

The University of Maine

DigitalCommons@UMaine

Honors College

Spring 5-2018

The Production, Characterization, and Upgrading of Biochars into Activated Carbon

Kasey Johnston
University of Maine

Follow this and additional works at: <https://digitalcommons.library.umaine.edu/honors>



Part of the [Chemical Engineering Commons](#)

Recommended Citation

Johnston, Kasey, "The Production, Characterization, and Upgrading of Biochars into Activated Carbon" (2018). *Honors College*. 345.
<https://digitalcommons.library.umaine.edu/honors/345>

This Honors Thesis is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Honors College by an authorized administrator of DigitalCommons@UMaine. For more information, please contact um.library.technical.services@maine.edu.

THE PRODUCTION, CHARACTERIZATION, AND UPGRADING OF BIOCHARS
INTO ACTIVATED CARBON

by

Kasey Johnston

A Thesis Submitted in Partial Fulfillment
Of the Requirements for a Degree with Honors
(Chemical Engineering)

The Honors College

University of Maine

May, 2018

Advisory Committee:

Dr. M. Clayton Wheeler, Professor of Chemical Engineering
Dr. Thomas J. Schwartz, Assistant Professor of Chemical Engineering
Dr. Sara Walton, Lecturer, Chemical and Biomedical Engineering
Dr. Sampath Gunukula, Postdoctoral Research Associate of Chemical and
Biomedical Engineering
Dr. Sally Molloy, Professor of Biochemistry and Honors

ABSTRACT

There is a growing demand for sustainable alternatives to petroleum based fuels to be used in the transportation sector. To this end, thermochemical pathways have been proposed for the conversion of renewable feedstock such as wood and corn stover to transportation fuels. Although it is recognized that renewable feedstock sources are environmentally superior to the current petroleum based fuels, the commercial production of renewable fuels via thermochemical pathways must also be economically advantageous. Thermochemical conversion of a renewable feedstock results in the production of a significant amount of biochar that has a low economic value. To improve the overall economics of the thermochemical pathways, there is a need for increasing the economic value of biochar by diversifying the use of biochar or by upgrading it to a higher-value product, such as activated carbon. This thesis analyzes the characteristics of biochar to provide insights in to the selection of derivatives as well as operating conditions for upgrading biochar.

To my parents for all their love and support,
And because I love them back; I don't ever expect them to read this.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor, Dr. Clayton Wheeler, for his expertise and guidance throughout this project. I'd also like to thank my committee members, Dr. Thomas Schwartz, Dr. Sara Walton, Dr. Sampath Gunukula, and Dr. Sally Molloy for their insight and willingness to help me succeed.

Additionally, I would like to thank Dr. Scott Eaton for teaching me to use the thermogravimetric analyzer and how to analyze the results. Finally, I would like to thank my roommates for (mostly) tolerating my complaining about my thesis all year.

TABLE OF CONTENTS

Introduction	1
Biochars: Production, Characterization, & Upgrading.....	3
Production of Biochars	3
Acid Hydrolysis and Dehydration.....	3
Pyrolysis.....	5
Characterization of Biochars.....	6
Surface Functionality	6
Thermal Decomposition.....	7
Upgrading Biochars	9
Physical Activation	9
Chemical Activation.....	11
Application to Water Treatment.....	13
Results and Discussion	14
Discussion and Conclusion.....	25
References	28
Appendices	30
Author's Biography	37

INTRODUCTION

In recent years, the issue of climate change has been in the limelight of both scientific communities and general society, alike. Carbon emissions play a large role in the phenomenon of climate change. One of the major contributors of carbon emissions in developed nations is the transportation sector. As of 2015, the Environmental Protection Agency listed the transportation sector to be culpable for 27% of the carbon emissions in the United States.¹ Currently, the U.S. Energy Information Administration states that 91% of transportation fuels are made from non-renewable petroleum feedstock.² This heavy reliance on only one feedstock for fuel puts financial risk on the transportation industry, and threatens the energy security of the United States of America. Growing concerns over climate change and the desire to reduce our dependence on petroleum have shifted the focus to make transportation fuels from renewable lignocellulosic feedstocks.

Many thermochemical, biochemical, and chemical catalytic technologies have been, and are being developed to convert lignocellulosic feedstock to transportation fuels. One such technology, which was developed at the University of Maine, produces renewable fuels from a biomass feedstock comprised of wood through the use of acid hydrolysis and dehydration (AHDH) and thermal deoxygenation (TDO) processes. In the AHDH process, the C₅ and C₆ sugars found in wood are converted to furfural, formic acid, and levulinic acid. The AHDH process results in a byproduct called biochar, while the calcium neutralized salts of formic acid and levulinic acid are subjected to the TDO process to produce renewable fuels.³

One of the more widely used thermochemical technologies used to make renewable fuels is pyrolysis. In this process, organic materials (*e.g.*, biomass) are heated in the absence of oxygen to cause thermal decomposition of the material into combustible gases. Pyrolysis can be done at temperatures between 270 °C and 800 °C.^{4, 5} The main byproduct of pyrolysis of a biomass feedstock is biochar. Qualities such as surface functionality and elemental composition of the resulting biochars vary with the conditions at which the pyrolysis was performed.⁶

The biochars derived from the AHDH and TDO processes are characterized by low porosity and high carbon content. The market price of these chars is low, around \$100/ton, and they are generally burned to generate energy.⁷ However, by using physical activation process to increase their surface area, the AHDH char and pyrolysis chars might be converted into activated carbon, which can have a market price of up to \$7,000/ton, depending on its characteristics.⁷ Biochars can be converted into activated carbon through the use of either physical or chemical activation. In physical activation, steam is used to increase the surface area of the biochar, and in chemical activation, inorganic compounds, such as zinc chloride, sodium hydroxide, potassium hydroxide, or phosphoric acid, are used to convert the biochar to activated carbon. The production of activated carbon is advantageous as it can be sold at a higher price than biochar. The ability to garner additional profit from byproducts such as activated carbon would bolster the economic strength of the biofuel process.

BIOCHARS: PRODUCTION, CHARACTERIZATION, & UPGRADING

Production of Biochars

Acid Hydrolysis and Dehydration

The acid hydrolysis dehydration process, a technology being developed by the University of Maine, is a process in which C₆ sugars are converted into organic acids. During AHDH, a wood feedstock is reacted under acidic conditions to produce levulinic acid, formic acid, furfural, and biochar. AHDH reactor conditions are 16 bar and 200 °C. The hemicellulose and lignin components of the wood feedstock end up as a biochar, a byproduct, while the theoretical yields of the furfural, levulinic acid, and formic acid are approximately 70%.³ The products, levulinic acid and formic acid, will be subjected to further reactions and the thermal deoxygenation process to ultimately produce renewable fuels.

Products from the AHDH reactor pass to a flash separator in which the vapor components of the stream, containing water and small amounts of formic acid, are sent to the furfural recovery section, while the liquid components are sent to a washing step. During this washing step, biochar is separated from the liquid furfural, levulinic acid, and formic acid by means of centrifuge. In this step, a series of centrifuges use counter-current washing with water. Following the washing step, the char is sent to a tube furnace. The char remains in the 470 °C tube furnace for 30 minutes to allow volatile organics to evaporate to further carbonize the char byproduct, as shown in Figure 1. At this point, the AHDH char could be used as a feedstock to an activated carbon production

process. For every 2,000 metric tons of bone dry wood used as a feedstock, 750 metric tons of AHDH biochar is made as a byproduct of the process.

The remaining liquid components that resulted from the AHDH reaction are sent to a solvent extraction column. In the solvent extraction column, levulinic acid, formic acid, and furfural are extracted into 2-methyltetrahydrofuran, an organic solvent. Calcium oxide is used to precipitate the formic acid and levulinic acid as calcium formate and calcium levulinate, respectively. The calcium formate and calcium levulinate are sent to the TDO reactor, operating at 1 atm and 450 °C, in which their thermal decomposition produces TDO oil. The stream, now composed of furfural and 2-methyltetrahydrofuran is sent to a solvent recovery section in which the 2-methyltetrahydrofuran is recovered with 99% purity of a weight basis. (5) Furfural is sent to a recovery section and the organic solvent is recycled back to the solvent extraction column.

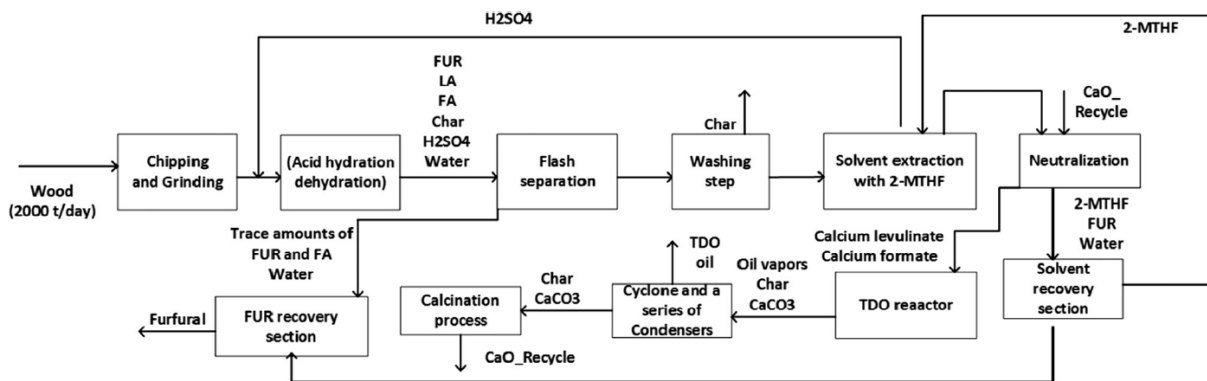


Figure 1: AHDH process flow diagram. Image sourced from “Techno-economic analysis of thermal deoxygenation based biorefineries for the coproduction of fuels and chemicals”, S. Gunukula *et al.*

Pyrolysis

Pyrolysis is a commonly used process in the production of biofuels. It is a process in which thermal decomposition of biomass occurs in the absence of oxygen. In this process, biomass is heated to temperatures, between 500 °C and 800 °C, at atmospheric pressure. The heating occurs rapidly, in less than two seconds. Then the products are rapidly cooled to stop the reaction. Products that result from biomass pyrolysis include biochar, pyrolysis oil, and combustible gases. Product yields are dependent on the process conditions, such as temperature and residence time, at which pyrolysis is performed.

