anhydro-MNF and 3,6-anhydro-GNF

When NAG dissolves in water it exists as both a furanose ring and an open chain species. The structural isomers that form in low yields as side products stem from ring closure reactions. The standard deviations of yields for Chromogen I (3.1 %) and Chromogen III (0.5 %) regardless of initial concentration provided evidence for first-order kinetics. This study on the production of

Chromogen I and III evaluated a NAG concentration range from 0.1 to 5.0 wt% and found that the product distribution did not change over that range.

Confirmation of the product identity (e.g. Chromogen I and Chromogen III) was achieved using HPLC and NMR spectroscopy. Chromogen I was observed in the highest yield at 180 ^{o}C and beyond that temperature it was further dehydrated into Chromogen III. Above 200 ^{o}C the Chromogen III compound was reported to degrade into various water soluble and insoluble chemicals. The authors do not divulge information about the residue formed during the reaction or propose any applications for said insolubles. The Chromogen research provides valuable insight into the additive-free transformation of NAG but is clearly influenced by the high pressure environment. The formation of Chromogen III is optimized at 220 ^{o}C with a yield of 23 mol% within 12 s but degrades completely within 1 minute. These conditions are environmentally friendly but present separation issues and large amounts of waste water would be generated due to the low sugar concentration for these reactions. Side product formation is a key obstacle to overcome and as such additives are employed to hinder these by-products. The neutralization of the water stream for alkaline and borate methodologies depends on the concentration and by-products.

1.2.3 : Previous Research on the Formation of 3-acetyl-5-acetamido-furan

Inspiration for the current research project came from previous work in the Kerton group based on ionic liquids (ILs) or dimethylformamide (DMF) as NAG processing solvents. This study demonstrated the formation of a renewable amide (3-acetamido-5-acetylfuran [3A5AF]) from N-acetyl-*D*-glucosamine in good yields (19, 20). Ionic liquids have been used as the

reaction medium for 5-HMF production via conventional heating (21, 22) as well as microwave heated experiments (23, 24). This research showed that NaCl increased yield of 3A5AF but their system was limited by water for its inhibitory effects. Ionic liquids can be considered green solvents due to their non-volatile, non-flammable and potential recyclability (25). Some disadvantages of employing ILs as reaction media involve the higher cost and overall higher energy involved during synthesis, as well as common chemicals used in their preparation (chlorobutane, hexafluorophosphate) are toxic for human health and the environment. Previous research involved the production of 3A5AF in ILs under moderate conditions and compared heating source (conventional, microwave) and solvents (water and organic) (19). This work demonstrated that the formation of 3A5AF is possible in good yields (40 mol% - 60 mol%) when employing ILs but showed decreased activity when water was added.

Renewable amines are considered an essential platform molecules for biorefineries of the future; although to produce some of these compounds, researchers have employed ammonia as the nitrogen source (26). One main benefit of this recent research stems from employing chitinous biomass as biologically fixated nitrogen and thus it is a renewable source of small amines. This fixation is a key part of the nitrogen cycle in marine environments and has implications for the terrestrial cycle. Since the majority of ammonia is produced synthetically, a more sustainable route would use biologically fixated nitrogen for (renewable) amine production

It is noteworthy that 3A5AF has been produced from the thermal degradation of NAG in low yields < 3 mol% in the late 20th century (27, 28). Previous experiments conducted by Omari et al., employed microwave radiation as the heat source for NAG conversion reactions in ILs (19). A variety of ILs were evaluated at 120 ^{o}C with reaction times within a matter of minutes,

with [BMim]Cl yielding 14.1% conversion into 3A5AF. Products were identified by GC-MS and ^{1}H NMR spectroscopy. These results emphasized the connection between anion within the IL and the 3A5AF yield; with bromides or acetates giving low yields and the chlorides demonstrated effective conversion. It is generally accepted that chloride ions can play an influential role in the conversion of sugars in water. The issue arising from this is the environmental toxicity of the ILs and how they are synthesized. The highest yield (60 mol %) was obtained with the 2:1 mole equivalent of boric acid to NAG; while being heated in an oil bath at 180 ^{o}C for 1 hour. IL decomposition products were observed in the GC results (eg. methylimidazole) and were also found to inhibit product formation. Figure 1.2 shows the general scheme for the conversion of NAG into 3A5AF in ILs. The pathway of interest is initiated by the release of protons from the boric acid whilst possibly forming a doubly coordinated complex with NAG. This opens the ring of the aldose that is now prime for nucleophilic attack by a hydroxyl group to form a 5-membered ring. This heterocycle continues to become dehydrated and yields 3A5AF after a proposed keto-enol tautomerization step (Figure 1.3).

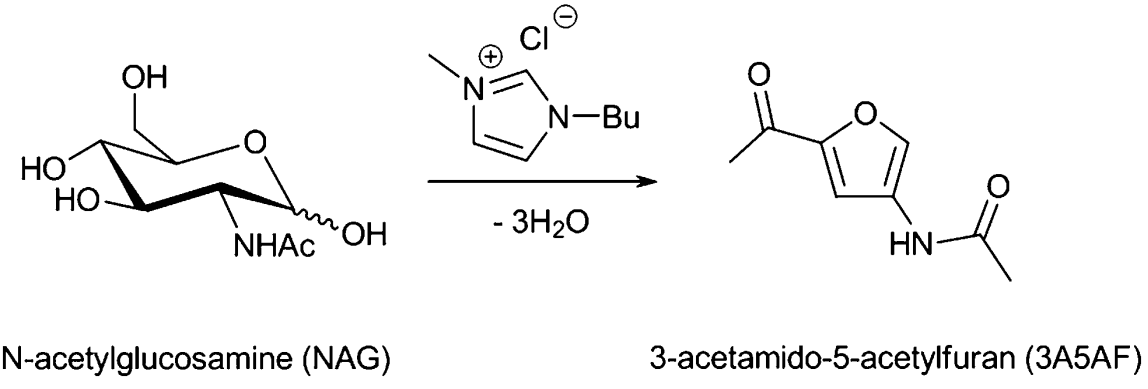


Figure 1.2 : General Scheme for the Conversion of NAG into 3A5AF in Ionic Liquids

This process was developed for the purpose of obtaining high yields of the versatile 3A5AF molecule. Authors of this study suggested that this furan might serve as a high-value precursor for proximicin (biologically active moiety) synthesis. Through the employment of ILs as the reaction medium the furan was readily separated via ethyl acetate extraction. The inherent green aspect of this research is use of a renewable feedstock and a non-volatile solvent. It was advocated that the main improvement for 3A5AF production would be use of a more sustainable and less toxic solvent which could display comparable selectivity.

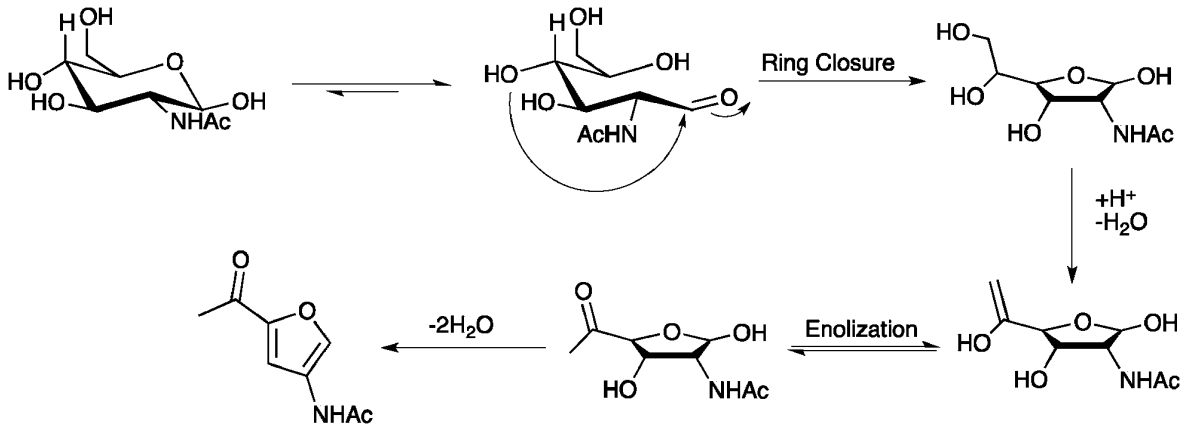
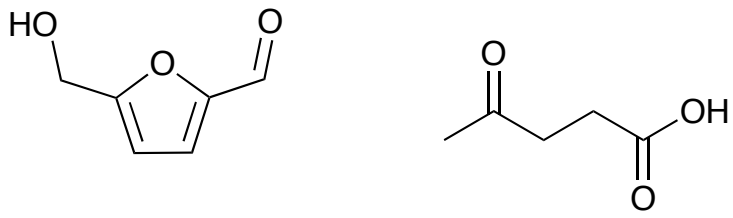


Figure 1.3 : Proposed Reaction Mechanism for NAG Conversion into 3A5AF via Enolization

1.2.4 : The Production of Platform Molecules from Amino-carbohydrates

A platform molecule is versatile and can be converted into a variety of other molecules or compounds. It was reported recently that glucosamine hydrochloride can be converted into levulinic acid (LA) (Figure 1.4) in moderate yields (59 mol %) under microwave radiation at 190

°C using $SnCl_4 \cdot 5 (H_2O)$ (19)**.** That particular research was evaluating the differences in reactivity for the polymer and monomer of chitin. Researchers have employed concentrated $ZnCl_2$ solutions as a reaction medium for the dehydration of glucose, fructose, maltose, sucrose and cellulose (29). The high activity of this system is attributed to the incomplete coordination of Zn^{2+} ions (when the H_2O:Zn ratio is less than 6) by the hydroxyl groups of the sugars (30). Subsequent work based on these findings was aimed to dehydrate glucosamine and N-acetyl-D-glucosamine ($GluNH_2$ and GluNHAc) with various co-catalysts (including $CrCl_3$, $SnCl_2$, $CdCl_2$, $CuCl_2$, NH_4Cl, $AlCl_3$ and $B(OH)_3$). Researchers obtained a mass yield of 2.8% 5-HMF when using N-acetyl-*D*-glucosamine as the starting material (29).



5-HMF **LA**

Figure 1.4 : Structures of 5-Hydroxymethylfurfural (5-HMF) and Levulinic Acid (LA)

The $GluNH_2$ was converted into 5-hydroxymethylfurfural (5-HMF) (Figure 1.4) in 21.9 mol% yield; thus showing the concentrated $ZnCl_2$ system more easily transforms the deacetylated aminosugar. The authors propose that the zinc chloride complexes with NAG in the pyranose form and converts it to an open chain form due to the selective interaction of Zn^{2+}; which the researchers acknowledge is also favored by Al^{3+} or B^{3+} (31). The deamination step is critical for the formation of 5-HMF but under certain conditions the nitrogen can be retained to yield renewable nitrogen compounds as discussed below. The weak interaction between the -NHAc

and Zn^{2+} is responsible for the poor yield of 5-HMF (2.8 mol%) and is probably due to steric hindrance (32). The formation of a metal-enediol species that then coordinates to a hydroxyl group is instrumental in stabilizing the transition state to isomerize a hexose into a 5 membered ring (33).

1.2.5 : The Role of Boric Acid in the Dehydration of Carbohydrates (Fructose and Glucose)

Recently some researchers have employed a 30 wt% fructose solution and achieved a 60% 5-HMF yield with 92% conversion by employing a catalytic amount of boric acid (34). 5-HMF was achieved with 65% selectivity when there are 100 g/L boric acid and 50 g/L of NaCl present in a biphasic water/MIBK (methy-iso-butyl-ketone) system. When the experiments were conducted with glucose (instead of fructose) the yield of 5-HMF dropped to 14% and the conversion reduced to 41%. Boric acid acts as a weak Lewis acid in water to form tetrahydroxyborate and a hydronium ion. It is this borate species that forms a complex with the sugar via its hydroxyl functionalities. It is postulated that the borate-hexose complex is doubly coordinated and liberates protons to acidify the solution while simultaneously initiating the dehydration. Once the sugar is dehydrated there will be an equilibrium reached for the furan species that can be controlled by minimizing the formation of levulinic acid and formic acid via re-hydration of 5-HMF (35). In the next paragraph the role of boron will be described in more detail.

The additional of salts for dehydration reactions of hexoses has been shown to be beneficial. In terms of environmental toxicity some salts will naturally be considered more green than others, with sodium chloride demonstrating synergetic effects it is a good economic choice

as an additive and furthermore it is environmentally compatible and publicly acceptable. A typical procedure (36) for the dehydration of sugars to 5-HMF involved filling a glass tube with a sugar solution, boric acid, alkaline salt and stir bar. The reaction vessel was heated conventionally (oil bath) for a period of time then cooled (no quenching) to room temperature. The dehydration products were extracted with a MIBK:water ratio of 4:1 then analyzed via HPLC. This analysis was performed with iso-propanol as the internal standard. The product yield, sugar conversion and product selectivity were calculated according to the equations in Figure 1.5 below. The optimized conditions were 150 ^{o}C for 45 minutes with a 50 g/L NaCl, 100 g/L $B(OH)_3$ for a 30 wt% fructose solution with MIBK (MIBK:water volume ratio 4:1) as the extracting solvent; this resulted in a fructose conversion of 70% and 46% 5-HMF yield.

$$\text{Product yield} = \frac{\text{Product conc.}}{\text{Initial sugar conc.}} \times 100\%$$

$$\text{Sugar conversion} = \left(1 - \frac{\text{Sugar conc.}}{\text{Initial sugar conc.}}\right) \times 100\%$$

$$\text{Product selectivity} = \frac{\text{Product yield}}{\text{Sugar conversion}} \times 100\%$$

Figure 1.5 : Quantification of Products for Fructose Dehydration

As mentioned above, in this work the authors suggest that boric acid forms a tetrahydroxyborate that then doubly coordinates to the hexose. This in turn liberates protons to acidify the solution that catalyzes the dehydration (Figure 1.6). It is possible to employ a glycol poisoning agent to occupy two of the hydroxyl groups of this borate species to determine the persistence of a doubly coordinated complex. The mild acidity of this process is an attractive

feature and would limit the need for corrosion resistant materials often used with mineral acids. Mineral acids (sulfuric and hydrochloric) have been used to degrade biomass for decades but controlling the product distribution catalyzed by these strong acids is difficult.

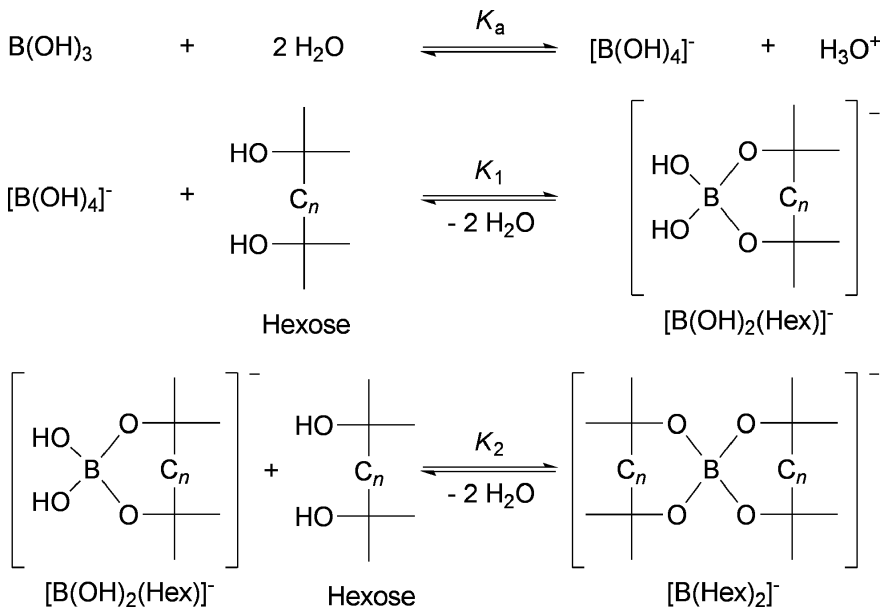


Figure 1.6 : Tetrahydroxylborate and Double Hexose Complex Formation

In 1987 Musau et al. demonstrated the dehydration of fructose into 5-HMF in DMSO without a catalyst at 150 ^{o}C in 2 hours with a 5-HMF selectivity of 92%; ethyl acetate (EtOAc) was the extraction solvent with dichloromethane (DCM) used in the silica gel chromatography (36). The extraction step in a chemical process may be critical in deciding whether a biomass transformation is environmentally friendly or not. The difficulties that arise in these processes (e.g selectivity) can be dealt with by employing a biphasic system that allows the 5-HMF to pass into the organic phase to prevent unwanted side reactions initiated by intermediates or degradation products (37, 38). Biphasic systems are able to achieve high yields of 5-HMF from

fructose but the toxicity of the organic solvent (assuming it is mixed with water) must be taken into account. With every chemical reaction, the solubility of the reactants and products can aid or hinder a desired outcome.

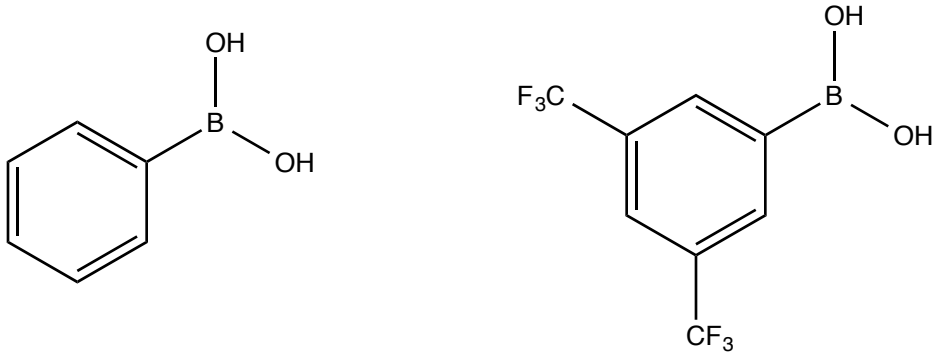
There is some speculation about the various roles of the dissolved salts in aqueous reactions of bio-sourced molecules; the salting out effect applies to the organics being formed but depending on the composition of the solution certain salts could hinder the process. The salting out effect takes place in aqueous solutions when water molecules shift from solvating an organic species and interact with salt ions. When there is sufficient salt ions present in solution the organic species can coagulate via hydrophobic interactions and their extraction (by an organic solvent) is enhanced. In a recent paper it was observed that 5-HMF yield could be increased from 5% to 13% with the addition of 50 g/L sodium chloride (34). The sodium and chloride ions presumably also function to stabilize intermediates and hence are critical for boosting desired yields. Out of the salts evaluated in this study, only lithium chloride and magnesium chloride displayed catalytic activity on par with sodium chloride. When economics are also taken into consideration, sodium chloride is the most cost effective. The effect of the anion was studied and sulfates displayed a lower selectivity than chlorides, with bromides and nitrates demonstrating similar activity to chlorides. Stronger Lewis acids such as aluminum or iron trichloride favored the formation of formic and levulinic acids via a re-hydration of 5-HMF. This study provides an overview of viable salts to combine with boric acid for carbohydrate dehydration but from a Green Chemistry perspective the relevant field of reagents is limited and NaCl is the most obvious and simplest choice.

1.2.6 : Boronic Acid as a Dehydration Catalyst

One research group has developed a process for glucose isomerization and subsequent in-situ extraction, which employed an organic phase with a hydrophobic aryl boronic acid (39). In this manner the role of the boronic acid is to liberate protons to acidify the aqueous solution and stabilize the intermediates for the extraction. This was applied to xylose and resulted in a furfural yields over 80 mol% at 110 ^{o}C (40).

In an area that gravitates towards chromium salt based catalysts it is seen as a benefit to replace them with a more environmentally benign reagent (41). Boric acid and its derivatives (arylboronic acids) are viewed as a more green catalytic system for the production of furan-containing platform chemicals (42). The first reported conversion of glucose into 5-HMF by using a phenyl boronic acid (Figure 1.7) was performed in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) (43). This was the starting point for a group of researchers collaborating in China and Singapore to study the role of borates in 5-HMF formation (42). Initially control reactions were performed without phenylboronic acid and it was observed that [EMIM]Cl could dehydrate fructose into 5-HMF but showed no activity for glucose conversion; the authors suggest this is because of its pyranose structure in the IL. It is postulated that this inertness stems from the stable ring structure between the sugar and the IL. The rate determining step to convert glucose into 5-HMF is the enolization before isomerization. These authors evaluated how changing the substituents on the phenyl ring can influence the 5-HMF yield through steric and electronic effects. It was observed that electron withdrawing groups (eg. nitro and carboxylic acid groups) had the strongest influence on the conversion of glucose to 5-HMF via strongly activating the arylboronic acids, whereas electron donating groups (eg. amine and methoxy groups) would

hinder the conversion. In terms of steric effects, the *tert*-butyl group gave about half the yield compared with the unsubstituted phenylboronic acid but the methyl group in the same position lowered the yield by 70%. The best reported yield of 50% was with 3,5-bis(trifluoromethyl) phenylboronic acid (Figure 1.7) and required a 20 mol% loading compared to 100 mol% with boric acid (optimized yield of 39%). What is remarkable about this system is how effective it is (34% yield of 5-HMF, and 12% LA) for generating platform chemicals directly from cellulose.



PBA **3,5-BPBA**

Figure 1.7 : Phenylboronic Acid (PBA) and 3,5-bis(trifluoromethyl)phenylboronic acid (3,5-BPBA)

In terms of mechanism differences for the isomerization in the first step, boric acid is proposed to catalyzed the transformation through an enediol intermediate whereas a hydride shift mechanism is central to a metal catalyzed isomerization (41,44,45). The boronic acid hydroxyl groups form a complex with sugar in a coplanar arrangement, with the cis-vicinal diol being more activated compared to the trans due to the distortion created by the latter (46,47). When the authors compared reactivity between glucose epimers (Figure 1.8: mannose and galactose) there

was a drop in yield from 13 - 45% that correlates with this distortion and leads to a heightened activation energy. In cases using an arylboronic acid, it is highly unlikely that a doubly coordinated complex could form with a sugar molecule despite the similarity in reactivity with boric acid which does form a doubly coordinated complex (44,45). Boron-containing species clearly remain a plausible replacement for chromium based catalysts for the conversion of carbohydrates in aqueous systems.

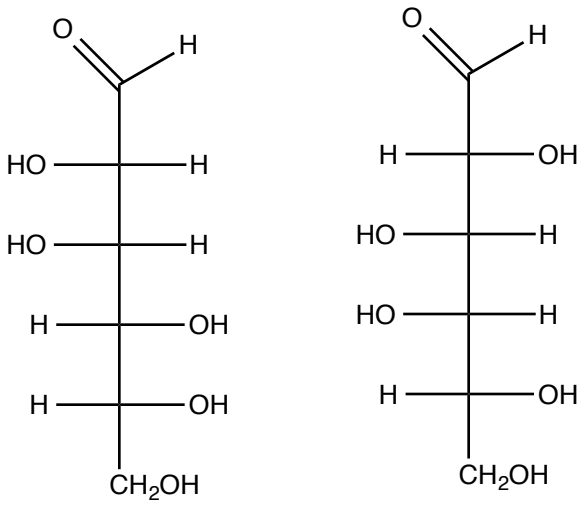


Figure 1.8 : Fischer Projections of D-Mannose and D-Galactose

1.3.0 : Applications of Platform Chemicals and By-products from Carbohydrates

With the cost of processing biomass being reduced annually through technology and innovation, there remains a number of hidden treasures waiting to be discovered. With the rise of biorefineries in the 21st century, the industrial landscape must decide on a group of platform chemicals that will be used as precursors for millions of chemicals, materials and fuels. A

promising compound for mass utilization in the chemical industry is 5-hydroxymethylfurfural (5-HMF) and it is primarily derived from renewable resources. This molecule can be converted to form 5-hydroxymethylfuranoic acid (HMFA), 2,5-furandicarboxylic acid (FDAc), 2,5 - dihydroxylmethyl furan (DHMF) and 2,5-furandicarboxaldehyde (FDAl) (seen in Figure 1.9) (48).

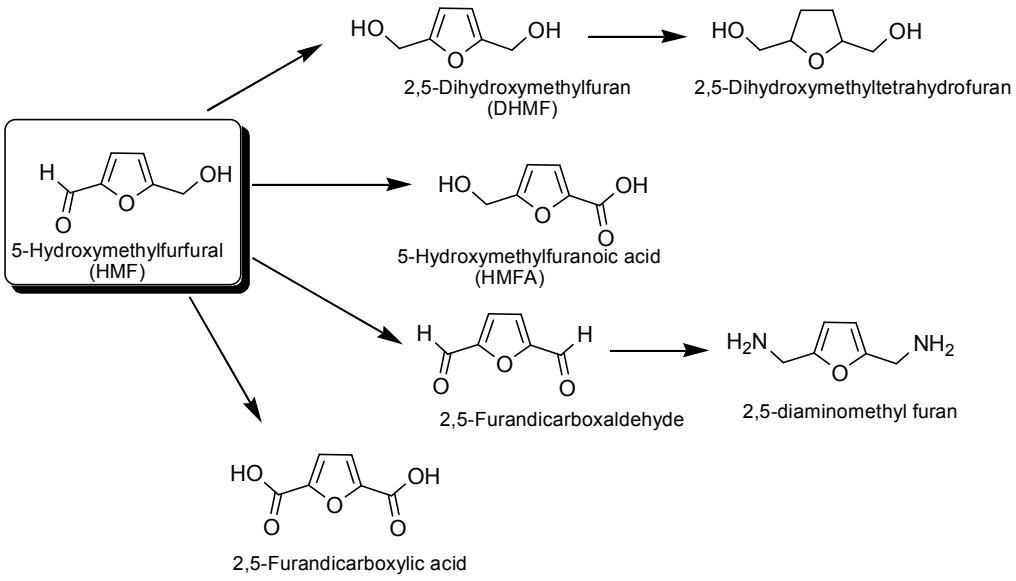


Figure 1.9 : Industrially Important Compounds Derived from 5-HMF

All of these compounds can be utilized as intermediates for more valuable products. The aldehyde can be employed for Schiff base synthesis and the diamino derivative is a green substitute for hexamethylenediamine for polyamide production. If the furan is fully saturated then a range of industrial industries (resins and artificial fibers) are within the realm of possibilities (49,50). The versatility of the original furan is remarkable and can greatly contribute

to the sustainability of the manufacturing industry. One of the versatile rewards from this platform chemical is the oxidation of 5-HMF into 2,5-furandicarboxylic acid (FDA) to replace terephthalic acid in polyester manufacturing (Figure 1.10) (34). The potential game changer is FDA since it has the ability to replace terephthalic (Figure 1.11), isophthalic and adipic acids for the production of polyamides, polyesters and polyurethanes (51,52) respectively. These sustainable replacements are an active area of focus in the field of polymer chemistry but such approaches have environmental and toxicological barriers as well as scale up issues to overcome.

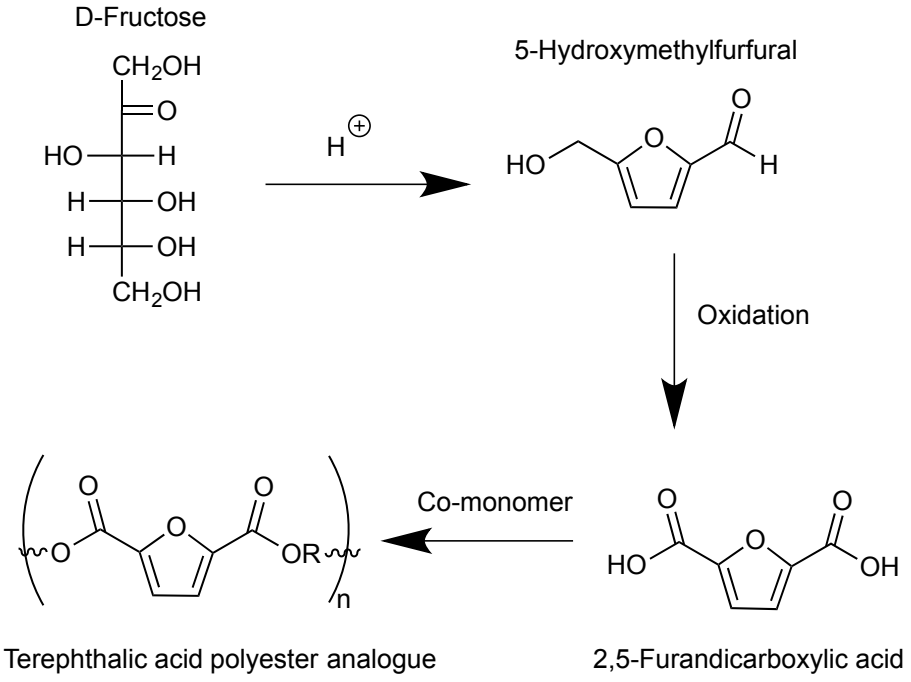
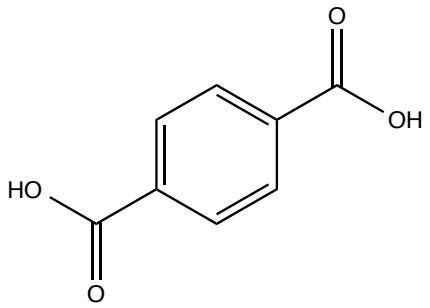


Figure 1.10 : The Conversion of D-Fructose to 2,5-furandicarboxylic acid



TPA

Figure 1.11 : Structure of terephthalic acid (TPA)

The reduction of 5-HMF to produce DHMF has been accomplished in the catalytic presence of nickel, copper, platinum and palladium under hydrogen (53). The main source of hydrogen is steam reforming of methane and as such depends on fossil fuels (an increasing amount of shale-derived methane in North America). In the future, hydrogen may be obtained via electrolysis of water. Future research in this area will most certainly develop an enzymatic-chemical approach for the reduction or oxidation of said furan. Recently there has been efficient heterogeneous oxidation systems for 5-HMF; the products include HMFA, 2,5-furandicarboxaldehyde and 2,5-furandicarboxylic acid (54). The oxidation route can be accomplished via the Cannizzaro reaction, which is a base-induced disproporationation of an aldehyde lacking a H-atom at the alpha position to the carbonyl group (48). During the reaction, one molecule of the aldehyde acts as the hydride donor while another acts as an acceptor to yield a carboxylic acid salt and an alcohol product. The main drawback for this process is the equimolar mixture of both products but when applied to 5-HMF the result is two valuable compounds of interest (DHMF and HMFA seen in Figure 1.12). An advantage for the Cannizzaro reaction is the relative low toxicity of dilute solutions of sodium hydroxide and simple operation.

Applying this to 5-HMF was first studied in the early 20th century (55) with the use of aqueous alkali solutions and more recently in ionic liquids (56).

A general procedure from a recent study involving the oxidation of 5-HMF via the Cannizzaro reaction is as follows (48): 1) dissolve 5-HMF in water and chill to 0 ^{o}C prior to NaOH addition, 2) stir at room temperature in a sealed environment for up to 36 hours, 3) evaporate water and perform extraction with ethyl acetate for diol (DHMF) separation, 4) isolate the carboxylate salt (HMFA) through recrystallization from ethanol, 5) wash diol (DHMF) to remove impurities. This study screened a variety of solvents (dry THF, water, CH_3CN) and bases (NaH, NaOH, KOBu) and yields were determined by proton NMR spectroscopy. Sodium hydride and hydroxide demonstrated the highest activity so the authors studied various substrates, solvents and time. The hydride achieved excellent yields within 4 hours when dry THF was the solvent. The hydroxide provided similar results in water but after 36 hours. From an environmental toxicity perspective, the hydride would present a greater risk due to the fact it reacts violently with water and thus requires more stringent handling/storing procedures. To run an industrial process that takes up to 36 hours per cycle would require the biorefinery to operate 24 hours a day and 7 days a week. Also the economics of employing dry THF instead of water would need to be considered before scaling up.

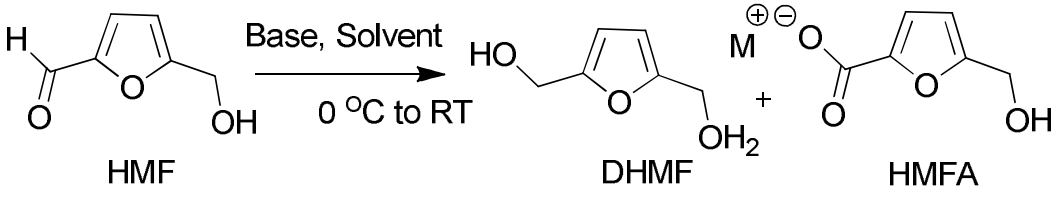


Figure 1.12 : General Scheme of the Cannizzaro Reaction Performed on 5-HMF

1.3.1 : Research on Hybrid Chemical Enzymatic Systems for Carbohydrate Transformations

It was reported that a chemical/enzymatic system was effective for glucose isomerization/dehydration in seawater (57). In this study the dehydration of hexoses into furans is initiated by an isomerization into a fructose/pentose species; which can be achieved by glucose isomerase under moderate conditions with high selectivity. Researchers have shown that by combining this isomerase with sodium tetraborate the fructose yield can significantly increase (50% to 88%) (58). This is a demonstration of the enhanced chelating ability of tetraborate with fructose (ketose) over glucose (aldose). The researchers also studied hexose/pentose isomerase for use in an aqueous environment on fructose, before being transferred to a biphasic system (water and 2-methyltetrahydrofuran 2-MTHF) for dehydration via oxalic acid. Both of these systems require an isomerized form of glucose to exploit the favorable chelating capabilities of sodium tetraborate and oxalic acid.

1.3.2 : Biocatalysts

One area that can significantly contribute to the upgrading of platform chemicals is bio-catalysis (isolated enzymes, whole-cell microorganisms). The power of yeast has been harnessed by people for centuries and thus it seems practical to evaluate its potential in Green Chemistry. Typical conditions for the reduction of organic compounds or fermentation are mild (R.T - 40 ^{o}C) and in an aqueous environment.

Baker's yeast has been employed for the selective reduction of ketones in organic solvents, ionic liquids and water (59). Isolating the product in organic solvents or ionic liquids tends to be less tedious than water but issues arise; such as biocatalyst deactivation, environmental toxicity and hazardous solvent disposal. In some cases the enzymes become deactivated in non-aqueous media although this can be mediated if there is a protective layer of water surrounding the biocatalyst (60). It should be noted that while the co-enzyme NADPH is recycled within the yeast in water, this does not occur in non-aqueous systems so the reaction is dependent on the initial concentration (61). To operate a catalytic process where the active species regenerates given a steady source of energy (small organic molecules) would hold an advantage over a system where the catalyst must be replaced and ex-situ regenerated.

A recent study has demonstrated the ability of baker's yeast to catalyze asymmetric reductions in various solvents (62). The purpose of this study was to use green techniques to achieve high selectivity towards chiral compounds. These compounds are used as building blocks for fine chemicals in the pharmaceutical, agrochemical and food science industries (63,64,65). There are three main advantages to employing whole cell biocatalysts compared to pure enzymes: 1) it avoids the costly process of extracting pure enzymes, 2) it supports co-factor regeneration, 3) greater tolerance to inhibitory reaction conditions. When employing a whole cell biocatalyst the reaction is generally slower due to the product diffusion through the cell membrane and enzymes can compete reducing selectivity.

Baker's yeast can be employed in the laboratory in its unsupported and immobilized form. The latter commonly includes alginate due to its easy preparation, low price and gel forming ability under mild conditions (66,67). The typical reaction runs for 1 - 5 days at

atmospheric pressure and between 30 - 37 ^{o}C but requires a large excess of yeast and a hydrogen source to oxidize such as sucrose or glucose. A remarkable feature of this biocatalyst is that the reaction conditions can influence its stereoselectivities between the *R*- and *S*- enantiomers by having oxygen present or absent (67, 68).

Petroleum based organic solvents can still play a role in the integration of baker's yeast into green chemical practices. The first reported use of a non-aqueous yeast reduction involved a mixture of isopropyl hexadecanoate and soybean phospholipids as the medium; although there was some water present to hydrate and protect the enzymes (69). A research group studied the enantioselective reduction of various beta-keto esters in light petroleum and obtained high yields (56 - 96%) and selectivity (94 - 99%) that were greater than in pure water (70). From the substrates evaluated, the authors observed that increasing the size of the ester group would require more yeast to balance the increased steric hinderance. ^{13}C NMR spectroscopy was used to study the deactivation of yeast in this solvent and after 24 hours the reductase enzymes displayed marginal activity (71). A complimentary study on yeast's tolerance to solvents concluded that as the polarity of the organic solvent decreased, the metabolic activity of immobilized and free yeast were increased (72). The researchers postulated that the rate of cell dehydration was accelerated as polarity increased.

Harnessing yeast and its enzymes for green conversion techniques offers a superior asymmetric reduction of chiral ketones because it does not require expensive hydrogen gas or potentially expensive homogeneous catalysts based on precious metals. The conversion of carbohydrates into novel building blocks does require the selective removal of oxygen and

further upstream processing. This opens the door for hybrid chemical/enzymatic systems for the sustainable production of platform chemicals.

1.3.4 : Biorefinery By-products: the Potential for Biochar and Applications

The overall sustainability of a process hinders on a holistic approach to by-product utilization and minimal waste going into the environment. During the hydrothermal processing of carbohydrates the initial compound(s) are transformed into three fractions (organic soluble, water soluble and residue). Literature discussed thus far has focused on the organic extract (furans) and touched on the hydrophilic compounds left in the aqueous (if water is the reaction medium) fraction. The residue that is formed at elevated temperature (>150 ^{o}C) has a variety of applications and its utilization is imperative for the carbon-neutral or negative outcome of these processes. This residue or biochar can be used for energy production, air and water purification and as a way to sequester carbon into the ground.

There is global interest in biomass pyrolysis for gas, liquid and char production due to the potential for carbon sequestration and biofuels through waste utilization. The gas is generally composed of CO_2, CO and CH_4; which can be converted into synthesis gas (CO and H_2) through reforming. Catalysts can be employed to convert the gas that is produced in these reactions into hydrogen, methane or alcohols via Fischer-Tropsch synthesis. The liquid (bio-oil) is typically an oxygen-rich mixture of organics with a relatively high water content (depending on original water content). This bio-oil can be upgraded into transportation fuels and is a suitable substitute (or blending agent) for petroleum oil. The biochar can be stored in agricultural lands to provide the dual benefit of helping to retain water and nutrients in the soil as well as a carbon negative

approach accompanying the production of energy. By harnessing the energy stored in the agricultural residues/wastes of the global biomass industries; it could be possible to offset up to 38% of global CO_2 emissions (73). The amount of food wasted or spoiled in developed countries can in some cases be greater than that consumed in developing countries.

About one-seventh of the CO_2 in the atmosphere is fixed each year by photosynthesis (74). This is balanced with approximately the same amount of CO_2 being released due to biomass decomposition. Carbon sequestration is limited to neutrality when using biomass as the medium. The opportunity in this situation is to lock the biomass carbon into a stable form to prevent its release into the atmosphere. The elemental analysis for an ash/nitrogen-free biochar has been reported to be in the range of 82% C, 3.4% H and 14% O (67). Biochar provides the vehicle to store carbon underground that could lead to a net-negative amount of CO_2 in the air. Storing biochar (charcoal) in the ground to improve the topsoil properties of the global agricultural regions can also be viewed as locking an energy reserve away for future generations/ or replacing the coal we have mined.

A recent study involving the pilot-scale (100 kg) pyrolysis of pine pellets resulted in a biochar formation of 26.3 kg (75). According to the calculations of the study, the amount of energy contained in the biochar was 28% of the total. The remaining energy is in the forms of hydrocarbon vapors and heat in the gas phase of the pyrolyzer. When steam was added to this mixture, the water gas shift reaction occurs to create synthesis gas with a higher overall hydrogen content. The resulting gas mixture was 47.6% H_2, 18.3% CO_2, 2.7% CH_4, 13.7% CO and 17.7% N_2.

When the biochar is produced at temperatures at or below 400 ^{o}C there tends to be a higher retention of functional groups (ketones, aldehydes, carboxylic acids and alcohols) than when pyrolysis temperatures are high (>800 ^{o}C) (77). These preliminary studies have shown that the biochar produced at the lower temperature had a great affinity at retaining fertilizer nutrients. Thus it is favorable to produce these solid carbon materials at lower temperatures. Since only the trace ash/mineral content of the biochar provides nutrients for plants, it is suggested that it be mixed with bicarbonate and urea salts for maximum carbon absorption into the soil. This is a more environmentally friendly option than nitrate-based fertilizers that leads (via runoff) to oxygen depletion in many coastal areas. This mixture then acts as a buffer to decrease the pH of the biochar from an alkaline position to one near neutrality. In a 2003 study (77), the chemisorption properties of biochar were evaluated and it is believed that the hydroxyl and carboxyl groups are responsible for the cation exchange capacity, specifically for ammonium and potassium ions in the soil that play key roles in sustained plant growth.

1.3.5 : Functionalized Carbon Materials

A wide degree of functionalization of HTC materials enables their use in a greater number of industries. The primary surface groups (-OH, -C=O and -COOH) are the active sites for reactions and can be selectively removed by thermal treatment. When the carbohydrate feedstock does not contain nitrogen, researchers have employed 3-chloropropylamine to graft amino groups to the surface to allow post-functionalization (78). Another common functional group to attach to the carbon surface is sulfonic acid; which is a simple manner of producing solid acid catalysts for biofuel production (79). Researchers have shown that to tailor the surface

functional groups it requires an inert atmosphere. To remove only the hydroxyl groups (they are converted to aldehydes or ketones) the post hydrothermal treatment of carbon must be at 350 ^{o}C or greater (80). When temperatures are raised to 500 ^{o}C, the carbonyl groups are removed and the surface consists of carboxylic acid groups (81). Above 600 ^{o}C the carbon is converted to material rich in aromatics with minimal surface oxygen species. Thus by simply increasing the temperature it is possible to synthesize a variety of carbon materials for specific applications.

Deriving these high value materials from waste or low value feedstocks is one of the main goals of hydrothermal carbonization research. A brief overview of the methodology employed to obtain a variety of functional carbon materials will be reviewed. There are several advantages of this carbonization process that are outlined as follows: 1) The temperatures are relatively low < 250 ^{o}C, 2) The process takes place in water with or without additives that enables the use of wet feedstocks (82), 3) Spherical micro-sized particles are the major product (83), 4) Porosity can be controlled by thermal treatment as well as the introduction of natural templates (84), 5) Silica (from rice husks (85)) is combined with carbon to form composites with unique properties (86), 6) The carbon particles have considerable amount of surface oxygenated groups that provide sites for functionalization (87), 7) The resulting carbon compounds can be considered "carbon negative" in the sense they have locked up CO_2 that was harnessed by photosynthesis (83).

