Valorization of Food Waste into Hydrochar

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Approval Sheet

It is certified that contents and form of thesis entitled "Valorization of food waste into hydrochar" submitted by Yarmiah Bukhari, Uzair Ahmad, Azeem Ullah have been found satisfactory for the requirement of the degree.

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Azeem Ullah

Dedication

Humans are made through all that build us. This thesis is dedicated to our families and friends that became family. Their love allows us to soar higher than the mountains and aim for the stars. This work is an acknowledgement to all those that have impacted our lives in a big or small manner, their contributions to our lives have enabled us to be here today.

Abstract

The dwindling fossil fuels that are being unsustainably exploited are soon going to finish. One of the major reasons for the exploitation of fossil fuels is their use as an energy source in industries. While we are nearing the end of our reserves, we are also running out of our carbon budget projected to remain within the 1.5℃. While the world battles with the unprecedented patterns of climate change it is important to look for alternate clean and renewable energy sources. Biomass as a source of renewable energy only contributes 0.9% of the total primary energy consumption by source. If we increase the percentage of renewable energy harvested from biomass we can reduce stress from fossil fuels and decrease carbon emissions due to the carbon neutrality of biomass. Hydrothermal carbonization is an attractive technology due to its several advantages like compatibility with varied moisture content, the lack of need for pretreatment and it results in hydrochar which is a carbon dense energy-rich material. Three fruits, apple, banana and orange were selected for the hydrothermal carbonization. Microwave-assisted hydrothermal carbonization resulted in a lower mass yield of hydrochar. The six samples that were analyzed banana peel hydrochar had an energy densification ratio of less than 1. In the critical analysis, it was later concluded that owing to the lesser lignin content than the other two fruits, banana peel resulted in a lower energy yield. The effects of mixed biomass were also investigated in the research. The combination of biomasses resulted in a higher mass yield, however, lower calorific values.

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Chapter 1

1 Introduction:

This chapter would introduce the motivation behind the project. It would highlight the current global energy trends and the various technologies available for energy harvesting through biomass. The chapter would also be introducing the objectives and mission statement of the research project.

1.1 Background:

When food is wasted, it wastes all the resources that went into the production of the food. It wastes the labour and energy that went into growing the food. Globally 36% of the food is wasted (EPA, 2018) and goes to landfills without treatment. In Pakistan, 36 million tons of food are wasted every year. (The News International, 2021). Throwing food into landfills is not just a sustainable solution to food waste management. Landfills are contributors to greenhouse gas emissions. While the energy potential of food is being wasted by dumping it into landfills without treatment, the world is moving towards an energy crisis.

Anthropogenic carbon emissions need to decline by 45% if there needs to be a limited or no increase more than the 1.5℃ target of 2030 (IPCC, 2018). However, while the industrialized and developed countries continue with the anthropogenic industry activities the world is running out of its projected carbon budget set for a 1.5℃ rise by 2030. In 2021, Earth reached its highest carbon emissions of 36.3 billion tons. (IEA, 2022). It is predicted that an average country would run out of its carbon budget by 2030. This might be escalated for developed leading countries with higher carbon emissions (IPCC, 2021). We need a permanent and sustainable solution to these fossil fuel emissions.

Out of the global greenhouse gas emissions, 67% are carbon emissions from anthropogenic industrial burning (US EPA, 2018). If the energy sources are replaced with renewable clean sources of energy we can curtail our carbon emissions. In the current global energy mix, biomass renewable energy only has a share of 0.9% (ourworldindata.org, 2022). In Pakistan's energy mix, coal provides 17.91% of primary energy while other renewables provide only 0.07% of the total primary energy consumption (ourworldindata.org, 2022).

The global fossil fuels are dwindling, and it is predicted that we would start running out of fossil fuels in 50 years (BP, 2016).

If we increase our portion of biomass energy in the global energy mix by treatment of food waste, we can reduce our reliance on fossil fuels for energy and can manage our climate change targets effectively all the while preserving our fossil fuel reserves for our future generations.

1.2 Theory:

There are various technologies that allow us to tap into the energy potential of the food.

1. Anaerobic digestion
2. Pyrolysis
3. Hydrothermal carbonization

Anaerobic digestion is a slow process that produces biogas. Pyrolysis along with incineration and gasification is considered unfavourable in aspects of energy consumption and respective energy release through the process.

Hydrothermal carbonization is a thermochemical conversion process which is done in a water medium. The use of water as a medium makes it ecologically safe and the abundance of water is an advantage. The process of hydrothermal carbonization results in an energy-dense solid product (hydrochar) which is quoted to have the same calorific value as that of coal.

There are various advantages of hydrothermal carbonization that make it an attractive technology for food waste to energy pathways.