Following the pyrolyzer, the products are sent to a series of cyclones that separate the pyrolysis biochar from the pyrolysis vapors. The pyrolysis vapors are sent to a condenser to remove the condensable product, pyrolysis oil. The non-condensable gases can be collected and used as fuels, or recycled back to the pyrolysis reactor to be used as a fluidizing gas. The pyrolysis oil is then upgraded into fuels such as diesel and gasoline, through the process of hydrotreating. Work by P.A. Case *et al.* indicated that yields of non-condensable gases, biochar, and pyrolysis oil, for the pyrolysis of pine wood at 500 °C are 57%, 12%, and 21%, respectively.¹⁰

Characterization Of Biochars

Surface Functionality

The conditions at which biochars are formed influence their physical and chemical properties. Pyrolysis processes can be used to convert a variety of different types of biomass feedstocks into biofuel. The biochars resulting from pyrolysis of different biomass feedstocks display varying elemental composition as well as surface

functionality. Additionally, pyrolysis can be done at a variety of temperatures with differing residence times. These operating conditions also influence the elemental composition and surface functionality of the resulting biochars. Test methods including Fourier transform infrared spectroscopy, Raman spectroscopy, carbon nuclear magnetic resonance, X-ray diffraction, and X-ray photoelectron spectroscopy have been used to measure the surface groups of biochars. Together, these technologies are used to detect non-aromatic functionality of the surface of biochars, to distinguish the reactive and structural features of carbonaceous structures, and measure the degree of crystallinity of the biochars.

Kim *et al.* examined the effect that pyrolysis temperature has on the pyrolysis of switch grass and pine wood.⁶ Results showed that as the temperature of fast pyrolysis was increased from 450 °C to 800 °C, biochar yields decreased. The yield of biochar from pine wood feed stocks decreased from 26.6% to 9.5%, while that from switch grass decreased from 31.3% to 11.4%. These decreases in yield were due to losses in volatile matter, including CO, H₂, and CH₄. As the fast pyrolysis temperature increases from 450 °C to 800 °C, the carbon content of resulting biochars also increases, from 49% to 90% for pine wood, and from 46% to 72% for switch grass. Regardless of the feedstock, the concentration of organic elements increased with increasing fast pyrolysis temperatures. However, switchgrass biochars were found to have between 2 and 10 times more organic elements than pine wood biochars made at the same conditions. Additionally, increasing the fast pyrolysis temperature leads to decreases in H/C and O/C atomic ratios; therefore, increased pyrolysis temperatures produce a greater number of recalcitrant carbon structures. This study also indicated that biochars made at 800 °C were composed mainly

of aromatic structures and that surface functionality was lost. Comparing switchgrass biochars to pine wood biochars suggested that switchgrass biochars produced more aromatic rings than pine wood biochars.

Thermogravimetric Analyzer

A thermogravimetric analyzer (TGA) was used to characterize the thermochemical decomposition characteristics of biochars made via fast pyrolysis of wood at 500 °C and 800 °C, and AHDH processes. Thermogravimetry measures the change in weight of a material as a function of temperature. Experiments were done in which samples of biochar, which were pretreated in a 100 °C oven to remove atmospheric moisture, were weighed as the temperature was increased at a rate of 10 °C per minute from room temperature to 800 °C. Some tests were run in the presence of air, and others in the presence of N₂. Additional experiments were run in which samples of each biochar were heated to 800 °C in the presence of N₂, allowed to cool to 30 °C and then heated again in the presence of air. An overview of experiments run is shown in Table 1. Each of the listed experiments were repeated three times.

Table 1: Overview of TGA experiments

Type of Char	Gas Present	Activity
Pyrolysis	Air	Ramp 10 °C/min to 800 °C
Pyrolysis	Nitrogen	Ramp 10 °C/min to 800 °C
Pyrolysis	Nitrogen & Air	Ramp 10 °C/min to 800 °C, allow to cool to 30 °C, ramp 10 °C/min to 800 °C
AHDH	Air	Ramp 10 °C/min to 800 °C
AHDH	Nitrogen	Ramp 10 °C/min to 800 °C
AHDH	Nitrogen & Air	Ramp 10 °C/min to 800 °C, allow to cool to 30 °C, ramp 10 °C/min to 800 °C

Upgrading Biochars

The main byproduct of both the AHDH and TDO processes is biochar. Biochar is a low-value byproduct of lignocellulosic biorefineries, which unless upgraded can only be used to burn to create energy. Generally, the biochar will be burned on the site of biorefineries to meet energy needs, and any excess energy produced from biochar can be sold to the electricity grid. The economic value of biochar can be improved by upgrading it to a variety of added value materials. Potential options for adding value to biochars include upgrading it into activated carbon or graphene, or using it as a biocomposite or for soil amendment. Of these options, this paper focuses on the production of activated carbon from biochar.

Activated carbon, which is classified as a specialty chemical, can be used for many applications due to its adsorption properties, which are present as a result of its high surface area and low-volume pores. Some of the applications for activated carbon include air purification, water purification, sewage treatment, and medicine. Its surface area must be increased to about 800 m²/g, dependent on the application, to upgrade the biochar produced during thermochemical processes into activated carbon. The surface area of biochars can be increased through the process of either physical or chemical activation.

Physical Activation

Physical activation can be achieved by treating biochars with oxidizing agents, most commonly steam or carbon dioxide, at temperatures between 500 °C and 1000 °C.

Compared to carbon dioxide, water is a smaller molecule, allowing faster reaction rates and penetration into the pores of the char. During this process, the gaseous oxidizer continuously flushes a sample of biochar in the presence of nitrogen. This process produces activated carbon that has high porosity. During activation, the oxidizing agent permeates the internal structure of the char and reacts with carbon atoms resulting in greater surface area. The amount of increase in the surface area of the resulting activated carbons is highly dependent on activation conditions.

The operating conditions of physical activation that influence the quality and yield of activated carbon produced are activation time, activation temperature, and the mass ratio of steam to char. Studies done by Dalai and Azargohar tested activation times between 0.9 hours and 4 hours, activation temperatures ranging from 600 °C and 900 °C, and mass ratios of steam to char between 0.4 and 2. Activation results improved the surface area from 10 m²/g to up to 950 m²/g. It was determined that surface area increased as burn-off increased, however, the maximum surface area per unit mass of biochar occurred between 40-50 wt% burn-off. Optimum conditions that balanced producing high surface activated carbon and a relatively high yield were determined to be achieved with an activation time of 1.39 hours, an activation temperature of 792 °C, and a mass ratio of steam to biochar of 1.06.¹¹

Experiments done by Bernardo Gusman del Campo, tested the influence of activation time and temperature for physical activation. These experiments were done using steam as an oxidizing agent. Biochar samples were flushed with steam at a rate of 1 mL min⁻¹ g⁻¹. Residence times between 5 minutes and 60 minutes were tested, and activation temperatures ranging from 400 °C to 800 °C were investigated. Again, studies

aimed to balance increasing the surface area and activated carbon yield, simultaneously. In this study, the surface area of activated carbons increased with increasing activation temperature, while each activation temperature had an optimum residence time for activation. The optimum activation conditions determined by this study were 800 °C and 5 minutes, resulting in an increase of surface area from 10 m²/g to 550 m²/g and a burn-off of 28%.⁷

Chemical Activation

Chemical activation of biochars can be achieved by employing activating agents such as phosphoric acid, potassium hydroxide, or zinc chloride. During the process of chemical activation, biochar is subjected to activating agents, treated with heat between 300 °C and 500 °C, and then the activating agent is removed by means of washing with an acid or base and water. The washing step of this process leads to the increase in surface area and highly porous pore structure.¹³

In a study done by Dalai and Azargohar, potassium hydroxide was used as the activating agent to test the effect that activation temperature, nitrogen flow rate, and potassium hydroxide to biochar mass ratio, had on the reaction yield and surface area. Activation temperatures between 550 °C and 800 °C were tested, along with nitrogen flow rates ranging from 80 cc/min to 250 cc/min, and mass ratios from 0.25 to 3. Chemical activation was achieved by exposing biochar to the desired amount of potassium hydroxide mixed with 100 mL of water, and allowing the mixture to sit for 2 hours at room temperature. Following this, samples were dried overnight at a temperature of 120 °C. 20 grams of the dried sample was put in a fixed-bed reactor and heated to a temperature of 300 °C at a rate of 3 °C/min, it was then held at 300 °C for 1 hour.