When employing lignocellulosic or chitinous biomass for HTC production, there are a number of complex reactions that take place. Dehydration and retro-aldol condensation reactions are responsible for the decomposition of sugar in sub-critical water (88). Dehydration is more dominant at lower (< 250 ^{o}C) temperatures and results in the formation of 5-

hydroxymethylfurfural (5-HMF) and furfural (89). The former is generated from hexoses while the latter from pentoses. This material can be referred to as humins (90), hydrothermal carbon (83) or hydrochars/biochars (91) depending on the reaction conditions. This material is composed of fused furanic moieties that have aliphatic regions as connections while hosting terminal oxygenated groups.

By following a holistic approach for the conversion of biomass in water, one can utilize the by-product (biochar) in several fields that aim to protect the environment. The area of nitrogen doped carbon materials has plenty of room to grow and play a role in the cleaning of water and air. The platform chemicals that can be derived from carbohydrates will be able to infiltrate the petroleum refining market but it is important to constantly look for ways to increase the green metrics of the process.

1.3.6 : Nitrogen-functionalized Carbon Materials

In-situ functionalization can take place when using amino-carbohydrates such as chitin, chitosan and glucosamine (92), or by addition of nitrogen containing proteins (93). In this paper, the Titirici research group demonstrated that HTC materials derived by glucosamine will retain their nitrogen up to 750 ^{o}C. This is attributed to the incorporation of nitrogen in the aromatic network via pyrrole and pyridinic functionalities which were formed by the in-situ generated ammonia. This approach enables the production of nitrogen doped carbon materials from a renewable source for applications such as catalyst support and selective adsorption membranes. Prawn and lobster shells remain one of the most abundant biomass source of nitrogen for novel

chemicals and materials. Waste protein streams are another viable source for renewable nitrogen compounds.

1.4.0 : Objectives of this Research

The aim of the research in this thesis was to:

1) Investigate whether water was a suitable medium for the conversion of amino-carbohydrates into 3-acetyl-5-acetamido-furan.

2) Optimize the following reaction parameters: temperature, time, additive content, sugar content and feasibility of solvent recycling

3) Perform reactions that have a minimum negative impact on the environment and human health.

4) Proof of concept for biotransformation of furans

5) Determine feasibility of biochar for multiple applications

Chapter 2. Experimental

2.1.0 Materials, Equipment and Instrumentations

N-acetyl-*D*-glucosamine (98%) (NAG), sodium chloride (99%) and boric acid (99%) were obtained from AK Scientific, Inc., ACF Chemicals and Sigma-Aldrich respectively. 5-Hydroxymethylfurfural (98%) and levulinic acid (98%) were purchased from Alfa Aesar. Deionized water was obtained from a Nanopure II system (manufactured by Barnstead/ Thermolyne, USA), Ethyl acetate (99.5% HPLC grade) obtained from Caledon Laboratory Chemicals.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer. Gas chromatography-mass spectrometry (GC-MS) was performed on an Agilent 7890A GC system coupled with an Agilent 5975C MS detector that was equipped with a capillary column db-5 (column length: 30.0 m and column diameter: 0.25 mm). Products were detected by a 5975C VLMSD with Triple Axis Detector (*m/z* 50-250).

2.1.1 General Procedure for the Dehydration of N-acetyl-*D*-glucosamine and Extraction of Products

A typical reaction was performed in a Parr reactor (300 mL) at temperatures between 180 ^{o}C and 220 ^{o}C. The time required to reach the desired temperatures was on average 26 minutes for the former and 35 minutes for the latter temperature. Specific amounts of NAG, sodium chloride and boric acid were poured into the reaction vessel and then the desired amount

of water was added. The vessel was stirred and heated to the desired temperature; once at this temperature the timing of the reaction started. Once the reaction was complete, it was quenched by placing the vessel in an ice water bath, where it was cooled to room temperature within 5 minutes. The reactor was opened and the aqueous mixture was filtered and the residue (biochar) was washed with ethyl acetate (3 × 100 mL). The aqueous phase was then extracted with a known amount of ethyl acetate. The organic phase was concentrated by rotary evaporation and the solvent in the trap was recycled for two more extractions (three in total) then was re-dissolved in ethyl acetate to be analyzed by a GC-MS.

2.1.2 Analytical Methods for Furan Identification

After dehydration of NAG, extraction with ethyl acetate and removal of solvent by rotoevaporation, the dried residue was dissolved in $CDCl_3$ or D_2O. The mixture of products was analyzed by ^{1}H-NMR and ^{13}C-NMR spectroscopy. GC-MS was the main analytical method used for the characterization and quantification of the product mixture. All solvent recycling experiments were performed in triplicates, with the values reported in this thesis being the average.

Reconstituted sample was injected through a 7683B Series Injector using a split mode of 50%. The GC separation was done at a flow rate of 1 mL/min He (99.999%). Products were detected at m/z 50-250 scan range. The method employed was programmed as follows: 50 ^{o}C heating to 150 ^{o}C at 30 ^{o}C/min, 10 ^{o}C/min to 190 ^{o}C then 30 ^{o}C/min to 260 ^{o}C (total run time = 11 minutes). The retention times for 3A5AF, 5-HMF, 5Ac3NH_2F and 3NH_2F were 7.030 +

5.950, 3.512, 4.710 and 2.203 respectively. Products were identified by retention time and MS spectral library while yield quantitation was based on relative peak area.

Molar yields for furans were determined from the mass of crude product obtained after (3 × 100 mL ethyl acetate) liquid extractions are complete and the sample was dried under vacuum. The residue (biochar) was dried overnight at 120 ^{o}C and weighed. There were negligible amounts of gaseous products formed during the reaction; hence the difference in mass between products (furan compounds and biochar) and initial substrate was assumed to remain in the aqueous phase (organic acids, soluble humins).

2.1.3 Analytical Methods for Biochar Identification

Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker ALPHA FTIR instrument with ALPHA-T sample compartment to determine functional groups of dried biochar samples. Elemental analysis (EA) was performed via combustion microanalysis on dried biochar samples to determine carbon, hydrogen, nitrogen, oxygen and boron content. 50 mg of each sample was dissolved in 1 mL of 8M Nitric acid. The solutions were then diluted to 30 g with nanopure water. 5 g of each sample solution was diluted to 10 g with 0.2M Nitric acid.Inductively coupled plasma mass spectrometry (ICP-MS) was performed using an ELAN DRC II ICP-MS instrument to determine the elemental content of biochar samples.

Chapter 3. Results and Discussion

3.1.0 : The Green Conversion of N-acetyl-*D*-glucosamine to Platform Chemicals

The purpose of this research is to produce versatile platform chemicals in a manner that does not negatively impact humans or the environment. This research focuses primarily on the catalytic dehydration of N-acetyl-*D*-glucosamine (NAG) in subcritical water (180 - 220 ^{o}C / 250 - 450 psi) for the production of substituted furans. Water was chosen as the solvent because of its bio-compatible, economic and toxicological properties. The studies focused on the influence of additives (boric acid, sodium chloride), NAG concentration and time/temperature on product distribution. The feasibility of solvent recycling and proof-of-concept for the biotransformation of furans are presented at the end of this chapter. This work was based on the investigation into the production of platform chemicals from NAG through a catalytic system that employs sodium chloride and boric acid (20). In that research the production of 3-acetamido-5-acetyl-furan (3A5AF) was achieved in dimethylacetamide (DMA) at 220 ^{o}C under microwave radiation for 15 minutes. This renewable amide molecule was also formed in ionic liquids with boric acid being the most catalytically active reagent when employed in a 2:1 boric acid:NAG molar ratio. Previous work in the Kerton group demonstrated that these additives were capable of producing 3A5AF in ionic liquids or organic solvents in good yields (50 - 60 mol%) but presented environmental drawbacks due to the volatility and toxicity of the solvents used.

The experimental research discussed in the following chapter will demonstrate that renewable amides can be produced from a sugar with a minimum toxicological impact. The main benefits with using water as the solvent is its intrinsic environmentally benign nature and tunable properties that exist between the range above the boiling point and below the critical point. We were able to not only produce the desired product but additional platform chemicals containing the furan moiety. These products includes primary amides and nitrogen-free furans. A general reaction scheme with the various furan products derived from the conversion of NAG is displayed in Figure 3.1. Every reaction performed in this project (including additive-free ones) produced an ethyl acetate insoluble residue that is hereon referred to as biochar. Products that were extracted in ethyl acetate were analyzed on an Agilent GC-MS instrument. Initial studies were focused on the influence of the NAG concentration and time on the distribution of products and yields with a fixed temperature and additive content.

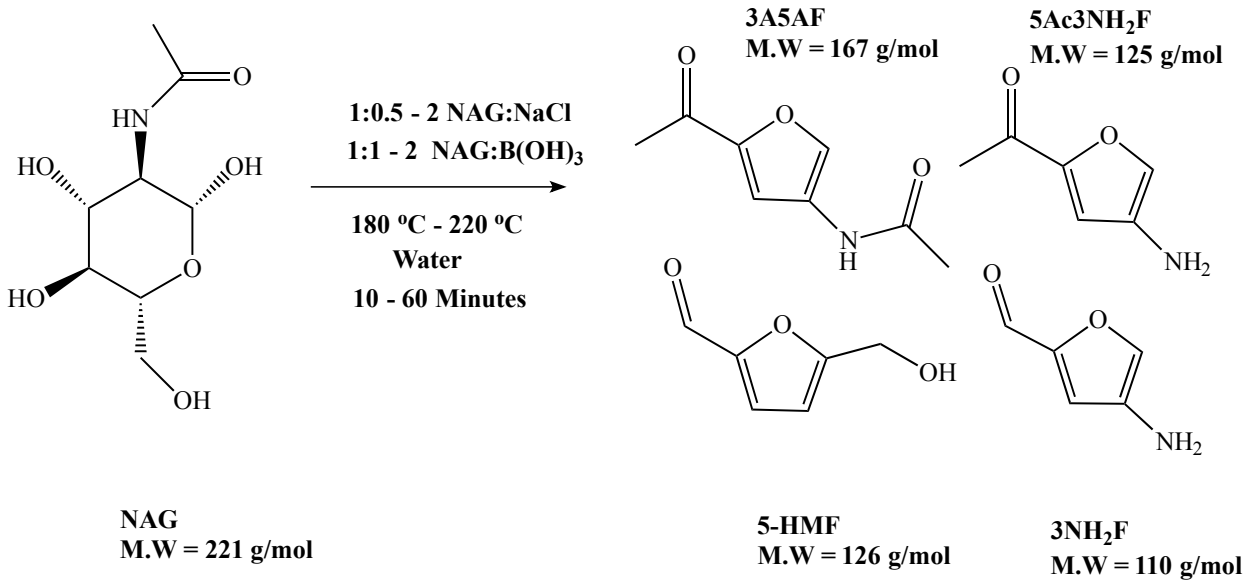


Figure 3.1 : The Conversion Scheme of NAG to 3A5AF, 5-HMF, $5Ac3NH_2F$ & $3NH_2F$ in Water

In Figure 3.2 below, results are presented on the distribution of products that were obtained by varying the NAG concentration between 10 and 40 minutes. When the reaction time is increased the water becomes more acidic and results in the formation of 5-hydroxymethylfurfural (5-HMF) in high selectivity (86.5%). During these longer reactions, the amount of biochar collected also increased. The distribution of products for shorter reactions was such that 3A5AF forms with high selectivity (>90%) along with 5-HMF and degradation products. In some cases there were two peaks with *m/z* = 167, the mass of 3A5AF and this might indicate the presence of another isomer but further studies are needed for confirmation. Different concentrations of NAG were evaluated to determine any dilution effect and potentially shed light into the reaction mechanisms.

By adjusting the molar ratios of additives, a selectivity of 93.4% with a molar yield of 70.0% for 3A5AF and 85.6% selectivity for 5-HMF with a molar yield of 69.4% were obtained under optimal conditions. These two molecules (3A5AF and 5-HMF) can be utilized for a variety of material and energy applications. The former was achieved in 20 minutes with a 5 wt% NAG solution and 1:2:1 NAG:$B(OH)_3$:NaCl ratio while the latter in 40 minutes at 7.5 wt% NAG at 220 ^oC and1:2:2 NAG:$B(OH)_3$:NaCl. The data for reactions conducted at 220 ^oC (Figure 3.2) indicate that time has a significant influence on yields when there are 2 molar equivalents of boric acid and sodium chloride for every 1 of NAG. By a small increase in reaction time it is possible to switch the selectivity in this reaction and add a practical dimension to the process if it were to be scaled up. These conditions provide information about the reagent's reactivity and established a mechanistic foundation for two distinct dehydration pathways.

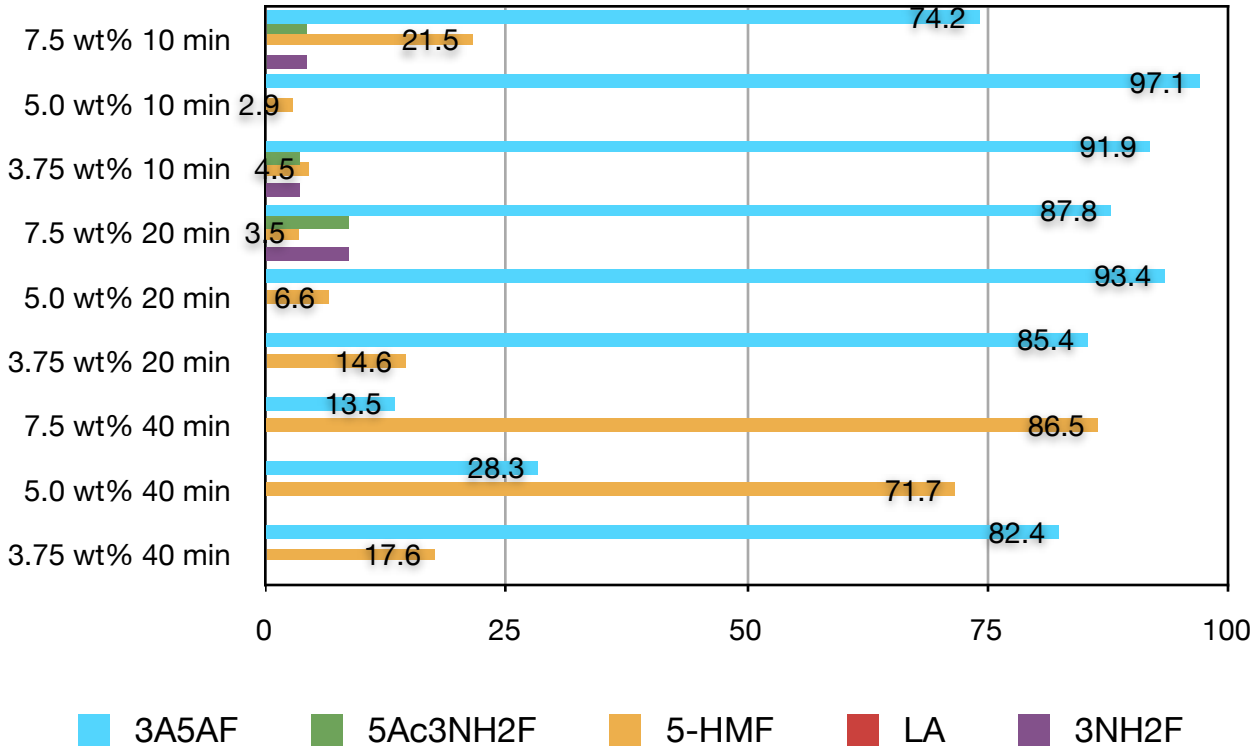


Figure 3.2: Product Selectivity : 1:2:2, NAG: NaCl: $B(OH)_3$ at 220 ^oC

3.1.1 Proposed Reaction Mechanism

The mechanism for the formation of 3A5AF is briefly discussed in the following section based on what was proposed by Omari et al. (19). When the water is added to the vessel containing the reagents, the boric acid immediately ionizes and forms an equilibrium with water. Depending on the exact conditions (eg. concentration) different amounts of $B(OH)_4^-$ (tetrahydroxyborate) and H_3O^+ (hydronium) form. Polyborate formation is also possible under basic conditions but that avenue will not be addressed in this study as the conditions are not basic. As the temperature is increased the hexose ring opens at the oxygen moiety to yield a hydroxyl and aldehyde group. The hydronium ions initiate this isomerization of the straight chain molecule into a 5 membered ring with a ethylene glycol substituent bonded at the 3 position and

acetamido at the 5 position (Figure 3.3) (19). As temperature increases the tetrahydroxyborate forms a complex with the furanose that makes it susceptible to dehydration. There is speculation that a doubly coordinated complex forms with NAG but preliminary studies within the group are inconclusive (Y. Liu, borate unpublished results). This doubly coordinated species would be an intermediate that enables the faster dehydration of the hexose, and would be rate determining if yields decreased significantly upon "poisoning" the boric acid. During this project there was ethylene glycol added (in equal molar amounts to the $B(OH)_3$) to the solution in the attempt to prevent formation of a double hexose/boron complex. The formation of 3A5AF still occurred in the presence of ethylene glycol but the yield decreased by 25%. This leads us to believe even if there is a doubly coordinated species it is not formed during the rate determining step of this reaction. The main transition state forms a 6 membered ring with the borate while the sodium chloride ions play a role in stabilization (19). The final amido-furan (3A5AF) undergoes degradation through deacetylation and the conditions that lead to that will discussed later on in this chapter.

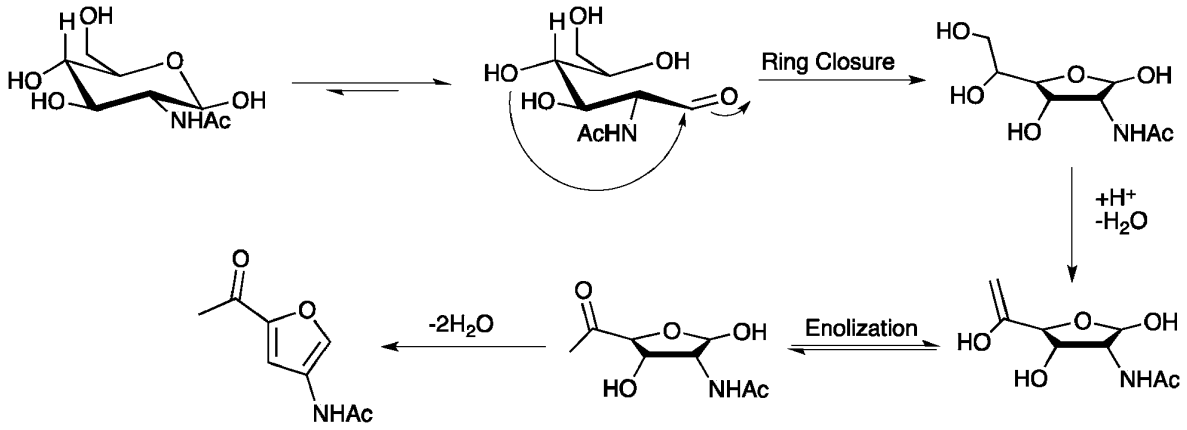


Figure 3.3 : General Mechanism for the Formation of 3A5AF from NAG

The formation of 3A5AF is significantly different than 5-HMF because the final furan substitution pattern is different. The formation of 5-HMF from NAG follows a similar mechanism to that mentioned above and is related to that for glucosamine dehydration presented by Omari et al. (20). Once ammonium hydroxide is generated there is a condensation reaction that closes the ring and yields a saturated heterocycle. The two remaining hydroxyl groups bonded to the ring are removed as water (acid-catalyzed dehydration) to result in the unsaturated 5-HMF. This six carbon platform chemical can rehydrate/decompose into levulinic acid (a five carbon chemical) and formic acid. Levulinic acid has the potential to be widely used in polymer production while formic acid can be used in a fuel cell to generate electricity. As mentioned in the literature review, 5-HMF itself can be oxidized in 2,5-dicarboxylic furan which is an ideal replacement for terephthalic acid (Figure 3.4). This acid is most commonly found as the commodity plastic PET (polyethylene terephthalate).

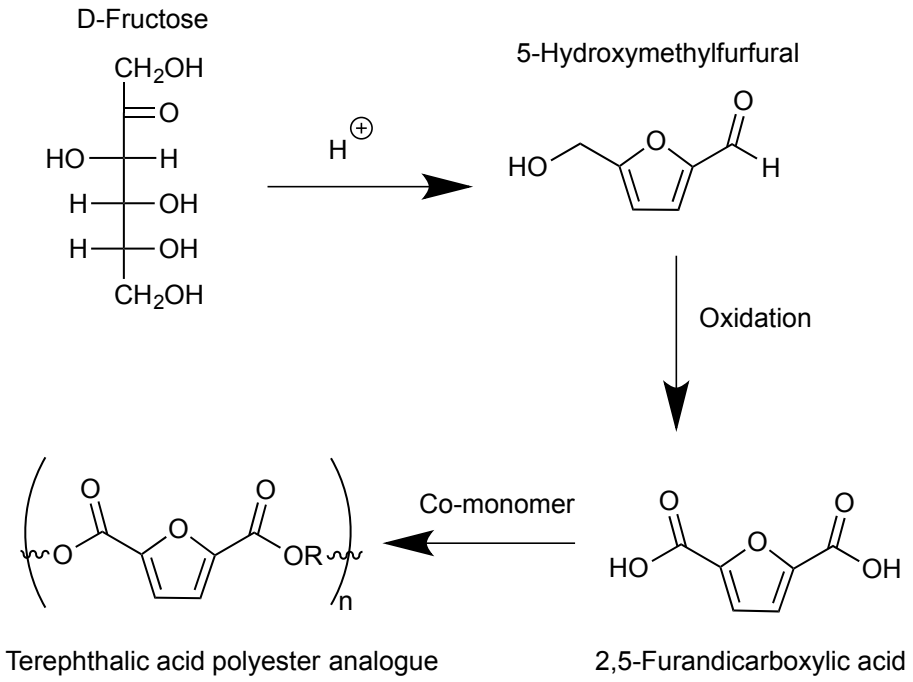


Figure 3.4 : 5-HMF Oxidizing into DCF and Compare to PET Analogue

From the beginning of the concentration study, it was observed that 3A5AF was the dominant product after 20 minutes. As the reaction progresses the products react under increasingly acidic conditions (acetic/organic acids form via autocatalysis). N-acetyl-*D*-glucosamine reaches an equilibrium in water between the ring structure and the open chain upon dissolving. By adjusting temperature, time and concentrations, the optimal conditions to sway the relative amounts of the ring and chain forms of the sugar to favor the retention of nitrogen in the product was observed. The primary goal of this research is the production of renewable amides so nitrogen retention is essential. The initial isomerization into a furanose is likely the rate limiting step and given analogous studies with glucose can occur over a short period of time. This isomerization reaction is acid-catalyzed in this study but can also be performed by enzymes, which is the slower of the two methodologies. Therefore, there is a trade off when using

enzymes that perform highly selective reactions over the course of days. With longer reaction times the conditions become favorable for the open chain form of NAG to undergo a retro-aldol condensation and form a Chromogen I precursor from an aminoacetaldehyde (Figure 3.5).

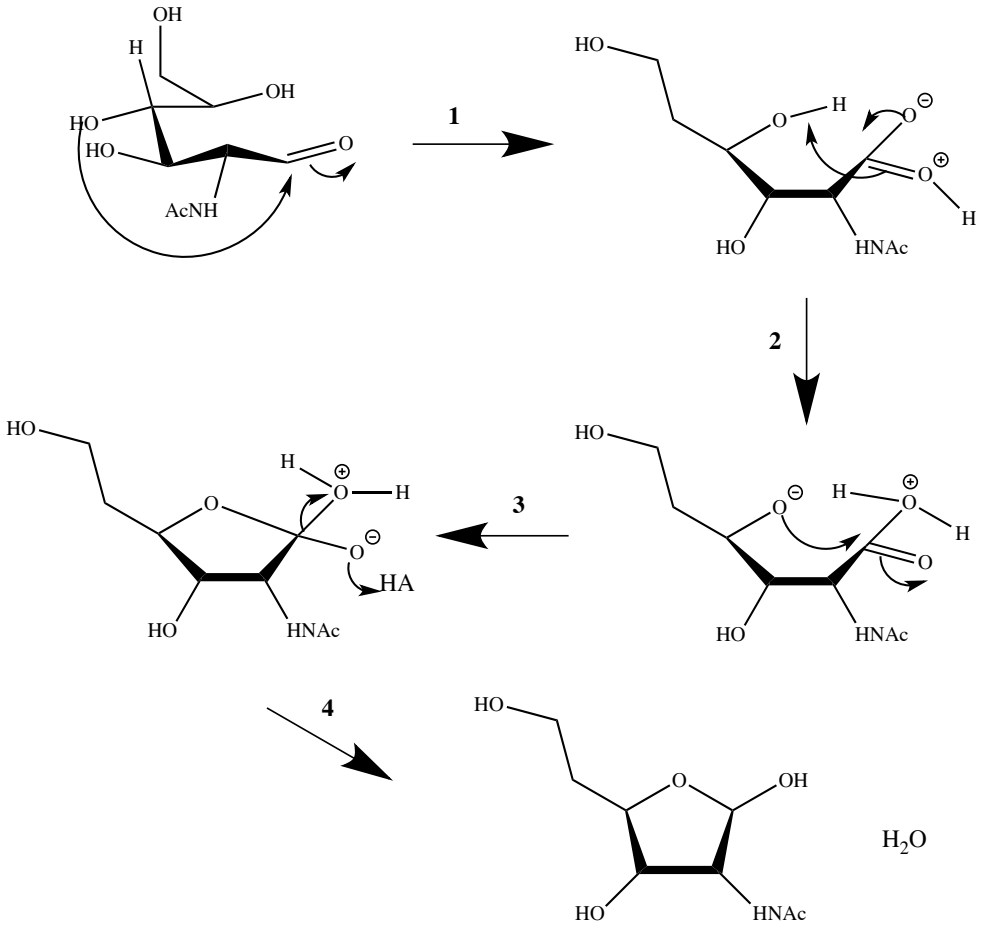


Figure 3.5 : Retro-Aldol condensation of aminoacetaldehyde into Chromogen I Precursor

A retro-aldol reaction is when a hydroxyl group undergoes deprotonation by a base and forms a carbonyl group as well as breaking a carbon bond to convert an adjacent carbonyl group into an enolate. Since this is a condensation the subsequent intermediate will form

simultaneously with a new water molecule. The dilute amount of boric acid employed during this study (1 - 4.5 wt%) provides sufficient hydronium ions that facilitate the loss of ammonium from the aminoacetaldehyde (under conditions that favor 5-HMF formation) and initiates the rehydration of the compound. After this there are two consecutive condensation reactions that yield a di-substituted furan. It is this step that requires the acidity of the boric acid the most; since in the literature the Chromogen I & III molecules have been reported from the high pressure autocatalysis of NAG in water (18). The first of these molecules has only one double bond in the furan ring, the latter is fully unsaturated, and they both contain two hydroxyl groups on the $CHCH_2$ moiety at the 3 position.

From the experimental data reported in Figure 3.7, reactions at 40 minutes led to 5-HMF being formed in significant amounts while not degrading into levulinic acid. It should be noted that in all reactions described in this thesis, no pyrrole or pyridine derivatives were detected. Those nitrogen-containing compounds (Figure 3.6 e.g pyrrole, pyridine) are formed through the process of the ammonium activation induced ring opening of a furan or through a NAG open chain self-condensation reaction.

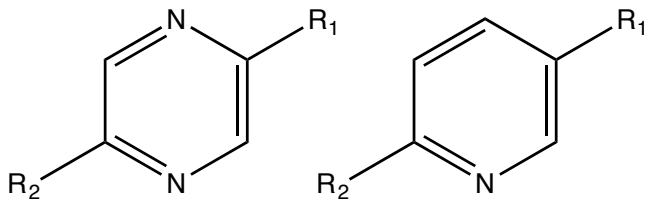


Figure 3.6 : Pyrazines and Pyridines Formed from NAG at High Temperature

This mechanism described above was seen when the molar ratio of NaCl and $B(OH)_3$ are 2:1 with NAG at 220 ^oC. The selectivity was evaluated under different reaction environments where the amount of one additive was reduced by half. From these next studies, it is possible to postulate how the stabilization of intermediates occurs under different acidic and saline concentrations and how these play a role in determining the distribution of products. The cooperative effect displayed between boric acid and sodium chloride is apparent while providing a reaction window suitable for multiple transformations.

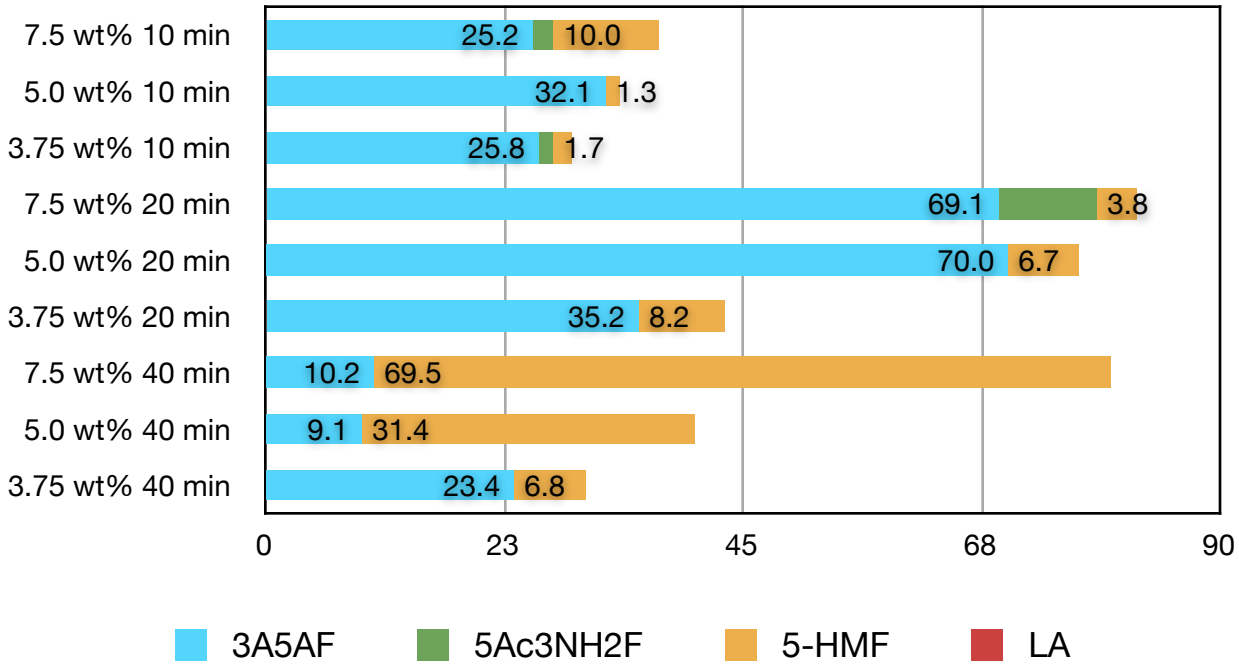


Figure 3.7: Molar Yields when 1:2:2, NAG: NaCl: $B(OH)_3$ at 220 ^oC

3.1.2 The Effect of Changing the Additive Mole Ratio to 1:2:1, NAG: NaCl: $B(OH)_3$

In the efforts to boost yields from an elevated salting out effect and to better understand NAG chemistry in a less acidic environment, studies were performed with a mole ratio of 1:2:1,

NAG: NaCl: $B(OH)_3$. The stark difference is the retention of nitrogen in the final product at longer reaction times. The selectivity for 3A5AF increased from 10.2% to 87.2% when the vessel contained a 7.5 wt% solution of NAG at 220 ^oC (Figure 3.8); compared to when 2 mole equiv. of NaCl and $B(OH)_3$ are present relative to NAG (Figure 3.7). When the reaction mixture is less acidic the formation of 5-HMF is hindered and the main product was 3A5AF after 40 minutes. Under these conditions (1:2:1 NAG:NaCl:$B(OH)_3$) the most concentrated sugar solution (7.5 wt % NAG) studies achieved highest selectivity (>90%) over the course of 40 minutes. But when taking time into consideration the 7.5 wt% NAG reaction at 20 minutes resulted in a mere 0.16% increase in 3A5AF; thus a 10 minute reaction window is advantageous because the yields are similar in half the reaction time. In this case where the by-products are valuable then the practical conditions are those with the higher (furan) molar yield. The results of the 40 minute reactions are the most interesting to discuss due to the large swing in yields; when the amount of boric acid is decreased by half, the yield for 3A5AF increases dramatically while 5-HMF formation drops significantly. This is an example of how delicate the equilibrium is when it comes to acidity. The excess chloride ions (relative to boric acid content) in solution give way to a preferential retention for the acetamido functionality to remain in the majority of the products. However, the effect of NaCl concentration on the effectiveness of aqueous extraction should also be considered.

Due to the chemical affinity that chloride ions possess for the hydroxyl groups of carbohydrates, the experiments under these conditions provide mechanistic insight into the role of different oxygenated species. When more Cl^- ions coordinate to the sugar derivatives, the less complexation occurs between boric acid and the sugars. When the mole ratio of boric acid is 1:1

with NAG (compared to 2:1), there is less boric acid protonation occurring and that translates into a less acidic environment. When the environment is less acidic, deacetylation takes place to a less extent and that equates to more nitrogen retention in the product; thus less 5-HMF is formed. With less acid present in the subcritical water, the acetyl group bonded to the amino group is subjected to less protonation and acts as a protecting group to retain the nitrogen in the final product (3A5AF). This decrease in protonation is a response to the increase in chloride ions as well as the lower degree of complexation taking place between tetrahydroxylborate. This results in a less acidic environment where 5-HMF formation is suppressed. The more dilute reactions (3.75 wt% NAG) tended to form more 5-HMF with the highest (25 mol%) yield occurring from 40 minute reaction. It should also be noted that the 2:1 mole ratio for NaCl:B $(OH)_3$ based reactions produced a small amount of levulinic acid (which was not observed when the ratio was 2:2). This research suggests that the rehydration of 5-HMF occurs more readily in a solution with more NaCl than $B(OH)_3$ or after 40 minutes at 220 ^oC. As the amount of NAG in solution decreases there is a relatively constant amounts of $5Ac3NH_2F$ and $3NH_2F$ formed due to the deacetylation of a acetamido group. This implies there are further degradation products formed (from all furan compounds) that remain in the water phase.

In Figure 3.9 the molar yields displays a [NAG] concentration effect with spikes or drops that is linked to the time at 220 ^oC. Overall the yields are lower than when there are two mole equiv. of boric acid, which was expected since overall the products are in a more hydrated form (lack of excessive acid in media). Since the two main products are formed by a triple dehydrations, the pH of the aqueous solution affects greatly the outcome of furans. The highest

yield achieved for 3A5AF 56.2 mol% with a selectivity of 72.7% when the concentration of NAG was 5.0 wt% and the time was 40 minutes.

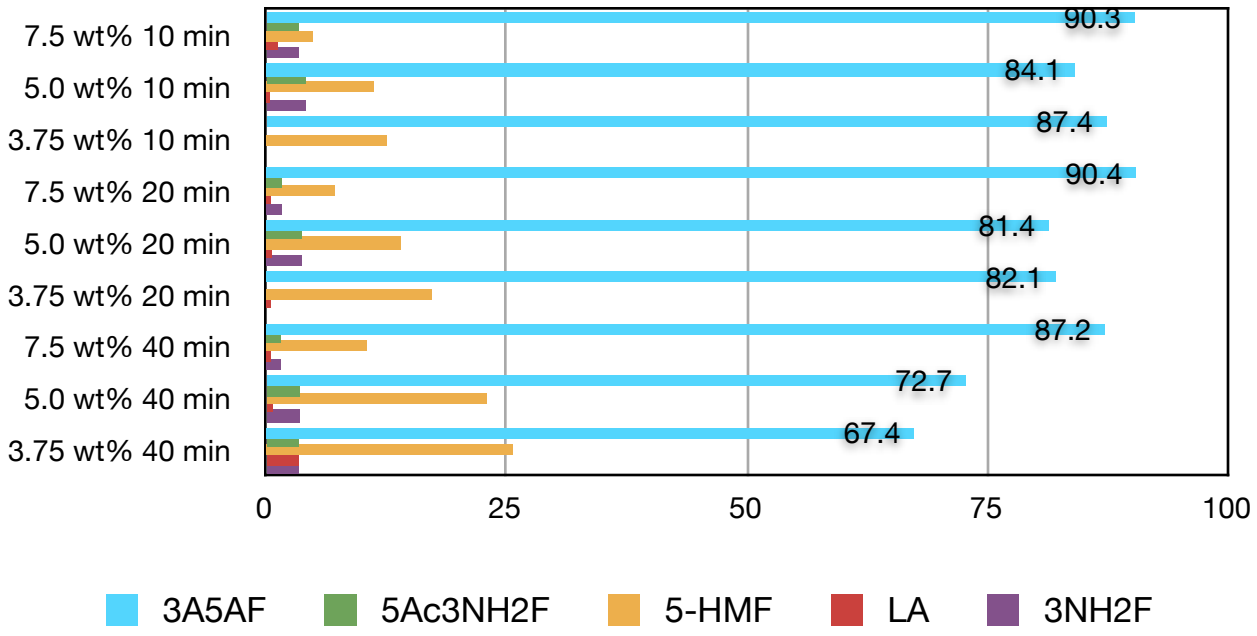


Figure 3.8 : The Influence of NAG Concentration and Time on Selectivity at 1:2:1 NAG: NaCl: $B(OH)_3$:NAG at 220 ^oC

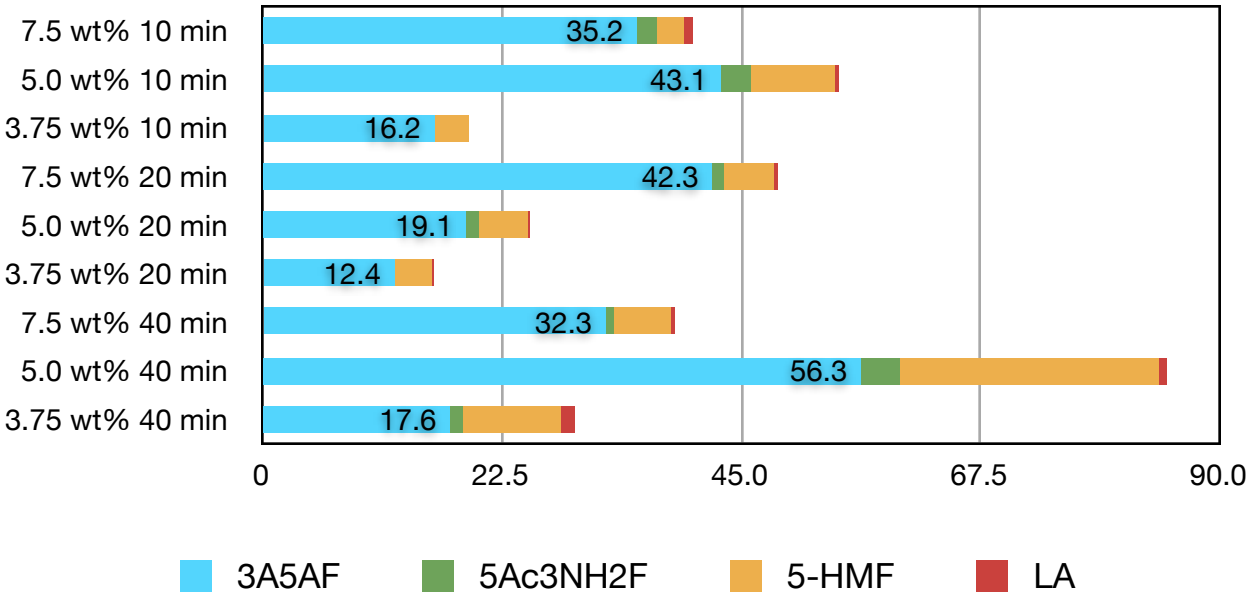


Figure 3.9 : The Influence of NAG Concentration and Time on Molar Yields 1:2:1 NAG: NaCl: $B(OH)_3$:NAG at 220 ^oC

3.1.3 Effect of Changing the Additive Mole Ratio to 1:1:2, NAG: NaCl: $B(OH)_3$

When there is twice the mole ratio of boric acid than sodium chloride (3.75 wt% NAG). The selectivity of 5-HMF increases from 11.7% to 24.6% between 10 and 40 minutes; while 3A5AF decreases from 84.0% to 69.9% (Figure 3.10). When there is less sugar relative to boric acid, the removal of nitrogen from the starting material was more favorable. For 3A5AF, the selectivity had a minor decrease from 90.6% to 90.2% as the reaction time was increased from 10 to 20 minutes. This result helped to support the optimal time for maximum 3A5AF production at 10 minutes.

When NaCl is present in equimolar amounts as NAG, the salt was less influential at destabilizing the acetamido functionality of NAG to yield acetic acid and a primary amine. Throughout this study, 5-HMF was produced in larger quantities when there was twice the

amount of NaCl (relative to NAG) and therefore, it can be assumed that chloride ions play a role in stabilizing an intermediate that forms during deacetylation that then leaves the primary amine susceptible to deamination. The synergy demonstrated between NaCl and $B(OH)_3$ during these experiments was not a rigid symbiosis but rather a tunable relationship that can be controlled through both acidity and the presence of chloride ions. The role chloride ions play in nitrogen removal needs further investigation.