1.2.1 Hydrothermal Carbonization:

“Thermochemical means of conversion through HTC transformed unprocessed waste into a hydro-char bearing a high calorific content and complemented with elevated levels of carbon content. A feedstock with 75%–90% moisture content is considered ideal for this process. HTC comprises three processes, namely, dehydration, decarboxylation, and decarbonylation, for which pretreatment or drying of the feedstock waste is not needed.”

1.2.2 Advantages of Hydrothermal Carbonization:

Hydrothermal carbonization works well with varying moisture content. This is an advantage because of the heterogeneous nature of food waste it’s difficult to determine one value of moisture content. Hydrothermal carbonization can be done for feeds with a range of moisture content. It does not require pre-drying of feedstocks. This is beneficial because food waste is known to have high moisture content. Other food-to-energy conversion technologies are energy inefficient because of the energy spent on drying the biomass.

Hydrothermal carbonization produces hydrochar which is a carbon-neutral solid fuel. The burning of hydrochar does not negatively impact the environment in the same way that coal does. Coal-burning adds new emissions to the environment however, carbon-neutral hydrochar when burned does not add new carbon emissions to the air. It rereleases the same carbon dioxide into the air which was absorbed during the photosynthesis for the synthesis of biomass.

1.2.3 Different Types of Hydrothermal Carbonization:

Hydrothermal carbonization can be divided into two different categories.

1. Conventional hydrothermal carbonization
2. Microwave-assisted hydrothermal carbonization

Conventional hydrothermal carbonization is done in autoclaves, pressurized vessels put in ovens for set time and temperature.

Microwave-assisted hydrothermal carbonization makes use of microwaves as a heating source. Through radiation, the targeted biomass is heated and then converted into hydrochar. The process is done in special microwave equipment with special fitted Teflon cups.

1.3 Problem Statement:

The fossil fuel reserves are dwindling because of their unsustainable and unprecedented use in industry for heating and energy uses. If fossil fuels are exploited at the current rate without keeping any precautions in mind, there would be less to no reserves left for coming generations.

The current carbon emissions from fossil fuel burning in anthropogenic activities had led to a decrease in the permissible carbon budget and contributed immensely to the climate crisis. One of the key strategies to manage the climate crisis is to decrease carbon emissions. This can not be done unless fossil fuel burning as a primary energy source is reduced.

Globally the potential of food is wasted when it is dumped into landfills without treatment. However, the treatment of food is problematic due to its varying moisture content and energy-intensive technologies available.

Hydrothermal carbonization produces a hydro car, a carbon-neutral solid fuel which would not increase the net carbon emissions. This increases the contribution of biomass to global energy reducing the reliance on fossil fuels. If we reduce the reliance on and exploitation of fossil fuels we can preserve our fossil fuels for coming generations.

1.4 SDG Mapping:

Sustainable development goals are set by United Nations. These goals are set as indicators to achieve a sustainable society for all keeping in mind the goals of intersectionality and inclusivity. The goals are indicators of a healthy, progressive society for all. The goals target various aspects like sanitation, education, poverty, sustainable energy, global peace and much more. There are 17 goals in total.

This research project is mapped with two sustainable development goals.

1.4.1 Target 7.2:

"By 2030, increase substantially the share of renewable energy in the global energy mix"

The target calls for access for all to modern, clean and renewable energy.

Hydrothermal carbonization that uses biomass as feedstock allows us to map the research with this SDG. It is renewable because it uses food waste as a feedstock for the reaction. Food waste is not a resource that we can run out of.

1.4.2 Target 12.3:

"By 2030, halve per capita global food waste at the retail and consumer levels and reduce food losses along production and supply chains, including post-harvest losses"

The food wastage along production and supply chains would be minimized by using hydrothermal carbonization. A lot of fruit portions of fruits are wasted in the food industry due to several reasons like quality defects or getting damaged during transportation. These fruits have no other use than to get dumped in landfills because they are discarded. Fruits like these or the remains of fruits which have no further use in the industry in the manufacturing process can be used as a feedstock for hydrothermal carbonization. This minimizes the wastage of food along with several levels.

1.5 Objectives:

The objectives for the research project are as follows:

1. To conduct hydrothermal carbonization with both methods, conventional and microwave-assisted and note if there are any differences in the production of hydrochar.

2. The effects mixed biomass can have on the production of hydrocahr.

3. Investigate how the composition of hemicellulosic biomass affects the heating value of hydrochar.

Chapter 2

2 Literature Review:

The literature review is an important part of research to establish a solid ground for future investigation and gather relevant information to conduct the research correctly with clear direction.