Following the temperature hold at 300 °C, the temperature was further increased at a rate of 3°C/min until it achieved the desired activation temperature. Once the desired temperature was reached, activation took place for 2 hours. The products were washed with water, then hydrogen chloride, then distilled water to remove unwanted compounds and salts. Finally, the sample was dried for 12 hours at a temperature of 110 °C.¹¹

The maximum surface area achieved during this study was greater than 1500 m²/g, and reaction yields ranged between 50 wt% and 82 wt%. Results indicated that higher activation temperatures lead to increased surface areas. Surface area increased as mass ratio of potassium hydroxide to biochar increased until a ratio of 1.93, in which the surface area started to fall again. Additionally, it was found that increasing nitrogen flow rate also increased the resulting surface area of activated carbon. The study concluded that the optimum operating conditions that best balanced the tradeoff between achieving a high surface area while having a relatively large yield occurred at an activation temperature of 680 °C, a nitrogen flow rate of 240 cc/min, and a potassium hydroxide to biochar mass ratio of 1.23. At these conditions, activated carbon with a surface area of 836 m²/g was produced with a yield of 78%. Costing \$750/ton, potassium hydroxide would cost \$1,180/ton of activated carbon produced.¹²

Application in Water Treatment

One application of particular interest for activated carbon is for the treatment of water. Activated carbon can be used as a filtering agent to remove chlorine and organic compounds from water to make it safer for human use. Removing either of these components prevents them from reacting with each other to produce carcinogens.

Organic compounds are removed from water through adsorption. This type of filter is most effective when the activated carbon pore sizes are small and the molecules to be removed are large. Additionally, activated carbon filters are most effective with organic molecules that aren't soluble in water that is fed at low temperatures and pH levels. As for chlorine removal, feed flow rates are normally high because dechlorination occurs quickly. To be successful, this process will require a large surface area and monitoring and replacing the activated carbon to ensure that it's effective.⁸

Activated carbon should have a surface area around 500 m²/g to be useful as a water filtering agent.⁹ This surface area can be achieved using either chemical or physical activation. For example, a surface area of 500 m²/g could be produced using physical activation by steam with a residence time of 5 minutes and temperature of 661 °C, with a yield of 76%, as indicated by the surface area response model determined by researchers at Iowa State University.⁷

RESULTS AND DISCUSSION

Table 1: Overview of TGA experiments

Type of Char	Gas Present	Activity
Pyrolysis	Air	Ramp 10 °C/min to 800 °C
Pyrolysis	Nitrogen	Ramp 10 °C/min to 800 °C
Pyrolysis	Nitrogen & Air	Ramp 10 °C/min to 800 °C, allow to cool to 30 °C, ramp 10 °C/min to 800 °C
AHDH	Air	Ramp 10 °C/min to 800 °C
AHDH	Nitrogen	Ramp 10 °C/min to 800 °C
AHDH	Nitrogen & Air	Ramp 10 °C/min to 800 °C, allow to cool to 30 °C, ramp 10 °C/min to 800 °C

Experiments with AHDH char in the presence of nitrogen indicated that there were consistent percentages of weight loss at a given temperature. This became clear when percent weight loss was plotted against temperature, and all three of the runs at these conditions followed the same line, as seen in **Figure 2**.

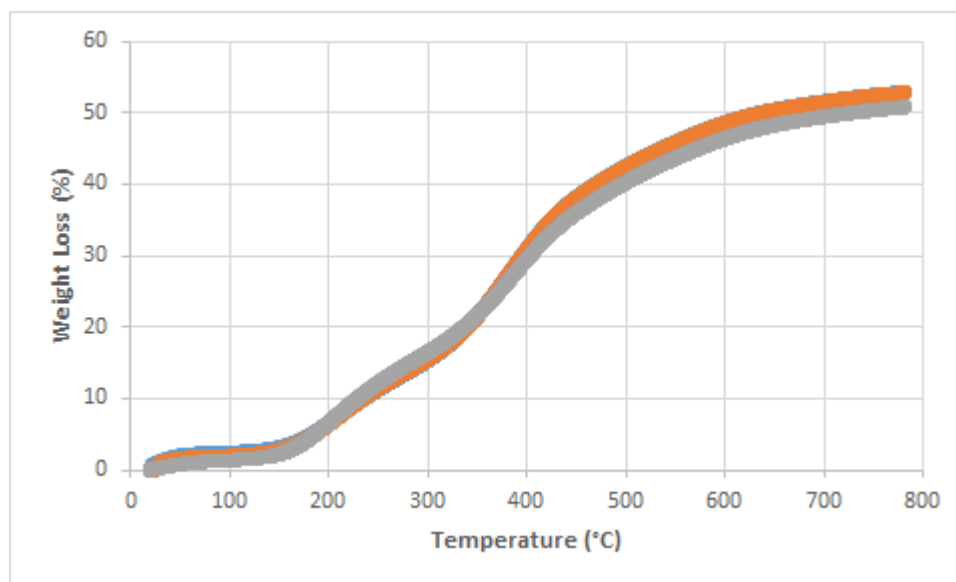


Figure 2: Percent weight loss as a function of temperature for AHDH char in the presence of N₂.

As indicated in **Figure 2**, the total percentage of weight loss approaches roughly 52% at the maximum experimental temperature, 800 °C. Additionally, weight losses below 100 °C are minimal due to the samples being pretreated in an oven. Looking at the graph of the derivative of the weight as a function of temperature indicates the temperatures at which the most major weight losses took place. As shown in **Figure 3**, there were high rates of change in sample weight around both 200 °C and 375 °C.

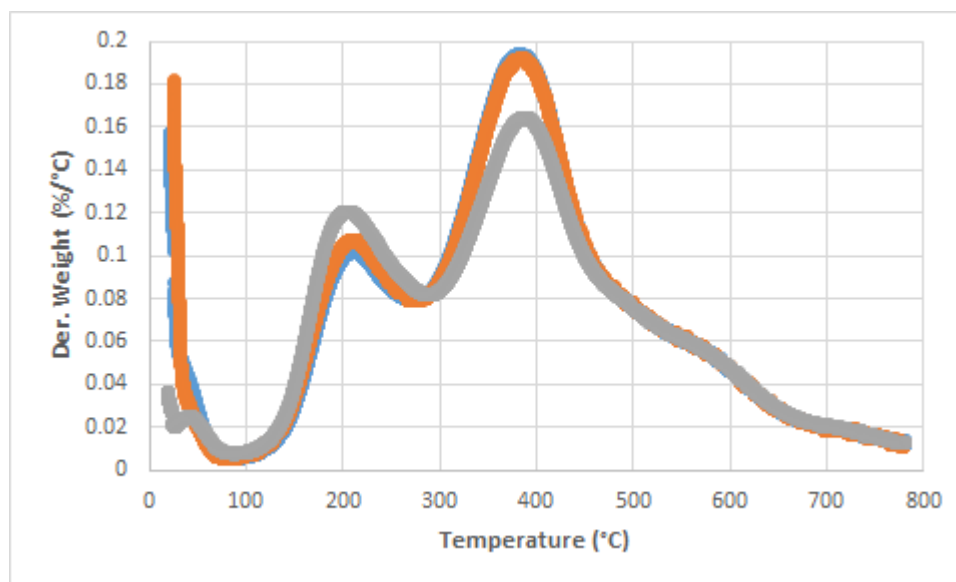


Figure 3: Derivative of weight loss as a function of temperature for AHDH char in the presence of N_2 .

Experiments that were run on AHDH char under the presence of air indicated that 100% weight loss would occur by about 560 °C. This suggests that components of the sample were reacting with oxygen at high temperatures. As shown in **Figure 4**, weight loss occurred between about 150 °C and 560 °C. The graph of the derivative of the weight as a function of temperature indicates that the temperature at which the rate of change of sample weight was the highest was around 500 °C, as seen in **Figure 5**.

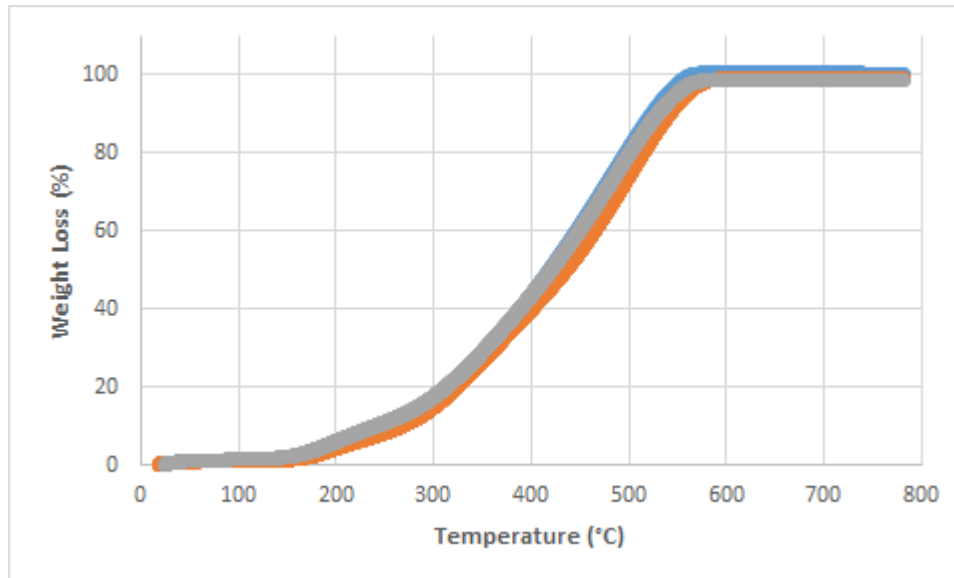


Figure 4: Percent weight loss as a function of temperature for AHDH char in the presence of air.