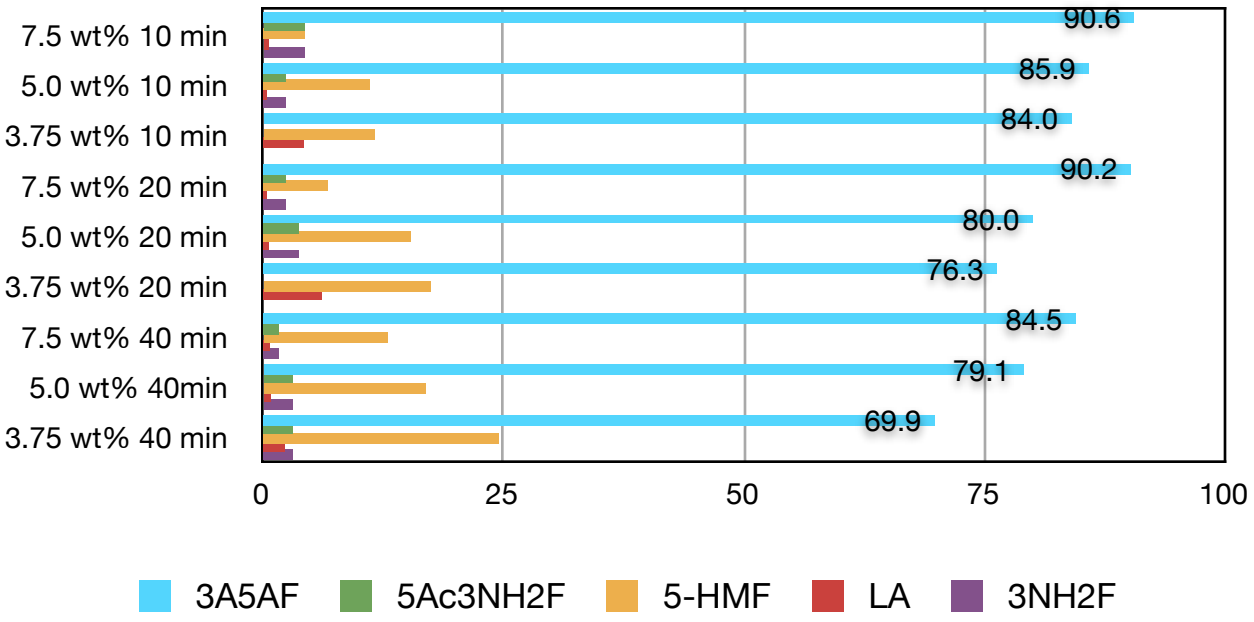


Figure 3.10 : NAG Concentration and Time Influence on Selectivity 1:1:2 NAG: NaCl: $B(OH)_3$ at 220 ^oC

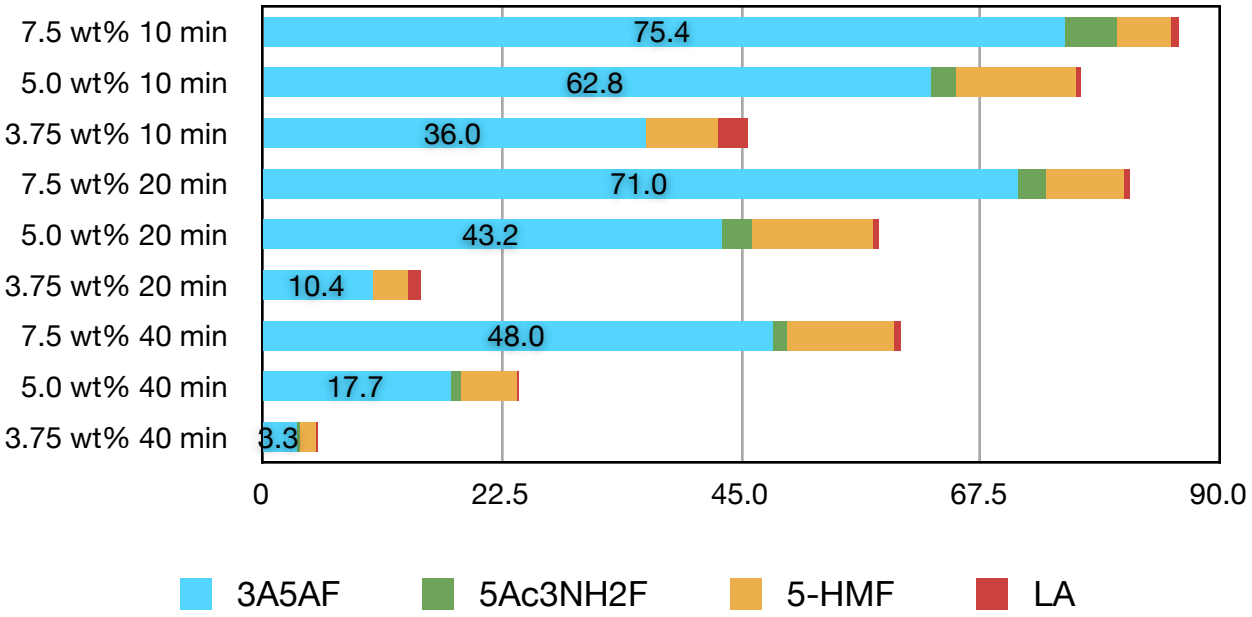


Figure 3.11 : NAG Concentration and Time Influence on Molar Yields

1:1:2 NAG: NaCl: $B(OH)_3$ at 220 ^oC

From studying the distribution of products over a range of conditions it was apparent that 3A5AF degraded in dilute solutions but remained the major product. As seen in Figure 3.11, when the mole ratio of NAG:$B(OH)_3$ is 1:2 the most dilute results give the lowest yields at 220 ^oC while overall yields decrease as time progresses. The shorter reaction time (10 minutes) was chosen as optimum because as time progresses the two main products begin to degrade into less versatile chemicals. As the highest NAG concentration favors the final incorporation of the nitrogen atom, the process optimization was focused on increasing amide yields. The highest selectivity (97%) for 3A5AF was obtained when NAG: NaCl: $B(OH)_3$ 1:2:2 molar ratio in a 5 wt % NAG solution at 220 ^oC within 10 minutes. Under these same conditions the highest selectivity of 5-HMF was achieved after 40 minutes with a 7.5 wt% NAG solution (Figure 3.2) Molar yields up to 75 mol % 3A5AF (Figure 3.11), and 69.5 mol% 5-HMF (Figure 3.7) were

obtained depending on conditions. Under those conditions there was at least 20 wt% biochar residues were produced. The biochar formation occurs more readily at higher temperatures and when there is more sodium chloride than boric acid. Section 3.3.0 will go further into detail about the insoluble residue (biochar) formed during this research.

3.1.4 : Cooperative Effect Between NaCl and $B(OH)_3$ after 40 Minutes

It can be seen in Figure 3.12 that as long as the mole ratios of boric acid to NAG is 1:1 or less then the selectivity towards 3A5AF remains high. From this figure the selectivity dips when the amount of sodium chloride doubles to 2:1 molar ratio with NAG; with the amount of 5-HMF decreasing by a half while the formation of LA doubles. Even after 40 minutes in a 7.5 wt% NAG solution these results agree with our earlier ones that salt increases 5-HMF formation.

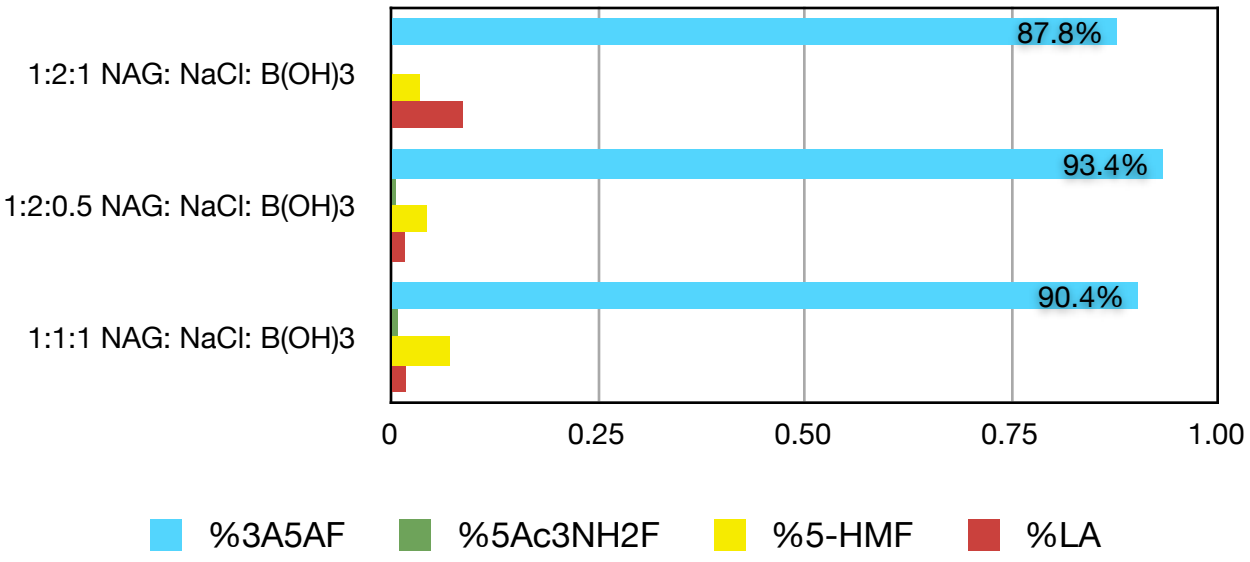


Figure 3.12 : Selectivity at 220 °C With a 7.5 wt% NAG After 40 Minute Reactions

Figure 3.12 shows that 3A5AF was the major product with a boric acid content of 0.5-1 mole ratios (relative to NAG) at high temperature (220 °C) after 40 minutes. When boric acid was in excess (e.g. 2 equivalents relative to NAG), it increased the acidity of the environment as it reacts to form $B(OH)_4^-$ and H_3O^+ that (after 40 minutes) favor the removal of ammonia from the main product. Acetic acid, which would be formed during deacetylation, has been detected by ^{1}H-NMR and its distinct odor was detected during work up. Figure 3.13 below depicts the distribution of products at 220 °C after 40 minutes with 0.5 - 1 mol equiv. of boric acid. When there are one or two mole ratios of sodium chloride the selectivity of 3A5AF remains relatively the same, although levulinic acid reaches a maximum at 10 mol% and a minimum at 0.9 mol% when the amount of boric acid is reduced from 1 to 0.5 mol equiv. The molar yields decrease by a half (69.1 mol% to 34.6 mol%) which indicates that an excess of chloride ions is detrimental to furan formation. Longer reactions demonstrate the stability of 3A5AF and can be tuned precisely but yields are not better than shorter reactions so 10 minutes was chosen as the optimal time.

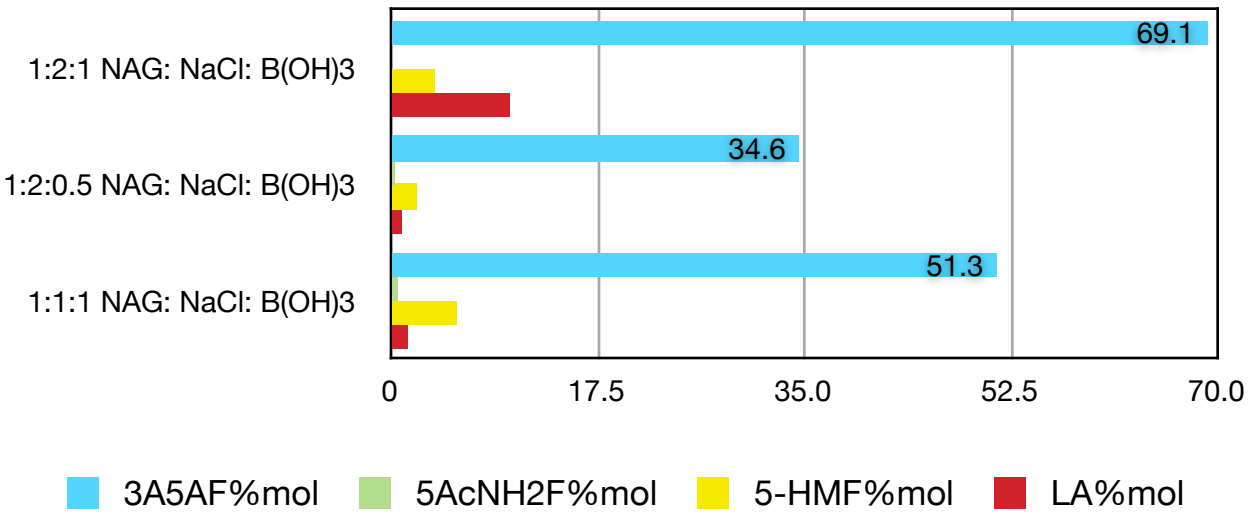


Figure 3.13 : Molar Yields for 40 Minute Reactions at 220 °C with 7.5 wt% NAG

3.1.5 : Benefits and Cooperative Effect of NAG Dehydration in Water

This optimum ratio of reagents (1:2:2 NAG: NaCl: $B(OH)_3$) is in agreement with previous studies in the Kerton group but the distribution of products in water is unique compared to organic solvents. Experiments presented in this thesis are an improvement that was built on the work of Omari *et al*., and demonstrate the commitment of the Memorial University Green Chemistry group has to sustainability (20). The reduction in salt (1:2 NAG:NaCl vs 1:4 NAG:NaCl) and the switch from organic to aqueous media are the key environmental benefits from this research. The effect of water addition to DMA was performed previously and found to inhibit the dehydration process. In that study it was observed that addition of up to 20 wt% water to reactions in DMA decreased 3A5AF yields from 40 mol% to below 10 mol% (20). It is noted that the previous work in the Kerton group was performed at a 5 wt% NAG solution in 4.5 mL of solvent; although some attempts to scale up were investigated (100 mL scale), although yields decreased. It has now been shown through these M.Sc studies that the conversion of NAG into nitrogen containing precursors for novel polymers or biofuels can be achieved in a system of dilute aqueous boric acid and sodium chloride (see in Figure 3.14).

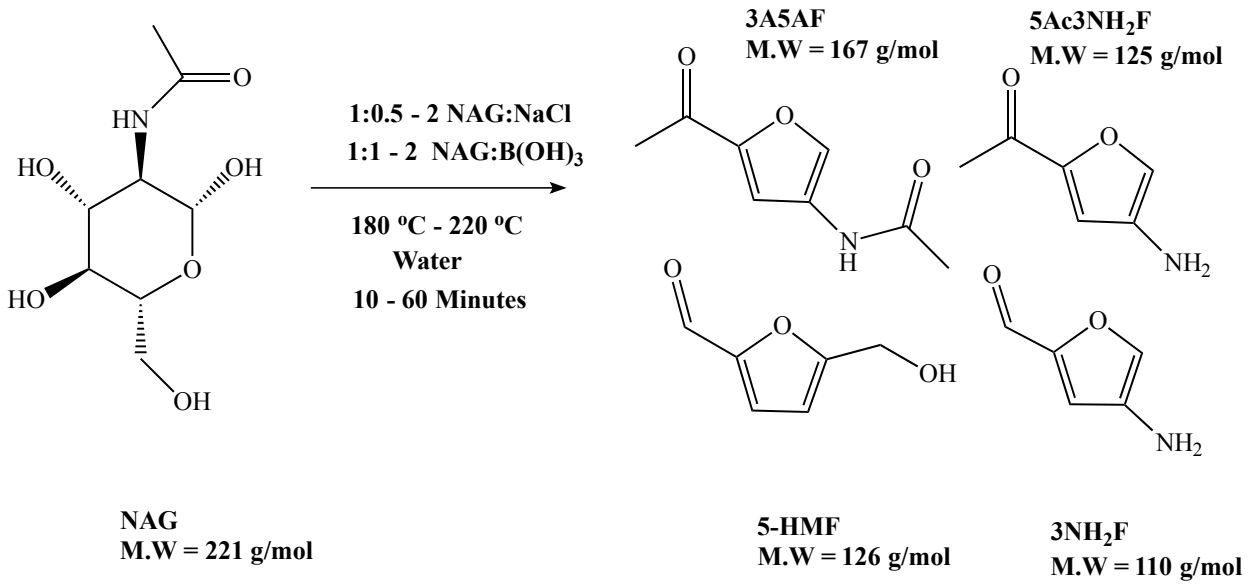


Figure 3.14 : The Conversion Scheme of NAG to 3A5AF, 5-HMF, 5Ac3NH_2F & 3NH_2F in Water

3.1.6 : Role of Chloride Ions

A cooperative effect was observed between boric acid and sodium chloride which has been harnessed to selectively yield 3A5AF or 5-HMF. This research shows that the molar yield of 5-HMF is high at 220 °C after 40 minutes. When more salt is present in solution the distribution shifts to more equal amounts of 3A5AF and 5-HMF. This might be attributed to the chloride ions or metal cations stabilizing intermediates that initiate the release of ammonia or the lower amount of boric acid preventing a crucial step or intermediate forming prior to 3A5AF formation. Note, when 3A5AF is heated in the presence of boric acid and NaCl, it does not form 5-HMF. Therefore, deamination likely occurs earlier in the mechanism (K. Omari and F. M. Kerton unpublished results). There is some speculation of the various roles of the dissolved salts

in aqueous reactions in particular the salting out effect applies to the organics being formed and may enhance the separation process. This may also be due to increased K_w at high temperature and the presence of more H^+ and OH^- ions from water. However the chloride ions presumably also function to stabilize intermediates and hence are critical for boosting desired yields (20). Chloride readily forms hydrogen bonds with hydroxyl groups and can stabilize the complex with a hexose. This could occur by stabilizing either the borate anion or the sugar portion of the complex. The exact role of chloride ions in carbohydrate conversion still needs further investigation.

3.1.7 Summary of Results of Additive Influence on Product Distribution

In accordance with the majority of our results, the reaction proceeds selectively towards 3A5AF formation. The minor product levulinic acid was produced with a 4.3 mol% yield with a 3.75 wt% NAG solution (at 10 minutes) and after 20 minutes peaks at 6.2 mol%. This small organic acid is a formidable platform chemical in its own right due to the biorefining potential. The levulinic acid yield drops to the lowest level after 40 minutes and that coincides with a general drop in total yields. The LA and $3NH_2F$ are low yielding by-products but nevertheless their minor accumulation over time would allow for feasible applications

Through this simple window of salinity the ability of product control was possible and hence the processing of amino-carbohydrates can be achieved for applications such as materials or fuels. When the nitrogen was retained in the product there are numerous gas separation and utilization processes that could benefit from an acetamido-containing furan. Even with 5-HMF as the main product there are opportunities to reduce to dimethylfuran or oxidize to furan diol. The

reduced form has characteristics that make it a remarkable biofuel while the oxidized version can be incorporated into polymers. The studies evaluating the influences of temperature, time, NAG concentration and additive content at 220 ^{o}C (previously determined optimal temperature from the Kerton group) were successful at producing high yields and selectivity of the two desired products (3A5AF, 5-HMF). The mixture of these furans resulted in a low melting orange/brown solid. From the experimental data reported above, it remains clear that conducting amino-carbohydrate transformations in subcritical water yields significant flexibility to choose between two novel platform furans (3A5AF and 5-HMF). Functionalized furans are set to influence manufacturing in the 21st century as benzene did in the 20th. Although since these reactions were not 100% selective, there was consistently minor and by-products formed.

3.1.8 : Recycling of Aqueous Phase from Reactions using NaCl and $B(OH)_3$ as Additives

Recycling the water phase was one of the main goals of this research. For the additive-free reactions, 200 mol% of NaCl and $B(OH)_3$ relative to NAG were used in the first and only fresh NAG was added to the 2nd and 3rd runs of the reaction, no additional water nor NaCl/B $(OH)_3$ were added. Three cycles were performed with each aqueous phase and the results are presented below. As seen in Figure 3.15, recycling the water when boric acid and sodium chloride remained from the first run displayed positive effects by increasing the 3A5AF selectivity. The third cycle conducted at 180 ^{o}C achieved a 3A5AF selectivity of 95.8%, which was an improvement of 23.7% from the initial run. During these cycles the amount of 5-HMF decreased from 22% to 4% due to the lack of additional boric acid and sodium chloride. This indicates that a certain amount of boric acid and sodium chloride was either left in solution in a

deactivated form or was incorporated in the insoluble residue (biochar) that was extracted. In the earlier parts of this chapter, it is clear these reagents are essential for the formation of 5-HMF from NAG. The inclusion of both of these elements can be advantageous for soil remediation because they are essential to plant health.

At 220 °C the 5-HMF that formed was partially rehydrated into levulinic acid and was likely incorporated into the residue. The $5Ac3NH_2F$ that formed dropped significantly after the first cycle while the 3A5AF selectivity peaked at 86% after the second cycle. The amount of biochar that formed will be discussed in the following section. As seen in Figure 3.16, the yield peaks at 44.8 mol% for the third cycle at the lower temperature (a 20% increase from the first cycle). Once the temperature was increased the maximum 3A5AF yield (36.1 mol%) was achieved for the second cycle. These initial results demonstrate that renewable amides can be produced in spent water while achieving reasonable yields in a 7.5 wt% NAG solutions with no additional boric acid or sodium chloride (after the initial loading).

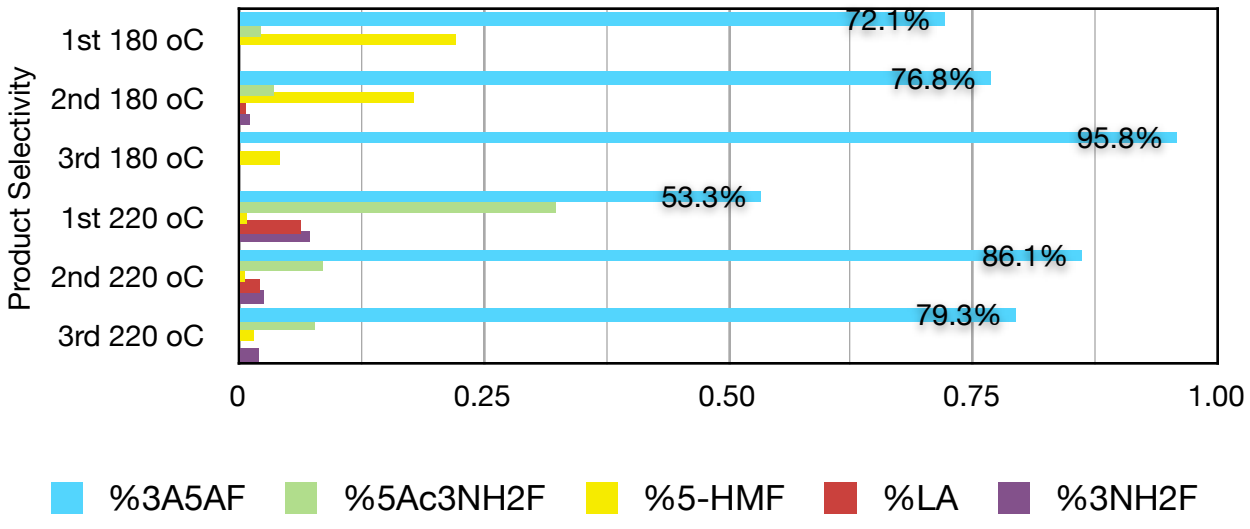


Figure 3.15 : Product Selectivity Upon Recycling Water with No Additional NaCl or $B(OH)_3$ at Two Different Temperatures

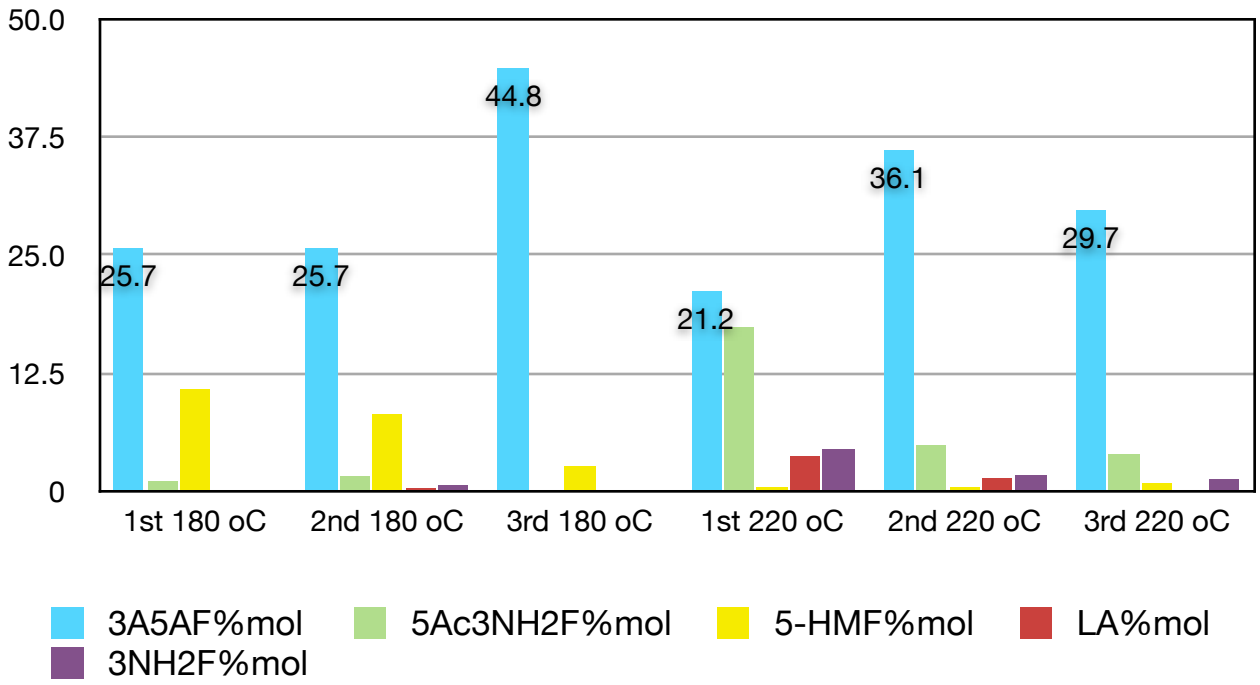


Figure 3.16 : Molar Yields of Recycled Water with No Additional NaCl or $B(OH)_3$ at Two Different Temperatures

Recycling the solvent with zero to minimal treatment vastly increases the sustainability of the process and equates to zero to minimal risk of environmental damage. By recycling the solvent even for three cycles the overall cost can be reduced and if experiments were conducted using a flow reactor system, then the product could be extracted to increase yields further. This represents a logical approach to convert intermediates left in the aqueous phase into desired products. When organic solvents are employed the chemicals need to be refined and their evaporation controlled. Employing concentrated solutions and toxic catalysts add to the treatment costs and increase the risk of accidents that cause environmental damage. Water is the most abundant liquid on Earth and processing of carbohydrates in ocean water rather than tap

water would be step further in the right direction. Ideally this water would be naturally purified but more about this subject will be discussed in the green aspects section.

When 200 mol% of each additive (relative to NAG) was added to each run of the recycled water the results are varied. For two 1st runs, selectivity was 91.5% +/- 7%. Assuming all reactions show similar fluctuations, there is no significant difference in selectivity towards 3A5AF but a wider range of products are seen when NaCl is added. The second run with NaCl displays a spike in 5-HMF formation from zero to 12% whereas during the second run with boric acid the 5Ac3NH$_2$F drops from 15% to 2% (Figure 3.17). The recycled water employed here now has up to 4 mol equiv. of sodium chloride in it and can more readily destabilize the acetamido group that ultimately results in 5-HMF formation. These reactions also produced the largest amount of biochar that was of a unique nature. The residue has the appearance of aggregated flakes with a higher than average ridge formation (Figure S30). When the levels of NaCl were further increased, the residue formed was caked to the reactor vessel to a larger degree than under any other conditions.

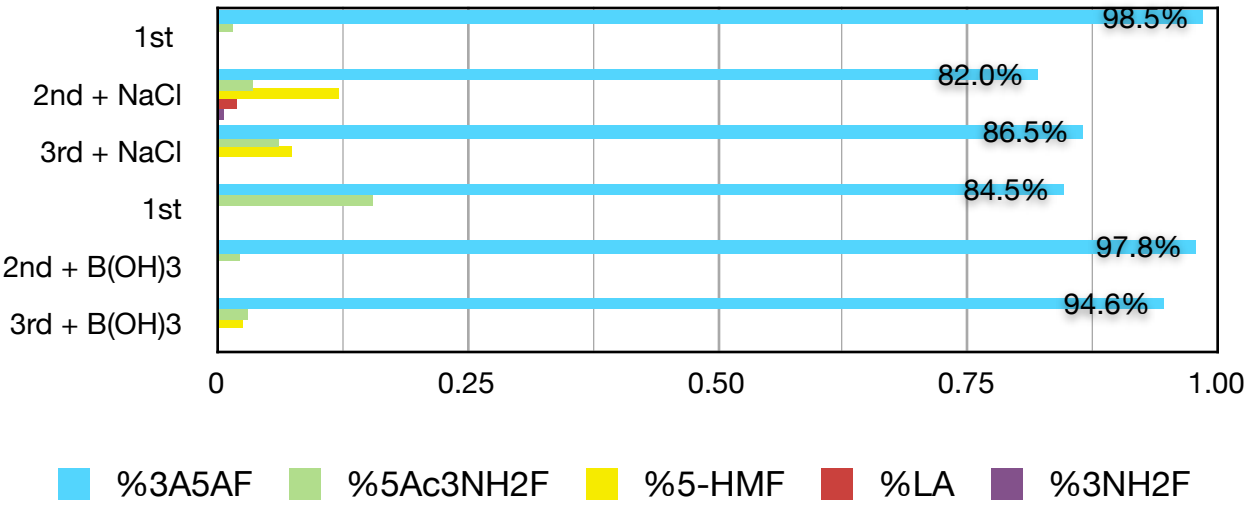


Figure 3.17 : Product Selectivity Upon Recycling Water with Additional Additives at 180 ^{o}C

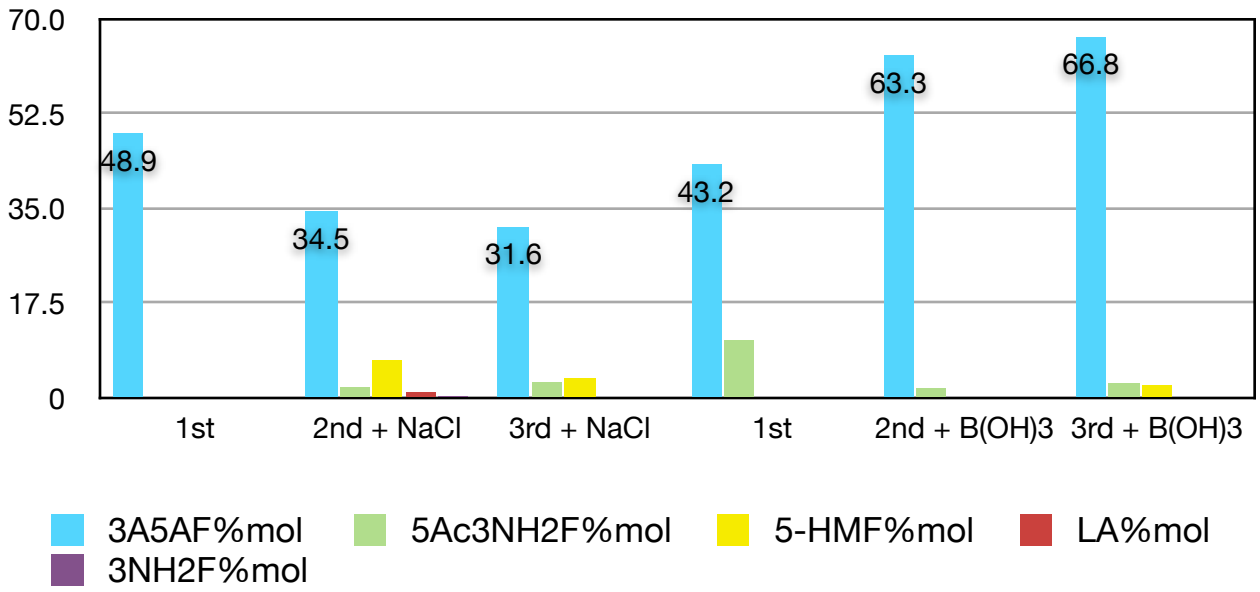


Figure 3.18 : Molar Yield of Recycled Water During 3 Cycles with Additional NaCl or $B(OH)_3$ at 180 °C

Figure 3.18 shows that a significant inhibitory effect that is caused by the increased salinity of the solution. The yield of 3A5AF decreased from 48.9 to 31.6 mol% after 3 cycles with additional NaCl; while with additional boric acid the yields increase. A molar yield increase of 23.6% (with additional boric acid), along with heightened selectivity makes the reaction at 220 °C a superior choice for high 3A5AF yields. These results agree with the previous experimental data about the advantages of additives, whereas this water recycling study reveals a large increase in yield (induced by extra boric acid) and selectivity when the temperature is 180 °C. The molar yields obtained with recycled water are amongst the highest achieved during this research project and add a substantial layer of sustainability to the aqueous phase reforming of NAG. When employing organic solvents or ionic liquids at elevated temperature there is an increased probability that they will react with themselves or with products to form undesirable

compounds. These issues are not a concern when water is the reaction medium. Thus by reusing the water phase in carbohydrate conversion processes (even for 3 cycles) the undesirable compounds will be reduced.

When the temperature was increased to 220 °C the yields and selectivity are significantly enhanced for reactions with added boric acid in recycled water. It can be seen in Figure 3.19, that the addition of more NaCl to the recycled water has negligible effect while added boric acid almost triples the 3A5AF yields. Throughout both of the additional additive reactions the amount of by-products decreases through the cycles. This decrease hints at 3A5AF precursors (possibly Chromogen I or III) remaining in the aqueous phase being selectively converted to the desired furan. At 220 °C, 3A5AF degrades into $5Ac3NH_2F$ and $3NH_2F$ but selectivities decrease by over 50% after the second cycle (Figure 3.20).

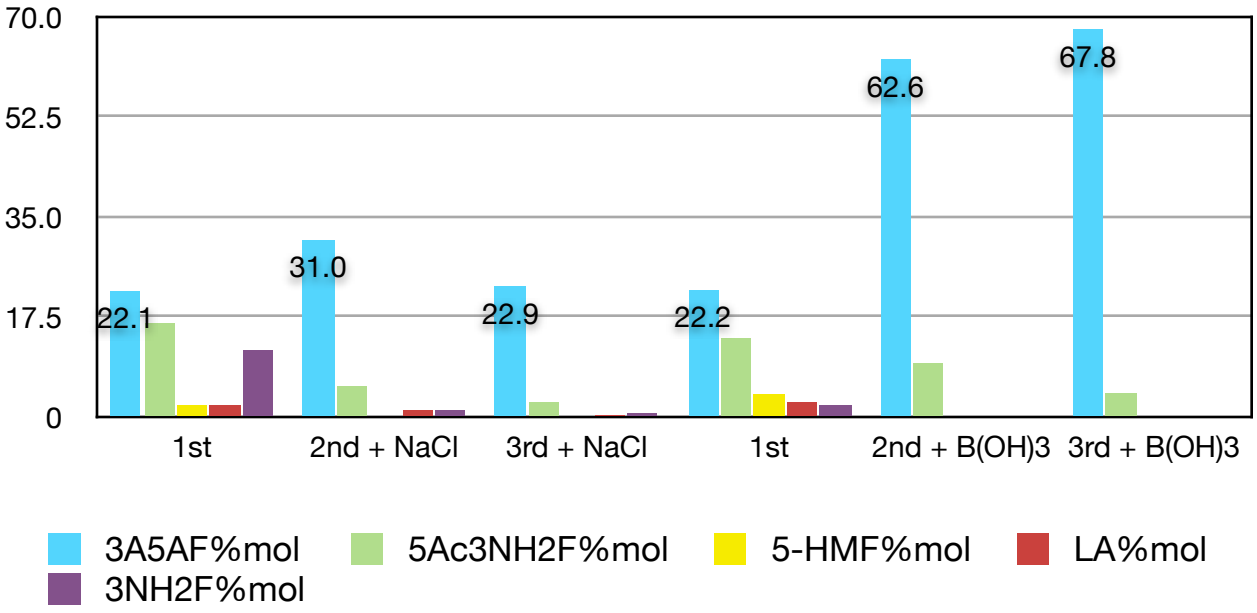


Figure 3.19 : Molar Yield of Recycled Water During 3 Cycles with Additional NaCl or $B(OH)_3$ 220 °C

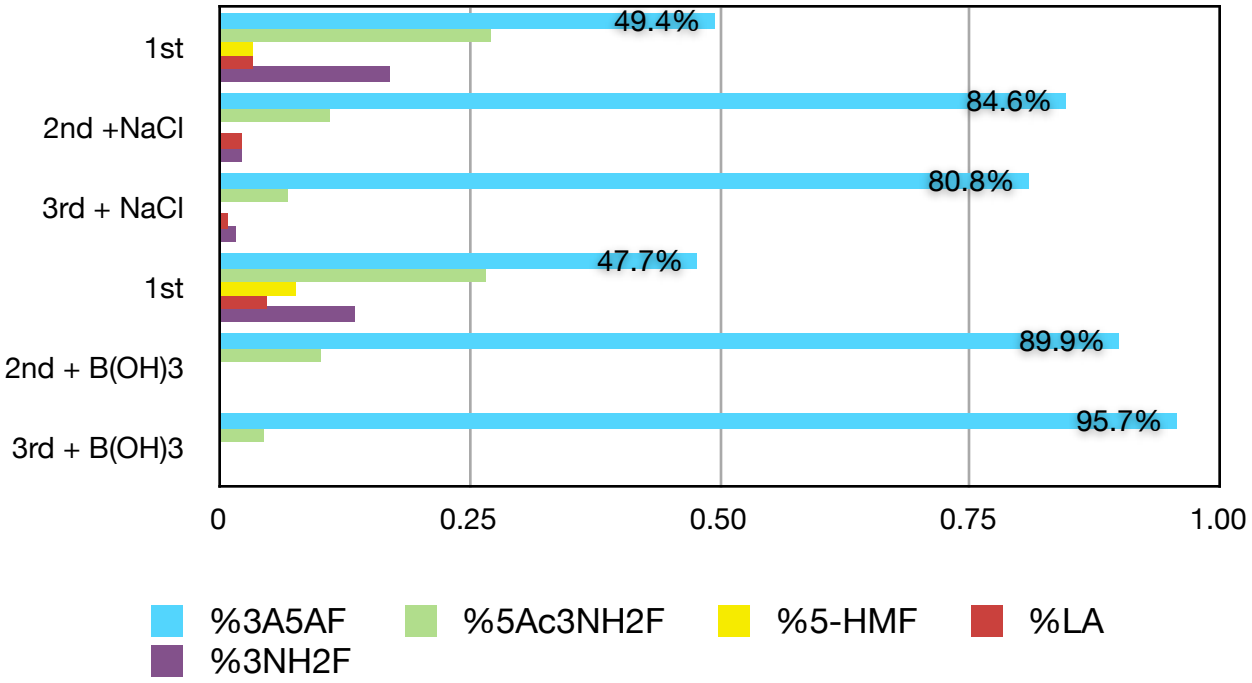


Figure 3.20 : Selectivity of Recycled Water During 3 Cycles with Additional NaCl or $B(OH)_3$

220 °C

3.2.0 : Formation of Nitrogen Compounds via The Maillard Reaction

There are small amounts (< 5% yield) of compounds detected by GC-MS (*m/z* = >174) that might indicate the reincorporation of ammonia into the product (via opening of the furan). It is also possible that mono and di dehydration products of NAG play a role in these rearrangements. In agricultural and food chemistry research that focuses on NAG, it has been shown that nitrogen containing compounds such as substituted pyridines and pyrazines are found in baked food and reformed carbohydrate mixtures (Figure 3.6) (14). Since this research operates under conditions similar to baking carbohydrates, the formation of compounds commonly found in food is possible.

As expected when heating carbohydrates, reactions similar to the Maillard reaction take place between the aldose form of NAG and any amine present. The chain form of the carbohydrate contains a carbonyl group that reactions with the connected amine group (nucleophile) to produce a variety of flavor compounds in baking. The aroma created during the Maillard reaction typically stems from nitrogen containing compounds that are formed at elevated temperature (>150 ^{o}C). This is different from the caramelization process, which consists of nitrogen-free reagents although both reactions take place simultaneously in baking and thus similar reactions occur during hydrothermal treatment of amino-carbohydrates. This goes some way to explain why after the furans and biochar have been extracted from the aqueous fraction it remains deep orange (furans) to dark brown (furans/biochar). Although a number of hydrophilic compounds remain in the water fraction, the mixture was so diverse that there was dozens of major signals observed when we analyzed by LC-MS. The major peaks in the aqueous phase were *m/z* = 234.1, 291.0 and 333.0 with in the *m/z* range of 125 to 455. The first peak at 234.1 could be equal to Chromogen III - 2H + B + OH + Na. This multitude of chemicals must be responsible for the brown/tan appearance of the crude residual mixture and the roasted oat and caramel odor.

In a 1998 study published in the *J. Agric. Food Chem*., researchers subjected NAG to pyrolysis at 200 ^{o}C with anhydrous sodium phosphate in equal molar amounts and 3A5AF, 3Ac3NH_2F, 3NH_2F and pyrazine were the main products (14). The authors in that study propose separate mechanisms for the formation of 3-acetamido-5-acetylfuran and 3-acetamido-furan. It was noted that acidic compounds were not analyzed due to their alkaline extraction conditions; and that the authors were interested in the pyrazine compounds for the flavor chemistry industry.

It was proposed that because 2,5-di(2-furyl)pyrazine was formed only in a glucosamine study that the N-acetyl group protects the amines from forming a pyrazine ring through sequential dehydration. The researchers suggested that furyl-pyrazines formed from double polyhydroxyl group undergoing dehydration. These types of compounds are certainly formed during the Maillard reaction in baking and thus are not detrimental to human health. Research in the area of conversion of biomass can benefit greatly from the food science industries with the prefect intersection being an organic vertical farm that also produces energy and materials.

3.2.1 Yields and Mechanistic Insight into Additive-Free Reactions

To better understand the influence of additives in the transformation of amino-carbohydrates it was imperative to conduct additive-free experiments without boric acid and sodium chloride. These reactions have much in common with recent work on Chromogen production from NAG **(**18). These reactions revealed similar product selectivity within the same temperature window (180 - 220 ^{o}C) but due to significant emulsion formation during extraction the workup was tedious. Attempts were made to salt out the products but the emulsion remained. The yields ranged between 1.7 - 10.4 mol % for furans with the rest as insoluble residue and water-soluble products. There are considerably lower yields of furans than produced in the the research on Chromogen I & III formation due to the lower pressure used. The highest pressure obtained during this research was 450 psi while the reference Chromogen work was performed at over 3500 psi. Due to the formation of organic acids from sugar in hot and compressed water the term autocatalytic is sometimes employed. This term is more logical than non-catalytic when referring to additive-free hydrothermal processing of biomass. The formation of organic acids

tends to be more favorable under higher pressure conditions. The low yields in this research highlight some of the benefits of utilizing sodium chloride and boric acid. Without additives the subcritical treatment of carbohydrates results in poor furan selectivity and a bounty of highly water soluble products (when conducted at a low pressure). The ease of product extraction is also an important factor for scaling up reactions. The low yields obtained in this research was not unexpected since Chromogens (I and III) can be formed in up to 23 mol % under autocatalytic conditions in high pressure water (15). According to the authors, these Chromogen I and III molecules have biomedical applications and consist of an unsaturated furan ring with hydroxyl groups bonded to that ring. It is the acetamido moiety that gives these molecules their biomedical versatility and is another avenue that benefits from sustainable production of renewable amines (Figure 1.1).

The first derivative has one double bond within the furan ring with an ethylene glycol moiety bonded to the 5 position. The 3rd derivative of this compound has two double bonds due to the removal of the ring -OH group; as well as the retention of $CH(OH)CH_2(OH)$. The dehydration of this functional group requires a catalyst that displays a chelating effect to bond to both of the hydroxyl groups.