2.1 Hydrothermal Carbonization as the Preferred Technology

The world is moving towards an energy crisis, and as the world struggles to find more renewable energy sources it is important to find attractive technologies that allow us to tap into the potential of biomass for energy purposes. A disadvantage of using wet biomass as feedstock for the energy conversion technologies is the need for one or more pretreatment steps before using them for the energy conversion process. Waste biomass has high energy content which makes it unsuitable for the energy conversion process because it yields less energy densification ratios and energy yields. The biomass decomposition during hydrothermal carbonization increases the carbon content of the biomass and the resulting hydrochar can be used as a carbon-neutral solid fuel. (Maniscalco, Volpe and Messineo, 2022)

One of the major problems faced by biomass conversion to energy-dense materials is the variable moisture content of the food waste. It is difficult to determine which waste would contain exactly what amount of moisture content. Treatment options like pyrolysis and gasification work well for dry biomasses. If these techniques are employed, biomass has to be dried first before treatment. The initial pretreatment makes these technologies energy-intensive technologies. Technologies that work well with variable and high moisture contents, a property of food waste are to be preferred for the energy conversion pathway of food waste. (Saqib et al., 2019)

Pyrolysis is an energy intensive method that runs on high temperatures (400-800℃). (Prurapark, et al., 2020). One of the reasons why hydrothermal carbonization is preferred to technologies like pyrolysis is the lack of pre heat treatment required to dry the wet feedstock. Hydrothermal carbonization is performed at lower temperatures than pyrolysis (180-350℃), which makes it less energy intensive than its counterpart technology which synthesizes biochar (Nasrollahzadeh, et al., 2021).

There are various problems that are associated with the food to energy pathway of gasification. The syngas mixture that is produced is a combination of several gases that require post treatment to treat syngas. Undesirable gases also have a chance of being present in the syngas mixture. (Molino, et al., 2016)

Hydrothermal carbonization uses water as a medium which makes it ecologically safe. Other techniques often require substances and chemicals which are often derived from fossil fuels. This is why hydrothermal carbonization is the preferred pathway for conversion of biomass to energy because of its ecological safety and being the sustainable solution. (Román, et al., 2018)

Hydrochar synthesized from hydrothermal carbonization has several applications. One of the key applications being as an adsorbant. Furthermore, hydrochars can be activated with certain substances to enhance their qualities. $KHCO_3$ activation of glucose synthesized hydrochar converts it into N-doped carbon spheres which later showed potential for carbon dioxide capture. (Shi, et al., 2022)

Hydrochars have an added application of being used as a soil additive. The hydrochars derived from agriculture residues have shown in soil conditioning. They promote carbon and nitrogen cycles to varying levels depending on the various parameters of the hydrochars synthesized. They are also shown to reduce the emissions of carbon dioxide and nitrogen dioxide. (Li, et al., 2022)

2.2 Hydrothermal Carbonization Parameters

Hydrothermal carbonization is a thermochemical conversion that degrades biomass. The parameters such as the temperature of the reaction and the residence time for the biomass for the reaction play affect the properties of the hydrochar. It is pertinent to choose reaction parameters that allow us to tap into the maximum energy potential for the hdyrochar. Reaction temperatures ranging from 180-250℃ are preferred to achieve higher calorific values of the hydrochar. (Vardiambasis et al., 2020)

Cellulosic biomasses are constructed of complex substrates. The substrates like hemicellulose, lignin and cellulose are commonly found in the hemicellulosic biomasses. It is difficult to distinguish which substrate is responsible for the higher calorific value of the hydrochar. It is also difficult to gauge the exact percentages of each substrate that make up the hemicellulosic biomass. Depending on the geography and other factors like the species of the fruit the component percentages tend to vary. In this aspect, it is important to choose a technology that can cater to various component percentages and varying moisture content. (Paritosh et al., 2017)

Achieving a good calorific value for hydrochar is an important aspect of the valorization of food waste. A higher calorific value of hydrochar would result in a higher amount of energy released when the hydrochar would be combusted. The studies show that biomass would higher lignin content tends to show higher calorific values than their counterparts. (Masoumi, 2021)

Initial biomass-to-water ratio affects the calorific values of the resulting hydrochar. It is pertinent to choose a ratio that results in maximum calorific value possible. When the set ratio of biomass-to-water starts to increase from 15%, the resulting hydrochar result in lesser heating values. (Oktaviananda, 2017)

Hydrothermal carbonization results in products like liquid phases and solid phases. The distribution of the phases is dependent on the kind of feedstock used and the conditions that have been provided to the feedstock (Yoganandham, et al., 2020).