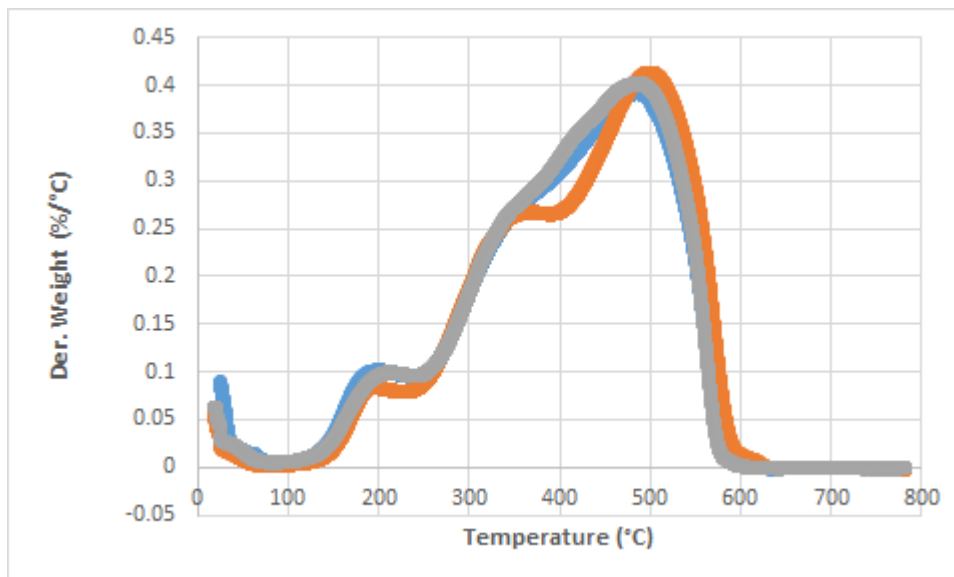


Figure 5: Derivative of weight loss as a function of temperature for AHDH char in the presence of air.

The experiments in which AHDH char samples were heated in the presence of N_2 , and allowed to cool to 30 °C before being heated again in the presence of air again indicates that the percentage of weight that will be lost with N_2 is roughly 52%, and 100% weight

loss with air, as seen in **Figure 6**. Unlike the experiments in which the sample was heated with air, and air only, 100% weight loss was achieved around 600 °C, rather than 560 °C. The graph of the derivative of the weight as a function of temperature indicates that the rate of change of sample weight was the highest was around 560 °C in the presence of air, as seen in **Figure 7**.

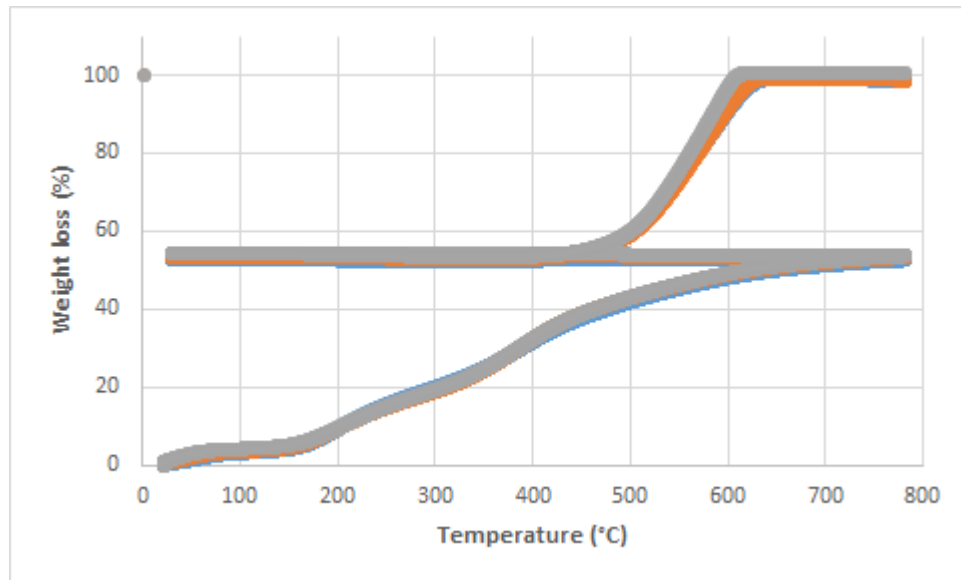


Figure 6: Percent weight loss as a function of temperature for AHDH char in the presence N_2 followed by air.

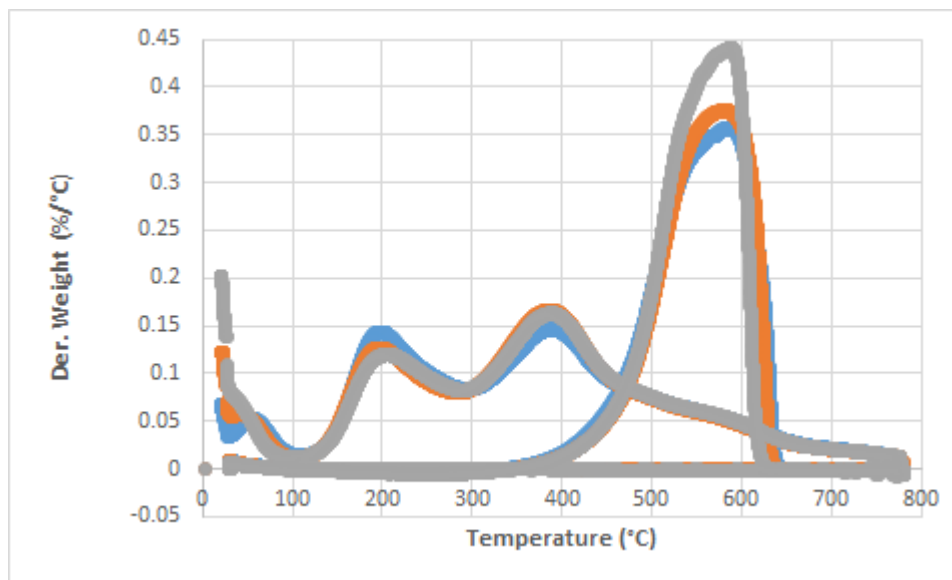


Figure 7: Derivative of weight loss as a function of temperature for AHDH char in the presence of N₂ followed by air.

Experiments with pyrolysis char in the presence of nitrogen indicated less consistent percentages of weight loss at a given temperature than the experiments done with AHDH char. When percent weight loss was plotted against temperature, all three of the runs at these conditions followed the same trend at low temperatures. However, the lines begin to diverge as they approach higher temperatures, as seen in **Figure 8**. The total percentage of weight loss is between 4% and 10% at the maximum experimental temperature, 800 °C. Again, weight losses below 100 °C were minimal due to the samples pretreating. Looking at the graph of the derivative of the weight as a function of temperature indicates the temperatures at which the most major weight losses took place. As seen in **Figure 9**, there was a high rate of change in sample weight at about 625 °C.

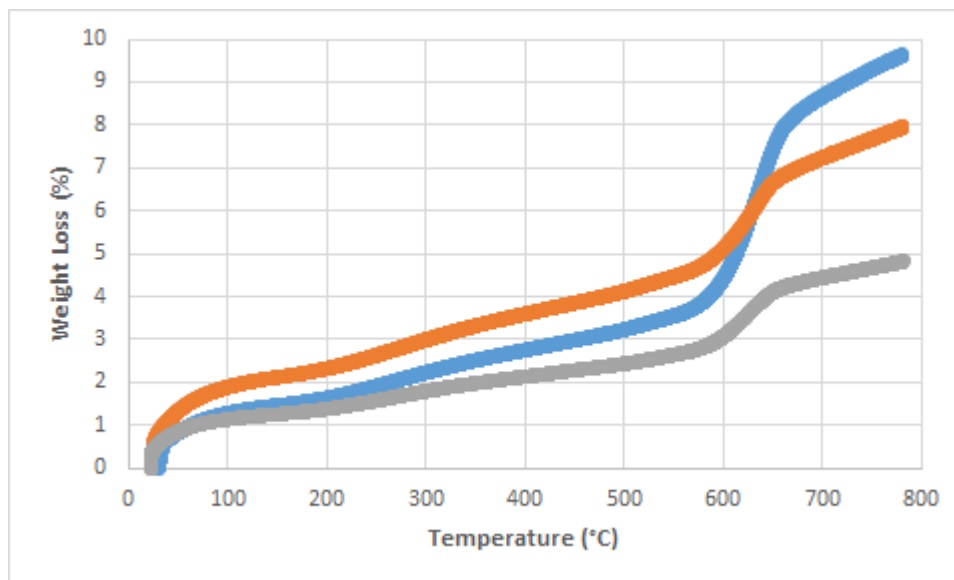


Figure 8: Percent weight loss as a function of temperature for pyrolysis in the presence of N_2 .