In that study there was additive-free experiments performed at the temperatures of 180 ^oC, 200 ^oC and 220 ^oC; which is within the range (120 ^oC - 220 ^oC) of the recent research on Chromogens. In the autocatalytic research on NAG conversion, highest amount of Chromogen I formed at 190 ^oC while Chromogen III at 210 ^oC. The control/additive-free experiments presented in this thesis revealed that 3A5AF can be produced via autocatalysis in water with yields being dependent on temperature and NAG concentration. As the solution becomes more

dilute the molar yields decrease while the influence of temperature (Figure 3.21 - 3.24) on yields, varies depending on NAG concentration. The data presented here are from reactions that were all performed in triplicates for 10 minutes. At more dilute concentrations, 3A5AF was the major product and 5Ac3NH$_2$F was the minor when temperature was above 200 ^{o}C. Figure 3.21 shows that when the solution contains 7.5 wt% there was an increase in 3A5AF degradation into 5Ac3NH$_2$F at 200 ^{o}C. The controlled degradation of a compound is a useful technique to better understand the structural stability. Over the concentration and temperature evaluated it was observed that 3NH$_2$F was produced in levels similar to 5Ac3NH$_2$F. Figure 3.21 presents data that agrees with the earlier experiments in that 3A5AF selectivity was highest at 180 ^{o}C.

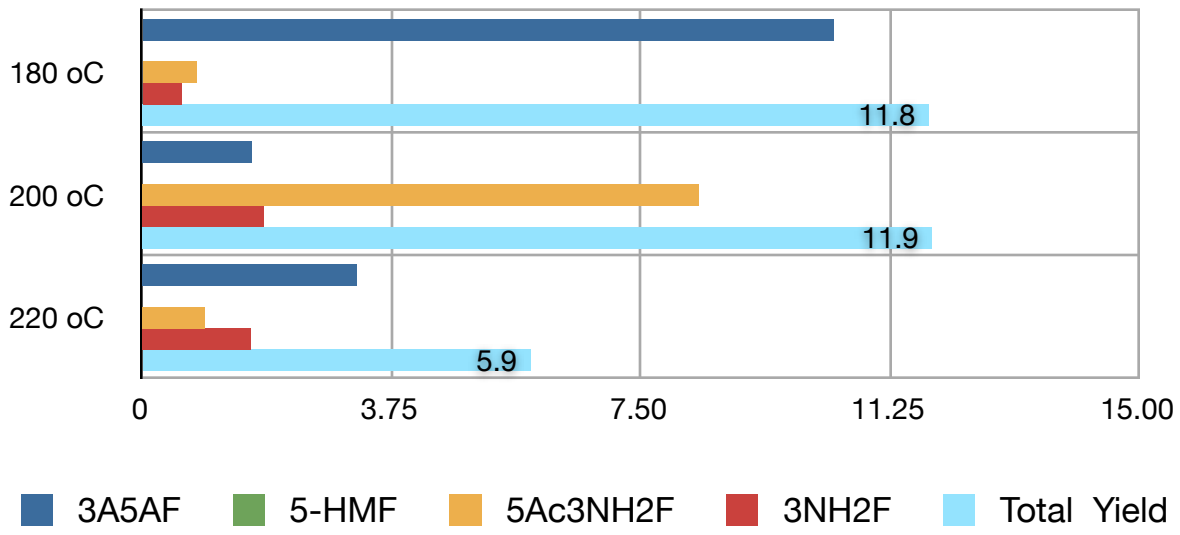


Figure 3.21 : Temperature Influence on Molar Yields for Additive-Free 7.5 wt% NAG Solution

Issues with the formation of emulsions during the additive-free reactions were the most troublesome of all. This provides incentive to add salt to assist in separating out organics. The

low molar yield, main product degradation and emulsion issues are evidence to support the use of additives to control product distribution and boost yields. As the concentration of NAG in solution decreases, the amount of a particular degradation product varies with temperature.

The increase in temperature benefited the total furanic yield for more dilute (5 wt%, 3.75 wt%) reactions at the expense of 3A5AF degradation. The limited amount (relative to reactions with additives) of 5-HMF formed indicates the organic acids produced do not acidify the solution to the degree that is required for the deamination reaction. The degradation of 3A5AF begins with the removal of the acetyl functionality that is bonded to nitrogen. It has been reported that the production of 5-HMF, furfural and 1,2,4-benzenetriol (BTO) can be achieved in high temperature water from D-glucose and D-fructose (34,35). Prior to the recent publication on Chromogen I and III formation from NAG, studies have been limited on the dehydration of amino-carbohydrates above the boiling temperature of water. At the time of this research, there are no reports on the conversion of NAG in supercritical water. Reactions performed at lower temperatures (<250 ^{o}C) do not require specialized reactors unlike the ones that can contain supercritical water. These Chromogen compounds along with 3A5AF are generally synthesized in-house for researchers to study and as such they are relatively expensive.

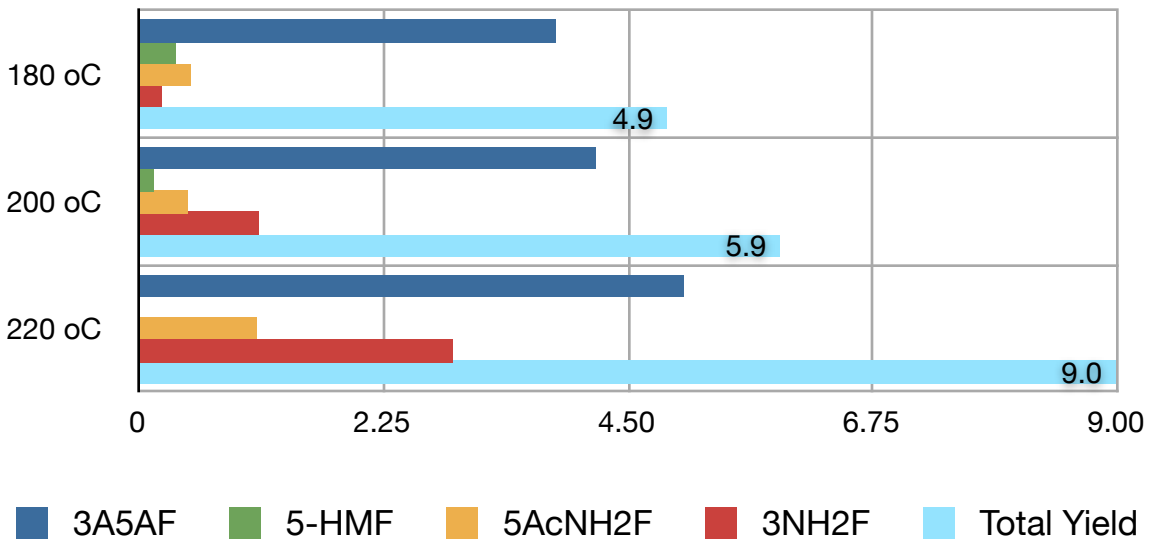


Figure 3.22 : Temperature Influence on Molar Yields for Additive-Free 5.0 wt% NAG Solution

By studying a system free of additives the influence of the elevated ion product constant of water ($K_w = [H^+][OH^-]$) at 180 - 220 ^oC can be better understood. The dissociation of water molecules into H+ and OH- is an endothermic process and (K_w) can increases to values of 5.2×10^{-12} and 8.4×10^{-12}, respectively at 25 MPa and 300 ^oC (31,32). This is significantly higher than at the boiling temperature for water and is a major contribution to the unique properties associated with water at high pressures and temperatures.

As in studies using additives, the formation of biochar also occurred during all control reactions. Due to the absence of a Lewis acid (e.g boric acids, metal chlorides) the majority of products are highly oxygenated and display low solubility in organic solvents (e.g ethyl acetate, ethyl ether, butanol). The water phase becomes a richer shade of orange but the chemicals responsible for the color are only extracted into the organic phase in minor amounts. All of the high 3A5AF yield reactions performed in this study changed the appearance of transparent ethyl

acetate into blood orange. It was observed (Figure 3.23) that at 200 °C the maximum amount of $3NH_2F$ is produced under all NAG concentration levels.

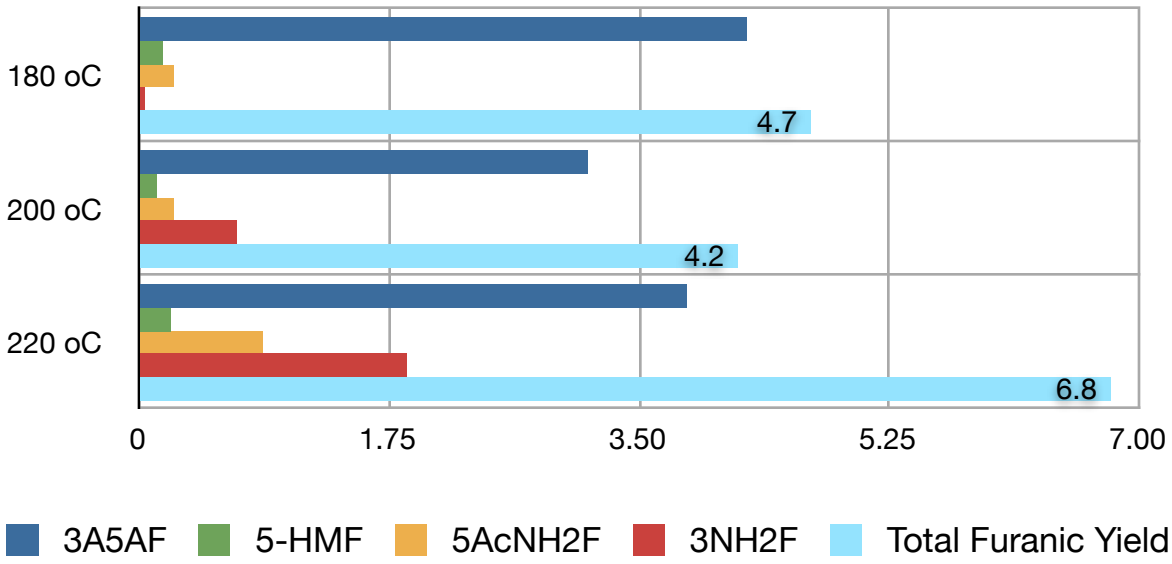


Figure 3.23 : Temperature Influence on Molar Yields for Additive-Free 3.75 wt% NAG Solution

5-HMF is not the largest secondary product until under the most dilute conditions of 1.875 wt% NAG. The nitrogen containing degradation products (from 3A5AF) was regularly the main furanic co-product for the majority of additive-free reactions, which indicates that this system has a delicate acidic equilibrium. When there was a high amount of NAG in solution the acetyl protecting group remained. With a low level of NAG in solution the water-derived hydroxide ion is able to react with the acidic amide proton (Yi Liu, unpublished results) moiety and possibly form NH_4OH. It is possible for the protonated primary amine species to form by an hydroxide attack on the carbonyl group which creates an acetate ion bonded to the nitrogen. This ion leaves

by abstracting a hydrogen (from hydronium) atom and forms RNH_3^+. The role of hydronium and hydroxide ions are hence better understood via the evaluation of control experiments.

With NAG, the dehydration differs from that of glucose because the removal of a hydroxyl group at C-2 (of the furanose form) does not result in the substituent on C-3 from leaving via an aldehyde forming rearrangement. In the case of glucose the second dehydration step removes the hydroxyl group on C-3; the last dehydration occurs at the C-3 site and yields an unsaturated furan. It is clear from the selectivity data in Figures 3.24a-d, that 3A5AF is the main product when initial sugar concentrations are equal to 5 wt% or less. These furan yields are lower than reported in recent (18) and past research that used borate catalysts (14, 30). Over this range it was observed that $3NH_2F$ levels increased as the temperature approached 220 ^oC. This trend demonstrates that 3A5AF can undergo deacetylation via autocatalysis. Since the purpose of this research was to create platform chemicals as bioplastic and biofuel precursors, the use of additives are quite advantageous for increased yields and selectivity. Also, concerns over neutralization are diminished compared to food additive and medical applications (e.g uses of Chromogen I and III) where impurities would have implication for regulatory approval. This can divide the applied research on amino-carbohydrates into using low pressure (for bioenergy, biomaterials) or high pressure (flavor chemistry, and medicine) subcritical water.

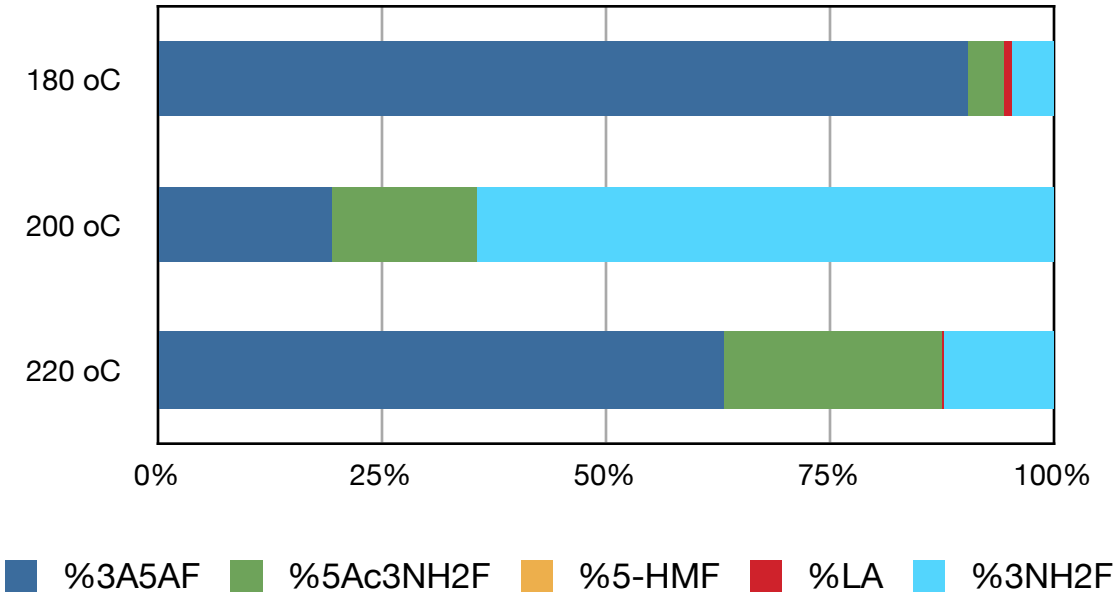


Figure 3.24a : Selectivity of Additive Free Reactions with a 7.5 wt% NAG Solution

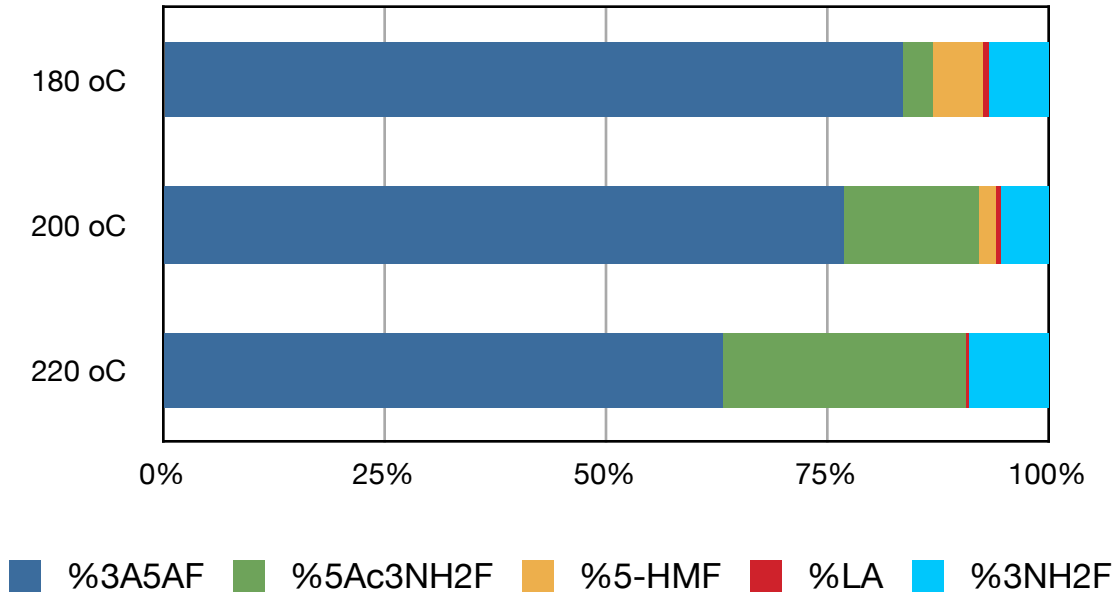


Figure 3.24b : Selectivity of Additive Free Reactions with a 5.0 wt% NAG Solution

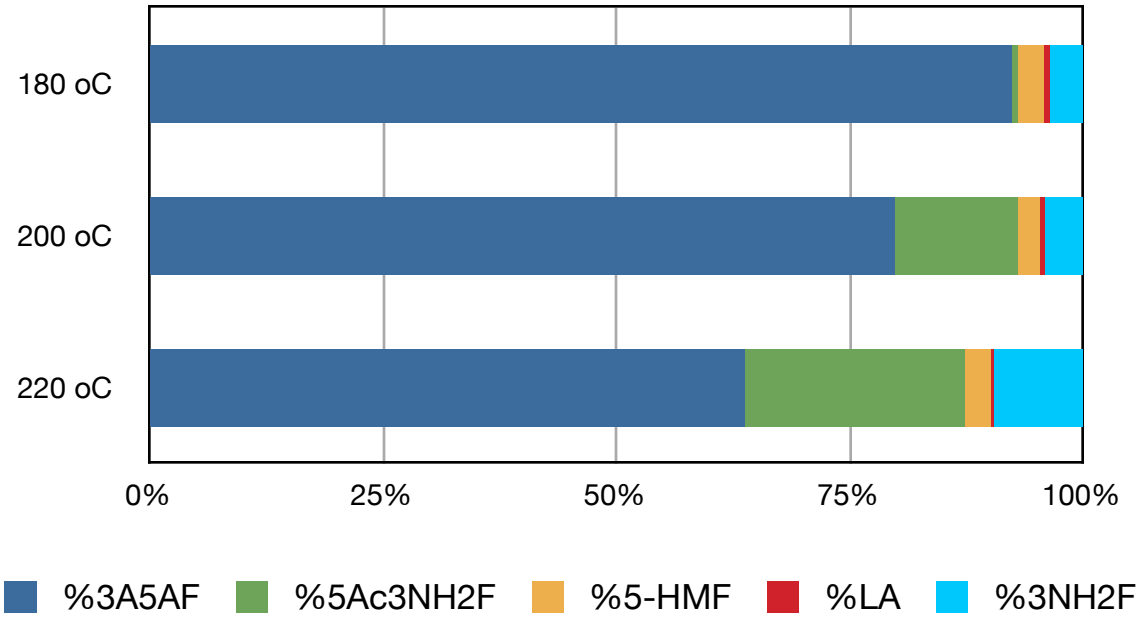


Figure 3.24c : Selectivity of Additive Free Reactions with a 3.75 wt% NAG Solution

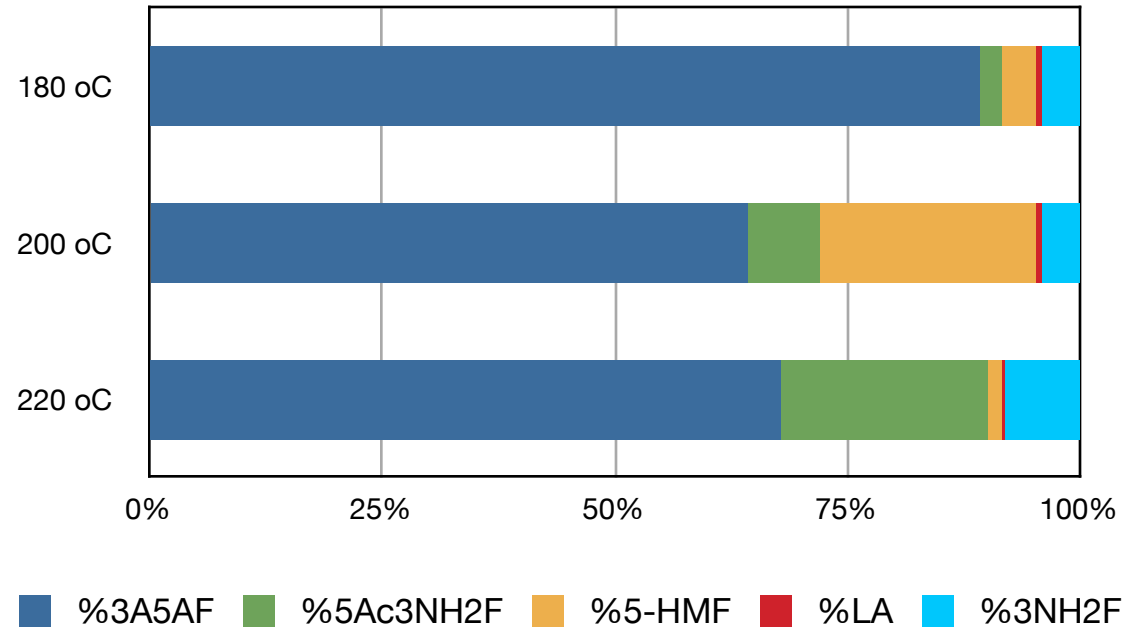


Figure 3.24d : Selectivity of Additive Free Reactions with a 1.875 wt% NAG Solution

3.2.2 The Degradation of 3A5AF Under Additive-Free Conditions

The GC chromatograms in Figures 3.25a-c show the degradation of 3A5AF as the temperature is increased for the reactions from 180 °C - 200 °C - 220 °C. The formation of the peak with a retention time of 3.2 min is at the expense of the compound at 3.7 min. Hence at elevated temperature, the removal of the acetyl group on the furan ring was favored for one isomer of 3A5AF. This leads to the formation of acetic acid after a nucleophilic attack of an hydroxyl group on the acetyl moiety at the 5 position (Figure 3.26).

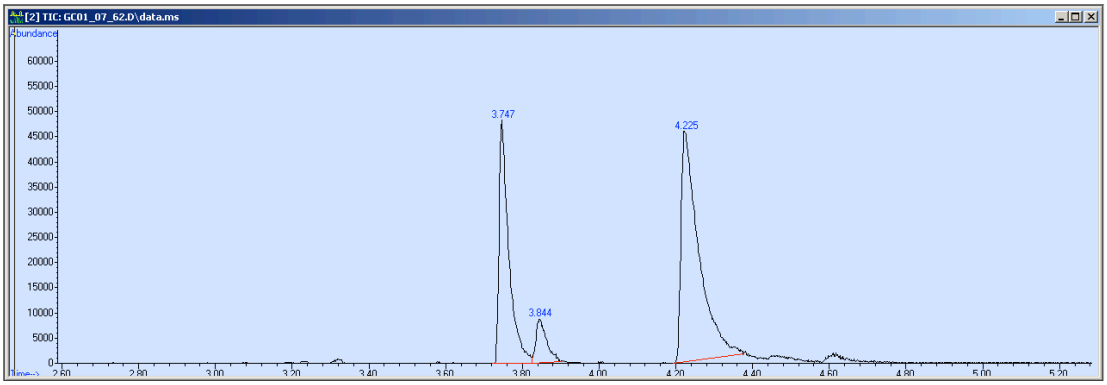


Figure 3.25a : GC Chromatogram of Additive Free Reaction Performed at 180 °C with 7.5 wt% NAG Solution

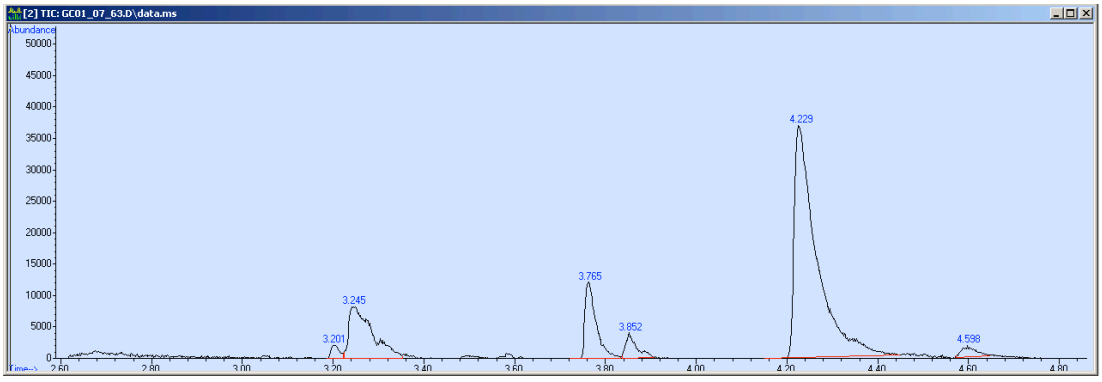


Figure 3.25b : GC Chromatogram of Additive Free Reaction Performed at 200 °C with 7.5 wt% NAG Solution

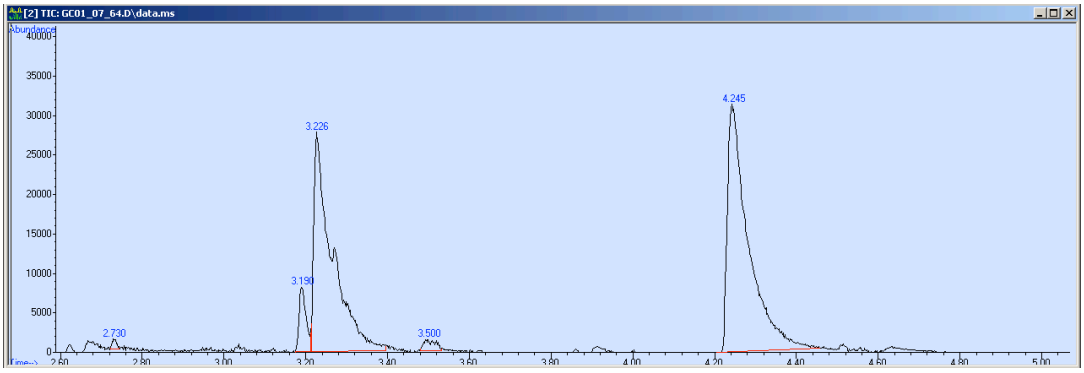


Figure 3.25c : GC Chromatogram of Additive Free Reaction Performed at 220 °C with 7.5 wt% NAG Solution

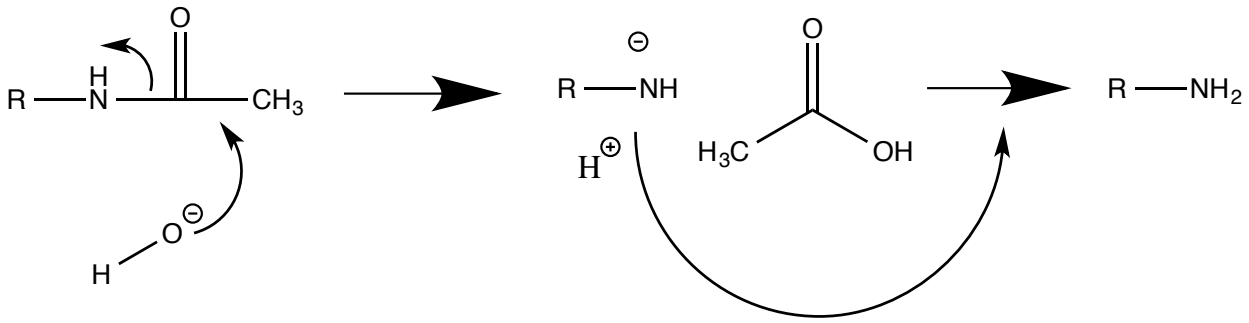


Figure 3. 26 : Hydroxyl Attack on Amide Carbonyl Group to Yield Primary Amine

The GC chromatograms above display the deacetylation of a 3A5AF isomer as temperature increases under additive-free conditions. This is the dominate pathway for the degradation of NAG in subcritical water that was observed in our aqueous based research. Note, the exact structural isomer of 3A5AF produced remains unknown. The isomer at 4.2 min RT is 3A5AF, the peak at 3.7 min has the same mass spectrum as 3A5AF.

The GC chromatograms presented above demonstrate that 3A5AF is stable in reaction mixtures at 180 °C but at 220 °C, near equal amounts of the primary amine furan are formed.

3A5AF is suitable for novel polymer synthesis due to functional groups at the 3 and 5 position as well as the hydrogen bonding that can occurs between the NH and C=O on nearby molecules that provide polymer strength. This opens the area of high strength/value polyamide synthesis for applications such as armor/personal protection, sports equipment, cookware and composite materials. These functionalized furans are a necessary platform chemical in future biorefining and if they are publicly promoted then a renewable replacement for polyurethanes could also be possible.

3.3.0 : Formation of Valuable Biochar

Biochar formation was relatively constant at 220 ^{o}C over the NAG concentration and time evaluated. Additives had more influence than concentration and it was observed an excess of NaCl (relative to NAG) increased the insoluble residue yield. As the environment becomes more acidic the rate of biochar formation increases exponentially over time; this subject will be addressed in further detail in the next section. The solid by-product (biochar) was characterized by Fourier-Transform Infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA). Through the former technique, the biochar was found to be rich in surface hydroxyl, carboxylic and carbonyl functionalities; thus making it ideal as a precursors for nanomaterials or solid acid catalysts.

The research conducted in this study can benefit the processing of biological waste (from fishing industries) by highlighting a highly selective conversion of N-acetyl-D-glucosamine. Conventionally the crustacean processing waste is minimally treated and dumped in the ocean. This group of furans and organic acids could form the foundation building blocks for oceanic

biorefineries and benefit the bioregion where this research was conducted (Atlantic Canada). It is a practical pursuit to conduct research that will benefit local industries.

3.3.1 Biochar By-Product Yields and Applications

During every reaction performed in this research project there was a brown residue or black insoluble by-product formed. This was expected due to the series of reactions that occur during the caramelization process under liquefaction temperatures and Maillard reactions amongst nitrogen containing compounds. The types of reactions that take place are isomerization, condensation, dehydration, fragmentation and polymer formation. Applications for biochar range include feedstock for carbon support materials to water purification and soil remediation. It is one of the goals of this study to produce a biochar that is 1) suitable for revitalizing soil with organic nitrogen and 2) suitable as a precursor for functionalized carbon materials.

All farmers know plants require potassium (K), phosphorus (P) and nitrogen (N) as macronutrients in their growing media so it is essential that these elements be in ample supply in the soil. Some micronutrients that help plants grow are boron (B), chlorine (Cl), iron (Fe), sodium (Na) and zinc (Zn). The biochar produced in these experiments could have sufficient amounts of N, B, Na and Cl along with ample organic compounds. These features can translate into biochar being beneficial for soil improvement as a way to lock carbon out of the atmosphere. Depending on the conditions for hydrothermal processing of amino-carbohydrates, a range of these macro and micronutrients would be present in the solid residue. Biochar samples were dried and analyzed via Fourier transform infrared spectroscopy (FT-IR) and

thermogravimetric analysis (TGA) to determine what surface type of carbon-oxygen bonds are dominant and its thermal integrity. Through TGA, we are able to observe what forms of carbon are present to better determine it's application potential based on the functional groups present. With FT-IR, one can observe hydroxyl, carboxyl, amine and carbonyl functionalities for the purpose of determining it's application potential. The biochar yields that are discussed below comes from the water recycling study and additive-free reactions. Experimentally, it was observed that at a lower temperature the addition of boric acid or sodium chloride increases the residue yield.

It can be seen in Figure 3.27 that the addition of sodium chloride increases the biochar yield at the expense of the ethyl acetate extractives. During the 2nd and 3rd cycle with additional boric acid the yield of furans are enhanced at the expense of the aqueous fraction. The product phases were calculated by mass balance of the dried biochar, furan products and water fraction. Although at a higher temperature the amount of biochar is greater on average; the amount of organic carbon compounds that remain in water after the first run decreases (Figure 3.38). These results show added benefits to recycling the water used in the subcritical dehydration of NAG. It is postulated that the water phase contains partially dehydrated compounds that are easily transformed into the desired furans after further addition of additives. In the case of NaCl, the intermediates left in the water phase contribute to the increase in biochar yield instead of being converted into 3A5AF. It is observed, at 180 ^{o}C, that the addition of boric acid to the recycled water phase has a net positive effect on furan yield but does still contributes to biochar formation. This was the most desirable outcome because it provides the largest amounts of the useful products (biochar and unsaturated furans). By recycling the intermediate products, it is

possible to obtain enhanced yields that are not achieved after one catalytic treatment. A major limitation of these reactions was that they were performed in a batch reactor, where the recycling of solvent is not as ideal as in a continuous flow reactor. Experiments conducted in a continuous manner would be a centerpiece of future research.

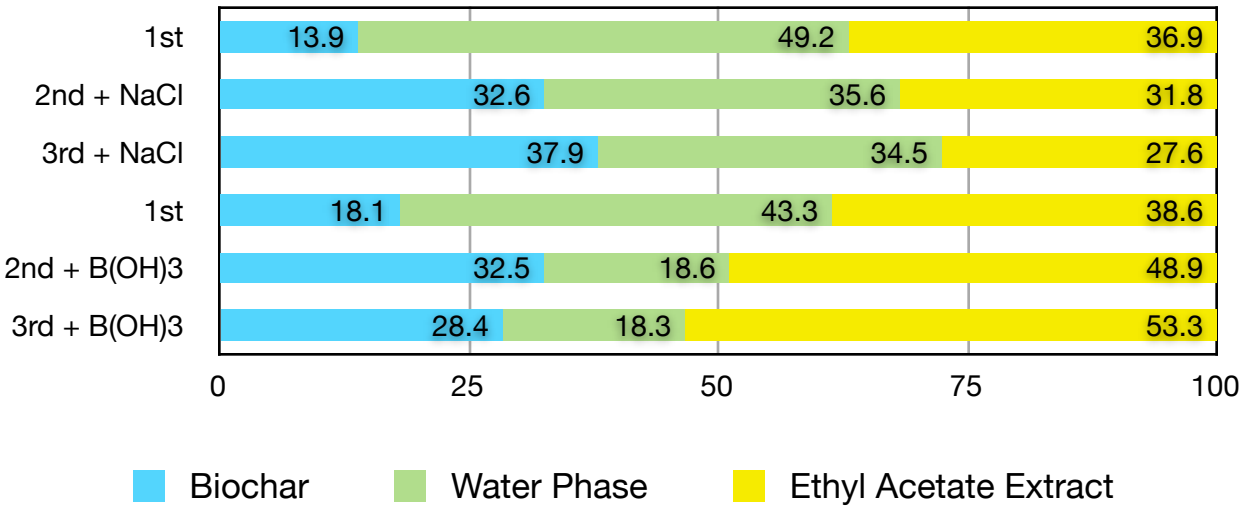


Figure 3.27 : Product Phases at 180 °C for Water Recycling Reactions that had Additional NaCl or $B(OH)_3$

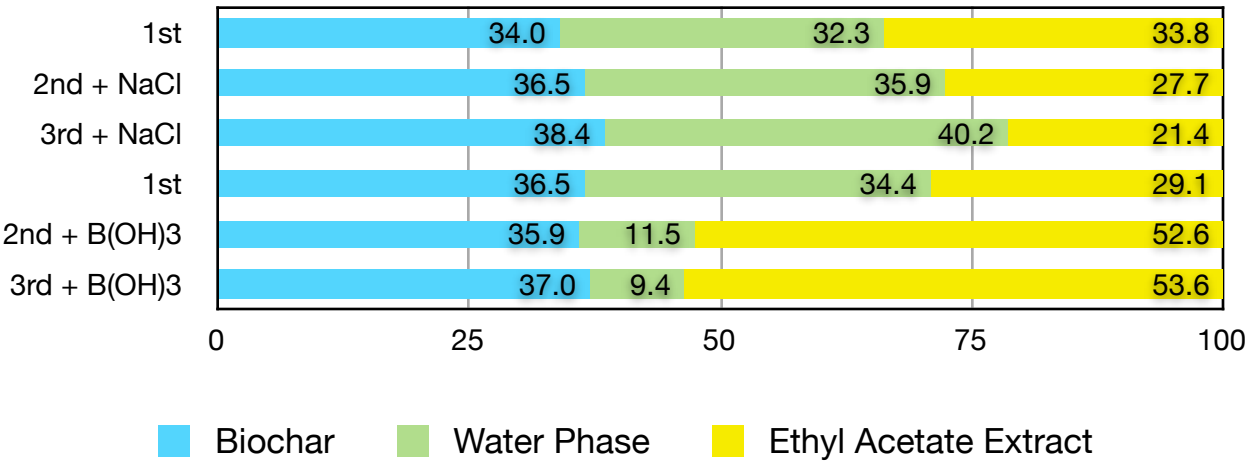


Figure 3.28 : Product Phases at 220 °C for Water Recycling Reactions that had Additional NaCl or $B(OH)_3$

Increasing the temperature to 220 ^{o}C has advantages and disadvantages. The clear advantage can be seen by comparing the 1st cycle at both temperatures. The mass that remains in the water phase was reduced and hits the lowest point (9.43 wt%) after the 3rd cycle; which was approximately half the amount formed at 180 ^{o}C. Throughout the solvent recycling study the addition of NaCl either significantly increased the biochar fraction (at 180 ^{o}C) or increased the water fraction (at 220 ^{o}C). Figure 3.28 shows boric acid was able to convert the intermediates in the water fraction into extractable furans; although this increase has a limit.

The spectra presented in this section display a variety of oxygenated carbon species. Since the biochar is formed in a significant amount (30 - 50 wt%) there is emphasis to utilize it for sustainable applications. Improving the quality of soil through the incorporation of macro and micro nutrients will result in healthier plants and less synthetic chemicals employed. Employing this functionalized carbon material for catalyst support synthesis would have environmental-friendly advantages as well.

When comparing the lower frequency region of wavelength in the FT-IR spectrums in Figures 3.29 and 3.30, the latter contains a broad peak at 1035 cm^{-1} that can represents the a C-O bond in an alcohol. Peaks at 1550 cm^{-1}, 1370 cm^{-1} and 1227 cm^{-1} are present in different magnitudes in both biochar fractions from reactions at 180 ^{o}C. Through the addition of boric acid to the recycled water, it was possible to produce carbon materials with a larger content of surface (non-phenolic) hydroxyl groups. Another interesting point is the ratio between the (carboxylic acid) peak at 1230 cm^{-1} and 1030 cm^{-1}, which is larger when additional NaCl is added compared to boric acid. The biochar from the additional salt reaction displays a stronger peak in the carboxylate region which could correlate with the surplus of sodium ions present. The small

peaks above 3500 cm^{-1} (O-H stretch) can represent low concentrations of phenolic alcohols and carboxylic acids. All of the FT-IR spectroscopic analysis on BC shows peaks that might be assigned to primary and secondary amine peaks (3000 - 3500 cm^{-1}).

Oxygenated surface groups (alcohol, carbonyl, phenolic alcohol and carboxyl) are the most versatile for post-functionalization. There are research groups employing biochar to make FT-synthesis and cellulose hydrolysis catalysts (94,95). In this catalysis research, the authors grafted -SO_3H and ionic liquids ([Bmim][Cl]) onto biochar or thermally activate it to yield iron carbide nanoparticles on the surface. The research in this thesis shows shows that biochar formed under more saline conditions has benefits for soil remediation applications while residue formed in a more acidic environment can be directed towards catalyst support development because of the absence and presence of surface oxygen functionalities. These results are based on FT-IR, TGA analysis and elemental analysis.

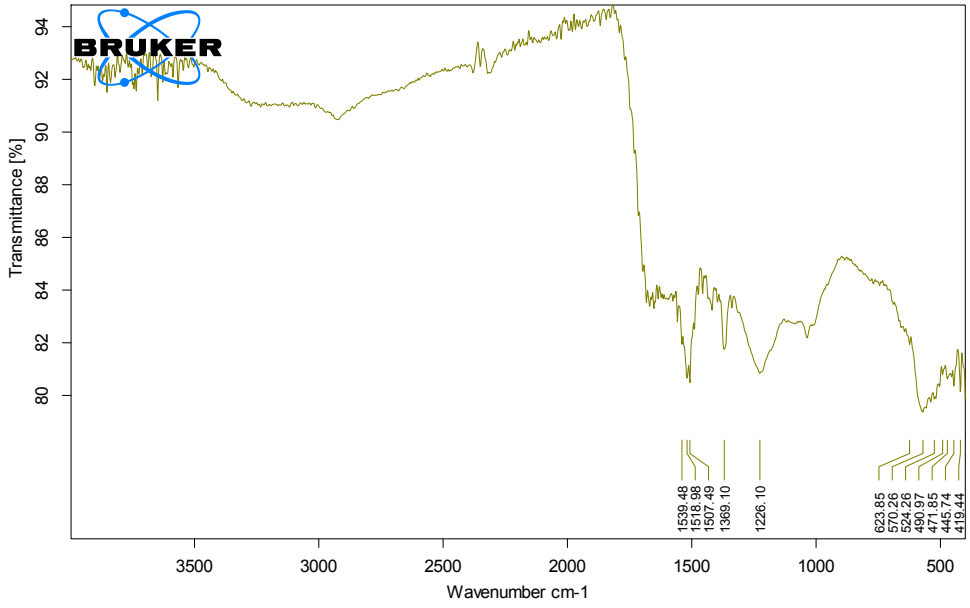


Figure 3.29 : FT-IR Spectrum of Biochar from the Water Recycling Study (3rd cycle at 180 ^oC with added NaCl)

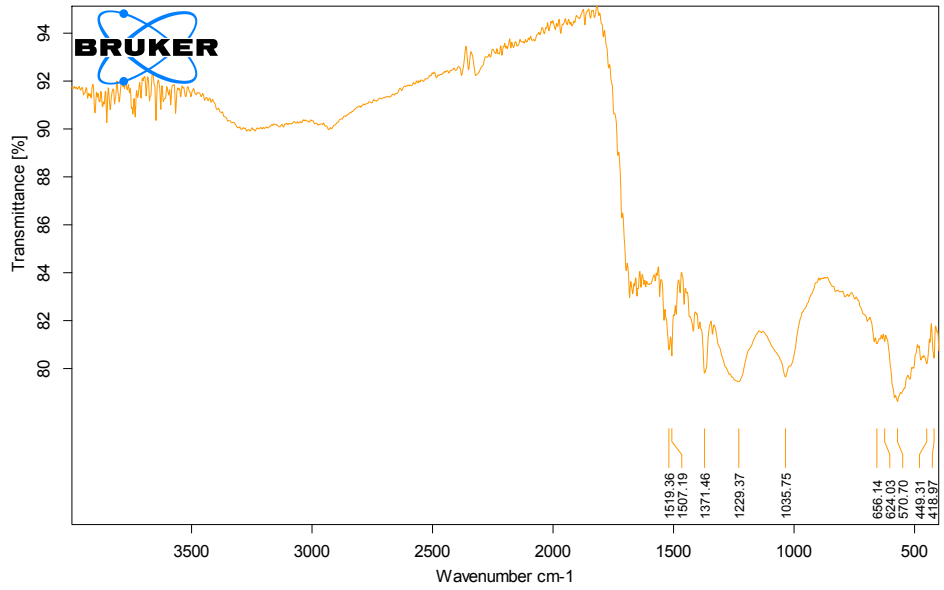


Figure 3.30 : FT-IR Spectrum of Biochar from the Water Recycling Study (3rd cycle at 180 ^{o}C with added Boric Acid)

The biochar that formed after the 2nd and 3rd cycle at 220 ^{o}C contains an array of surface oxygen species. Figure 3.31 shows that after the 2nd cycle with added NaCl the material has less oxygenated species such as carboxyl and carboxylate acid functional groups, as seen by the smaller peak at 1100 cm^{-1} (relative to Figure 3.32). The absence of bands between 950 and 1710 cm^{-1} indicate less oxygen species present, so this material would have a higher carbon and hydrogen content and as such is suitable for black carbon to deposit in the soil. Polycyclic aromatics in the 1400 - 1600 cm-1 region are seen through the biochar samples (94). After the 3rd cycle the biochar changes dramatically through the generation of numerous phenolic and carboxylic functionalities. The broad band at 3185 cm^{-1} represents the overlapping O-H stretch (seen in Figure 3.32) (95). These results show that biochar characteristics can be tailored depending on the extent of solvent recycling.