When residence times are increased the mass yield percentage decreases. The extended residence time would cause an increase in coke content of hydrochar. If the reaction temperature is increased, it can be seen that the calorific value of the hydrochar also increases. If the residence time and temperature are increased simultaneously the mass yield of hydrochar would decrease while the ash content of the hydrochar would increase. (Czerwińska, et al., 2022)

Increasing temperature and residence time can lead to lower mass yields but increased carbonization and higher energy densification ratios. (Soh, et al., 2022)

2.3 Substrate Concentration Effects on Calorific Values

Food waste is heterogenous in nature. It’s difficult to determine the exact percentages of different components of hemicellulosic biomasses. It’s important to investigate that which component of hemicellulosic biomass is affecting the calorific value of hydrochar, an important performance parameter for hydrochars. Studies show that foods with higher lignin content show higher calorific values and lignin has been the component with the highest impact on the calorific values of hydrochars (Masoumi, et al., 2021)

2.4 Methods for characterization of hydrochar:

The hydrochar obtained must be characterized for its various properties to determine its suitability as a replacement for solid fuels. There are different tests that have to be performed to gather sufficient results to reach this conclusion. A proximate analysis test is performed to check the percentage of volatile compounds present in the hydrochar. The ultimate analysis is performed to check the quantitative elemental composition of the hydrochar. The calorific analysis tells us about the heating value of the hydrochar. This is an important parameter to test if hydrothermal carbonization is used to recover energy from wasted food. There are other testing techniques that can be used to test the physical properties of hydrochar. Scanning electron microscopy for its structural analysis can also be used (Tippayawong, et al., 2020).

Chapter 3

3 Methodology

The chapter would be introducing the research methodology and all the steps that were taken for the synthesis of hydrochar.

3.1 Preparation of feedstock

3.1.1 Determination of Feedstock

The research would focus on the valorization of orange, apple and banana peels. These three are lignocellulosic biomasses and fruits that are abundantly found in Pakistan. The fruits were chosen according to their seasonal availability. From September to February, oranges are grown in Pakistan. Bananas and apples are abundantly available throughout the year. The rationale behind choosing these specific fruits was the lignocellulosic nature and the seasonal variability.

3.1.2 Separation of Peels

The project aims to consider those peels that are wasted along with the production processes. The peels were collected from fruit shops from Concordia 1 of the National University of Sciences and Technology. This replicates the local situation of Pakistan where there is plenty of wastage in fruit shops, juice shops or jam industries.

3.1.3 Grinding the Peels

To minimize the particle size of the peels, it is important to grind them. The peels were ground in biomass ground for sixty seconds. To ensure that the size of the grains is smaller than 10mm they were passed through the sieve number 10. After all the peels were ground, they were stored in polythene bags to avoid further degradation. It is important to prevent further increase in moisture of the peels because that would not represent the true condition of the peels and can disturb the results of the research.

3.1.4 Drying the Peels

In later stages, the biomass is ought to be submerged in water for the reaction. The amount of water including the existing moisture content is supposed the total ratio of water to biomass ratio. However, it's difficult to calculate the exact moisture content for biomass samples. Hence, the peels were dried beforehand. The temperature used was 65℃ for 12 hours. This temperature is used for biodegradable masses. After the peels were dried, they were again stored in polythene bags in a desiccator. This is to ensure that peels remain dry till further experimentation.

3.2 Experimentation

3.2.1 Biomass Suspension

The dried peels were in the form of hard rocks, they are ground using mortar and pestle to break down the particle size.

Hydrothermal carbonization uses water as a medium to conduct the reaction. The biomass to water ratio affects the properties of hydrochar. Biomass to water ratio increasing more than 15% results in a lower calorific value of hydrochar. (Oktaviananda, et al., 2017)

The suspension was established weight to a weight basis. 5 grams of biomass would reflect 50ml of water used for the reaction.

Distilled water is used for the reaction. Distilled water is free from extra salts which can affect the reaction or contribute to result in distortions later.

A homogenized slurry is required to allow uniform heating of the target biomass. The solution formed is then turned into a homogenized slurry using a magnetic stirrer with a residence time of five minutes.

The homogenized slurry mixture is then transferred to the reaction vessel.

In those samples where mixed biomass has to be used, a 1:1 ratio of both biomasses is maintained. This is reflected as 2.5 grams of both fruit waste peels being added to 50ml of water.

There were 6 samples prepared in total for the hydrothermal carbonization.

Orange peels hydrochar was the first batch that was tested. Orange peels were used to synthesize hydrochar through both methods of hydrothermal carbonization.

The first objective of the research calls to analyze if there are any differences in the results of microwave-assisted hydrothermal carbonization and ordinary hydrothermal carbonization. For the first batch of peels, both methods would be used. However, after analysis of the initial results microwave-assisted hydrothermal carbonization would not be used for the next batches of peels.

3.2.2 Microwave-Assisted Hydrothermal Carbonization

As mentioned above, there are two different modes of heating that can be chosen for hydrothermal carbonization. Microwave hydrothermal carbonization uses microwaves to heat the targeted biomass. Instead of using hot air ovens, special Teflon tube fitted microwaves are used for this purpose.

The slurry mixture was poured into the Teflon tubes of the microwave. The microwave was then turned on at 180℃ for the residence time of 1hour.