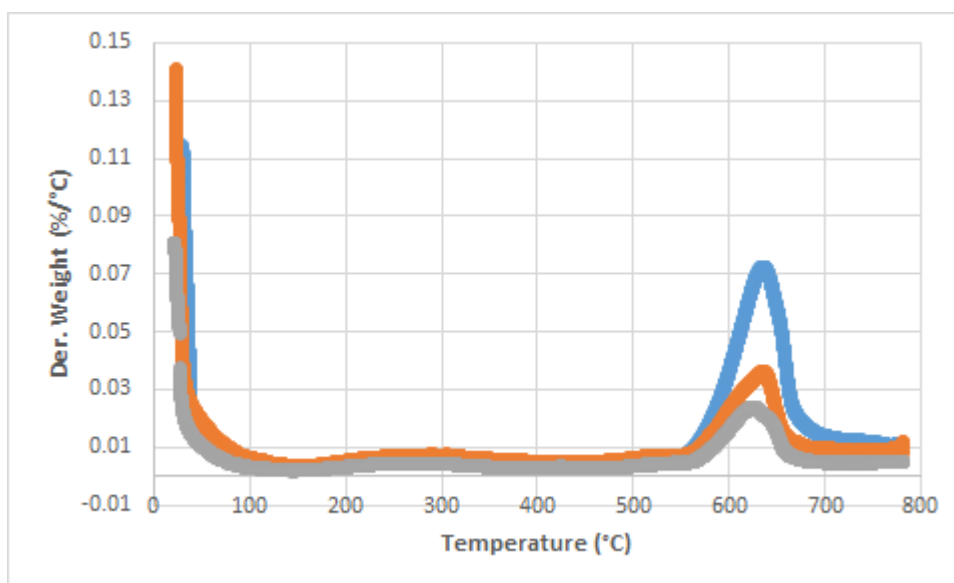


Figure 9: Derivative of weight loss as a function of temperature for pyrolysis char in the presence of air.

Experiments that were run on pyrolysis char in the presence of air indicated that 100% weight loss would be reached between 600 °C and 700 °C. Again, this suggests that components of the sample were reacting with oxygen at high temperatures. As seen in **Figure 10**, the majority of weight loss occurred between about 400 °C and 700 °C. The graph of the derivative of the weight as a function of temperature indicates that the temperature at which the rate of change of sample weight was the highest was between 500 °C and 550 °C, as seen in **Figure 11**. Additionally, there was another smaller peak on the weight derivative plot between the temperatures of 600 °C and 700 °C.

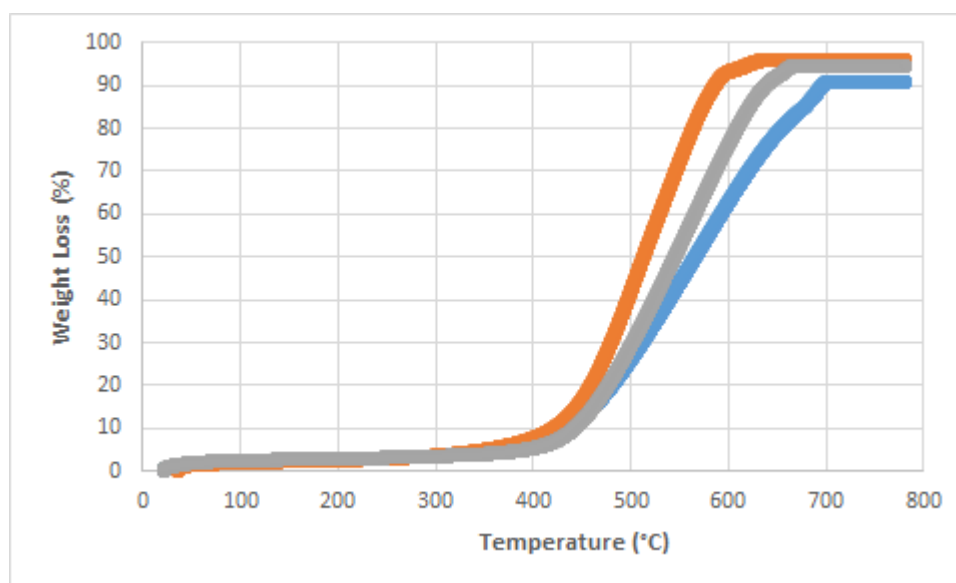


Figure 10: Percent weight loss as a function of temperature for pyrolysis in the presence of air.

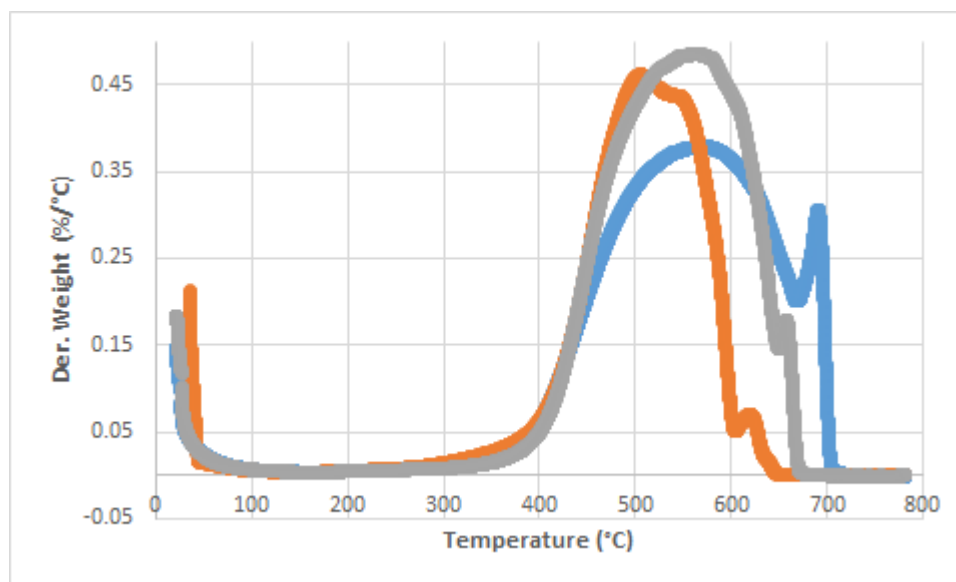


Figure 11: Derivative of weight loss as a function of temperature for biochar in the presence of air.

The experiments in which pyrolysis char samples were heated in the presence of N_2 , and allowed to cool to 30 °C before being heated again in the presence of air again indicated that the percentage of weight that will be lost with N_2 is roughly 10%, and about 94% weight loss could be achieved with air, as seen in **Figure 12**. This is unlike the experiments in which the sample was heated with air, and air only, in which 100% weight loss was achieved. Instead of achieving 100% weight loss around 550 °C, 94% weight loss was achieved by 700 °C. The graph of the derivative of the weight as a function of temperature indicates that the rate of change of sample weight was the highest between 550 °C and 600 °C in the presence of air, as seen in **Figure 13**.

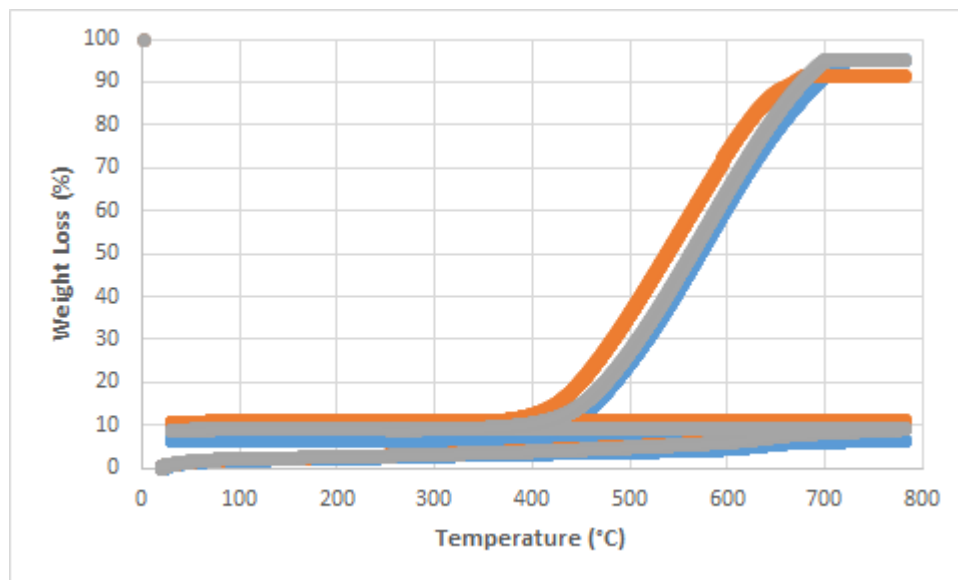


Figure 12: Percent weight loss as a function of temperature for pyrolysis in the presence of N_2 followed by air.