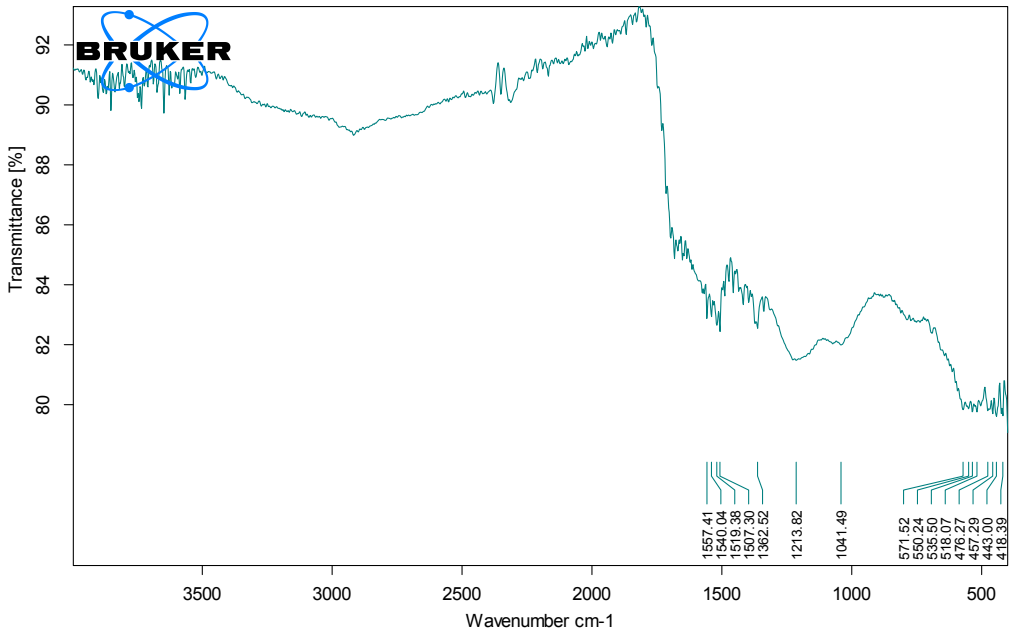


Figure 3.31 : FT-IR Spectrum of Biochar from the Water Recycling Study (2nd cycle at 220 °C with added NaCl)

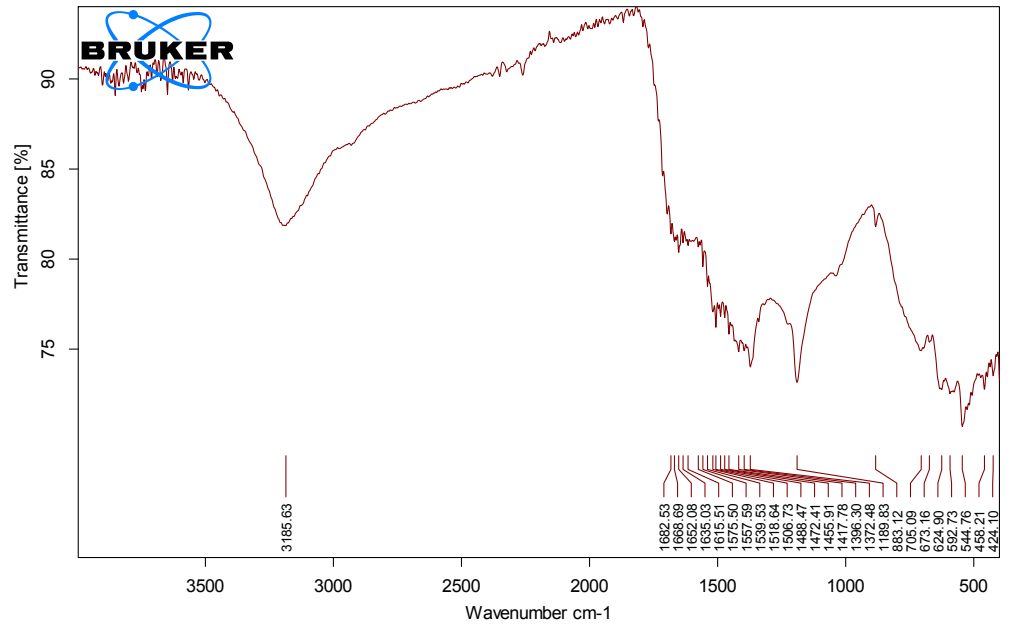


Figure 3.32 : FT-IR Spectrum of Biochar from the Water Recycling Study (3rd cycle at 220 °C with added NaCl)

The residue formed during the reaction is designated as biochar (BC) during this discussion. When two molar equivalents of both additives are present in the reactor, the amount of BC formed at 180 ^{o}C averages (triplicates) to 23.9 wt%. Elevating the temperature to 220 ^{o}C results in an almost 15 % increase (37.8 wt%) in solids collected during filtration. When there is more salt than boric acid in solution the amount of BC increases proportionally. Depending on the reaction conditions there are two distinct forms of residue collected; which are distinguished by their morphology and appearance. The main residue is a sandy powder (at the bottom of the vessel) that is black with some brown while the other appear as shiny black flakes that form above the propeller. Since our studies have shown that longer reactions (when there is twice as much boric acid as NAG) result in 5-HMF as the major product, it is postulated that ammonium hydroxide and acetic acid contributes to the increase of BC. This ethyl acetate insoluble fraction was primarily characterized by FT-IR spectroscopy, which shows a variety of oxygen moieties present. The BC from the water recycling study are compared to additive-free control reactions later on in this chapter. The BC is dried overnight at 120 ^{o}C in an oven and analyzed once cooled. The hydroxyl group is dominate in the FT-IR spectrum when compared to the crude product mixture of furans (Figure S19). Further FT-IR and TGA characterization of the insoluble fraction revealed versatile surface properties that allow a range of post-functionalization that can be applied.

The thermal stability of biochars were studied by TGA for their thermogravimetric (TG) and derivative thermogravimetric (DTG) curves. In Figure 3.33 - 3.35, the DTG curves are different due to the increasing temperature of the reaction (180 ^{o}C, 200 ^{o}C and 220 ^{o}C). In all

three figures there is a small decline in the TG curve above 100 °C, which is assigned to the evaporation of adsorbed water molecules. The biochar produced at 180 °C has the highest thermal stability with 0.5 wt% of the sample remaining at 719.2 °C; whereas at 200 °C and 220 °C there was 0.8 wt% and 0.7 wt% remaining at 594.9 °C and 604.6 °C respectively. These temperatures are taken from the TG curve where it flatlines at the end of the run and likely represents the furthest degree of carbonization that has occurred with each sample.

Each of the three figures of TGA data show a DTG peak between 297.9 °C/84.0 wt% (220 °C) and 320.5 °C / 86.6 wt% (180 °C). For the biochar produced at 180 °C (Figure 3.33), the first peak dips at 427.8 °C/67.8 wt% before increasing to the second and final peak at 608.6 °C/ 21.8 wt% (then decreasing to 719.2 °C/0.5 wt%. Between the temperatures of 320.5 °C and 608.6 °C there is a mass loss of 64.9 wt% and can be attributed to the surface oxygenated groups (e.g carbonyl, carboxylic, hydroxyl). The loss of 21.2 wt% between 608.6 °C and 719.2 °C originates from the further carbonization that occurs as the organic matter fuses into connected aromatic rings. These demonstrates the high thermal stability of biochar produced at 180 °C under additive-free conditions; whereas 99.2 wt% of the sample is present at 180.1 °C, which implies the biochar is suitable to convert to a solid acid catalyst for use under mild conditions.

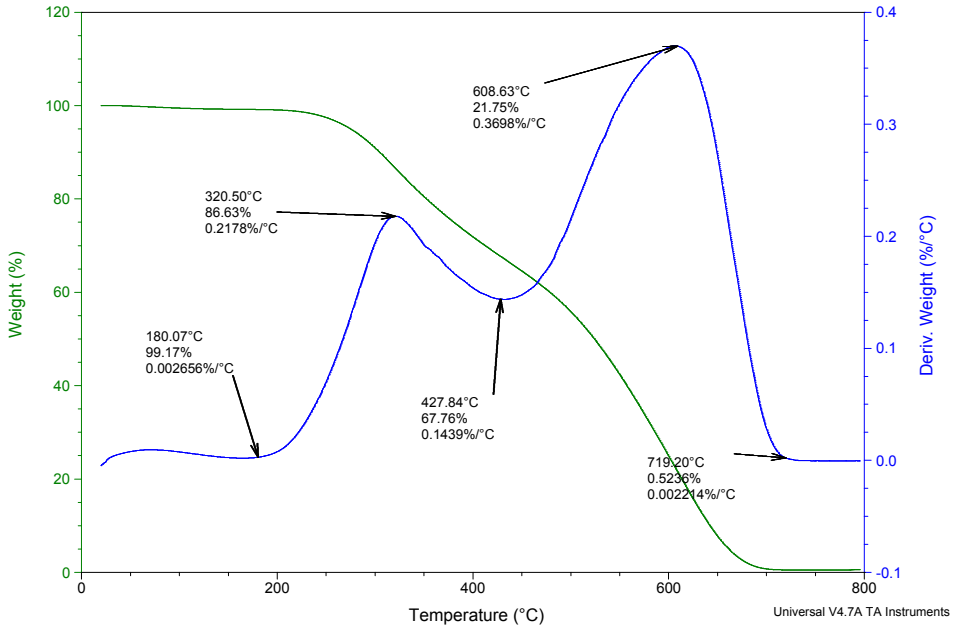


Figure 3.33 : TGA of Biochar Produced from Additive-Free Reaction at 180 °C for 10 minutes at 7.5 wt% NAG

The TGA profiles for biochar produced at 200 °C and 220 °C exhibit similar thermal properties (Figure 3.34 and 3.35). The weight loss between the two peaks for the lower temperature was 55.6 wt% and 56.5 wt% for the higher temperature. Both of these thermal stability profiles show less than 1 wt% of sample left around 600 °C and thus highlight the fact that oxygenated species are retained to a larger extent on the biochar when it was produced at 180 °C. The difference in thermal stability and surface composition between reactions conducted at 180 °C and 220 °C (or 200 °C) divides the biochar into two categories.

The two categories are for soil remediation and precursor for catalytic material. In terms of soil remediation, biochar can retain water and nutrients more efficiently when the number of surface oxygenated species is relatively high. This surface trait is also beneficial to post-

functionalization for the purpose of solid acid catalyst synthesis by providing ample sites for SO_3H- to bond to. The higher thermal stability from biochar that was produced at lower temperatures is a desirable trait for the production of catalytic carbide species or nanomaterials.

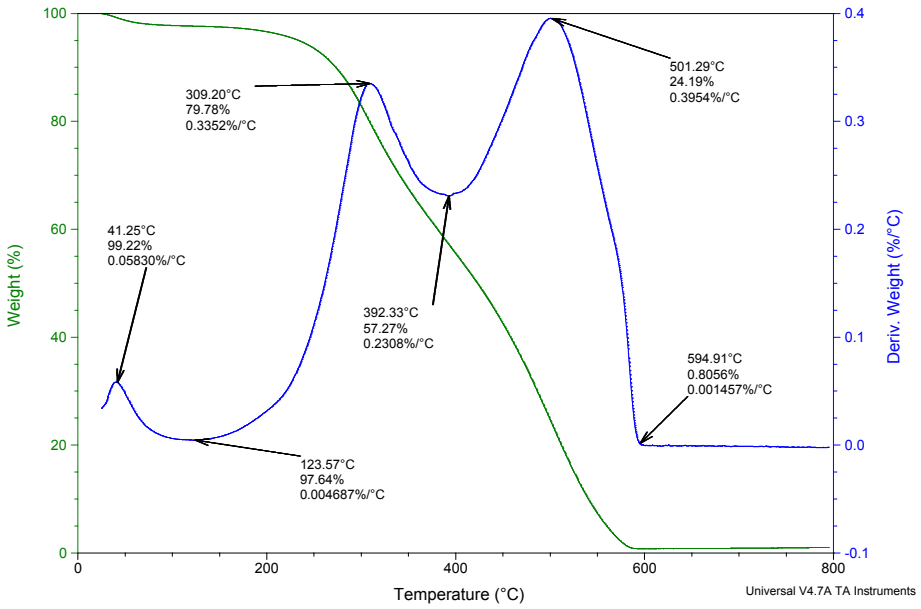


Figure 3.34 : TGA of Biochar Produced from Additive-Free Reaction at 200 ^oC for 10 minutes at 7.5 wt% NAG

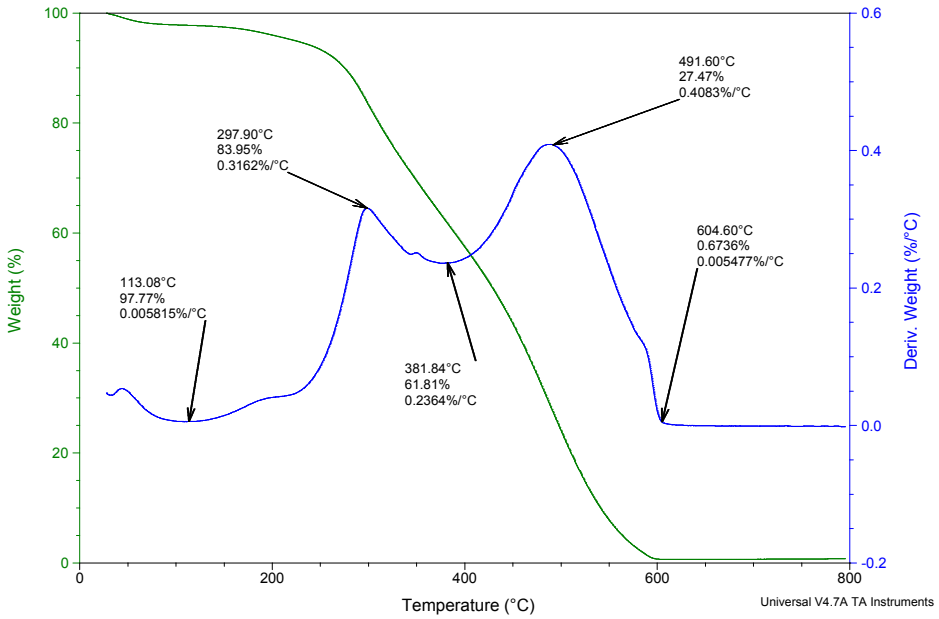


Figure 3.35 : TGA of Biochar Produced from Additive-Free Reaction at 220 °C for 10 minutes at 7.5 wt% NAG

The role of boric acid was studied further by its influence on the thermal stability of biochar. In Figure 3.36, the TG and DTG curves are presented for a reaction conducted at the following conditions: 220 °C, 10 minutes, 7.5 wt% NAG and 1:2:2 NAG:NaCl:$B(OH)_3$. As the temperature increases the weight of the sample decreased from 99.4% (140.5 °C) to 5.2% (630.4 °C). There are two distinct thermal events during the thermogravimetric analysis: i) a broad peak with apexes at 286.6 °C (87.3%) and 416.6 °C (45.1%) and ii) a sharp peak with the apex at 557.8 °C (14.1%). The broad peak represents the conversion of oxygenated species (carboxylic acids, ethers and alcohols) to more thermally stable carbonyl and cyclic ether structures through a series of dehydrogenation, condensation, isomerization and hydrogen

transfer reactions. The sharper peak can be attributed to the carbonization process that occurs between the range of 500 - 600 °C.

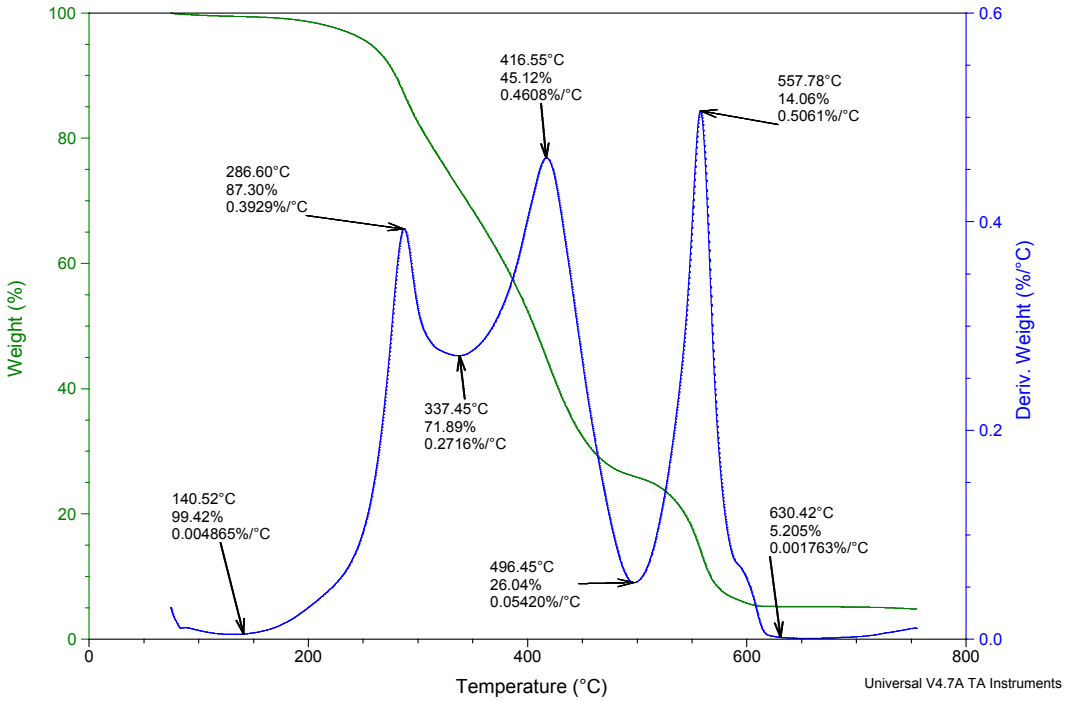


Figure 3.36 : TGA of Biochar from 1:2:2 NAG:NaCl:$B(OH)_3$, 7.5 wt% NAG at 220 °C

When boric acid was not present in the reaction mixture (Figure 3.37), the thermal processes change in amplitude. The TGA profile was similar to a biochar produced with boric acid but the first broad peak has significantly diminished. The apexes of that peak were 304.4 °C (87.7%) and 414.9 °C (63.4%). The second apex has a higher weight on the DTG curve (63.4%) than when boric acid was present (45.1%). This increase can be attributed to higher thermal stability of biochar that was achieved in the absence of boric acid. The higher thermal stability of biochar generally occurs because a higher content of carbon and a decreased amount of

oxygen. The sharp peak that represents the carbonization process occurs at 544.87 °C (33.36%) in the absence of boric acid and 557.8 °C (14.06%) with it present. Biochar has a larger amount of the initial sample undergo carbonization when the reaction vessel contained only water, NAG and NaCl. This indicates a higher carbon and lower oxygen content of biochar when the only additive was NaCl. Samples were sent for analysis to determine of what extent the incorporation of chloride ions into biochar has occurred.

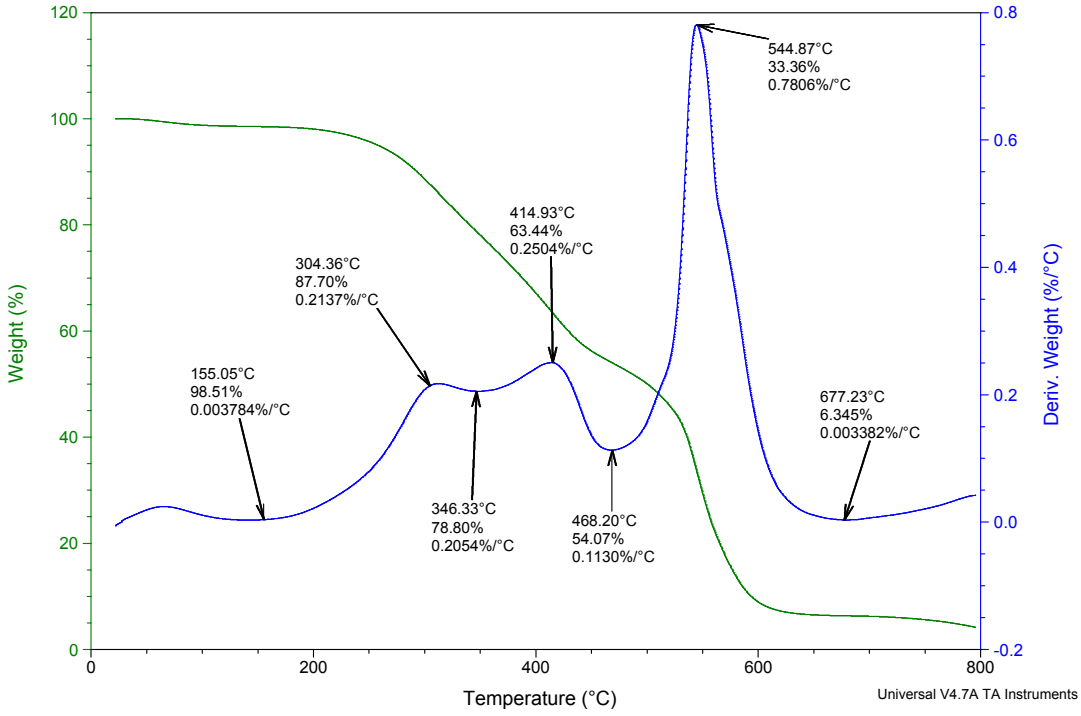


Figure 3.37 :TGA of Biochar from 7.5 wt% NAG, 1:2 NAG:NaCl at 220 °C

3.3.2 : Additive Influence on the Elemental Composition of Biochar

The elemental composition of biochar produced from biomass is dependent on the source feedstock and the conversion conditions. The biochar produced from the processing of NAG in

subcritical water has a slightly higher carbon content when conducted without additives (Figure 3.38). The elemental composition of NAG is as follows: 43.43% C, 43.40% O, 6.84% H and 6.33% N. The total C and N content of all biochars increased while O and H decreased regardless of additives or temperature. One of the main by-products that reduced the oxygen content was water. A major goal of this research was for the retention of nitrogen from the starting material; this was achieved via the renewable amide (3A5AF) and N-containing biochar.

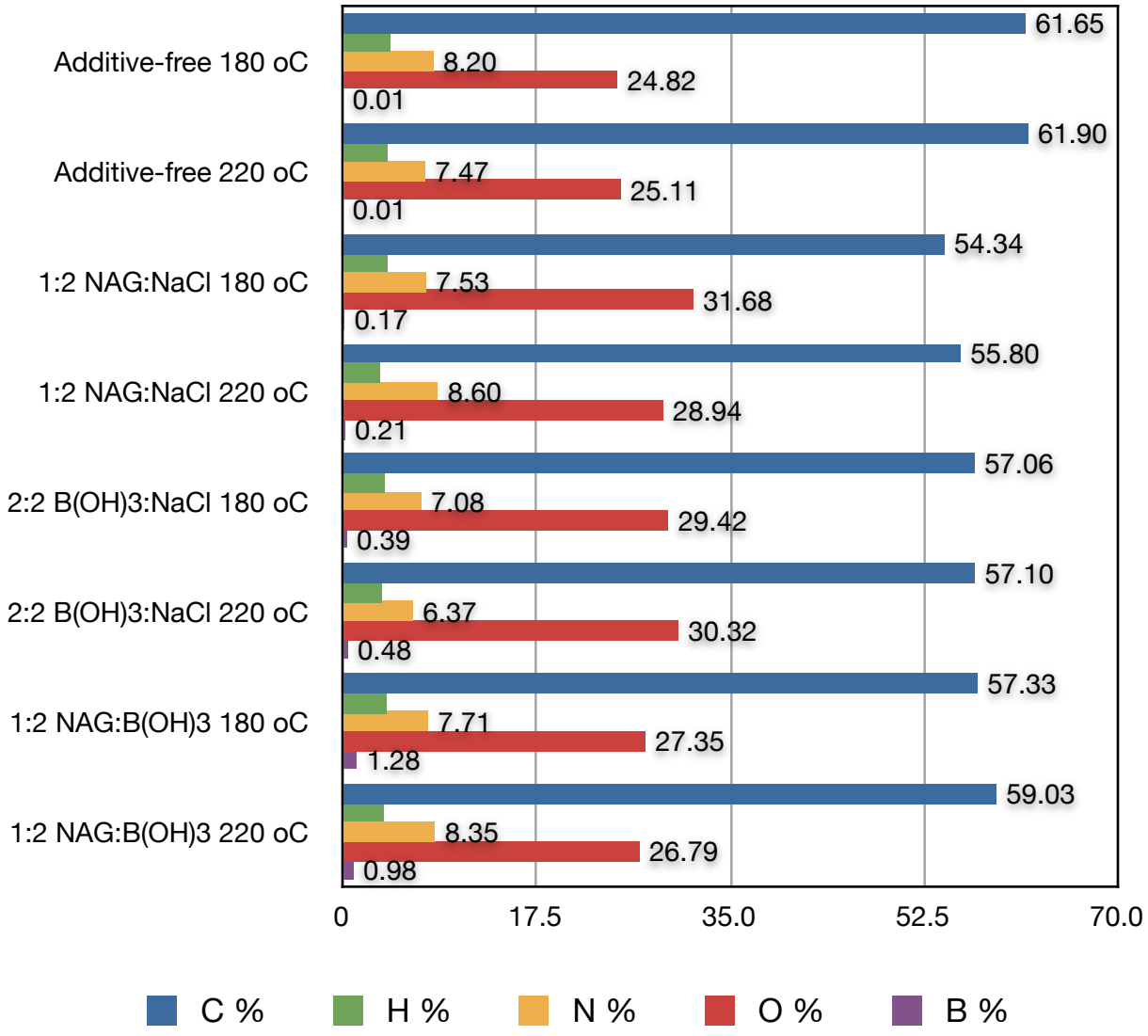


Figure 3.38 : Elemental Composition with and without Additives

An interesting note from the elemental analysis was the inclusion of boron into the biochar occurred more readily at a lower temperature and was hindered by NaCl. At 220 ^{o}C, the nitrogen content was 8.35% when boric acid was the only additive and compared to when sodium chloride was present the nitrogen content dropped to 6.37% (close to the initial NAG N content of 6.33%). A similar result was obtained from the NaCl only reaction at 220 ^{o}C; whereas the N content decreased from 8.60% to 6.37%. These results indicate that reactions performed with only boric acid as an additive lead to the greater retention of boron and nitrogen while increasing the carbon content and decreasing the oxygen.

For the purpose of plant health, the inclusion of boron and nitrogen into biochar at levels higher than NAG (> 0% B, > 6.33% N) would be essential and that was achieved under the conditions analyzed. It is important to note that the values in Figure 3.38 do not add up to 100% and therefore sodium and/or chloride atoms are most likely present since they were the only other elements included in the reactions. Since small amounts of sodium and chloride are beneficial to plant growth, these biochars could be suitable to increase the nutritional content of soil.

3.4.0 : The Development of a Task-Specific Polymer based on 3A5AF

3-Acetamido-5-acetylfuran is a renewable amide that is a valuable and versatile platform chemical with potential in the area of CO_2 capture technology and gas purification. This can be accomplished when the ketones are reduced to hydroxyl groups to have a more favorable interaction with CO_2. The most commonly employed CO_2 capture system involves mono- or di-

ethanolamine as a slurry that flue gas is passed through. The carbamate formed by the amine and CO_2 is removed and the CO_2 is released by increasing the temperature and hence is energy intensive and presents corrosion issues. The disubstituted furan (3A5AF) that is the focus of this project has the potential to replace such a system on environmental merits alone. Cost is normally the deciding factor for gas processing technologies and by employing 3A5AF derivatives for CO_2 capture there would be several advantages. The solubility would be favorable for a less energy intensive release of gas and the use of renewable feedstocks is more sustainable. The cost of corrosion would decrease due to the decreased reactivity of a secondary amine compared to a primary. Developing a polymeric organic membrane based on the 3A5AF moiety is a future goal of our research group. The two ketones or the furan ring could be used as sites to anchor a monomer for polymerization. Another application would be to reduce the ketones of the compound into hydroxyl functionalities. There are several ways to accomplish this goal but the one that best overlaps with the principles of green chemistry is the baker's yeast (BY) catalyzed reduction in water. A series of preliminary reactions were conducted to determine the feasibility of the BY bioreduction of furan platform molecules and will be discussed further on in this section.

3.4.1 : The Nature of Biotransformations

The catalytic transformations of C-O functionalities are an ubiquitous part of Nature and are often facilitated by enzymes. One can consider enzymes to be complex homogeneous catalysts that are typically assisted by other molecules. Many enzymes are in the oxidoreductase category and their efficiency depends on co-factors. Enzymes can be utilized in the laboratory in

their pure form or embodied in a whole cell biocatalyst (yeast, fungi, bacterium). When isolated enzymes are employed, they are controlled by the biochemistry of proteins and their co-factors and/or co-enzymes. Whole cell biocatalysts are governed by internal mass transfer, cellular metabolism, protein synthesis and growth of the cell. Biocatalytic processes are generally divided into two categories: 1) biotransformations and 2) fermentations. With the former typically employing a cheap sacrificial substrate (such as glucose, glycerol or small organic acid) to serve as the energy source and reduction equivalents for cell health and most importantly for co-factor regeneration. In fermentations, the desired target chemical is produced from the carbon in solution. The bio-reduction of ketones into optically active alcohols can take place through whole cell biocatalysts (typically baker's yeast (BY)) by utilizing alcohol dehydrogenases (ADHs) that require nicotinamide (NAD(P)H) co-factors (96-99). These alcohols can be of great industrial or pharmaceutical importance and as such their production via bio-catalysis are a very environmentally benign approach. Typically these reactions are performed in water due to the non-detrimental effects on the baker's yeast (*Saccharomyces cerevisiae*) and its enzymes but issues arise such as low solubility of organic reagents/intermediates, side reactions and tedious separation techniques.

3.4.2 : The Attempted Bio-reduction of 3A5AF and 5-HMF by Baker's Yeast

A proof-of-concept investigation was conducted on the bio-reduction of mixed substituted furans in water. The goal of this study was to create diols or other alcohols that can be used as renewable monomers or biofuels. These reactions took place at 25 ^{o}C in 100 mL of water over 3 days. Standard baker's yeast was obtained from a grocery store and was employed without

modification. The highest amount of recovered products (46.41 wt%) was achieve with a mass ratio of 1:4 of furans to baker's yeast (BY) (Figure 3.39). As the amount of yeast introduced into the system increases, the amount of recoverable furans decreases to 18.43 wt% (with 16 grams of BY). When 20 grams of yeast was used there was a tendency for the flask to foam over within 24 hours of starting the biotransformation. The organic products were extracted with 3 x 100 mL of ethyl acetate and each fraction was concentrated by rotary evaporation. During ethyl acetate extractions and workups the yeast odor similar to bread baking was strongly apparent. This is an example of the overlap between green chemistry and food science.

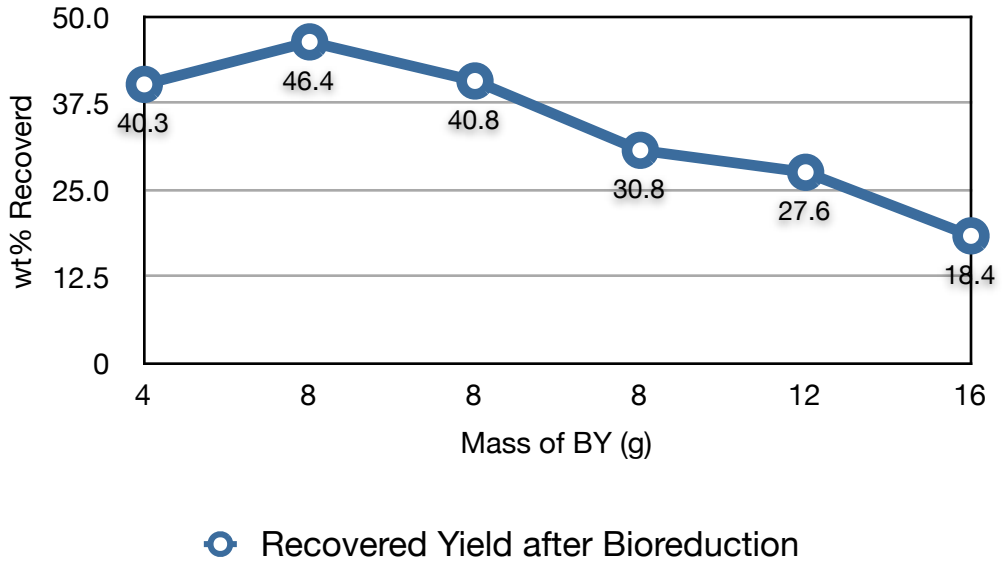


Figure 3.39: Baker's Yeast Loading Influence on Yield Under Identical Conditions with Different Furan Mixtures

There was no observed bio-reduction of 3A5AF and the cause of this requires further experimentation. It is possible for the species with a ketone and acetamido group to form a stable dimer through hydrogen bonding. The enzymes present in baker's yeast must not have been able

to form a stable complex with 3A5AF. However 5-HMF was found to be readily susceptible to bio-reduction by baker's yeast (Figure 3.40) to the diol. The selectivity between an aldehyde and ketone functionality may also play a role with this particular species of yeast. Converting 5-HMF into 2,5 dihydroxymethylfuran was a goal of this proof-of-concept study; for the purpose of future work on the co-polymerization for bioplastic production (100).

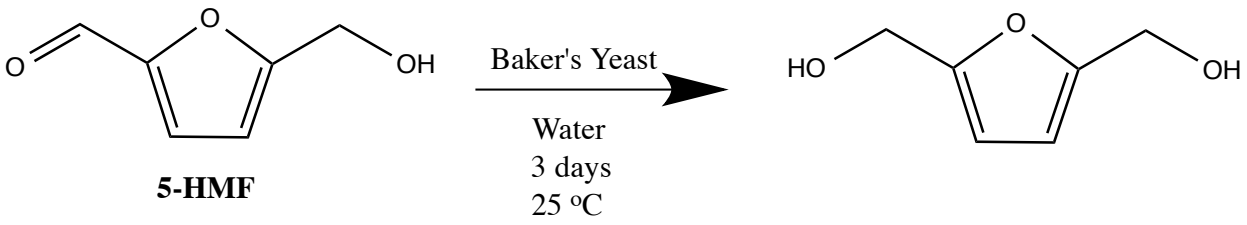


Figure 3.40 : General Scheme of the Bio-reduction of 5-HMF to 2,5 Dihydroxymethylfuran in Water

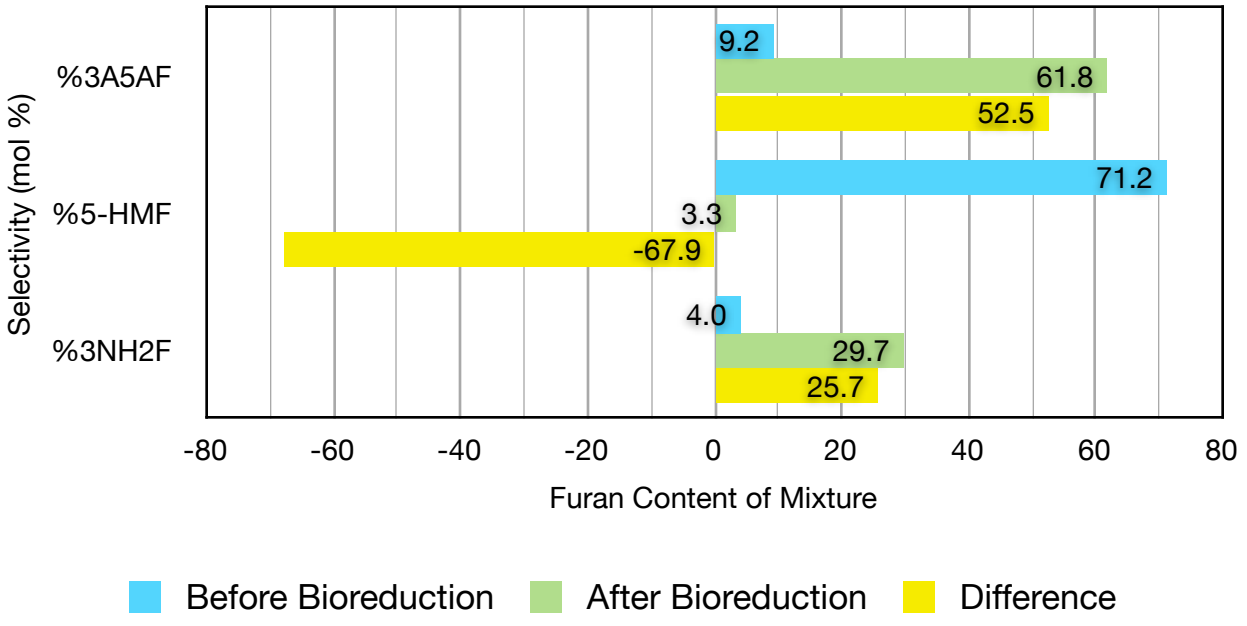
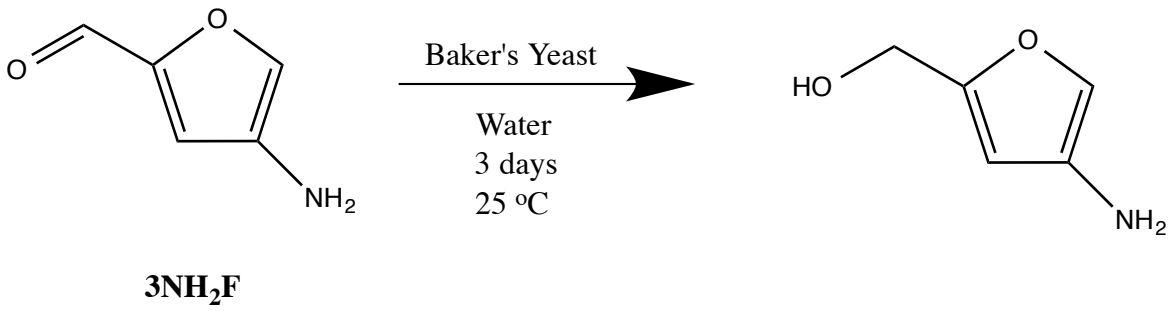


Figure 3.41 : Bio-reduction of 5-HMF when 2:1 BY wt% : F wt% and 2:1 BY:Glucose

In Figure 3.41, 3A5AF was the minority of the furans in the original sample but became the dominant product after bio-reduction. This furan mixture was intentionally chosen to see if 5-HMF could be selectively reduced. This sample was primarily composed of 5-HMF (71 mol%) and after the biotransformation we observed a reduction of 95% into the diol. This is the first time 5-HMF has been converted into a diol with common baker's yeast. This is the most significant result achieved in this study and demonstrates the feasibility of baker's yeast for diol production. It was anticipated that all of the furans would undergo biotransformation to some degree. It is interesting to note that the BY was more selective towards the nitrogen-free furan (5-HMF). This could be related to the concentration of furans or to the influence of the nitrogen atom. If concentration had a greater influence, it would be expected that the low levels of nitrogen-containing furans would be saturated with enzymes and their ketones would completely convert into hydroxyl groups. From the results presented in this thesis, it appears that the nitrogen atom possesses the greater [inhibitory] influence over the alcohol dehydrogenases (ADH). The acetamido functionality has the ability to coordinate with the zinc atom at the center of ADH's catalytic site. The general scheme for the bio-reduction of $3NH_2F$ to an alcohol is presented in Figure 3.42. Through the data presented in Figure 3.43, it was observed that the bio-reduction of nitrogen-rich furans behave differently if the group is an amine rather than an amide. The zinc atoms are coordinated to certain amino acids (in ADH) and the acetamido group would naturally imitate a different interaction with the metal ion than RNH_2. These experiments provide evidence that the BY is inactive towards reducing acetamido groups; although they are able to convert an acetyl group across from a primary amine ($5Ac3NH_2F$) when the ratio of BY to furans is 4:1. It was observed that the $3AcNH_2F$ molecule had decreased in concentration by

61%, however, the product identity is unknown. The ability of the acetamido moiety to hinder the bio-reduction of 3A5AF draws parallels to the protecting ability of the acetyl group in retaining the nitrogen into platform chemicals as described before in this study.