3.2.3 Ordinary Hydrothermal Carbonization

Ordinary hydrothermal carbonization is performed using a hot air oven.

For the degradation of biomass into its comprising components, it needs a consistent uniform heating source.

The slurry mixture is poured into an autoclave vessel and the autoclave is sealed. The pressurized vessel is then put into the hot air oven at the temperature of 180℃ for a residence time of 1 hour.

3.3 Post Treatment of Hydrochar

3.3.1 Filtration

The resulting mixture obtained after hydrothermal carbonization contains both liquid and solid fractions. Hydrochar is the solid fraction. The liquid and solid fractions need to be separated before the characterization can take place.

The solid and liquid fractions of the resulting mixture are separated using a filtration assembly. The filter paper size was 20µm. The filtration assembly with the help of applying vacuum separated the liquid fraction and collected it in the flask at the bottom. However, the hydrochar was collected at the top of the filter paper.

3.3.2 Washing of hydrochar

The collected hydrochar after filtration has to be washed thoroughly with distilled water before it can be used for characterization. It is imperative to wash the hydrochar to remove any remains of the liquid fraction.

To obtain a clean and pure sample of hydrochar, the sample has to be repeatedly washed with distilled water. Acid washing is avoided for hydrochar because it can react and damage the existing structure of hydrochar, decreasing its capability as an adsorbent.

3.3.3 Drying the Hydrochar

The obtained wet hydrochar has to be dried before further characterizations and usage. The hydrochar is dried in a muffle furnace for 24 hours at the moisture removal temperature of 105℃.

3.3.4 Storage

The dried hydrochar is removed and stored in a desiccator to prevent any external moisture from disrupting the properties of the hydrochar.

3.4 Characterizations

Characterizations are important because they allow us to profile the quality and properties of the hydrochar obtained.

3.4.1 Proximate Analysis

Proximate analysis is a test that is used to calculate the amount of volatile matter, ash content and fixed carbon. This test is important because good quality coals don’t have a high amount of ash content present in them. If the hydrochar obtained contains a high amount of ash, it would not be considered suitable for combustion.

A sample is pre-weighed and put in the muffle furnace for 7 minutes at a temperature of 950℃. The change in weight would show the amount of volatile matter present.

$$\frac{\mathrm{w1}-\mathrm{w2}}{\mathrm{w1}} * 100\% = \%\ \text{of volatile matter present}$$

In the next step, the sample is heated at 700℃ until the mass becomes constant. This is checked by weighing the remaining samples a minimum of twice. If the remaining sample weighs the same that means we are only left with ash.

$$\frac{\mathrm{w2}-\mathrm{w3}}{\mathrm{w2}} * 100\% = \%\ \text{of ash content}$$

The fixed carbon content can be easily quantified by removing ash content and volatile matter percentages from 100.

$$100 - (ash\ content) - (volatile\ content) = fixed\ carbon\ \%\ present$$

3.4.2 Ultimate Analysis

The percentages of key elements (C, H, O and N) were calculated using the formula of Nhuchhen (Poomsawat and Poomsawat, 2021).

$$C = -35.992 + 0.7698(VM) + 1.3269(FC) + 0.3250(Ash)$$

$$H = 55.3678 - 0.4830(VM) - 0.5319(FC) - 0.5600(Ash)$$

$$O = 223.6805 - 1.7226(VM) - 2.2296(FC) - 2.2463(Ash)$$

The remaining fraction after subtraction of C, H, O and ashes was assumed to be the nitrogen content.