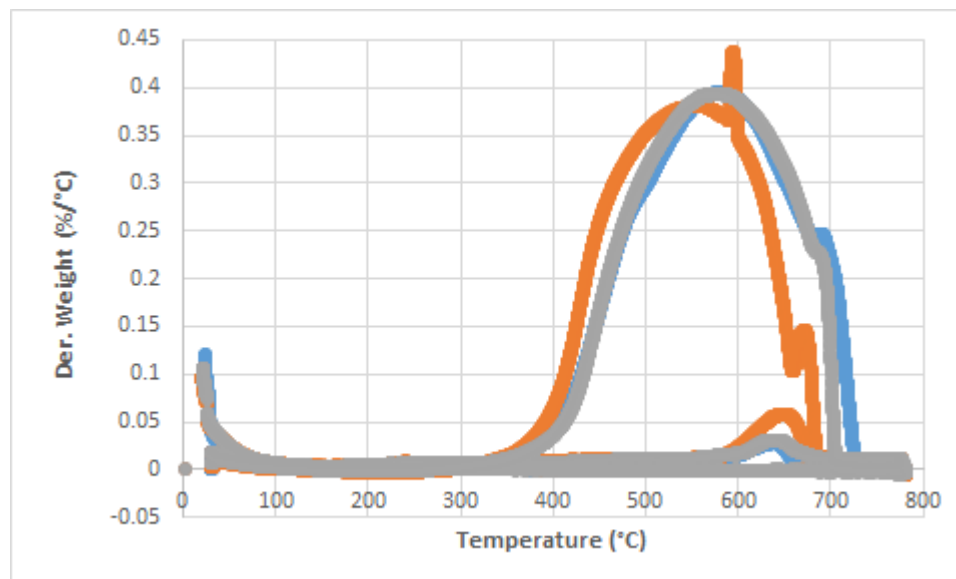


Figure 13: Derivative of weight loss as a function of temperature for pyrolysis char in the presence of N_2 followed by air.

An overall comparison of weight losses as a function of temperature for experiments run under N_2 and air can be seen in **Figure 14**. When compared, it is clear that pyrolysis chars have lower ultimate weight loss percentages than AHDH chars. The weight losses in AHDH char in the presence of nitrogen is about 5 times higher than that of pyrolysis char. In addition to having a lower final weight loss, pyrolysis chars also reached their final weight losses at a higher temperature, around 625 °C as opposed to 575 °C for AHDH chars.

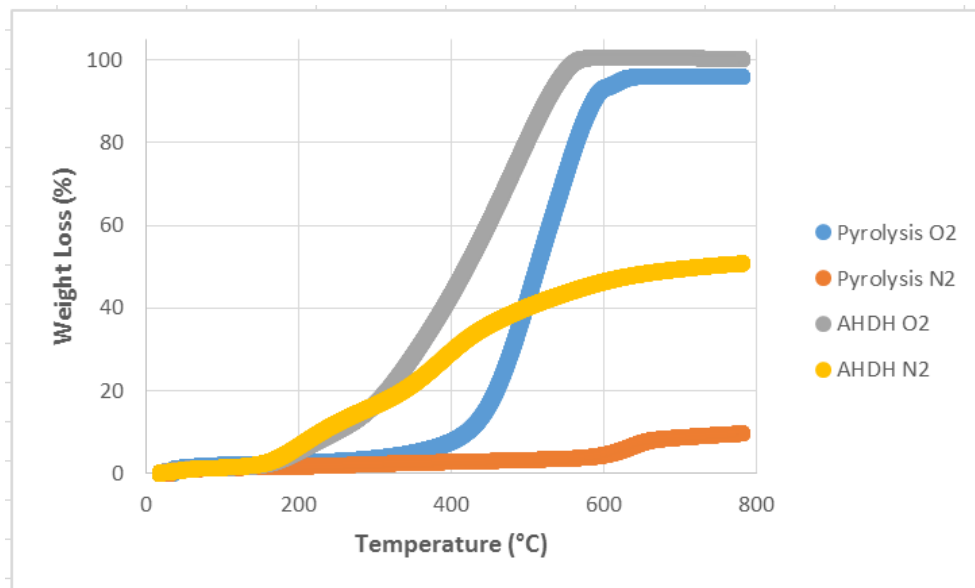


Figure 14: Comparison of percent weight loss as a function of temperature for pyrolysis chars and AHDH chars in the presence of air and N_2 .

DISCUSSION AND CONCLUSION

Both biochar feedstocks and activation methods have different strengths in terms of economic advantages. Pyrolysis and AHDH have very different biochar yields, 12% and 37.5%, respectively. If 1960 metric tons of biomass is fed to a process per day, the AHDH process produces 296,000 tons of biochar annually, whereas a pyrolysis process will produce only 95,000 tons of biochar per year. This means that there is a greater opportunity for upgrading biochars from the AHDH process. Empirical models developed by Gusman del Campo, and Dalai and Ramin were used to determine the operating conditions to make activated carbon with the surface area of 500 m²/g via physical and chemical activation of biochar, respectively.^{7,11} The physical activation model indicates that activated carbon that could be used for water treatment could be produced with an activation temperature of 661 °C and an activation time of 5 minutes, and would result in a 76% activated carbon yield. A variety of different combinations of chemical activation operating conditions could result in 500 m²/g activated carbon. An activation temperature of 660 °C, a 1:1 potassium hydroxide to biochar mass ratio, and an 80 cm³/min flow rate of nitrogen scaled to the size of an industrial reactor achieved the desired surface area for the lowest price. With a 2-hour activation time, activated carbon could be produced via chemical activation at a yield of 71.7%.

Although both models indicate that 500 m²/g activated carbon can be produced from pyrolysis char, neither of these processes would be profitable when considering operating costs. With the activated carbon selling price of \$2,140/ton, the annual revenue of \$154 million is generated. The annual operating costs, including costs of utilities,

labor, and maintenance, would total \$22 million, indicating that this project has a potential to be profitable. With the chemical activation of pyrolysis char to activated carbon, an annual revenue of \$145 million can be generated with a plant capacity of 184 metric ton per day of activated carbon. The annual operating costs of this chemical activation plant would be \$90 million dollars, which would be profitable.

While there are no models to suggest the appropriate operating conditions to upgrade AHDH char into activated carbon, the thermal decomposition trends constructed using the thermogravimetric analyzer sheds some light on the operating conditions that would be necessary as compared to pyrolysis char. Both AHDH char and pyrolysis char reached 100% weight loss in the presence of air, however, AHDH char experienced total weight loss around 560 °C while pyrolysis char didn't experience it until 650 °C. These major weight losses due to combustion indicate that organic volatile matter existing in the char is reacting with O₂ at high temperatures. The presence of such a large quantity of organic matter could indicate the conversion capabilities of the AHDH and pyrolysis processes could be improved to convert a greater quantity of the feedstock into biofuel. While pyrolysis char displayed 7% total weight loss at 800 °C in the presence of nitrogen, AHDH char had 52% total weight loss at this temperature. At all temperatures tested using the TGA, AHDH char had greater weight loss at lower temperatures when compared to pyrolysis char. This suggests that AHDH char has a lower activation energy than pyrolysis char, and as a result, it would likely create aromatic rings and lose surface functionality at lower temperatures than pyrolysis char. Because of these qualities, AHDH char could likely be activated via chemical or physical activation at milder conditions than pyrolysis char. The ability to gain high surface area activated carbon at

milder operating conditions would mean lower operating cost than pyrolysis char. The ability to upgrade AHDH char at milder operating conditions, paired with a higher biochar yield from the AHDH process suggests that the net revenue per ton of biomass feed stock would likely be higher for AHDH char.

REFERENCES

1. “Fast Facts on Transportation Greenhouse Gas Emissions.” *EPA*, Environmental Protection Agency, 26 Sept. 2017, www.epa.gov/greenvehicles/fast-facts-transportation-greenhouse-gas-emissions.
2. “Energy Use for Transportation.” *Energy Use for Transportation - Energy Explained, Your Guide To Understanding Energy - Energy Information Administration*, U.S. Energy Information Administration, www.eia.gov/energyexplained/?page=us_energy_transportation.
3. Gunukula, Sampath, *et al.* “Techno-Economic Analysis of Thermal Deoxygenation Based Biorefineries for the Coproduction of Fuels and Chemicals.” *Applied Energy*, vol. 214, 2018, pp. 16–23., doi:10.1016/j.apenergy.2018.01.065.
4. Jones, Susanne, *et al.* “Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Fast Pyrolysis and Hydrotreating Bio-Oil Pathway.” Jan. 2013, doi:10.2172/1126275.
5. Scott, Donald S., *et al.* “The Role of Temperature in the Fast Pyrolysis of Cellulose and Wood.” *American Chemical Society*, 1988, doi:10.1021/ie00073a003.
6. Kim, Pyoungchung, *et al.* “Surface Functionality and Carbon Structures in Lignocellulosic-Derived Biochars Produced by Fast Pyrolysis.” *Energy & Fuels*, vol. 25, no. 10, 2011, pp. 4693–4703., doi:10.1021/ef200915s.
7. del Campo, Bernardo Gusman, "Production of activated carbon from fast pyrolysis biochar and the detoxification of pyrolytic sugars for ethanol fermentation" (2015). *Graduate Theses and Dissertations*. 14691. <https://lib.dr.iastate.edu/etd/14691>
8. “Activated Carbon Filters.” *Activated Carbon Water Treatment | Activated Carbon Filters*, Water Professionals, 2018, www.waterprofessionals.com/learning-center/activated-carbon-filters/.
9. Reiff, Fred. “Activated Carbon and Water Treatment.” *Water Quality and Health Council*, 15 Apr. 2016, waterandhealth.org/safe-drinking-water/activated-carbon-water-treatment/.
10. Case, Paige A., *et al.* “Formate Assisted Pyrolysis of Pine Sawdust for in-Situ Oxygen Removal and Stabilization of Bio-Oil.” *Bioresource Technology*, vol. 173, 2014, pp. 177–184., doi:10.1016/j.biortech.2014.09.075.