$3NH_2F$

Figure 3.42 : General Scheme of the Possible Bio-reduction of $3NH_2F$ from Carbonyl to Alcohol in Water

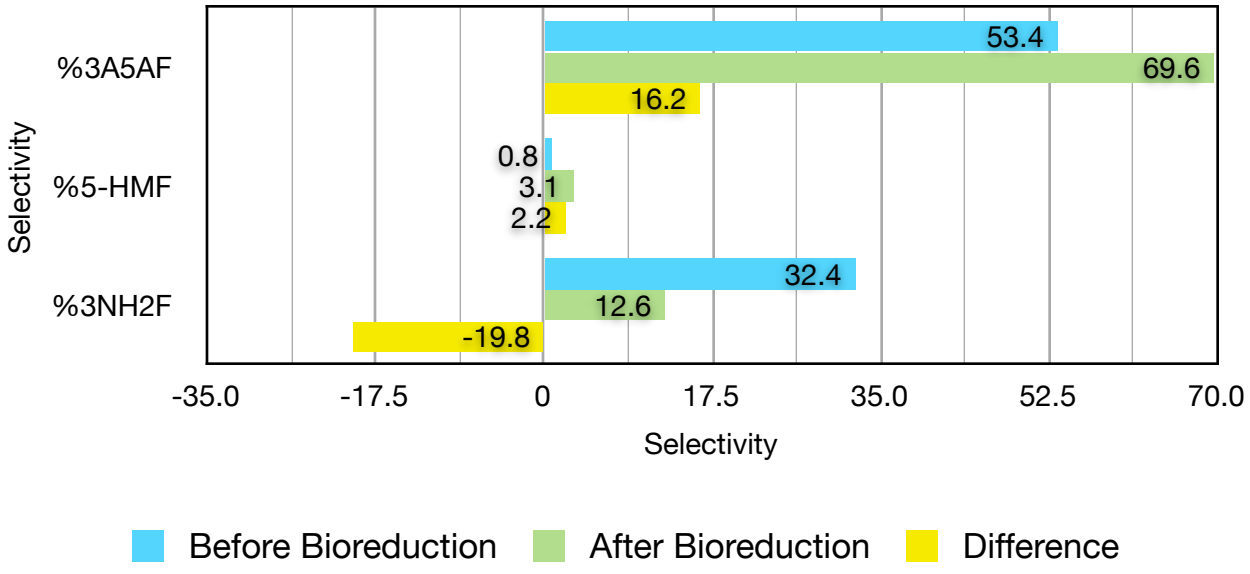


Figure 3.43 : Bio-reduction of $3NH_2F$ when 4:1 BY wt% : F wt% in the Absence of Glucose

For experiments that were conducted with higher loadings of BY on both nitrogen-rich and nitrogen-poor furan mixtures, a boost in conversion but a lower recovery yield was revealed. Figure 3.44 shows that a ratio of 8:1 for BY:F results in a bio-reduction of 83% but the recovered mass decreases 12%. When mixtures of 3A5AF and $3AcNH_2F$ are combined with BY and incubated for 3 days at 25 ^oC the only reduction that occurred was for the primary amine molecule. When a 5-HMF rich mixture was subjected to these incubation conditions, there was a reduction of the aldehyde group into an alcohol. This preliminary study has shown that whole cell biocatalysis for the conversion of carbonyl groups (aldehyde) can readily occur on substituted furans but does not occur on 3A5AF due to the possible destabilizing effect brought on by the acetamido functionality.

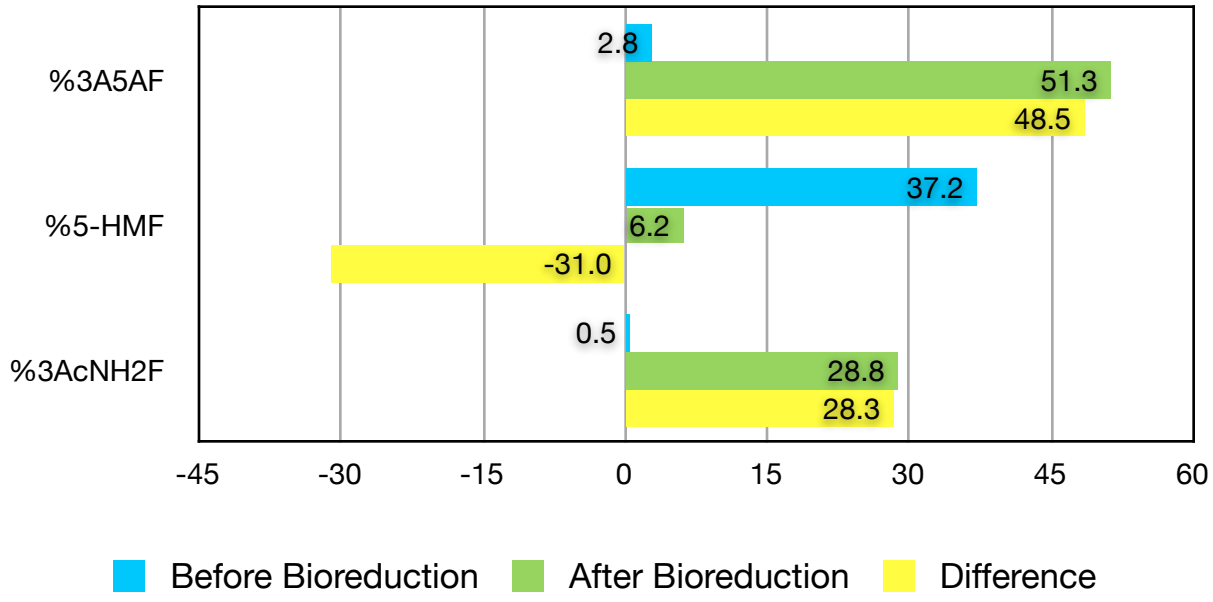


Figure 3.44 : Bio-reduction of 5-HMF when 8:1 BY:F in the Absence of Glucose

The results presented in this chapter demonstrate that the conversion of NAG into 3A5AF can readily occur in water when catalyzed by boric acid and sodium chloride. Water remains to be the most environmentally friendly solvent for a biorefinery, although supercritical carbon dioxide and mechanochemistry offer similar green advantages. Renewable amides will remain an important class of platform chemicals for future sustainable applications as long as the overall process from raw material to final product can be conducted in a green manner. Chapter 4 will go into more detail about the relationship of this research and Green Chemistry. The future prospects of this research will be discussed in a green context.

Chapter 4. Green Research Potential and Future Prospects

4.1.0 : 12 Principles of Green Chemistry

Chemists and engineers can use the 12 principles of Green Chemistry when designing and conducting research and development for the production of chemicals (101). The chemical industry has rapidly developed over the past century and has in many cases placed economic gain over environmental sustainability. Applied scientists can find inspiration for their research through the intricate inner workings of biological systems that have evolved in Nature. In Nature, all of the chemical building blocks are renewable and travel through ecosystems via elemental cycles (e.g C, N, O, H_2O). The by-products that are released are utilized or undergo biodegradation. Just as the nutrients in soil must be balanced to sustain agriculture, the gases in Earth's atmosphere must stay within a range that supports our growing industrial societies.

It is important to note that for the chemistry to be green, the process does not need to satisfy all of the 12 principles of Green Chemistry (101). The research in this thesis focused on principles 1, 2, 3, 4, 5, 6, 7 and 10.

1) Prevention: it is more green to prevent waste than to treat or clean it up after it was created.
2) Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials in the process into the final product.
3) Generation of Little or No Toxic Chemicals: Synthetic methods should be designed to generate as a small and treatable amount of hazardous waste or nothing toxic.

4) Green Chemicals: Chemical products should be designed to effect their desired function while minimizing their toxicity.
5) Green Solvents: The use of solvents or separation agents should be minimized and posses environmentally friendly properties.
6) Design for Energy Efficiency: Energy requirements of the chemical processes should have their environmental and economic impacts minimized. Ideally reactions are conducted at ambient temperature and pressure.
7) Use of Renewable Feedstocks: A raw material or feedstock should be renewable whenever possible compared to depleting resources.
8) Reduce Derivatives: Unnecessary derivatization should be minimized or avoided.
9) Catalysts: Catalytic reagents are superior to stoichiometric regents.
10) Design for Degradation: Chemical products should be designed to breakdown into innocuous degradation products and not persist in the environment.
11) Real-time Analysis for Pollution Prevention: Analytical methodologies need to further develop into real-time, in-process monitoring and control prior to the formation of hazardous substances.
12) Safer Chemistry for Accident Prevention: Processes are to be developed to minimize chemical accidents such as explosions or fires.

For the green conversion of NAG to 3A5AF and 5-HMF presented in this thesis, the co-products have value and through the recycling of water can be further converted into 3A5AF. The relative toxicity of NAG towards human or environmental health is insignificant because it is

biocompatible and biodegradable. NAG dehydration experiments were conducted in aqueous solutions of boric acid and sodium chloride. Excluding the section on the water recycling study where additional additives are used, the highest concentration of NaCl was 3.97 g per reaction and 4.20 g $B(OH)_3$ per reaction. It is important to note that experiments conducted in solutions greater than 100 mL (e.g 150 - 250 mL) would posses a diminished environmental footprint via dilution. These additives used at these concentrations have low toxicity and conducting all of the research in water did not increase the environmental risk. NAG is a renewable feedstock obtained primarily from the ocean ecosystem and along all other reagents used in this process, would not persist in the environment.

4.1.1 : Green Aspects of this Research

All reactions were performed with air present under subcritical water conditions in a 300 mL batch (Parr) reactor. High selectivities for 3A5AF (> 95%) and 5-HMF (> 85%) were achieved within a narrow temperature window (40 ^oC). Dilute aqueous solutions of boric acid (< 5 wt%) and sodium chloride (< 5 wt%) that were employed in this research are relatively environmentally friendly and cost effective. From an environmental standpoint, this research is more green when compared to i) the Kerton group's previous results for 3A5AF synthesis in organic solvents or ILs (20), ii) employing concentrated $ZnCl_2$ aqueous solutions for conversion of sugar into 5-HMF (30) and iii) Chromogen I and III production from autocatalytic conversion of NAG in high pressurized water (11). The replacement of organic solvents or ionic liquids with water was a major accomplishment in this study based on the principles of green chemistry. A main advantage of this research was avoiding concentrated catalytic reagent solutions (67 wt%

$ZnCl_2$), which increase costs and present issues with corrosion due to HCl formation upon heating. The recent work on the conversion of NAG to Chromogen I and III via autocatalytic conversion highlights the food and medical applications of 3A5AF derivatives. The results presented in this thesis with additives has resulted in almost triple the furan yield compared to the autocatalytic studies. These additives demonstrate the effective dehydration of NAG into furans within a short period of time under aqueous conditions. It should be noted that under similar conditions using glucosamine hydrochloride, 5-HMF is produced as the only product (Kerton, unpublished results).

When comparing this approach to the research on the autocatalytic formation of Chromogen I and III, the main difference is their conditions require special vessels for high pressure (> 3000 psi) and presents separation issues (excess of water soluble products). Results presented in this thesis were conducted at a lower pressure (150 - 450 psi) and separation was less problematic (compared to additive-free reactions) due to the salting out effect while products are dehydrated to a further extent. A wide variety of chemicals translate into a wide range of applications although if optimization cannot lead to high selectivity of a valuable product then economics take over the industrial feasibility. The research presented in this thesis on the aqueous dehydration of NAG does not require a high degree of treatment for the wastewater. The results presented have demonstrated that recycling the water three times has advantages and immediately reduces the overall solvent usage. An alkaline approach would require a more energy intensive waste water treatment compared to a borate catalyzed reaction. In Chromogen I and III synthesis, an additive-free approach makes the products more suitable as food additives or precursors for medicinal compounds due to the significantly decreased risk of contamination

(18). To make this process more environmentally friendly, a replacement for boric acid should be evaluated.

Another benefit from this research is the potential replacement of petroleum-derived monomers for the production of engineering plastics. By incorporating a nitrogen functionalized compound into a polymer it might be possible to create Kevlar^{TM}-like (aromatic polyamide) material due to the similarities of the functional group positions that link the polymer (Kevlar^{TM} 3 & 6, 3A5AF 3 & 5). Polycarbonates are another engineering plastic and are one of the materials being developed for polymer (3rd generation) solar cells. This research contributes to sustainable development by providing renewable platform chemicals for the production of novel materials.

4.1.2 : Environmental (E) Factors from the Conversion of NAG into 3A5AF, 5-HMF and Biochar

The largest source of waste from the conversion of NAG into 3A5AF and 5-HMF is generated from the extraction step. When 100 mL of water was used for a reaction the extraction step required 300 mL of ethyl acetate. If the amount of water was increased, the amount of ethyl acetate was increased accordingly (water:ethyl acetate 1:3). It is possible to produce this organic solvent from renewable sources since it can be formed through the esterification reaction between ethanol and acetic acid. Ethyl acetate has a low toxicity since it formed commonly in fruits and wines and is a main component of fruit-like smells. Over time ethyl acetate will oxidize in the presence of air and can produce acetaldehyde, which gives spoiled wine a sharp vinegar-like aroma.

One of the limitations of E-factor as a green metric is that the value does not represent the environmental risk of the reagents used. For a reaction that has 2 mole ratios of NaCl and $B(OH)_3$ (relative to NAG) the total waste is 384.75g when conducted in 100 mL of water. The E-factors (Table 4.1) for this reaction are 134.95 (50 mol% yield), 112.16 (60 mol% yield) and 95.16 (70 mol% yield). These numbers are quite poor but they do highlight how higher yields are very important to minimize environmental impacts. Including biochar as a product substantially increases the greenness of the reaction by reducing the E-factor from 134.95 (no biochar) to 78.66 (2 g biochar). It is important to note that by including 1 g of biochar in a reaction with a 50 mol% yield; the E-factor is lower than a reaction with a yield of 70 mol% without biochar. The E-factors calculated support the atom economy conclusion of the NAG dehydration process; which is that the reaction is more sustainable when 3A5AF is the major product.

The environmental (impact) factors for the production of 3A5AF and 5-HMF are reduced by over half when biochar is taken into account. In Table 4.2, the E-factors are presented that are based on the water recycling study discussed in the results section. By recycling the water and EtOAc while also considering biochar a product the E-factor can drop from 304.6 to 1.00.

Total Reactants (g) = 384.75g	Total Product (g)	Total Waste (g)	E-Factor (A = 50 mol%)	E-Factor (B = 60 mol%)	E-Factor (C = 70 mol%)
7.5g NAG, 3.96g NaCl, 4.19g $B(OH)_3$ 100 mL Water 300 mL EtOAc	A) 2.83g B) 3.40g C) 3.96g 3A5AF	A) 381.92g B) 381.35g C) 380.79g	134.95	112.16	95.16
E-factor = total waste (g) / product (g)	1g Biochar	A) 380.92g B) 380.35g C) 379.79g	94.46	86.44	76.57
	2g Biochar	A) 379.92g B) 379.35g C) 378.79g	78.66	70.25	63.56
Total Reactants (g) = 384.75g	**Total Product (g)**	**Total Waste (g)**	**E-Factor (A = 50 mol%)**	**E-Factor (B = 60 mol%)**	**E-Factor (C = 70 mol%)**
	A) 2.14g B) 2.57g C) 2.99g 5-HMF	A) 382.61g B) 382.18g C) 381.76g	178.79	148.71	127.68
	1g Biochar	A) 381.61g B) 381.18g C) 380.76g	121.53	106.77	95.43
	2g Biochar	A) 380.61g B) 380.18g C) 379.76g	91.93	83.19	76.10

Table 4.1 : The Influence of Molar Yield on E-Factor for 3A5AF Production With and Without Biochar

Total Reactants (g) = 384.75g	Total Product (g)	Total Waste (g)	E-Factor (no Biochar)	E-Factor (1g Biochar)	E-Factor (2g Biochar)
1st) 384.75	1st 180 °C) 2.45g 3A5AF	382.3g	156.04	110.52	85.46
2nd 180 °C) 7.5g NAG, 3.96g NaCl 2nd 220 °C) 11.46g	2nd 180 °C) 1.95g 3A5AF 2nd 220 °C) 1.76g 3A5AF	2nd) 9.51g 2nd) 9.70g	2nd) 4.88 2nd) 5.51	2nd) 2.89 2nd) 3.15	2nd) 1.90 2nd) 2.05
3rd 180 °C) 7.5g NAG, 3.96g NaCl 3rd 220 °C) 11.46g	3rd 180 °C) 1.79g 3A5AF 3rd 220 °C) 1.30g 3A5AF	3rd) 9.67g 3rd) 10.16g	3rd) 5.40 3rd) 7.82	3rd) 3.11 3rd) 3.98	3rd) 2.02 3rd) 2.47
Total Reactants (g) = 384.75g	**Total Product (g)**	**Total Waste (g)**	**E-Factor (no Biochar)**	**E-Factor (1g Biochar)**	**E-Factor (2g Biochar)**
1st) 384.75g	1st 220 °C) 1.26g 3A5AF	383.49g	304.36	169.24	117.02
2nd 180 °C) 7.5g NAG, 4.19g $B(OH)_3$ 2nd 220 °C) 11.69g	2nd 180 °C) 3.58g 3A5AF 2nd 220 °C) 3.54g 3A5AF	2nd) 8.11g 2nd) 8.15g	2nd) 2.27 2nd) 2.30	2nd) 1.55 2nd) 1.58	2nd) 1.10 2nd) 1.11
3rd 180 °C) 7.5g NAG, 4.19g $B(OH)_3$ 3rd 220 °C) 11.69g	3rd 180 °C) 3.78g 3A5AF 3rd 220 °C) 3.84g 3A5AF	3rd) 7.91g 3rd) 7.85g	3rd) 2.09 3rd) 2.04	3rd) 1.45 3rd) 1.42	3rd) 1.02 3rd) 1.00

Table 4.2 : The Influence of Water Recycling for 3 Cycles on E-Factor at 180 °C and 220 °C for 3A5AF Production With and Without Biochar.

The value of 304.36 comes from the 1st cycle of the reaction conducted at 220 ^{o}C with two mole ratios of NaCl and $B(OH)_3$. Since the water and ethyl acetate are recycled, the reactants are simply more NAG and NaCl or $B(OH)_3$; which significantly reduces the amount of waste generated. An E-factor was calculated as 1.00 when 2 g of biochar is counted as a product after the 3rd cycle at 220 ^{o}C with additional $B(OH)_3$. From the trend observed in this study, the highest molar yield of 67.8 mol% (obtained after 3 cycles at 220 ^{o}C with additional $B(OH)_3$) could increase further with additional cycles and potential reduce the E-factor close to zero. Recycling (reagents, solvents, by-products) is essential for a sustainable chemical process and the information in this section supports that claim.

4.1.3 : Atom Economy for the Conversion of NAG into 3A5A5, 5-HMF and Biochar

The atom economy (A.E) for the conversion of NAG to 3A5AF and 5-HMF are quiet different (Table 4.3). When NAG (M.wt = 221.21 g/mol) is converted to 3A5AF (M.wt = 167.12 g/mol) with a 95% selectivity the A.E is 71.7% if the yield is 100 mol%. When the selectivity for 5-HMF (M.wt = 126.11 g/mol) is 85% the A.E is 48.5% if the yield is 100 mol%. Since those are the highest selectivities achieved it is apparent that the chemical process presented in this thesis is more sustainable when 3A5AF is the major product. Although the highest yields obtained for 3A5AF were between 60 and 75 mol% while the highest reported yield for 5-HMF was 65.5 mol %. The atom economy for the reactions change significantly when the yield departs from the theoretical maximum. It is noted that under certain conditions (220 ^{o}C, 7.5 wt% NAG, 10 minutes, 1:1:2 NAG:NaCl:$B(OH)_3$) the yield for 3A5AF was 75.4 mol% (selectivity of 90.6%)

while the remainder of the product mixture consisted of 4.9 mol% 5Ac3NH$_2$F, 5.0 mol% 5-HMF and 0.8 mol% LA (total platform chemical yield 86.1 mol%).

The biochar yield is generally between 1 and 2 g per reaction with the remainder of NAG-derived organics left in the spent water. The co-product (from NAG dehydration) is water and if the process could achieve 100% selectivity/molar yield, there would be 2.44 g of water generated (along with 7.56 g 3A5AF when the initial amount of NAG is 10.00 g). The water generated does not pose any human or environmental risk and thus it is considered a green by-product. Overall, the conversion of NAG to 3A5AF, secondary platform chemicals, biochar and water creates "waste" material that can be recycled or used in sustainable applications.

Product	A.E at 65%	A.E at 75%	A.E at 85%	A.E at 95%
100 mol% 3A5AF	49.1%	56.6%	64.2%	71.7%
100 mol% 5-HMF	37.1%	42.8%	48.5%	54.2%
Product	**A.E at 65%**	**A.E at 75%**	**A.E at 85%**	**A.E at 95%**
65 mol% 3A5AF	31.9%	36.8%	42.9%	45.6%
65 mol% 5-HMF	24.1%	27.8%	31.5%	35.2%

Table 4.3 : The Influence that Selectivity has on Atom Economy for the Conversion of NAG to 3A5AF and 5-HMF

4.1.4 : Life- Cycle Analysis of the Conversion of NAG into 3A5AF, 5-HMF and Biochar

Life-cycle analysis (LCA) is a tool to measure and predict the environmental impact of a product or process over its entire life cycle. A life cycle is a holistic approach that requires the environmental impacts of raw material production, manufacturing/processing, distribution, use and disposal to be taken into consideration to assess the sustainability of a process. This is often described as a cradle-to-grave analysis for it takes into consideration from the extraction of the raw material to the fate of the material at the end of its lifetime (disposal); although the phrase cradle-to-cradle can be used if the product is recycled or converted into energy at the end of its life.

Typically a LCA impact assessment is used to quantify the environmental impacts of the following (101): 1) Abiotic depletion - the depletion of non-renewable sources relative to the reserves of that resource, 2) Acidification potential - acid releases in terms of their potential to form H_3O^+ relative to SO_2, 3) Aquatic toxicity - the sum of the toxicity factors of a certain emission multiplied by the amount, 4) Eutrophication potential - potential to cause over-fertilization of water and soil, which can cause uncontrolled growth of algae due to PO_4^{3-}, NH_4^+ and NO_x, 5) Global warming potential (GWP) - a value based on known global warming factors for gases such as N_2O, CH_4, various organic solvents, expressed relative to CO_2, 6) Human toxicity potential - total potential is the sum of the different releases in different media (soil, water, air), 7) Ozone depletion potential - this is calculated in a similar manner to GWP and is expressed relative to trichlorofluoromethane (CFC-11), and 8) Photochemical oxidant creation potential - the measurement of the process to generate smog and is relative to ethene.

The research presented in this thesis was inspired by the principles of Green Chemistry and was intended to have minimal negative environmental impacts. The conversion of NAG to 3A5AF had minimal potential to induce eutrophication, release global warming or ozone depleting gases as well as photochemical oxidants. The boric acid and sodium chloride used as catalytic additives are derived from minerals that are non-renewable but can be recycled. There is however potential for aquatic and human toxicity when using boric acid but the effects were minimized by working in a closed system under dilute conditions.

Chemical transformations that are performed on dilute feedstock solutions are only feasible if the product is of very high value. For the extraction of as much valuable furans as economically feasible the use of boric acid and sodium chloride are advocated. The energy to heat and move this aqueous solution around an industrial facility could be derived from renewable energy but the economics of that are largely determined by geography. The window of time between when 3A5AF can be generated and when it begins to degrade is larger under low pressure conditions than higher ones and as a result it takes up to 10 minutes compared to 39 seconds; as in the recent work on Chromogen III formation.

A preliminary LCA for the conversion of NAG to 3A5AF was performed to highlight the relative mild nature of this process. The raw materials are either renewable or can be recycled via minerals while the desired products are high value and can be incorporated into sustainable or eco- technology (biofuels, biomaterials, soil remediation, water purification). The major drawback of the process presented in this thesis is the amount of energy required to heat 100 mL of water to 220 ^{o}C for 10 minutes. Since the boric acid and sodium chloride catalytic system has demonstrated high activity for selective dehydration of NAG at this temperature, then it would

be advantageous to source the electricity from a renewable source. To assist in the carbon cycle, the application of biochar for soil remediation would be necessary as well as reducing the overall carbon footprint of the process.

Inputs	System Boundary	Outputs
Raw materials: NAG, NaCl, $B(OH)_3$, H_2O, EtOAc Thermal energy for reaction: NL Hydro mostly but Holyrood thermal electric generating station*	<u>Raw Material Acquisition</u> A) Processing crustaceans to isolate chitin then depolymerize it into NAG. B) Mining the NaCl and B(OH)3 and purifying them from minerals. C) Using activated carbon (AC) filtration to purify the distilled water. D) Producing EtOAc from ethanol and acetic acid (which can both be derived from renewables)	Emissions to air, water and land: A) Creating alkaline waste water that must be treated and producing mineral by-products from the shells. B) The machines that dig up land to mine for minerals would release GHGs and mining waste must be treated to prevent land and water contamination. C) Producing AC from biomass and using energy to distill the water. D) Fermentation to produce ethanol and acetic acid as a pulp & paper facility by-product.

Inputs	System Boundary	Outputs
Water, ice cubes, electrical energy and EtOAc	Processing Using a 300 mL high pressure vessel up to 220 ^{o}C for 10 - 60 minutes requires energy to heat 100 - 200 mL of water. Ice bath to quench the vessel is required as well as energy to concentrate a series of extractions from the water-EtOAc mixture.	Products (3A5AF, 5-HMF) and co-products (biochar) are isolated through liquid-liquid extraction and filtration.
Ethanol, acetone, soap, water and methanol	Use/Reuse/Maintenance The reaction vessel is cleaned with ethanol and acetone as well as sonicated in soap and water. Samples are stored in glass vials and analyzed on a GC-MS in methanol. Water recycling study proved that high yields and selectivity can be achieved up to 3 cycles. Ethyl acetate is recycled from rotary evaporator and re-used for successive extractions.	Waste ethanol, acetone, water and methanol

Inputs	System Boundary	Outputs
Waste ethanol, acetone, water and methanol	Recycling/Waste Management Recycle: organic solvents (ethanol, acetone and methanol) are collected and recycle within reason of contamination. Spent reaction water is recycled for further dehydration reactions. Disposal: eventual treatment of spent water with dissolved boric acids, NaCl and NAG-derived organics.	Waste generated: water with dissolved $B(OH)_3$, NaCl, NAG-derived organics, ethyl acetate

Table 4.4 : Life-Cycle Analysis of NAG Conversion to 3A5AF, 5-HMF and Biochar

4.1.5 : Ecosystems and Soil Remediation

The research presented in this thesis directly relates to fishery [chitin] waste utilization, which provides a low-cost feedstock for future ocean-based biorefineries. By approaching this process in a holistic manner, the valorization of co-products can be achieved via applications in biofuels (5-HMF), bioplastics (3A5AF) and gas selective membranes (biochar-derived materials). When ecology is included into the processing equation, this green process may be considered an Ecotechnology. Ecotechnology is the integration of ecosystem consideration into the development of sustainable technologies. A main environmental benefit of this research is the diversion of renewable waste from a special landfill or being dumped in the ocean. Due to the short time, good yields and low cost of chemicals; this process could be developed cooperatively amongst regional fish processing facilities. Since this research was conducted in Atlantic Canada, there are a large number of fish processing facilities that could benefit from the waste-to-value ecotechnology to supplement revenues.

With the global population expected to rise to 10 billion before the turn of the century it is imperative that societies produce enough food that is rich in nutrients and doesn't cause pollution (102). Synthetic fertilizers are causing algal blooms throughout the world; these blooms lead to dead zones where fish cannot survive due to lack of oxygen. Biochar for soil remediation can play an essential part of sustainable farming and through tailoring can contain a variety of nutrients from a natural source. The combined benefits from healthier soil and locking atmospheric carbon up will be shared by future generations of people, plants and animals. Biochar has tremendous potential as a carbon sequestration tool to assist in mitigating climate change. The boost in agricultural productivity of soil that is mixed with biochar makes it a

feasible replacement for synthetic fertilizers that increasingly wreck havoc on the environment (103). Biochar has the capability to reduce nutrient leaching while aiding in the retention of water; which better prepares farmers for drought. Since it is the largest non-furan product of this research, the utilization of it can increase the sustainability of this ecotechnology.

Chapter 5. Conclusion

5.1.0 : Relative Benefits of this Research

These initial results were encouraging and are a good example of how versatile amino-carbohydrates are and highlights their potential to replace petroleum based chemicals as the building blocks of our industrial world. Historically, in scientific research the use of borate solutions for the conversion of carbohydrates was performed for several hours at temperatures above 100 ^{o}C. Typically these reactions produced an array of compounds and due to the severity required a neutralization step. The water produced from this particular carbohydrate research did not require that step for the pH was approximately neutral post-reaction. This supported the assumption that the boron is incorporated into the biochar and that is beneficial for soil remediation. On a regular occurrence the inside of the Parr (300 mL) reactor would become blackened with caramelized sugar, residue and biochar. This proves that the environment is not fiercely corrosive due to the low amount of boric acid used and the oxygenated char by-product. The chemistry at work is similar to what occurs in the food science industry; which is why the modern work on NAG degradation at elevated temperature was published in agricultural journals in the 1980s and 1990s. These studies were generally on the pyrolysis of the dry compound with additives to simulate baking chemistry. By employing water as the reaction medium we are preventing the heating of volatile organic solvents and the utilization of toxic ionic liquid precursors. When the reactions were being worked up through successive ethyl acetate extractions there was the distinct acetic acid odor coming from crude that was high in 5-HMF.

Acetic acid is another valuable chemical that can be used industrially or to generate electricity via a fuel cell.

5.1.1 : Benefits of Biotransformations

Employing baker's yeast for the synthesis of chiral alcohols would be in agreement with the opinion of Nobel Prize (Chemistry) winner Ryōji Noyori. Dr. Noyori is passionate about asymmetric synthesis and the principles of Green Chemistry (104). During his keynote address at the Second International Conference on Green and Sustainable Chemistry (2005), he encouraged scientists to be more politically active by influencing governments to work together on sustainability. Biotransformations have enormous potential for industrial chemistry in the area of energy and materials production.

Whole cell reactions have the robust benefit over pure enzymes catalyzed reactions but the latter can take place at a high rate (mass transfer and catalytic site saturation). Cross over reactions from the food science industry into the field of Green Chemistry can inspire and initiate innovation to create sustainable products. The influence biotechnology has on the daily operations of (industrial) society will continue to grow and can increase overall sustainability (compared to fossil fuels). Further studies with baker's yeast will be conducted on platform chemicals with the goal of being incorporated into a hybrid chemical-enzymatic process.

5.1.2 : The Intersection of Technology with Biology

The rise of the biorefinery (oceanic and lignocellulosic) in the 21st century is essential to revitalize the forestry, agriculture and aquaculture industries as well as shift away from

petroleum refineries that dominate the energy and polymer industries. The 20th century saw the integration of technology with creative thinking and in some cases (e.g nuclear weapons) resulted in incredible destructive powers. Materials and energy are what drive our global economies and the intersection of technology with biology can provide this in the most sustainable manner.

The proof-of-concept study presented in this thesis on the biotransformations of furans, was successful for the production of bioplastic precursors and provides incentive for continued use of baker's yeast. This type of reaction is possible through strictly chemical means although yeast are more environmentally benign and given an energy source can regenerate their enzymes and co-factors. It is this regeneration or "living catalyst" approach to biorefining that holds great potential in hybrid systems and boosts sustainability. Future work with common yeast or other whole cell microorganisms (bacteria, fungi) would focus on developing a process where the main product is continuously extracted (a flow reactor system).

The surface functional groups on the carbon residue by-product can be tailored by the amount of additives in the solution, temperature and time. The retention of macro and micro nutrients in the residue dictates that the utilization of biochar for soil remediation would help improve soil properties and effectively lock carbon in the ground. To better determine the ideal applications for all the products; further NMR characterization of all furan derivatives would be required to carry on this project as well as extensive elemental/morphological analysis of insoluble biochar.

5.1.3 : The Role of Boron and Polyborates in Future Research

Future research that builds on these findings will centre on developing a whole process to convert fishing industry by-products into advanced biofuels and novel plastics. Employing enzymes in water to depolymerize chitinous biomass into N-acetyl-D-glucosamine would be the first step in this process. Chemical and mechanical depolymerization are also viable methods to produce NAG from chitin/chitosan. To further enhance the green nature of this research, a mineral form of boron [polyborates such as: kernite ($Na_2B_4O_6(OH)_3 \cdot 3(H_2O)$), borax ($Na_2B_4O_5(OH)_4 \cdot 8(H_2O)$ or boracite ($Mg_3B_7O_{13}Cl$)] would be employed as the catalytic reagent(s). Kernite or borax can react with hydrochloric acid to form boric acid and sodium chloride in a 2:1 ratio; which in this thesis is the optimal ratio found to produce superior yields of 3A5AF from NAG. Although HCl is not an environmentally friendly chemical it is consumed in the process ($Na_2B_4O_5(OH)_4*8H_2O + 2HCl \rightarrow 4H_3BO_3 + 2NaCl + 5H_2O$). Due to the presence of chloride in boracite, it may be worth investigating this mineral for the catalytic dehydration of NAG in subcritical water.

Sigma-Aldrich offers a few different types of borax and their prices is as follows: 1) (> 99.5%) borax decahydrate $125/2.5 kg, 2) sodium tetraborate (99%) $63/500 g and 3) borax, anhydrous (98%) $361/1 kg. In comparison to 99.5% borax bought at the local grocery store for $6/2 kg for the purpose of boosting the effectiveness of laundry detergent. It would be remarkable to include everyday household cleaning items into laboratory research for the purpose of clean reactions. Green Chemistry principles would vote for the laundry detergent booster because of the low cost and could make a conversion process more economic viable. Another option would be to use seawater as a source of ions; although the variation of ions

would greatly depend on the following: i) which sea the water came from, ii) what season the water was taken, and iii) the depth (relative to shoreline) the water was taken.

An important aspect of the future research based on this thesis is eluding to the catalytically active boric acid species present under different conditions (eg temperature, concentration, time, salinity). One of the goals of the future research is to discovery which polyborate species has the highest catalytic activity to convert NAG in 3A5AF and apply this to other carbohydrates as well as biological polymers. It is interesting to note that the ideal boric acid species for dehydration of NAG could be formed in aqueous solutions through dehydration (Figure 5.1). Metaboric acid is formed by the dehydration of boric acid and occurs above the melting point of the latter acid (170 ^{o}C). This dehydrated form then undergoes trimerization to form a 6 membered ring metaboric acid. Since this reaction takes place in an aqueous environment at elevated temperatures there is an equilibrium between the monoclinic and orthorhombic metaboric acid that shifts between a molecule and an polyborate (Figure 5.2).

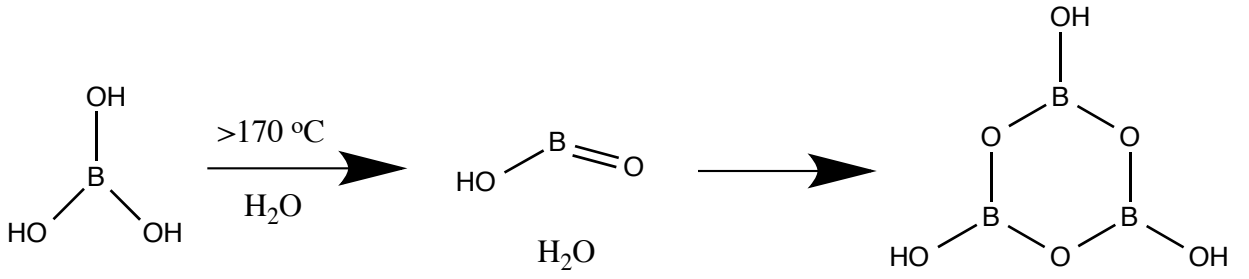


Figure 5.1 : The Dehydration of Boric Acid into the Stable Trimer of Metaboric Acid

Above 170 ^{o}C, the formation of a polyborate is possible from orthorhombic metaboric acid. In the monoclinic form, the metaboric acid has a higher melting point and different

solubility than the orthorhombic form. If the polyborate is catalytically active for dehydrating NAG then a possible mechanism could involve a conveyor belt in which a series of metaboric acids perform the steps to form 3A5AF. Reactions conducted at higher temperatures can allow for other boric acid species to form that could behave similarly or differently in terms of catalytic ability.

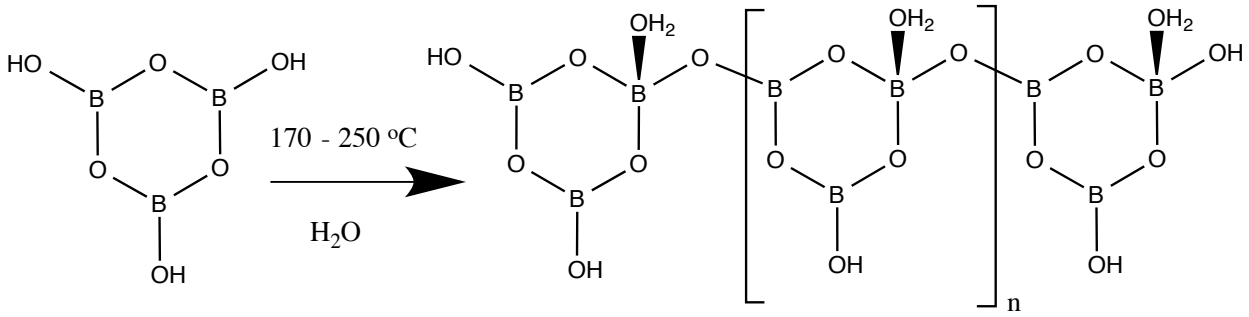
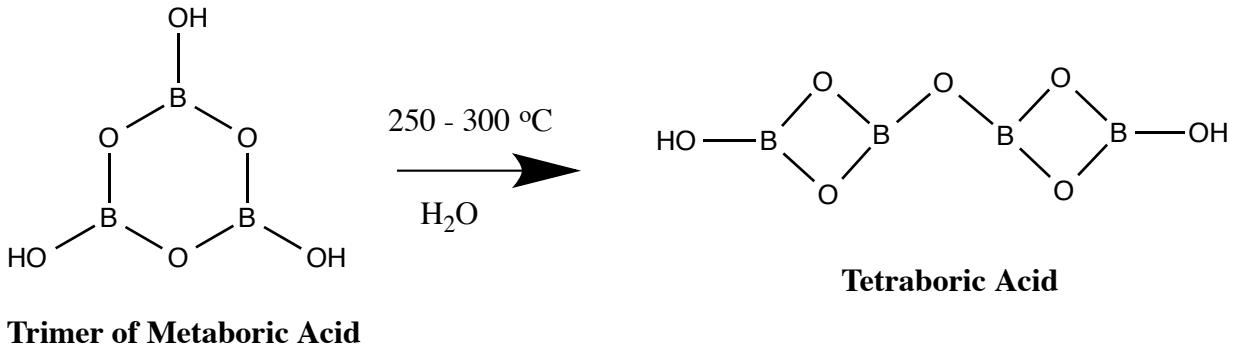


Figure 5.2 : The Formation of the Polyborate (Monoclinic) Metaboric Acid

When temperature increases to above 250 °C, the trimer of metaboric acid can further dehydrate into tetraboric acid (Figure 5.3). Tetraboric acid is naturally found in boron minerals such as borax (sodium tetraborate) and can function as a water-softening (chelating) agent to remove calcium and magnesium by releasing sodium into the water. The research presented in this thesis did not work at temperatures higher than 220 °C so this polyborate was not of immediate concern. Future work on the liquefaction and/or reforming of chitin/chitosan into 3A5AF will be conducted at temperatures between 250 - 350 °C; where the catalytic abilities of tetraboric acid would relevant. It is interesting to note that tetraboric acid has the greatest amount of hydrogen bond acceptor oxygen atoms (relative to metaboric acid and boric acid). This

chemical trait would allow for interactions with larger species in solution and has potential as a catalyst for reforming chitin into 3A5AF.



Trimer of Metaboric Acid

Tetraboric Acid

Figure 5.3 : Dehydration of Metaboric Acid into Tetraboric Acid at Elevated Temperature

5.1.4 : Optimization of NAG Conversion to 3A5AF and 5-HMF

The optimization of the main process described in this thesis led to the conclusion that 7.5 wt% solutions of NAG are most suited for selective conversion. This research study has demonstrated that 3A5AF and 5-HMF can be obtained in good molar yields (>60 % 3A5AF/ >60% 5-HMF) with high selectivity (>90% 3A5AF/ >80% 5-HMF) from NAG. These results show the benefits of incorporating green principles into the chemical conversion of amino-carbohydrates. It takes approximately 27 minutes for the reactor to equilibrate at 180 °C and 35 minutes at 220 °C; the reaction lasts 10 minutes then it is quenched in an ice bath for 30 - 45 minutes. In a batch [reactor] environment a total time of 90 minutes is relatively fast but this could be vastly reduced under continuous flow conditions. Employing low-cost reagents ($B(OH)_3$, NaCl, H_2O) gives this approach an advantage over more expensive solvents (organic, ionic liquid).

The 3A5AF selectivity remains dominant through the experiments that take place between 10 and 20 minutes. The formation of 3A5AF in water took place more readily than in organic solvents due to higher mass transfer properties of N-acetyl-D-glucosamine, boric acid and sodium chloride when in an aqueous environment. Under certain conditions (220 ^{o}C, 40 minutes) our results show that 5-HMF is the major product. As the reaction progressed there was an increasing amount of hydronium ions formed due to boric acid complexation with the hydroxyl groups of the sugar molecule. This has the effect of increasing by-product formation via deamination reactions. The best yield (70.0 mol% / 93.4% selectivity) for 3A5AF occurred under the following conditions: 220 ^{o}C, 5 wt% NAG, 20 minutes and 2:2 mole ratios of NaCl and $B(OH)_3$. A 75.4 mol% / 90.6% selectivity yield for 3A5AF was obtained under the following conditions: 220 ^{o}C, 7.5 wt% NAG, 10 minutes and 1:2 mole ratios of NaCl and $B(OH)_3$ relative to NAG. Another high yield (67.8 mol% / 95.7% selectivity) occurred after the 3rd recycling of water with addition boric acid at : 220 ^{o}C, 7.5 wt% NAG and 10 minutes. The best yield (69.5 mol% / 86.5% selectivity) for 5-HMF occurred at : 220 ^{o}C, 7.5 wt% NAG, 40 min and 2:2 mole ratio (relative to NAG) of NaCl & $B(OH)_3$. It is interesting to note that the highest yield of 5-HMF has 10.2 mol% of 3A5AF present, which proves that despite the more acidic environment the retention of the acetamido group can occur after 40 minutes. Boric acid and sodium chloride are cost competitive reagents that don't present a large danger to the environment (in dilute solutions) and boost the yield of 3A5AF and 5-HMF considerably when compared to additive-free reactions.

The reactions that achieved the highest selectivity towards 3A5AF were those from the water recycling study. When more boric acid is added to the water from the first cycle, the yields

significantly improve whereas additional sodium chloride hinders the conversion. The initial concentration of boric acid in water is 4.2 wt% from the first cycle with an additional 4.2 wt% added for the second and third cycle. Theoretically this can bring the boric acid concentration up to 12.6 wt% in the aqueous solution for the third cycle while sodium chloride levels would be below 3.96 wt% because there was no additional salt added. It is possible for the cyclic metaboric acid species that forms above 170 ^{o}C to react with water and form an open ring structure (Figure 5.4). Given the increase in boric acid concentration, it is possible for the open ring form to undergo a condensation reaction to yield a dimer. This dimer would have 8 hydroxyl groups in total and could facilitate the dehydration of NAG to 3A5AF in a more selective manner. This dimer species could be responsible for the high (>95%) selectivity of 3A5AF after the third cycle (of water recycling with additional boric acid added) due to it having two areas of the compound that could doubly coordinate to NAG. Since the trimer of metaboric acid forms above 170 ^{o}C it is possible that at 220 ^{o}C (where high selectivity of 3A5AF and 5-HMF occur) the species the open ring form where it is more catalytically active (than the trimer).