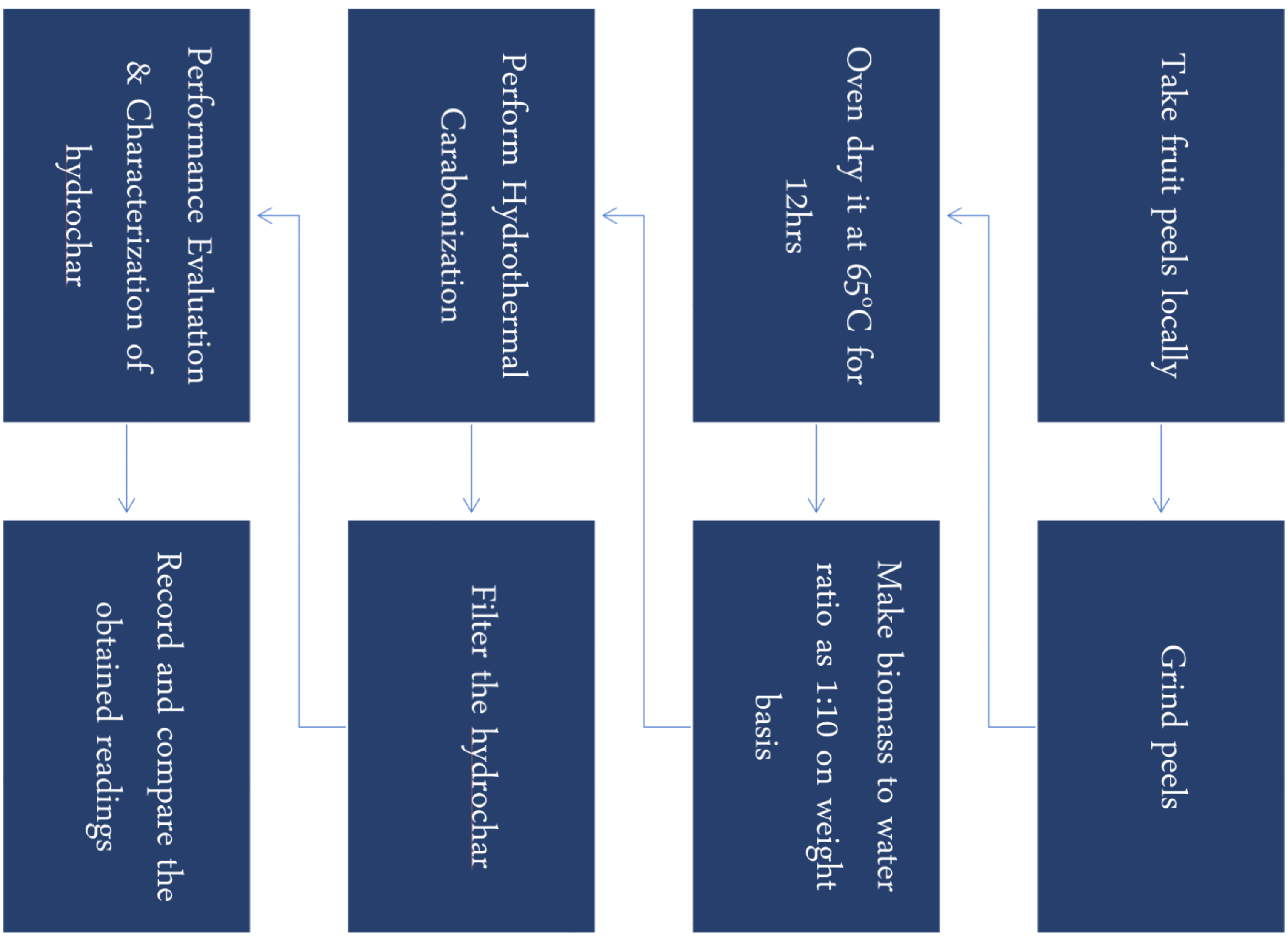
Elemental composition is important because good quality coals have a high carbon content. These allow us to characterize the hydrochar obtained as a particular type of coal.

3.4.3 Calorific Value Analysis

For the calorific value analysis, the samples were sent to USPCASE NUST. The samples were burned in an oxygen bomb calorimeter to accurate values for the calorific value of hydrochar. The research aims to quantify if Pakistani fruit made hydrochar has sufficient heating value to be used as a solid fuel which is carbon neutral with minimum environmental impact.

The quality of coal can also be determined by the amount of heat that is liberated per unit mass from coal. If the resulting values from hydrochar are similar to that of coal, it would mean that hydrochar manufactured in Pakistan can potentially substitute coal as a solid fuel.

3.5 Methodology Pathway



Chapter 4

4 Results and Discussion

This chapter would analyze the collected data and explain the trends observed.

4.1 Source of Heating

In the beginning orange peels, and hydrochars were synthesized from microwave and hot air ovens. This was done to analyze if there are any changes to the produced hydrochar. Mass yield % is used to analyze the results in this case. Mass yield is an important aspect of hydrochar synthesis. If the percentage yield is too low then the process is not feasible.

Two different samples A and B were taken of the same amount while one was heated with microwaves and the other with the conventional method of hot air oven heating.

Sample A

1. Oven-dried at 65^{o}C for 12 hours
2. Microwave-assisted -HTC at 180^{o}C for 1 hour

Sample B

1. Oven-dried at 65 ^{o}C for 12 hours
2. Hot air oven hydrothermal carbonization at 180^{o}C for 1 hour

All of the parameters were kept the same except for the heating source, this is to ensure that the only observed variable is the effects of the two different modes of heating.

4.1.1 Observations of Mass Yield

Sample A	Yield %
Sample 1	45.7
Sample 2	46.8
Sample 3	47.8

Table1: Mass yield results for sample A

$$\frac{\text{Mass output (g)}}{\text{Mass input (g)}} * 100\% = \%\ \text{yield of hydrochar}$$

Sample A were the orange peels that were put for reaction through the microwave-assisted pathway. The experiment was done three times to give it statistical importance.