11. Dalai, Ajay K., and Ramin Azargohar. "Production of Activated Carbon from Biochar Using Chemical and Physical Activation: Mechanism and Modeling." *ACS Symposium Series Materials, Chemicals, and Energy from Forest Biomass*, 2007, pp. 463–476., doi:10.1021/bk-2007-0954.ch029.
12. "Potassium Hydroxide Price." *Potassium Hydroxide Price Wholesale, Potassium Hydroxide Suppliers - Alibaba*, www.alibaba.com/showroom/potassium-hydroxide-price.html.
13. Alcañiz-Monge, J., and M.j. Illán-Gómez. "Insight into Hydroxides-Activated Coals: Chemical or Physical Activation?" *Journal of Colloid and Interface Science*, vol. 318, no. 1, 2008, pp. 35–41., doi:10.1016/j.jcis.2007.10.017.

APPENDICES

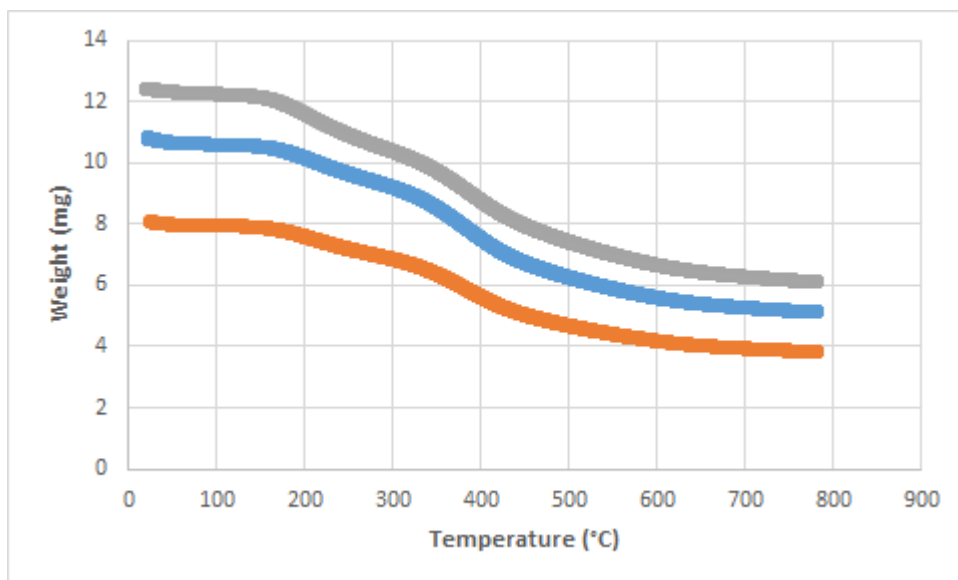


Figure A1: Weight as a function of temperature for AHDH chars in the presence of N₂.

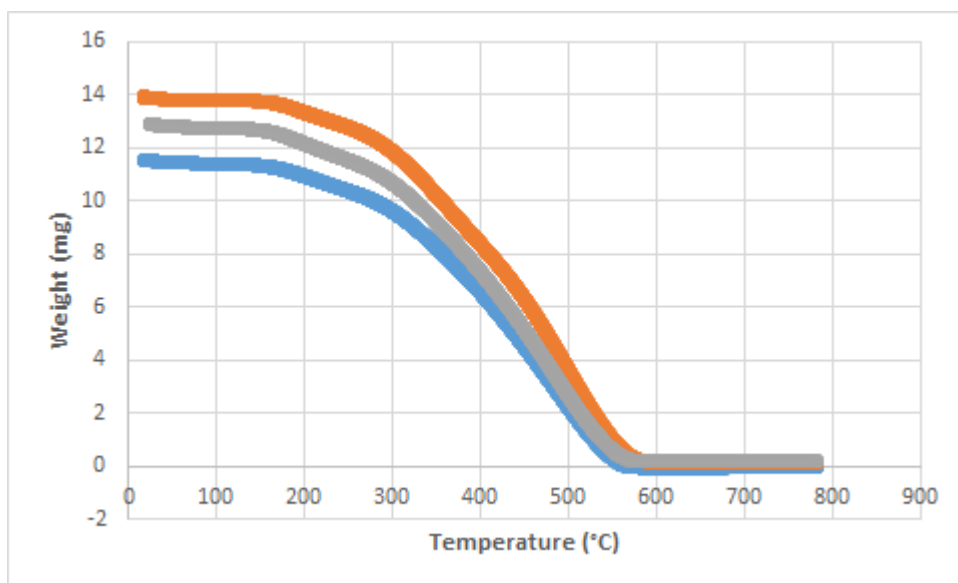


Figure A2: Weight as a function of temperature for AHDH chars in the presence of air.

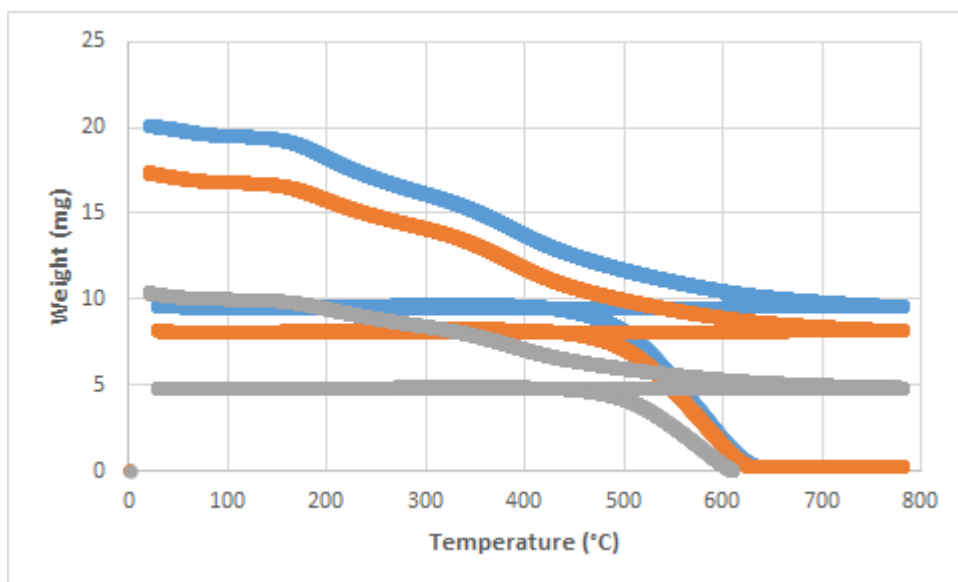


Figure A3: Weight as a function of temperature for AHDH chars in the presence of N₂ followed by air.

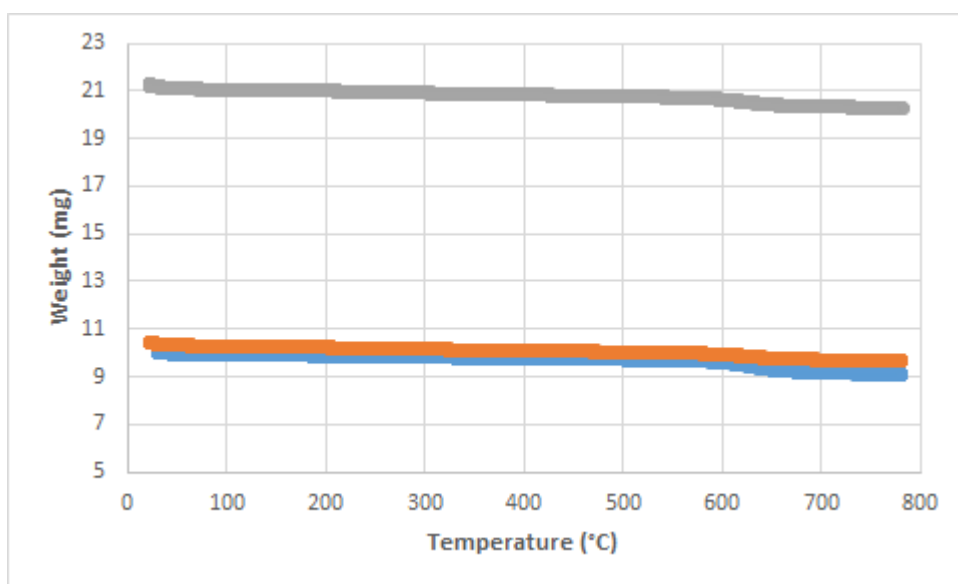


Figure A4: Weight as a function of temperature for pyrolysis chars in the presence of N₂.