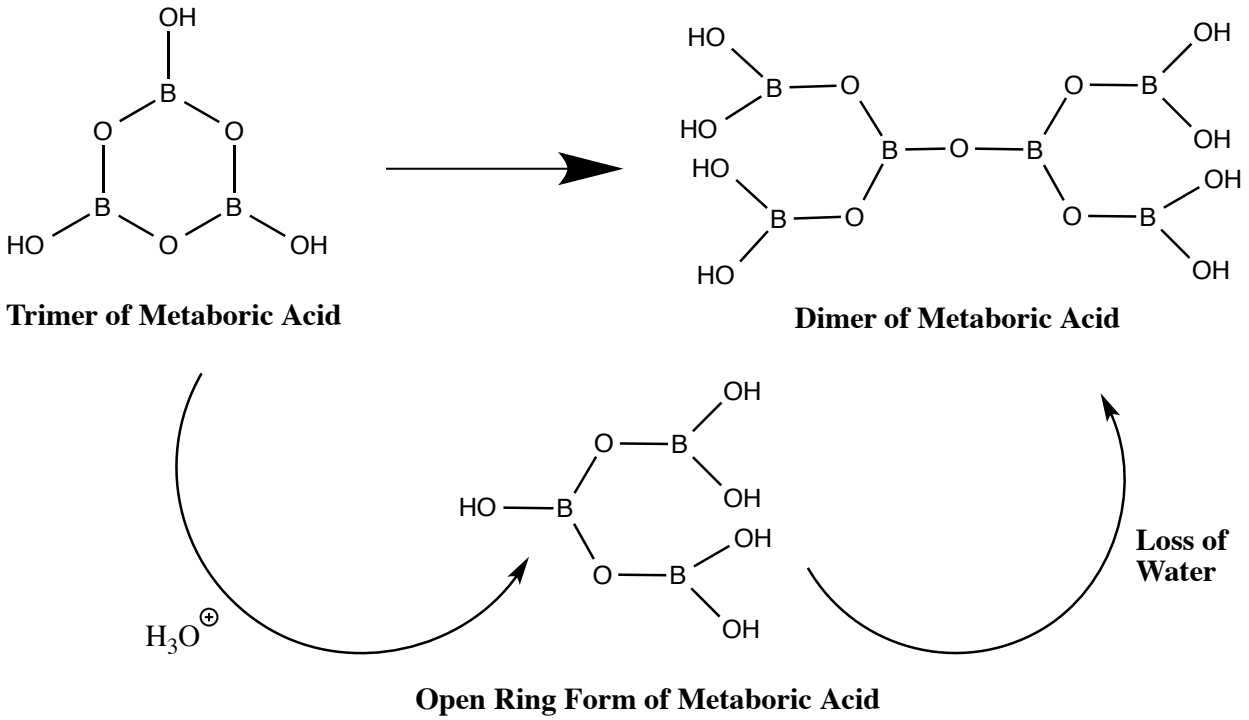


Figure 5.4 : Possible Dimer of the Open Ring Form of Metaboric Acid

5.1.5 : Research Goals Achieved

The aqueous dehydration of N-acetyl-D-glucosamine in subcritical water was successfully achieved to produce 3-acetamido-5-acetylfuran (3A5AF), 5-hydroxymethylfurfural (5-HMF) and biochar. The catalytic process optimized in this research was performed in a more desirable manner (increased yields and selectivity) than autocatalytic reactions in the literature and emphasized green methodology (water recycling and environmentally-benign reagents). The results are an improvement from previous research on 3A5AF formation in organic solvent and/ or IL due to the slightly higher (5 - 10 mol%) yields and lower sodium chloride used (50% reduction). The catalytic system in this research proved successful and the synergy between boric acid and sodium chloride was demonstrated for amino-carbohydrate conversion. Important

benefits from the production of 3A5AF include its high value (relative to starting material), multiple functional groups to manipulate and reduction in CO_2 in the atmosphere via burying it's by-product (biochar).

The research goals of this project were as follows: 1) utilize a waste/low-value feedstock, 2) achieve high selectivity and conversion, 3) employ or produce chemicals that are non-toxic to human health and the environment, 4) demonstrate water as a suitable dehydration solvent for carbohydrates, 5) achieve good yields rapidly at moderate temperatures, 6) prove the feasibility of amino-carbohydrates for renewable amine production and 7) re-use the solvent with minimal treatment. These goals were primarily achieved by: 1) using N-acetyl-D-glucosamine as the feedstock, which was derived from the fishery by-product: crustacean exoskeletons (crab, shrimp and lobster), 2) obtaining 90 - 95% selectivity with a 65 - 75 mol% yield for 3A5AF, 3) using environmentally benign reagents (dilute aqueous solutions of NAG, NaCl and boric acid) and producing chemicals that can form during the cooking of food, 4) obtained 3A5AF yields comparable to organic solvents or ILs with water, 5) 10 minute reactions suitable at 180 ^{o}C for high 3A5AF production, 6) demonstrated NAG can be employed as a suitable feedstock for renewable amide di-substituted furans and 7) observed enhanced selectivity and molar yields with recycled water.

5.1.6 : A Green Future

The influence of the acetamido functionality in NAG was examined in an attempt to see the possible advantages of amino-carbohydrate utilization. The experimental data consistently indicates that the acetyl group of the secondary amine acts as a protecting group. This suggests

Nature has designed a sugar molecule with a protected nitrogen that scientists and engineers can harness. Nitrogen is as essential for life as it is for high tech industries.

The research presented in this thesis represent the commitment to Green Chemistry that takes place at the Memorial University of Newfoundland. The main product (3-acetamido-5-acetylfuran) is a versatile renewable amide that will continue to be evaluated for its potential as a precursor for novel polymers and for CO_2 capture and separation of gas mixtures. This aqueous based process is built on the previous work in our group and when compared to recent Chromogen research demonstrates superior yields and selectivity are obtained with boric acid and sodium chloride. The green methodology presented in this thesis would compliment well with regional fishing industries in Atlantic Canada and other traditional aqua-cultural regions in the world. It is the sustainable goal of the Kerton group to continue with research in the area of amino-carbohydrates conversion for the production of novel materials.

REFERENCES

1) http://www.theage.com.au/world/two-years-on-burma-struggles-to-recover-from-cyclone-nargis-20100808-11qbg.html (Accessed July 10, 2014)

2) http://www.usatoday.com/story/news/nation/2013/10/29/sandy-anniversary-facts-devastation/3305985/ (Accessed July 10, 2014)

3) http://climate.nasa.gov/climate_resource_center/24 (Accessed July 10, 2014)

4) http://www.cbc.ca/news/world/indonesia-surpasses-brazil-in-deforestation-1.2691405 (Accessed July 10, 2014)

5) http://www.aljazeera.com/indepth/opinion/2012/10/201210993632838545.html (Accessed July 10, 2014)

6) http://www.cbc.ca/news/canada/10-worst-household-products-for-greenwashing-1.1200620 (Accessed July 10, 2014)

7) http://blog.cifor.org/8929/charred-lands-fertile-grounds-for-sustainable-agriculture-in-kalimantan#.U77DYChUMdI (Accessed July 10, 2014)

8) F. M. Kerton, Y. Liu, K.W. Omari, K. Hawboldt,. *Green Chem*., **2013.** 15, 860 – 871.

9) AMEC Earth & Environmental Limited, Management of Wastes from Atlantic Seafood Processing Operations, Report for Environment Canada Atlantic Region, **2003**.

10) M. Healy, A. Green,A. Healy, *Acta Biotechnol*., **2003**. 23, 151 – 160.

11) P. Kandra, M.M. Challa, H.K.P. Jyothi,. *Appl. Microbiol.Biotechnol.*, **2012.** 93, 17 – 29.

12) H. Sashiwa, S. Fujishima, N. Yamano, N. Kawasaki, A. Nakayama, E. Muraki, S.-I. Aiba,. *Chem. Lett.,* **2001.** 308 – 309.

13) C. Shu, *J. Agric. Food Chem.* **1998**. 46, 1129 − 1131.

14) J. Chen, C. Ho, J. Agric. Food Chem. **1998**. 46, 1971 − 1974.

15) M. Osada, C. Miura, Y. S. Nakagawa, M. Kaihara, M. Nikaido, K. Totani, *Carbohydr. Polym.*, **2013**. 92, 1573 – 1578.

16) M. Ogata, T. Hattori, R. Takeuchi, T. Usui, *Carbohydr. Res*., **2010**. 345, 230 – 234.

17) R. Kuhn, G. Kruger, *Chem. Ber*., **1957**. 90, 264 – 277.

18) M. Osada, K. Kikuta, K. Yoshida, K. Totani, M. Ogata, T. Usui.,. *Green Chem.*, **2013.** 15, 2960 - 2966.

19) M. W. Drover, K. W. Omari, J. N. Murphy, F. M. Kerton., *RSC Advances*, **2012**. 2, 4642 – 4644.

20) K. W. Omari, L. Dodot, F. M. Kerton., *ChemSusChem*, **2012**. 5, 1767 - 1772.

21) G. Yong, Y. Zhang, J. Y. Ying, *Angew. Chem., Int. Ed*., **2008**. 47, 9345 - 9348.

22) X. Qi, M. Watanabe, T. M. Aida, R. L. Smith, Jr., *Green Chem*., **2008**. 10, 799 - 805.

23) T. S. Hansen, J. M. Woodley, A. Riisager, *Carbohydr. Res*., **2009**. 344, 2568 - 2572.

24) F. M. Kerton, Alternative Solvents for Green Chemistry, RSC Publishing, Cambridge, **2009**.

25) T. Buntara, S. Noel, P. H. Phua, I. Melian-Cabrera, J. G. de Vries, H. J. Heeres, *Angew. Chem., Int. Ed.*, **2011**. 50, 7083 - 7087.

26) J. Chen, M. Wang, C. Ho, *J. Agric. Food Chem*., **1998**. 46, 3207 - 3209.

27) R. A. Franich, S. J. Goodin, *J. Anal. Appl. Pyrolysis*, **1984**. 7, 91 - 100.

28) K. W. Omari, J. E. Besaw, F. M. Kerton, *Green Chem*., **2012**. 14, 1480 - 1487.

29) Y. Wang, C. Pedersen, M. Deng, T. Qiao, Y., Hou, *Bioresource Technology.,* **2013**. 143, 384 – 390.

30) T. S. Deng, X. J. Cui, Y. Q. Qi, Y. X. Wang, X. L. Hou, Y. L. Zhu, *Chem. Commun*. **2012.** 48, 5494 – 5496.

31) A. J. Varma, S. V. Deshpande, J. F. Kennedy, *Carbohydr. Polym*., **2004**. 55, 77 – 93.

32) A. Gamage, F. Shahidi, *Food Chem*. **2007**. 104, 989 – 996.

33) F. Jiang, Q. J. Zhu, D. Ma, X. M. Liu, X. W. Han, *J. Mol. Catal. A Chem*. **2011**. 334, 8 – 12.

34) S. Hansen, J. Mielby, A. Riisager, *Green Chem*., **2011**. 13, 109 – 114.

35) L. Cottier, G. Descotes, *Trends in Heterocycl. Chem*., **1991**. 2, 233 - 248.

36) R. M. Musau, R. M. Munavu, *Biomass,* **1987**. 13, 67 - 74.

37) Y. Roman-Leshkov, J. N. Chheda, J. A. Dumesic, *Science*, **2006**. 312, 1933 - 1937.

38) Y. Román-Leshkov, J. A. Dumesic, *Top. Catal*., **2009**. 52, 297 - 303.

39) B. Li, P. A. Relue, S. Varanasi, *Green Chem*., **2012**. 14, 2436 – 2444.

40) B. Li, S. Varanasi, P. A. Relue, *Green Chem*., **2013**. 15, 2149 – 2157.

41) H. B. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**. 316,1597 – 1600.

42) D. H. Lukamto, P. Wang, Teck-Peng Loh., *Asian J. Org. Chem*. **2013**. 2, 947 – 951.

43) E. A. Khokhlova, V. V. Kachala, V. P. Ananikov, *ChemSusChem* **2012**. 5, 783 – 789.

44) T. Ståhlberg, S. Rodriguez-Rodriguez, P. Fristrup, A. Riisager, *Chem. Eur. J*. **2011**. 17, 1456 – 1464.

45) T. Ståhlberg, W. J. Fu, J. M. Woodley, A. Riisager, *ChemSusChem* **2011**. 4, 451 – 458.

46) D. G. Hall in Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine, Wiley-VCH, Weinheim, **2005**.

47) J. M. Sugihara, C. M. Bowman, *J. Am. Chem. Soc*. **1958**. 80, 2443 – 2446.

48) S. Subbiah, S.P. Simeonov, J.M.S.S. Esperanca, L.P.N.Rebelo and C.A.M. Afonso., *Green Chem.*, **2013**. 15, 2849 - 2853.

49) British Petroleum Co., Process for production of furfural and 5-(hydroxymethyl)-furfural and corresponding hydrogenated derivatives, France, 2556344 14, **1985**. June.

50) A. Gandini, *ACS Symp. Ser*., **1990**. 433, 195 - 208.

51) (a) A. Gandini, M. N. Belgacem, *Prog. Polym. Sci*., **1997**. 22, 1203 - 1379 (b) A. Gandini, Green Chem., **2011**. 13, 1061 - 1083

52) (a) C. Moreau, M. N. Belgacem, A. Gandini, Top. Catal., **2004**. 27, 11 - 30. (b) S. Dutta, S. De , B. Saha, *ChemPlusChem,* **2012**. 77, 259 - 272. (c) T. Buntara, S. Noel, P. H. Phua, I. M-Cabrera, J. G. de Vries, H. J. Heeres, *Top. Catal.*, **2012.** 55, 612 - 619.

53) (a) A. Faury, A. Gaset, . P. Gorrichon, *Inf. Chim.*, **1981**. 214, 203 - 209. (b) V. Schiavo, G. Descotes, J. Mentech, Bull. *Soc. Chim. Fr*., **1991**. 704 - 711. (c) G. C. A. Luijkx, N. P. M. Huck, H. V. Bekkum, F. V. Rantwijk, L. Maat, Heterocycles, **2009**. 77, 1037 - 1044. (d) M. Chidambaram, A. T. Bell, *Green Chem*., **2009**. 12, 1253 - 1262.

54) (a) A. Villa, M. Schiavoni, S. Campisi, G. M. Veith, L. Prati, *ChemSusChem*, **2013**. 6, 609 – 612. (b) M. Krystof, M. Péréz-Sánchez, P. Domínguez de Maria, *ChemSusChem*, **2013**. 6, 826 – 830.

55) (a) J. J. Blanksma, *Recl. Trav. Chim. Pays-Bas*, **1910**. 29, 403 - 406. (b) J. A. Middendorp, *Recl. Trav. Chim. Pays-Bas*, **1919**. 38, 1 - 71.

56) E. S. Kang, D. W. Chae, B. Kim, Y. G. Kim, *J. Ind. Eng. Chem*., **2012**. 18, 174 - 177.

57) P. M. Grande, C. Bergs, d. M. P. Dominguez, *ChemSusChem*, **2012**. 5, 1203 – 1206.

58) R. Huang, W. Qi, R. Su, Z. He, *Chem. Commun*., **2010**. 46, 1115 – 1117.

59) J. Howarth, P. James and J. Dai., *Tetrahedron Letters*., **2001**. 42, 7517 – 7519.

60) Katyar, S. S. De Tapas, K. *Biochem. Ind*. **1990**. 20, 1127 - 1135.

61) L. Y. Jayasinghe, A. J. Smallridge, M. A. Trewhella, *Tetrahedron Lett.* **1993.** 34, 3949 - 3950.

62) A. Wolfson, C. Dlugy , D. Tavor., *Org. Commun*., **2013.** 6, 1 - 11.

63) B. Cornils, W. A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds. Wiley-VCH, Weinheim, **2002**.

64) R. A. Sheldon, Chirotechnology, Marcel Dekker, New York, **1993**.

65) M. Beller, C. Bolm, Transition Metals for Organic Synthesis, Building Blocks and Fine Chemicals. Wiley-VCH, Weinheim, **1998**.

66) D. Poncelet, R. Lencki, C. Beaulieu, J. P. Halle, R. Neufeld, *J., Appl. Microbiol Biotechnol*. **1992**. 38, 39 - 45.

67) A. C. Hulst, J. Tramper, K. Van't Riet, J. M. Westerbeek, M., *Biotechnol. Bioeng*. **1985**. 27, 870 - 876.

68) J. Peters, T. Zelinski, M. R. Kula, *Appl. Microbiol. Biotechnol.* **1992**. 38, 334 - 340.

69) T. Haag, T. Arslan, Seebach., *Chimia* **1989**. 43, 351 - 353.

70) C. Medson, A. J. Smallridge, M. A. Trewhella, *Tetrahedron: Asymmetry* **1997**. 8, 1049 - 1054.

71) C., Medson, A. J. Smallridge, M. A. Trewhella, *J. Mol. Catal. B: Enzymatic* **2001**. 11, 897 – 903.

72) E. M. Buque, I. Chin-Joe, A. J. J. Straathof , J. A. Jongejan, J. J. Heijnen, *Enzyme Microb. Technol*. **2002**. 31, 656 – 664.

73) J. W. Lee, B. Hawkins, D.M. Day, D. C. Reicosky., *Energy Environ. Sci.*, **2010**. 3, 1695 – 1700.

74) R. J. Geider, E. H. Delucia, Primary productivity of planet earth: biological determinants and physical constraints in terrestrial and aquatic habitats, Global Change Biology **2001**. 7, 849 – 882.

75) K. C. Das, K. Singh, R. Adolphson, B. Hawkins, R. Oglesby, D. Lakly and D. Day., *Appl. Eng. Agric*., **2010**. 26(1), 137 – 146.

76) D. Day, R. J. Evans, J. W. Lee, D. Reicosky., *Energy*, **2005**. 30, 2558 – 2579.

77) M. J. Antal, M. Gronli., *Ind. Eng. Chem. Res*., **2003**. 42(8), 1619 – 1640.

78) M.-M. Titirici, A. Thomas, M. Antonietti, *J. Mater. Chem*., **2007**. 17, 3412 – 3418.

79) J. A. Macia-Agullo, M. Sevilla, M. A. Diez and A. B. Fuertes, *ChemSusChem*, **2010**. 3, 1352 – 1354.

80) Z. Chen, L. Ma, S. Li, J. Geng, Q. Song, J. Liu, C. Wang, H. Wang, J. Li, Z. Qin,S. Li, *Appl. Surf. Sci.*, **2011**. 257, 8686 – 8691.

81) S. Kubo, I. Tan, R. J. White, M. Antonietti, M.-M. Titirici, *Chem. Mater.*, **2010**. 22, 6590 – 6597.

82) J. A. Libra, K. S. Ro, C. Kammann, A. Funke, N. D. Berge, Y. Neubauer, M.-M. Titirici, C. Fuhner, O. Bens, J. Kern, K.-H. Emmerich, *Biofuels*, **2011**. 2, 89 – 124.

83) M. M. Titirici, M. Antonietti, N. Baccile, *Green Chem*., **2008**. 10, 1204 – 1212.

84) L. Zhao, L.-Z. Fan, M.-Q. Zhou, H. Guan, S. Qiao, M. Antonietti, M.-M. Titirici, *Adv. Mater*., **2010**. 22, 5202 – 5206.

85) N. Baccile, F. Babonneau, B. Thomas and T. Coradin, *J. Mater. Chem*., **2009**. 19, 8537 – 8559.

86) R. Demir-Cakan, Y.-S. Hu, M. Antonietti, J. Maier, M.-M. Titirici, *Chem. Mater.*, **2008**. 20, 1227 – 1229.

87) S. Kubo, I. Tan, R. J. White, M. Antonietti, M.-M. Titirici, *Chem. Mater*., **2010**. 22, 6590 – 6597.

88) F. S. Asghari, H. Yoshida, *Ind. Eng. Chem. Res*., **2007**. 46, 7703 - 7710.

89) J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, *Green Chem*., **2007**. 9, 342 – 350.

90) S. K. R. Patil and C. R. F. Lund, *Energy Fuels*, **2011**, 25, 4745 - 4755.

91) M. Sevilla and A. B. Fuertes, *Carbon*, **2009**, 47, 2281 – 2289.

92) Z. Li, N. Baccile, S. Gross, Z. Yuanjian, W. Wei, S. Yuhan, M. Antonietti, M. M. Titirici, *Carbon*, **2010**. 48, 3778 – 3787.

93) N. Baccile, M. Antonietti and M.-M. Titirici, *ChemSusChem*, **2010**. 3, 246 – 253.

94) C. Zhang, Z. Fu, Y. C Liu, B. Dai, Y. Zou, X. Gong, Y. Wang, X. Deng, H. Wu, Q. Xu, K. R. Steven and D. Yin., *Green Chem*., **2012**. 14, 1928 – 1934.

95) Q. Yan, C. Wan, J. Liu, J. Gao, F. Yu, J. Zhangc and Z. Caid., *Green Chem*., **2013**. 15, 1631 – 1640.

96) A. Liese, K. Seelbach and C. Wandrey, Industrial Biotransformations, Wiley-VCH, Weinheim, **2006**.

97) W. Hummel, in Advances in Biochemical Engineering/ Biotechnology, ed. T. Scheper, Springer, Berlin, **1997**. pp. 145 – 184.

98) W. Kroutil, H. Mang, K. Edegger and K. Faber, *Adv. Synth. Catal.*, **2004**. 346, 125 – 142.

99) W. Kroutil, H. Mang, K. Edegger and K. Faber, *Curr. Opin. Chem. Biol*., **2004**. 8, 120 – 126.

100) A. Gandini, *Polymer Chemistry*, **2010**. 1, 245 - 251.

101) Green Chemistry An Introductory Text: Mike Lancaster, RSC Publishing, 2nd Edition, **2010**. p. 5 - 7.

102) http://blogs.ei.columbia.edu/2013/07/15/world-population-projected-to-cross-11-billion-threshold-in-2100/ (Accessed May 18th, **2014**)

103) http://www.organicvalley.coop/why-organic/synthetic-fertilizers/ (Accessed May 18th, **2014**)

104) http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2001/noyori-lecture.pdf (Accessed May 18th, **2014**)

Appendix A. Supplementary Data

Spectra (Data for 3A5AF obtained from Optimized Reaction with 5-HMF, 5Ac3NH_2F and 3NH_2F data obtained from Product Mixture Spectra)

	3A5AF (S7 and S8)	5HMF (S2 and S3)	3AcNHF	3$NH_2$5F
H-NMR ($CDCl_3$)	2.08 ppm (3H, s, C(7)Me), 2.39 ppm (3H, s, C(8)Me), 7.11 ppm (1H, s, C(3)H), 8.14 ppm (1H, s, C(5)H), 8.45 ppm (1H, s, NH)	4.64 ppm (s, CH2OH), 6.53 ppm (d, CH), 7.22 ppm (d, CH),9.62 ppm (s, CHO).	(-NH_2) 2.78 ppm	(2d, C-H) 7.03 ppm, or 8.09 ppm
C-NMR ($CDCl_3$)	22.66 ppm (C1), 25.82 ppm (C2), 109.69 ppm (C3), 126.40 ppm (C4), 136.14 ppm (C5), 167.92 ppm (CX), 175.66 ppm (C7),187.4 ppm (C8)	57.43 ppm (C-OH), 196.58 ppm (H-C=O)	(C-NH_2) 40.59 ppm or 57.43 ppm 163.64 ppm (amide)	
FT-IR	1660.89 cm^{-1} (C=O amide stretch,C=O ketone stretch), 1376.89 cm^{-1} (C-O-C furan)	1188.71 cm^{-1} (C-O hydroxyl stretch)	(-NH_2) 701.62 cm^{-1} N-H wag	C-H “oop” aromatic 883.29 cm^{-1} or 925.87 cm^{-1}

Table S1 : NMR and FT-IR Identification of the Four Furans

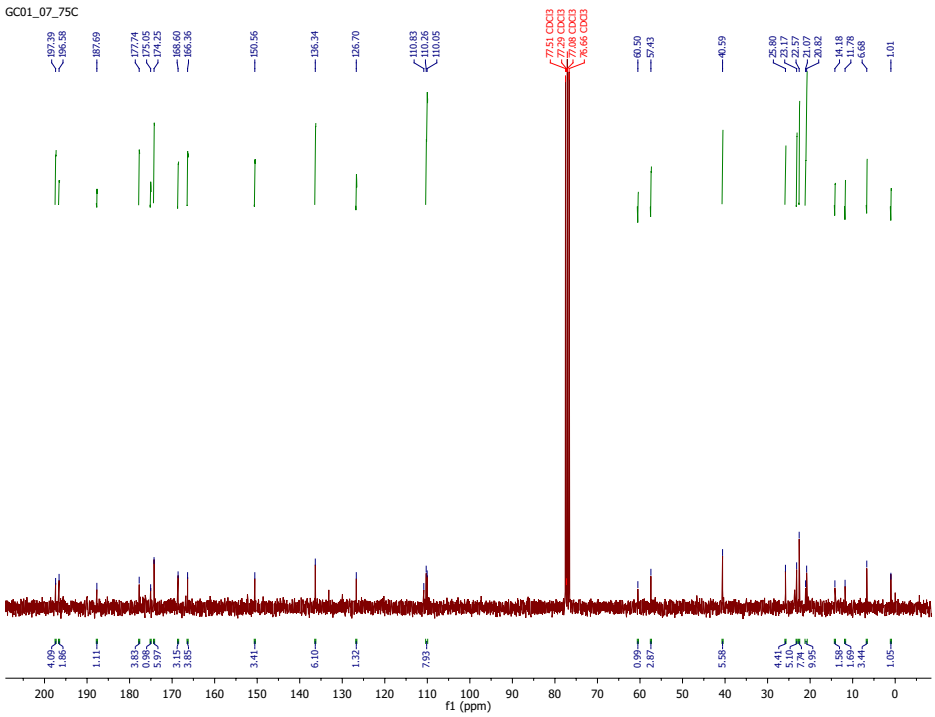


Figure S2: ^{13}C-NMR of Product Mixture

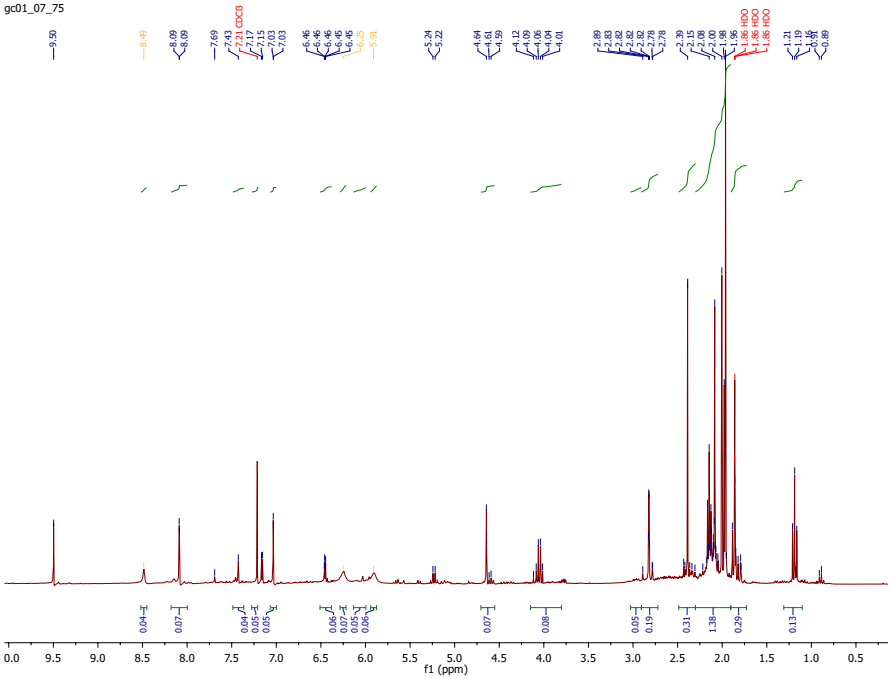


Figure S3: ^{1}H-NMR of Product Mixture

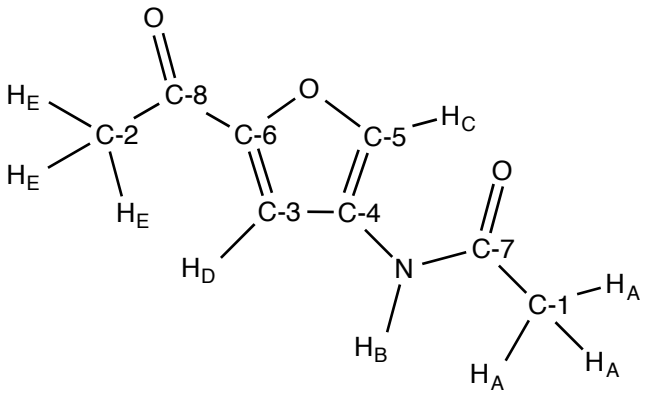


Figure S4 - 3A5AF Labeled for NMR Spectra

^{1}H-NMR (298 K, 500MHz; $CDCl_3$; Me_4Si) 2.05 (3H, s, C(7)Me), 2.40 (3H, s, C(8)Me), 7.07 (1H, s, C(3)H), 8.17 (1H, s, C(5)H) and 8.45 (1H, br s, NH)

^{13}C-NMR (298 K, 300 MHz; $CDCl_3$) 23.3 (C-1), 25.8 (C-2), 109.7 (C-3), 126.4 (C-4), 136.5 (C-5), 151.0 (C-6), 167.9 (C-7) and 187.0 (C-8).