In all the results it can be seen that the mass yield of microwave-assisted hydrothermal carbonization came out to be lesser than 50%. This is an important aspect to note because that would mean that larger amounts of peels would result in less than that amount of hydrochar generated if microwave-assisted hydrothermal carbonization is used for future purposes.

Sample B	Yield %
Sample 1	65.4
Sample 2	66.8
Sample 3	67.3

Table 2: Mass yield results for Sample B

It is evident that sample B hydrochar that was synthesized using a hot air oven yields better results than microwave-assisted hydrothermal carbonization.

This can be attributed to the fact that microwave-assisted hydrothermal carbonization resulted in a larger fraction of liquid product, but hot air oven hydrothermal carbonization resulted in a larger fraction of the solid product.

This is important to note that mass yields are important to assess the feasibility of any product. If a larger amount is required initially to produce smaller output, it would not be deemed fit for commercial use.

Once both methods were batch tested and the results were analyzed it was decided to use hot air oven hydrothermal carbonization for the latter steps of the research. This concluded the results of objective 1. Both methods were tested under the same conditions and the difference in the yields of hydrochars was noted.

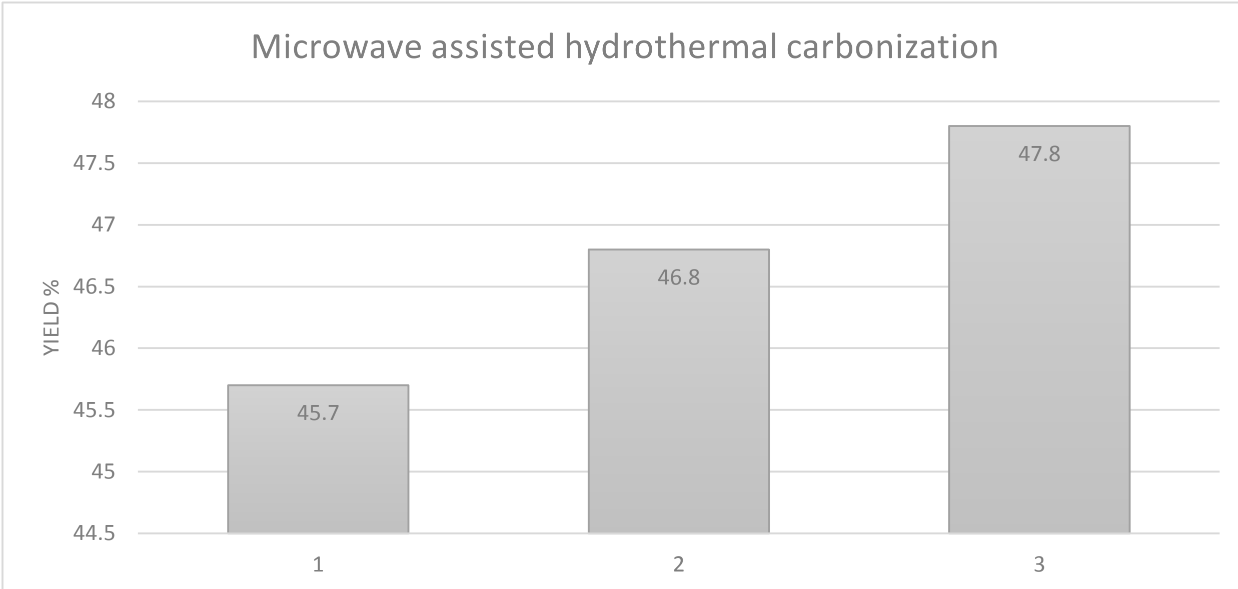


Figure 1: Graph of mass yields of Sample A

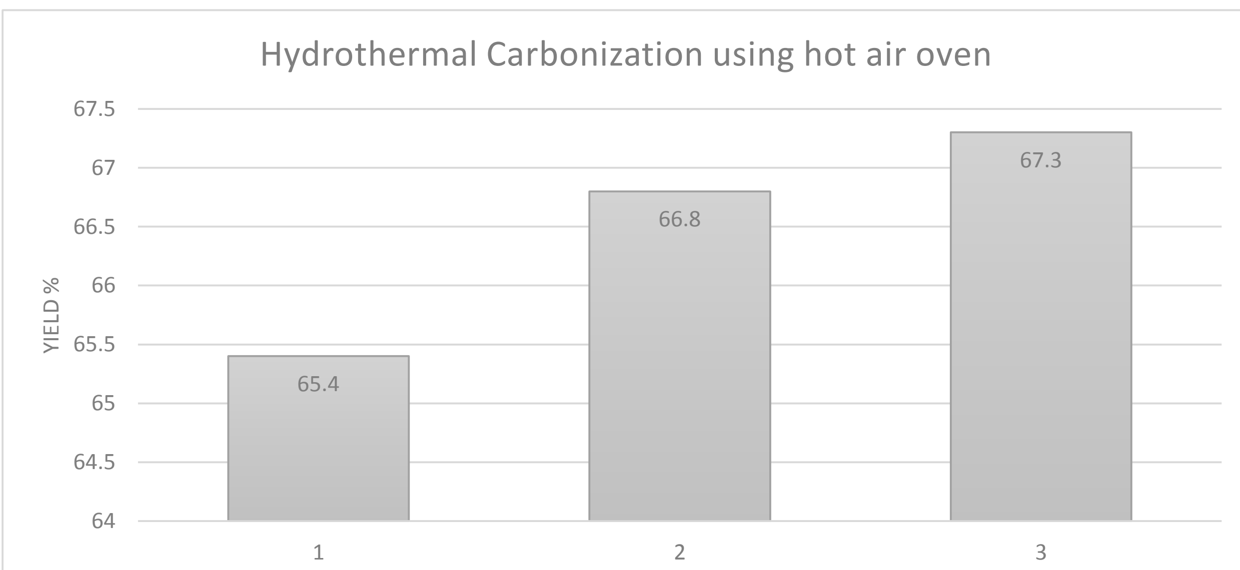