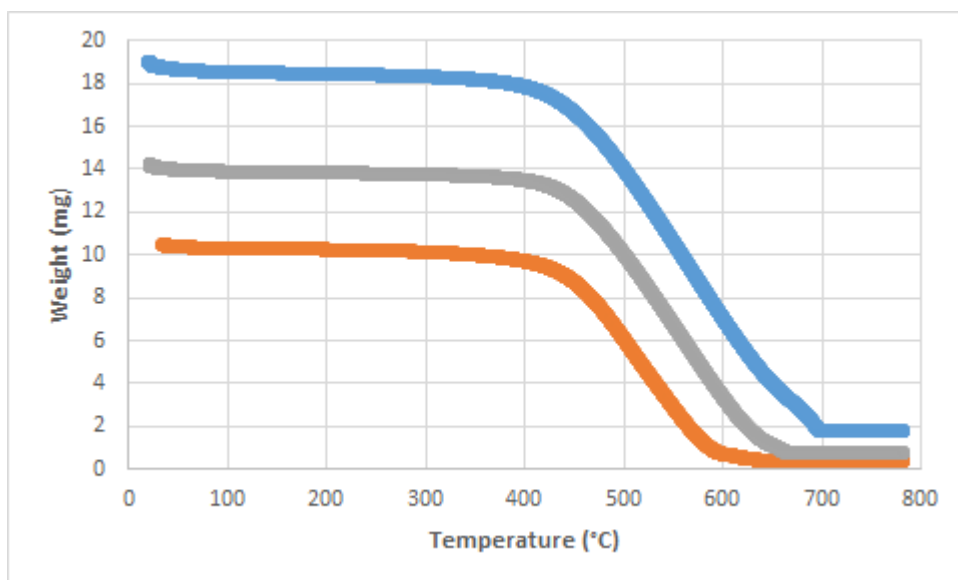


Figure A5: Weight as a function of temperature for pyrolysis chars in the presence of air.

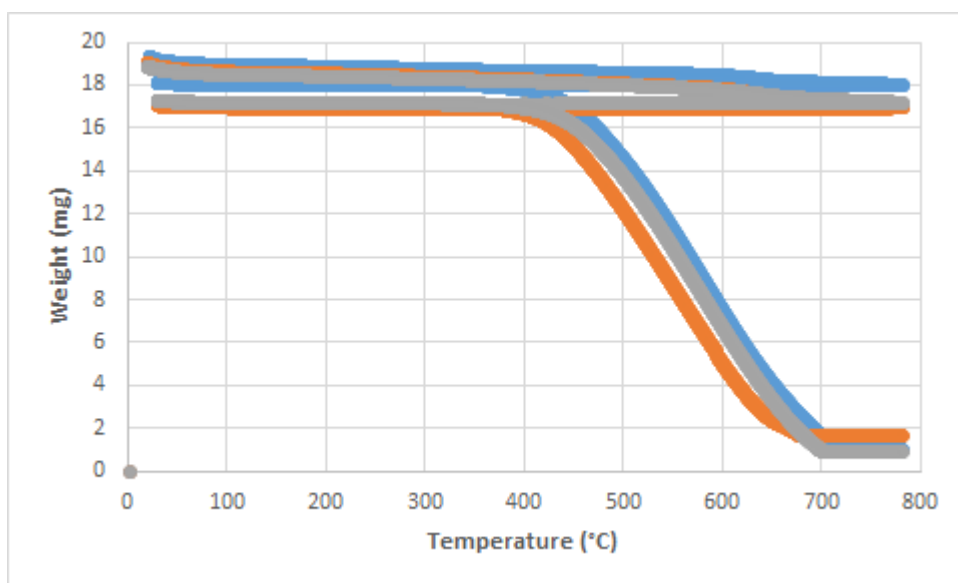


Figure A6: Weight as a function of temperature for pyrolysis chars in the presence of N₂ followed by air.

SAMPLE CALCULATIONS

Biomass feed:	$biomassfeed := 1960 \frac{\text{tonne}}{\text{day}}$
Biomass fed annually:	$biomassyr := biomassfeed \cdot 1 \text{ yr} = (7.891 \cdot 10^5) \text{ ton}$
37.5% of biomass ends up as AHDH char:	$AHDHchar := biomassyr \cdot .375 = 295918.796 \text{ ton}$
12% of biomass ends up as pyrolysis char:	$Pyrochar := biomassyr \cdot .12 = 94694.015 \text{ ton}$
Desired surface area of AC for water treatment application:	$5400 \frac{\text{ft}^2}{\text{gm}} = 501.676 \frac{\text{m}^2}{\text{gm}}$
AC selling price:	$price := 501.676 \frac{\text{m}^2}{\text{gm}} \cdot 0.0000047 \frac{\text{¤}}{\text{m}^2} = 2139.03 \frac{\text{¤}}{\text{ton}}$

Physical Activation of Pyrolysis Char:

Steam to biomass ratio:	$steamR := 2 \frac{kg}{1 kg}$
Steam price:	$steamprice := 16.64 \frac{\text{¤}}{1000 kg}$
Nitrogen to biomass ration:	$nitrogenR := 2 \frac{kg}{1 kg}$
Nitrogen price:	$nitroprice := 0.004 \frac{\text{¤}}{m^3}$
Nitrogen density:	$nitroD := 1.25 \frac{gm}{L}$
Yearly steam requirement:	$steamneed := steamR \cdot Pyrochar$ $steamneed = (1.894 \cdot 10^5) ton$
Cost of yearly steam requirement:	$steamcost := steamneed \cdot 16.64 \frac{\text{¤}}{1000 kg}$ $steamcost = (2.859 \cdot 10^6) \text{ ¤}$
Yearly nitrogen requirement:	$nitroneed := nitrogenR \cdot Pyrochar \cdot nitroprice \cdot \frac{1}{nitroD}$ $nitroneed = (5.498 \cdot 10^5) \text{ ¤}$
Yearly operating costs:	$opcost := (nitroneed + steamcost) + 18.8 \cdot 10^6 \text{ ¤}$ $opcost = 22208709.017 \text{ ¤}$
Activated carbon produced with 76% yield:	$ACmade := Pyrochar \cdot 0.76$ $ACmade = (7.197 \cdot 10^4) ton$
Activated carbon selling:	$ACsold := ACmade \cdot price$ $ACsold = 153940552.613 \text{ ¤}$
Yearly net revenue:	$netrev := ACsold - opcost$ $netrev = (1.317 \cdot 10^8) \text{ ¤}$

Chemical Activation of Pyrolysis Char:

Heat transfer coefficient:	$HTC := 5 \frac{BTU}{hr \cdot ft^2 \cdot \Delta^\circ F}$
Activation time:	$actime := 2 \text{ hr}$
Activation temperature:	$activtemp := 660$
Lab nitrogen flow rate:	$F := 80 \frac{cm^3}{min}$
Activated carbon yield:	$yield := .71722$
Potassium hydroxide price:	$PHprice := 750 \frac{\$}{ton}$
Potassium hydroxide to biomass ratio:	$ratio := \frac{1 \text{ kg}}{1 \text{ kg}}$
High pressure steam cost:	$energyprice := 9.83 \frac{\$}{GJ}$
Reactor volume:	$reactvol := \frac{Pyrochar}{yr} \cdot \frac{actime}{0.7 \frac{gm}{cm^3}} = 28 \text{ m}^3$
Reactor surface area:	<div> <div> Constraining Values </div> <div> $SA := 10 \text{ ft}^2 \quad L := 5 \text{ ft} \quad D := 5 \text{ ft}$ $\frac{L}{D} = 3 \quad SA = \pi \cdot \left(\frac{D}{2}\right) \cdot 2 \cdot L$ $\pi \cdot \left(\frac{D}{2}\right)^2 \cdot L = reactvol$ </div> </div> <div> <div>Solver</div> <div> $\begin{bmatrix} SA \\ L \\ D \end{bmatrix} := \text{find}(SA, L, D) = \begin{bmatrix} 49.08 \text{ m}^2 \\ 6.846 \text{ m} \\ 2.282 \text{ m} \end{bmatrix}$ </div> </div>
Reactor energy requirement:	$energyreq := HTC \cdot (activtemp - 25) \Delta^\circ C \cdot SA$ $energyreq = (8.848 \cdot 10^5) \text{ W}$
Energy cost:	$energycost := energyreq \cdot energyprice$ $energycost = (2.745 \cdot 10^5) \frac{\$}{yr}$

Potassium hydroxide cost:	$PHcost := ratio \cdot PHprice \cdot Pyrochar$ $PHcost = (7.102 \cdot 10^7) \text{ €}$
Yearly operating cost:	$opcost := PHcost + energycost \cdot yr + 18.8 \cdot 10^6 \text{ €}$ $opcost = 90094990.53 \text{ €}$
Activated carbon produced:	$ACmade := Pyrochar \cdot yield = (6.792 \cdot 10^4) \text{ ton}$
Activated carbon sold:	$ACsold := ACmade \cdot price = 145275319.928 \text{ €}$
Yearly net revenue:	$netrev := ACsold - PHcost - (energycost \cdot yr)$ $netrev = (7.398 \cdot 10^7) \text{ €}$

AUTHOR'S BIOGRAPHY

Kasey Johnston was born in Lockport, New York on January 19th, 1996, where she grew up and graduated in the top 1% of her class from Lockport High School. The following fall, she came to the University of Maine to pursue a degree in chemical engineering with a minor in Mathematics. During her four years at UMaine, Kasey played rugby for UMaine's Women's Rugby Team and was a member of Maine Student's for Climate Justice. In her spare time, Kasey enjoys hiking, running, and eating Thai food. After graduation, Kasey plans to spend a year volunteering in Southeast Asia and then pursue a master's degree in biomedical or chemical engineering.