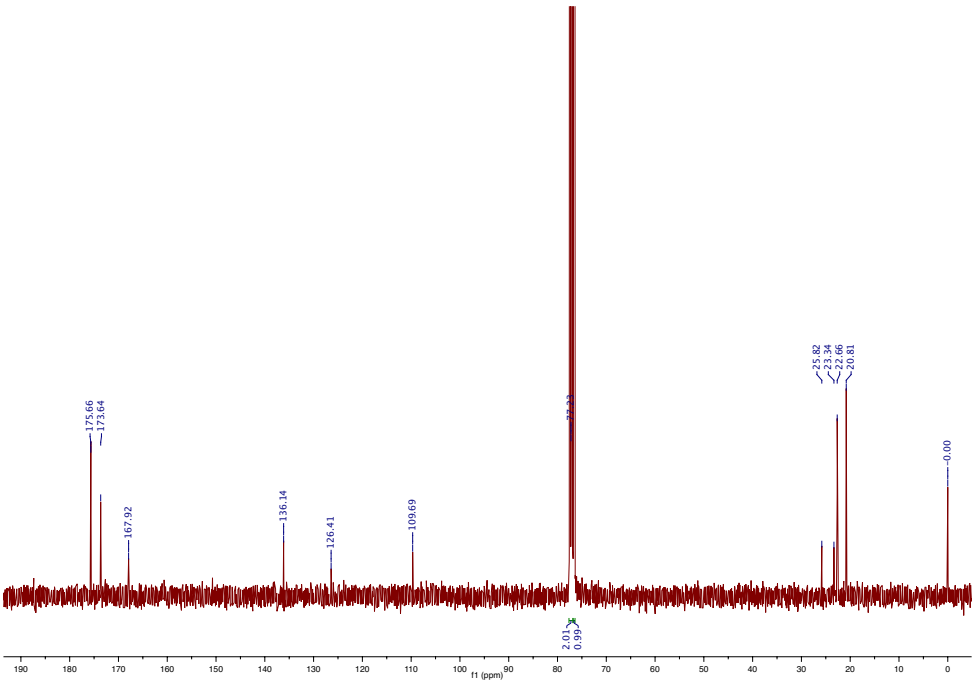


Figure S5 - Overnight ^{13}C-NMR of 3A5AF from Optimized Reaction

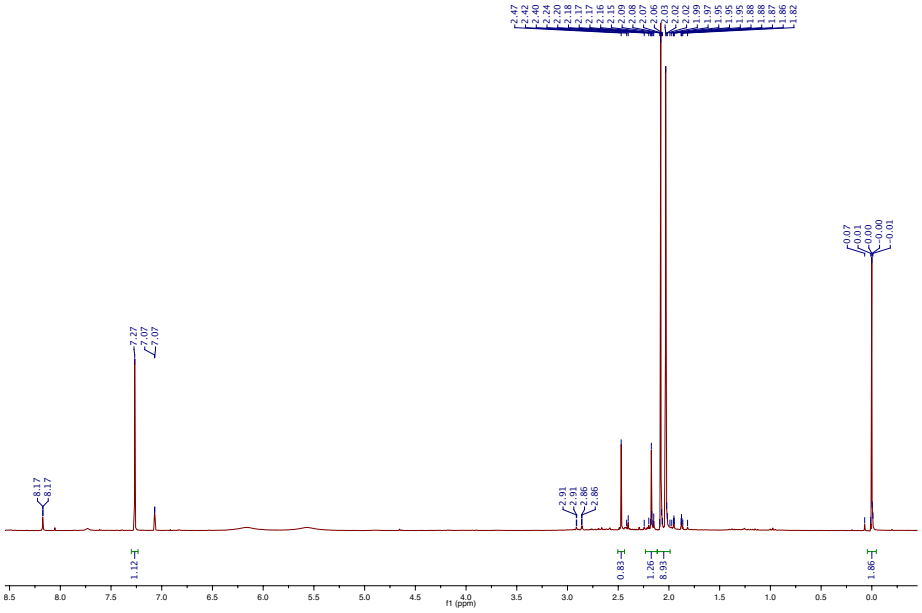


Figure S6 - ^{1}H-NMR of 3A5AF from Optimized Reaction

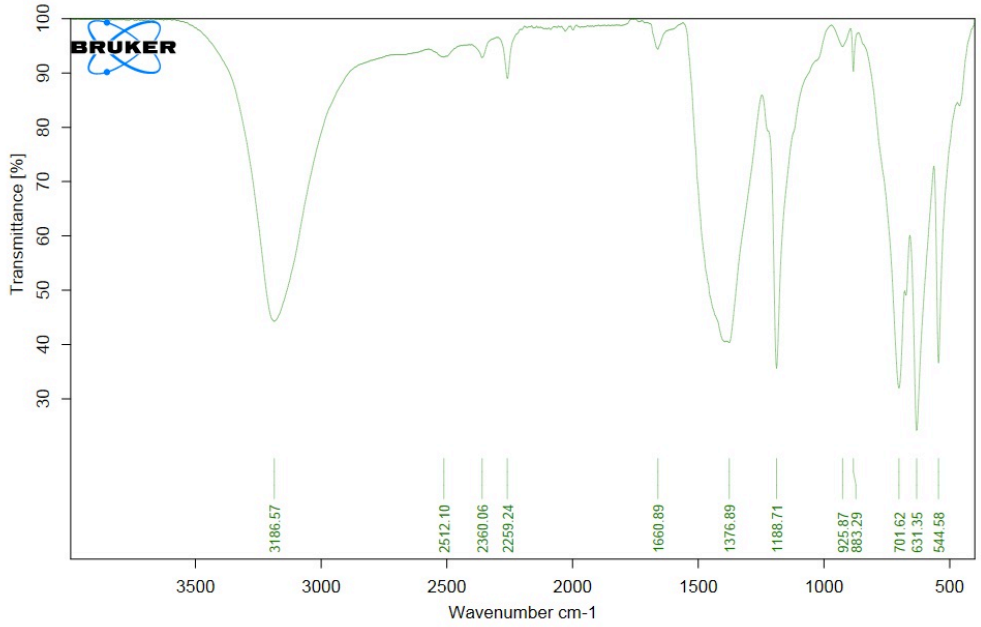


Figure S7: FTIR Spectrum of Product Mixture from Optimized Reaction

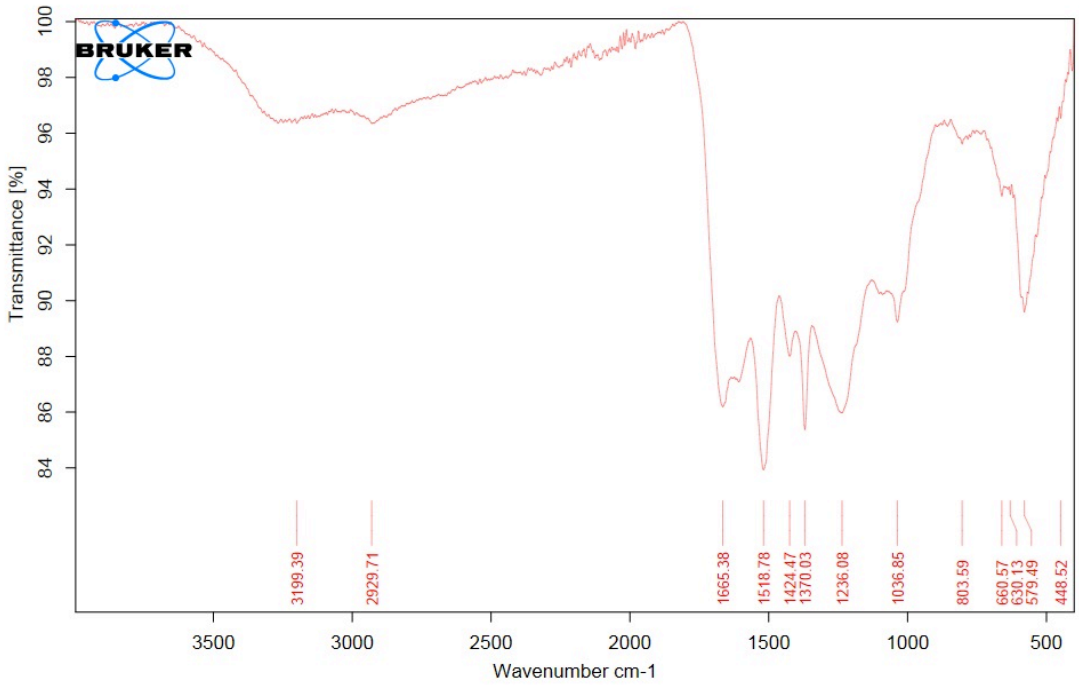


Figure S8: FTIR Spectrum of Biochar from Optimized Reaction

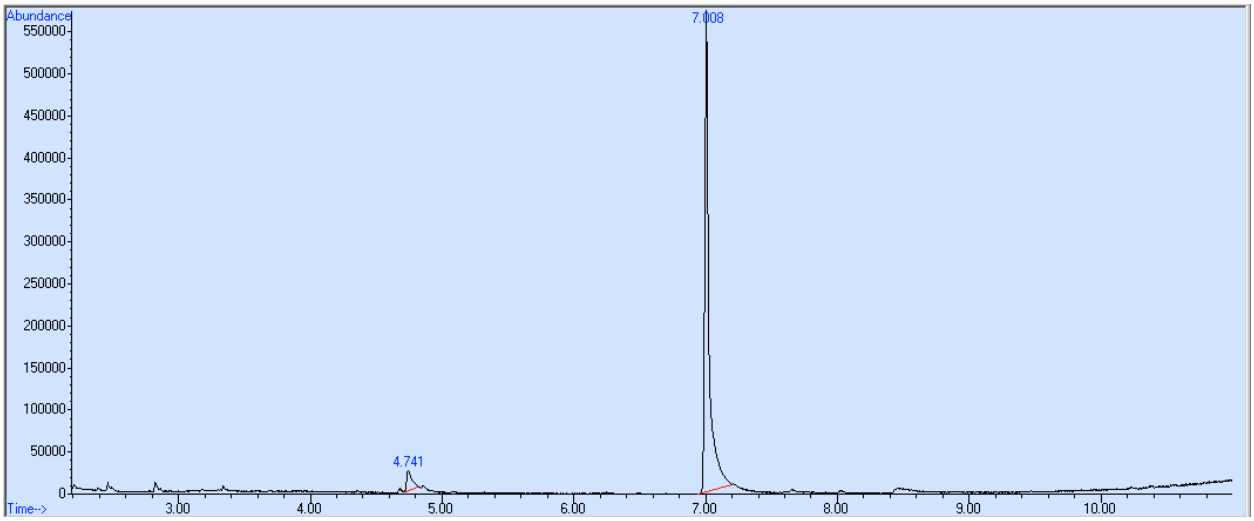


Figure S9 - Gas Chromatograph of 3A5AF from Optimized Reaction

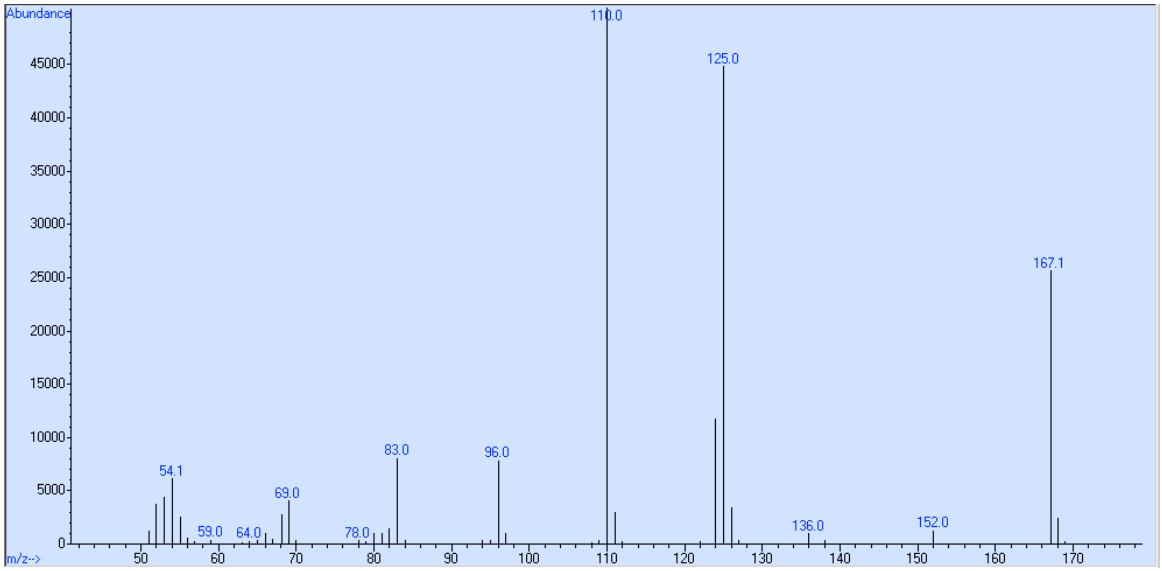


Figure S10 - Mass Spectrum of 3A5AF compound with *m/z* = 167

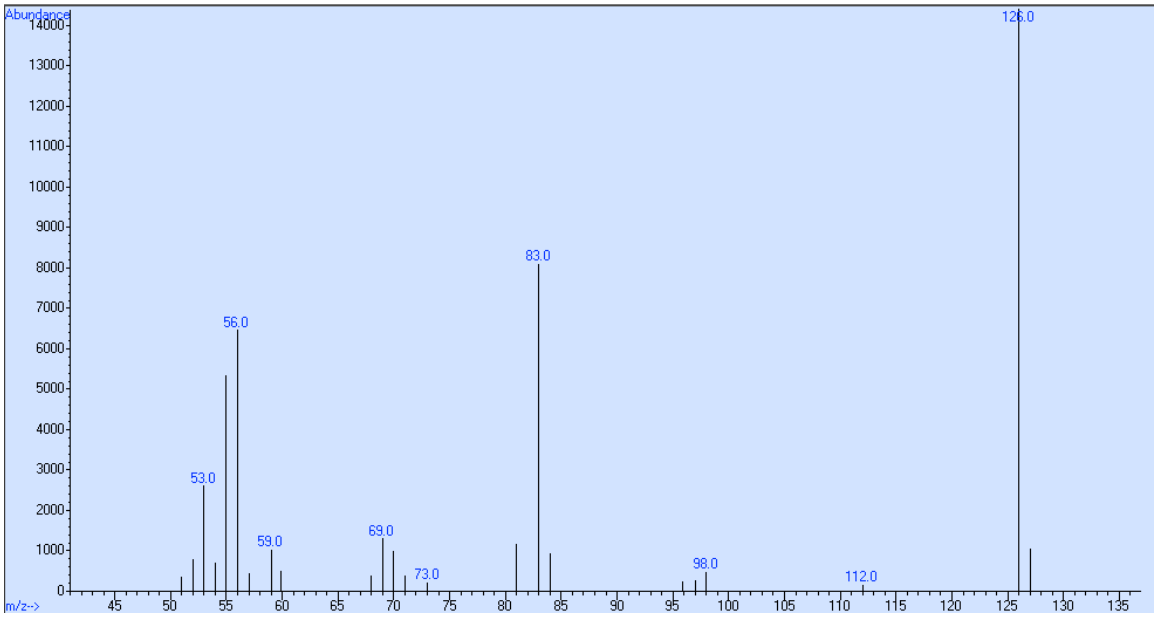


Figure S11 - Mass Spectrum of 5-HMF compound with *m/z* = 126

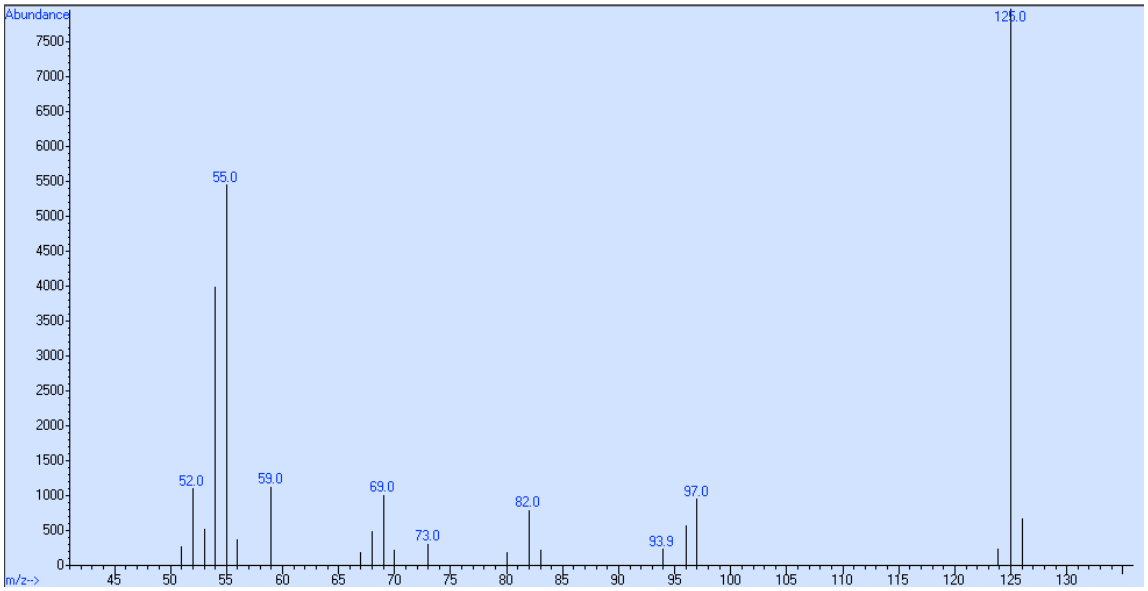


Figure S12 - Mass Spectrum of 5Ac3NH$_2$F with *m/z* = 125

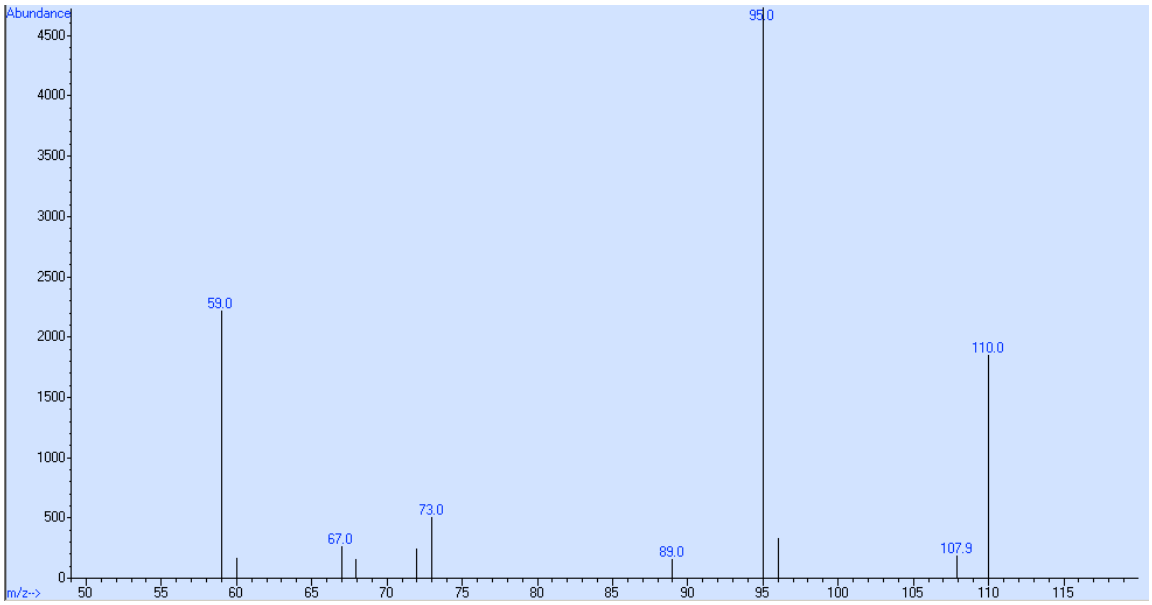


Figure S13 - Mass Spectrum of 3NH$_2$5F with *m/z* = 110

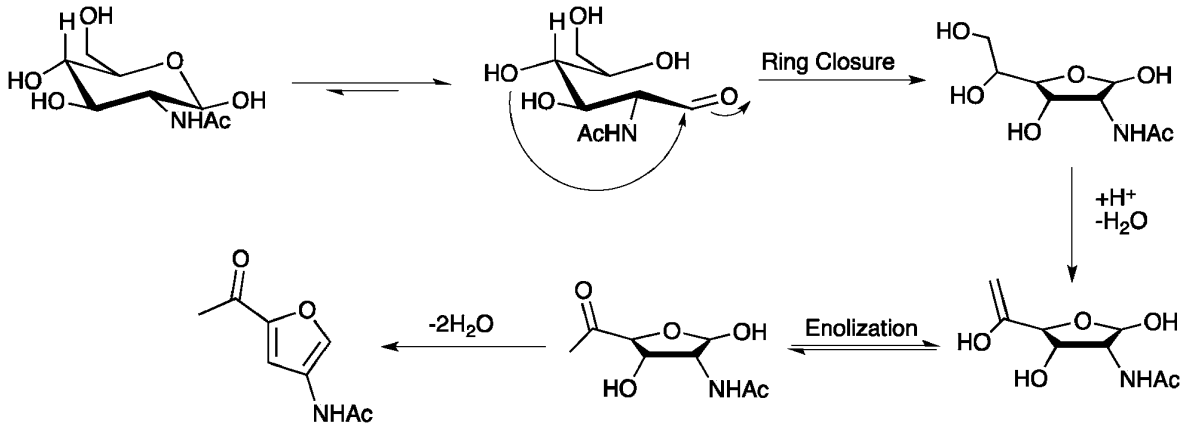


Figure S14: 3A5AF Formation from NAG from *RSC Advances*, **2012**, 2, 4642 – 4644

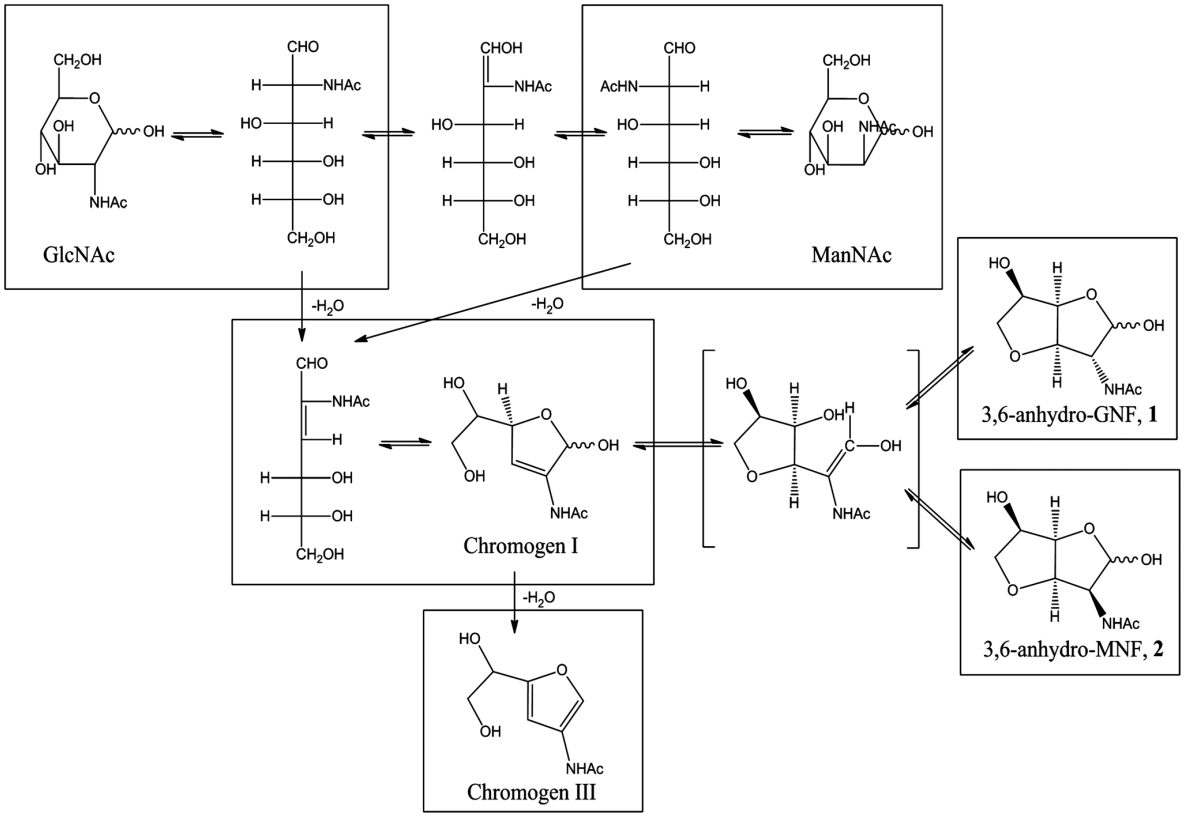


Figure S15: Chromogen I and III Formation from NAG from *Green Chem.*, **2013**, 15, 2960 – 2966

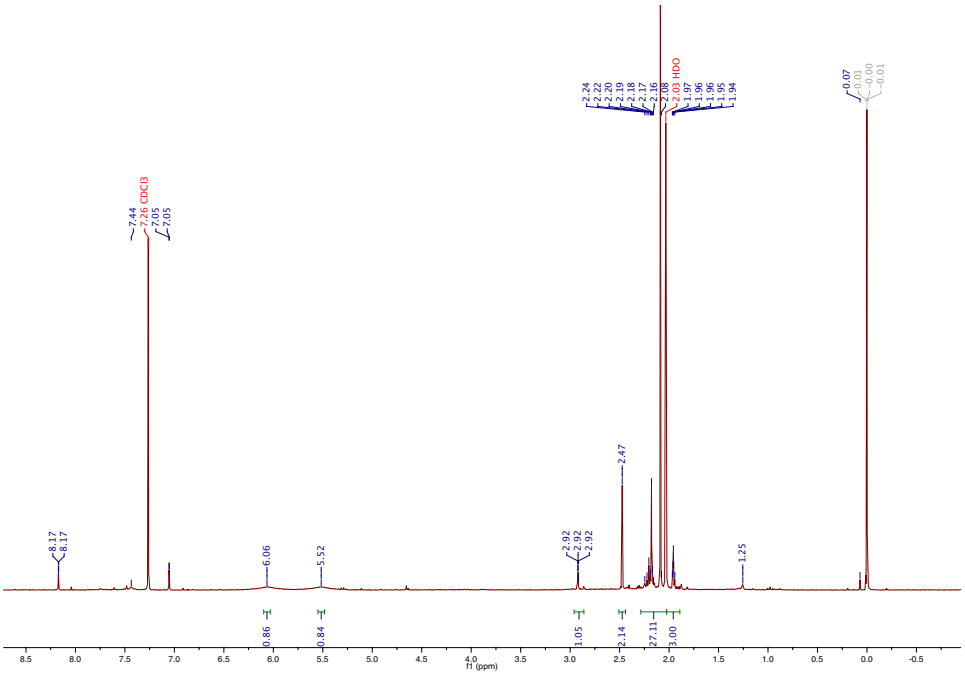


Figure S16: ^{1}H-NMR in $CDCl_3$ for a Reaction with 1:2 NAG:$B(OH)_3$ at 180 ^{o}C of 95% Pure 3A5AF

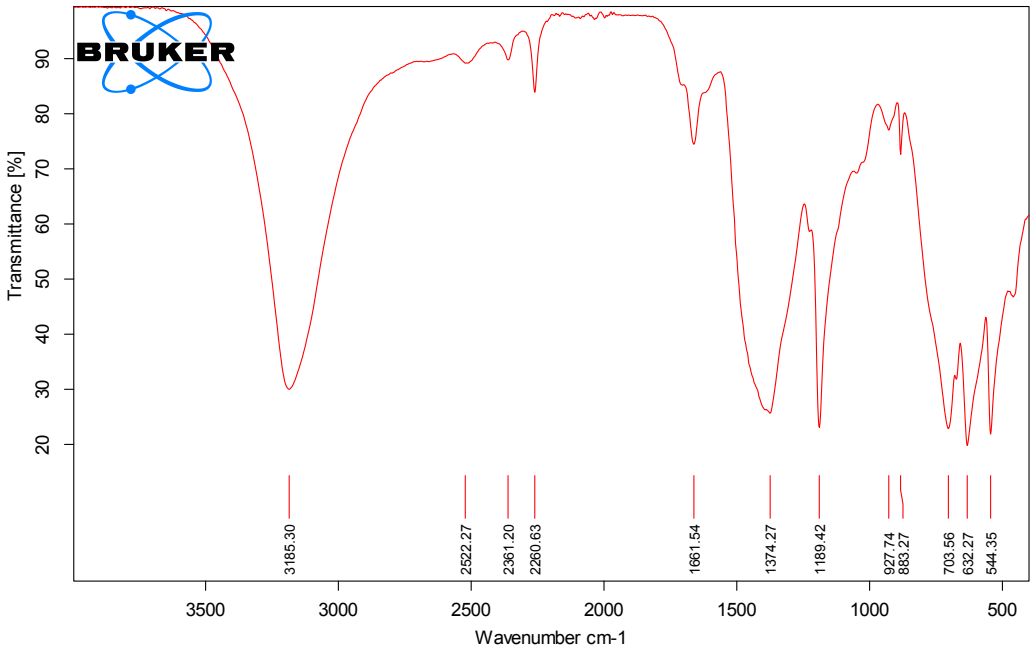


Figure S17: FT-IR Spectrum for a Reaction with 1:2 NAG:$B(OH)_3$ at 180 ^{o}C of 95% Pure 3A5AF

Figure S18: FT-IR Spectrum for Biochar Produced at 220 °C under Additive-free Conditions

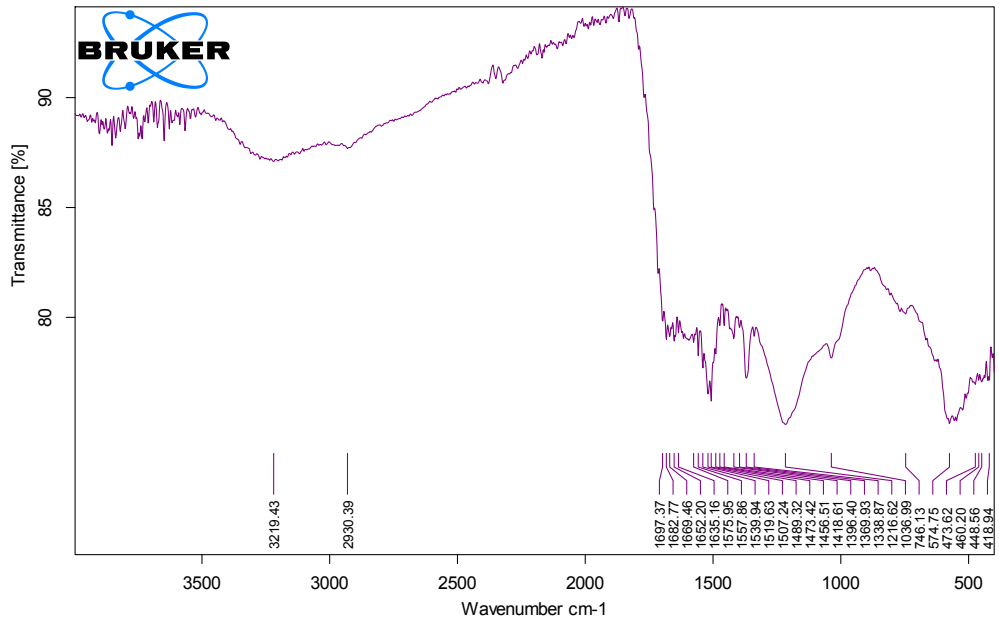


Figure S19 : FT-IR Spectrum for Biochar Produced at 180 °C under Additive-free Conditions

Figure S20: FT-IR Spectrum for Biochar Produced at 180 ^{o}C under 1:2:2 NAG:NaCl:B(OH)$_3$ Conditions

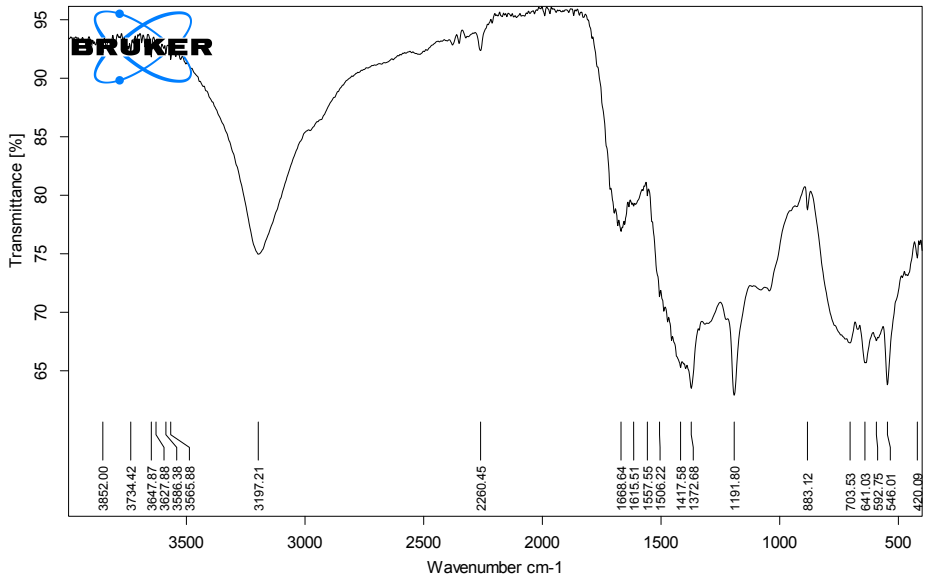


Figure S21: FT-IR Spectrum for Biochar Produced by Poised Reaction with Ethylene Glycol 1:1 with Boric Acid at 180 ^{o}C with 1:2:2 NAG:NaCl:B(OH)$_3$

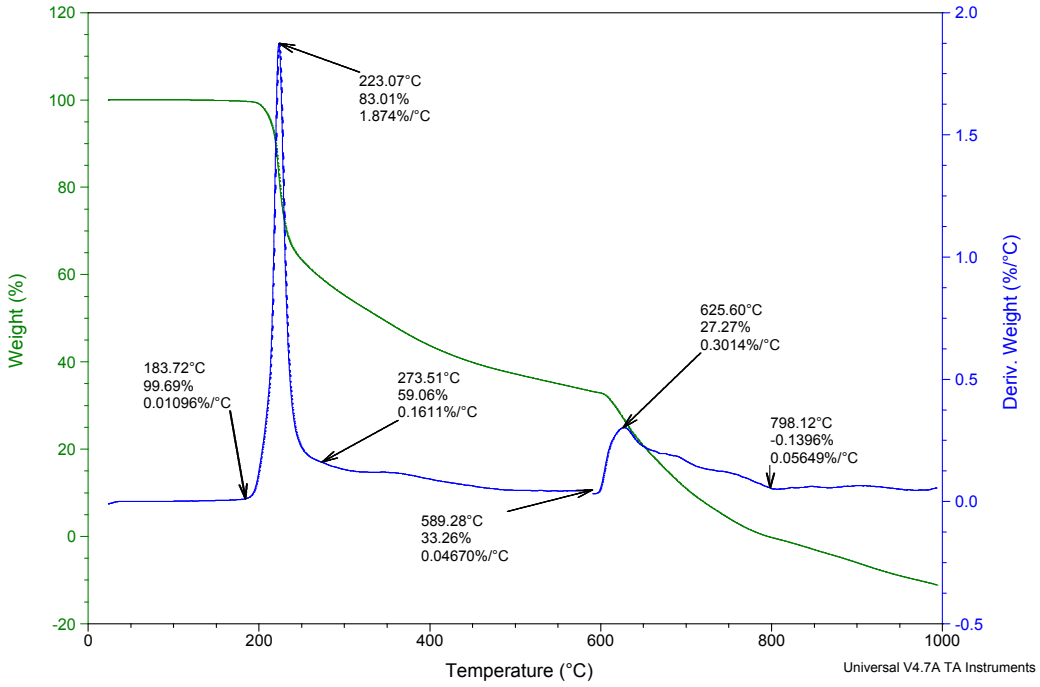


Figure S22 : TGA Profile of N-acetyl-*D*-glucosamine

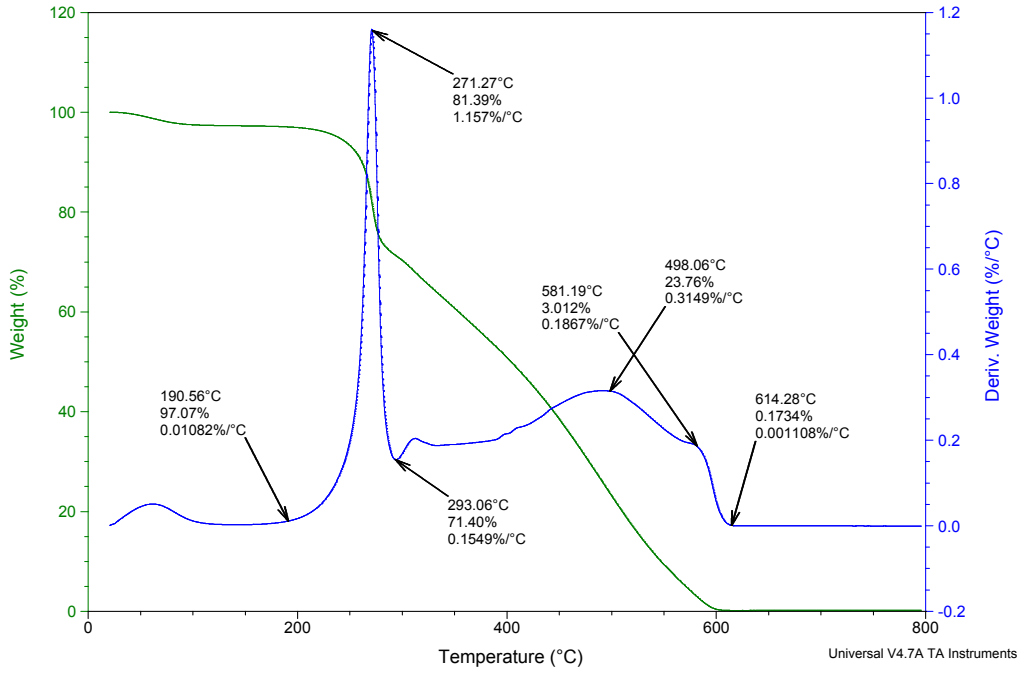


Figure S23 : TGA Profile of Furan Mixture under Additive-free Condition at 180 °C & 5.0 wt% NAG

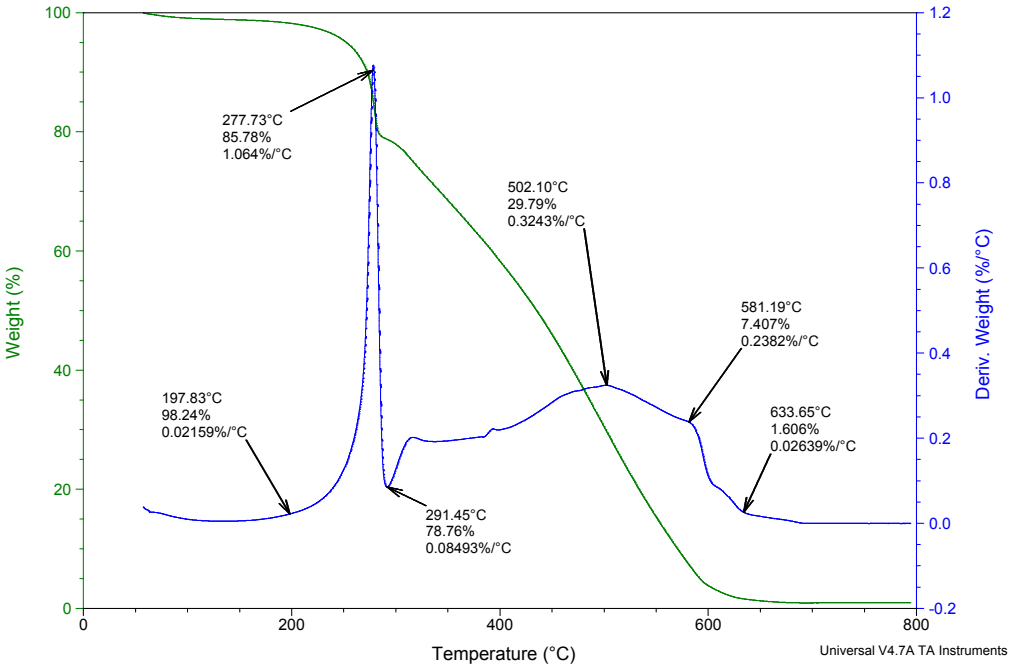


Figure S24 : TGA Profile of Furan Mixture under Additive-free Condition at 200 °C & 5.0 wt% NAG

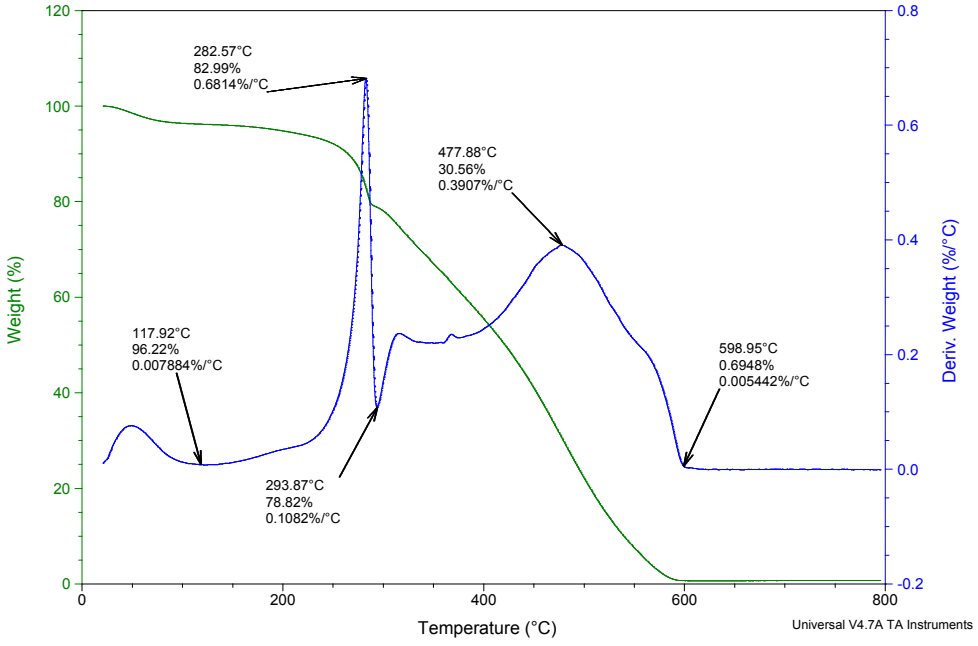


Figure S25 : TGA Profile of Furan Mixture under Additive-free Condition at 220 °C & 5.0 wt% NAG

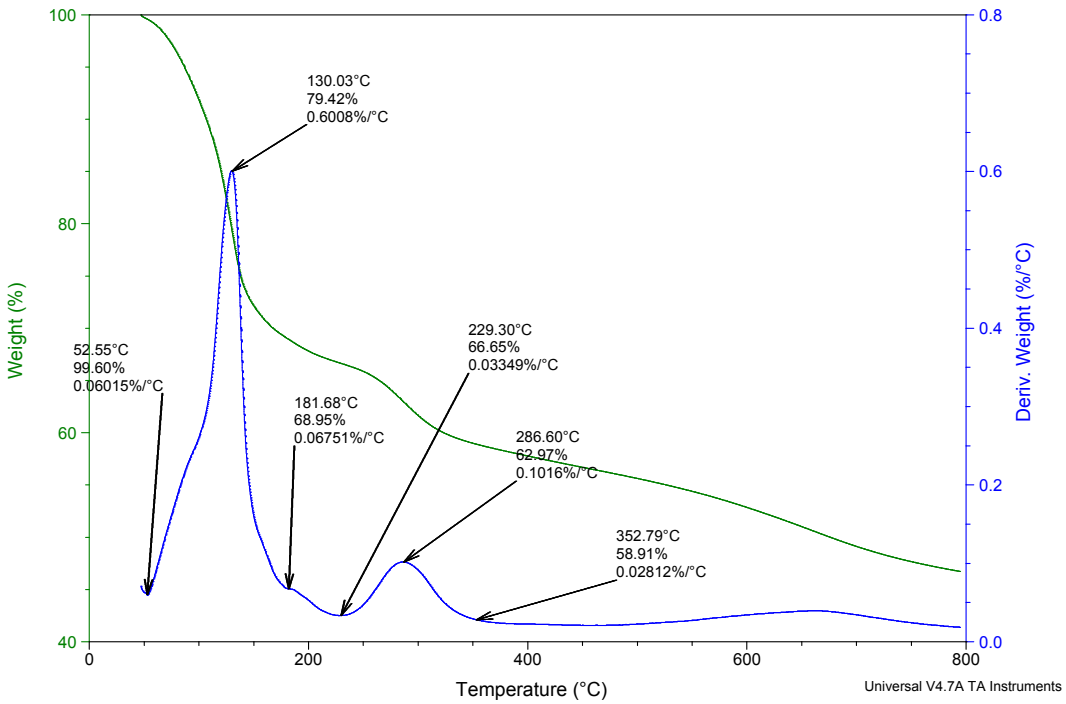


Figure S26 : TGA Profile of Furan Mixture at 220 ºC with 1:1:2 NAG:NaCl:$B(OH)_3$

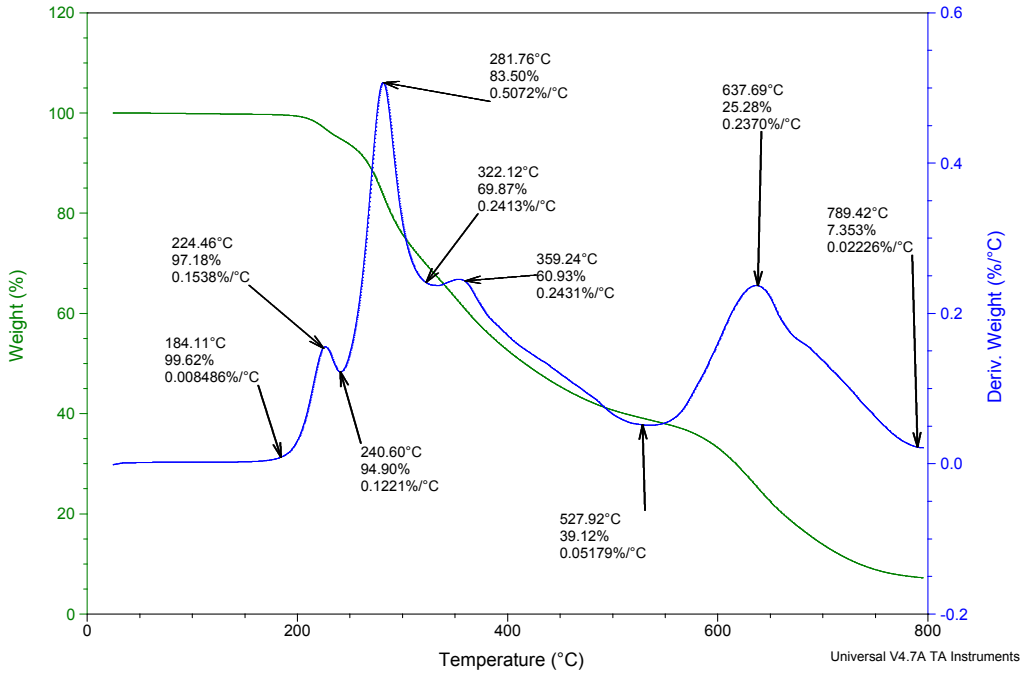


Figure S27 : TGA Profile of Bio-reduced Furan Mixture with a Mass Ratio of 4:1 BY:F with 2:1 Glu:F

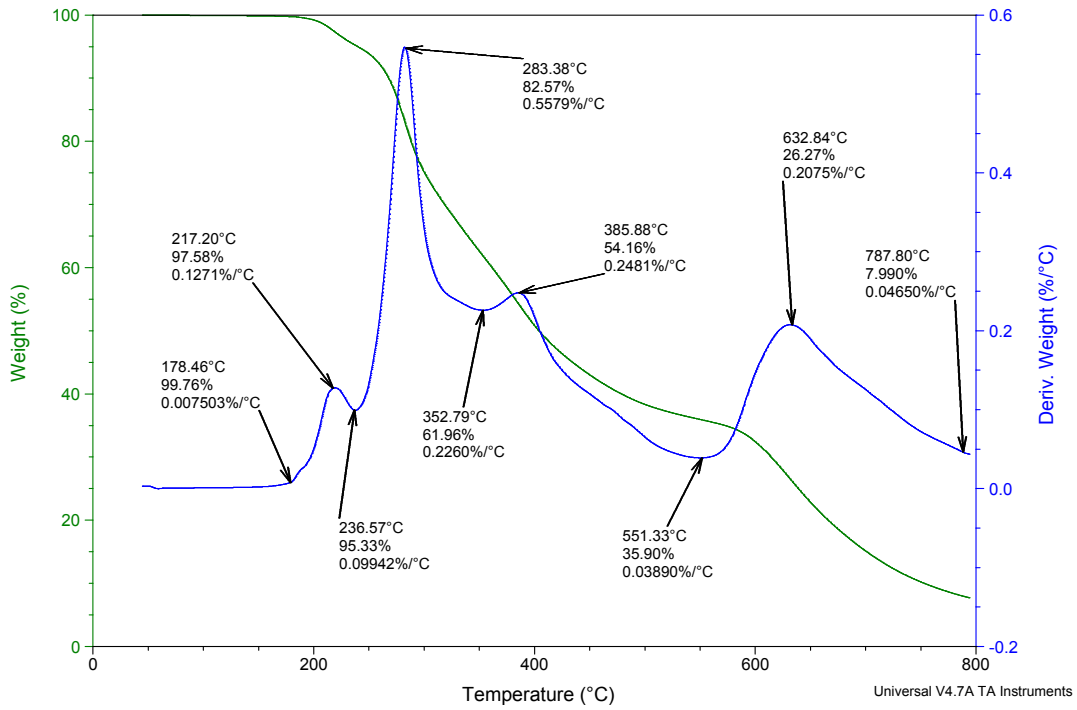


Figure S28 : TGA Profile of Bio-reduced Furan Mixture with a Mass Ratio of 4:1 BY:F without Glu

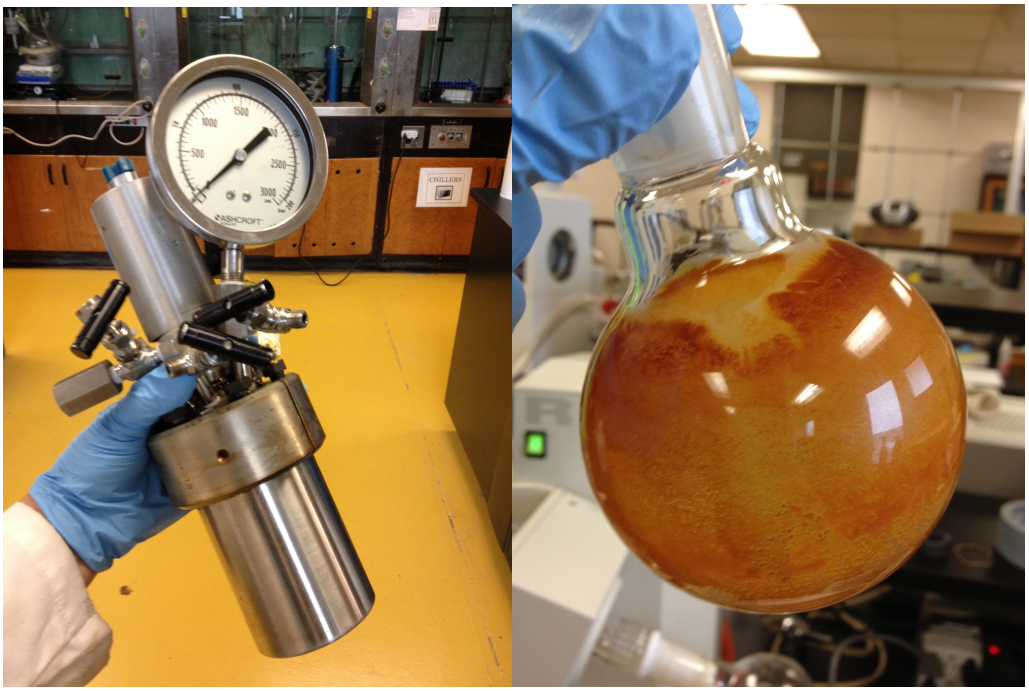


Figure S29: Parr Reactor and Fresh (95% Selective) 3A5AF Mixture

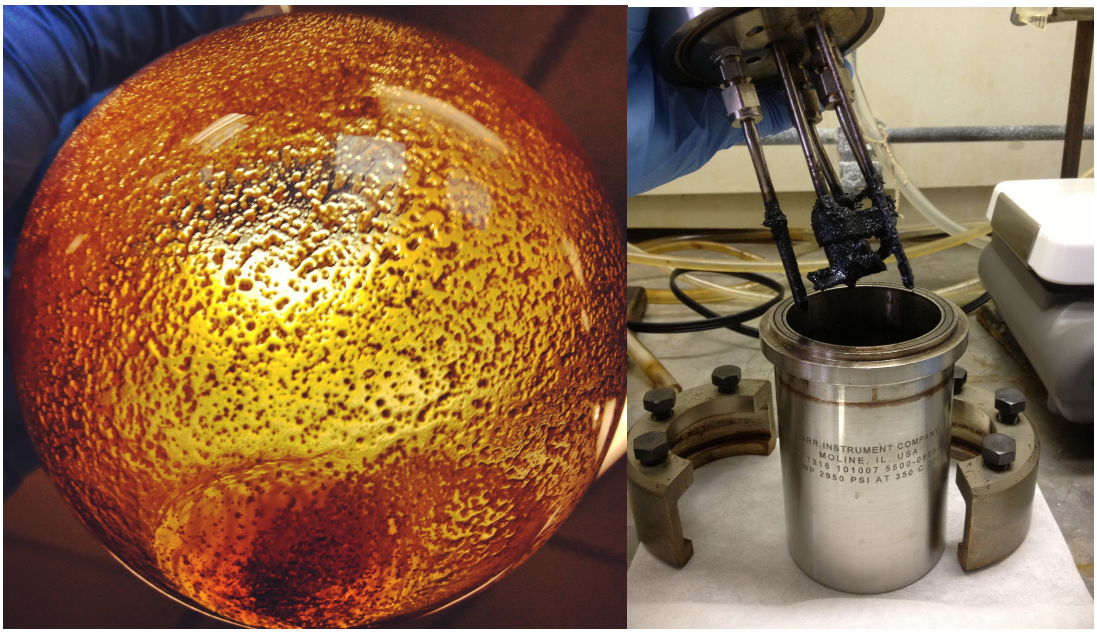


Figure S30: Freshly Worked up Furan Mixture and Biochar after Reaction

Figure S31: Crude Furan “Cookie” and Liquid/Solid Furan Mixtures

Figure S32: Filtrate from Baker's Yeast Attempted Reduction and Foamed Over Reaction

Figure S33: View from the Lab Window of the MUN Clock Tower