Figure2: Graph of mass yield results of Sample B

4.2 Hydrochar Yield

Six samples were analyzed over the course of the research. The six samples were:

- Pure Apple peel hydrochar
- Pure Banana peel hydrochar
- Pure Orange peel hydrochar
- Apple peel and Banana peel hydrochar
- Apple and Orange peel hydrochar
- Banana and Orange peel hydrochar

As mentioned in chapter 3, the mixtures of biomasses were prepared in the weight/ weight ratio of 1:1.

4.2.1 Observations of Hydrochar Yield

Sample	Yield %
Apple peel HC	65.7
Banana peel HC	68.53
Orange peel HC	65.35
Apple and Banana HC	69.58
Apple and Orange HC	69.46
Orange and Banana HC	71.05

Table3: Mass yield results of hydrochar synthesized from six different samples of fruit peels

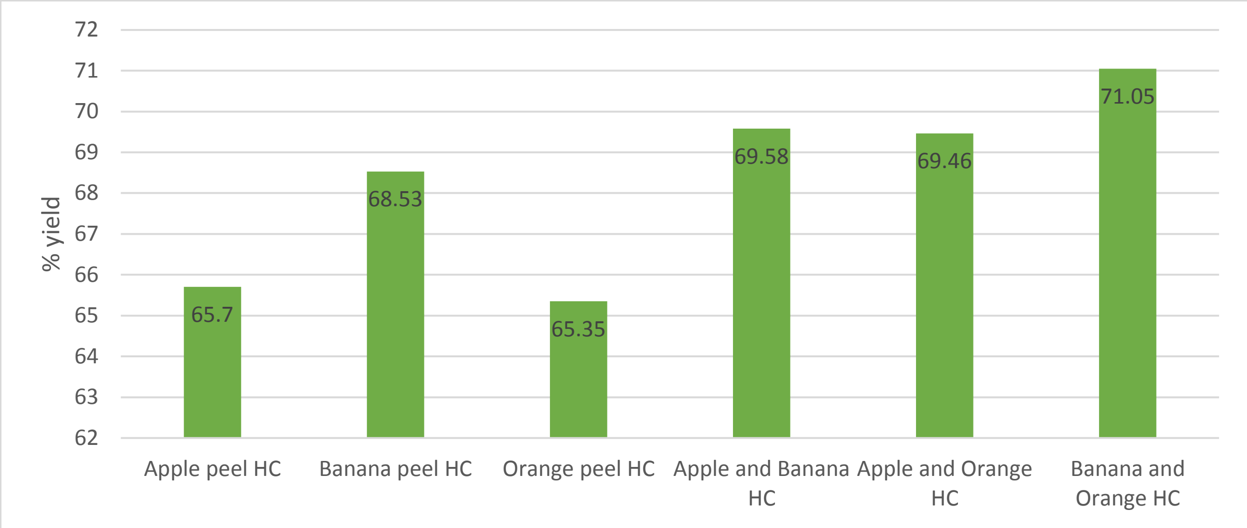


Figure 3: Graph of yield results of the samples

All the samples returned yield results higher than 60%. This is an improvement from microwave-assisted hydrothermal carbonization that returned values of less than 50%.

The graph shows that mixed biomass samples returned higher values of mass yields. This makes it an attractive feature. Mixed waste can be directly used without segregation for the synthesis of hydrochar with high values of mass yields

4.3 Calorific Analysis

4.3.1 Observations

Sample	HHV (BTU/lb)
Apple peel HC	11,000
Banana peel HC	5300
Orange peel HC	9000
Apple and Banana HC	7000
Apple and Orange HC	5000
Banana and Orange HC	8300

Table 4: Calorific values of samples

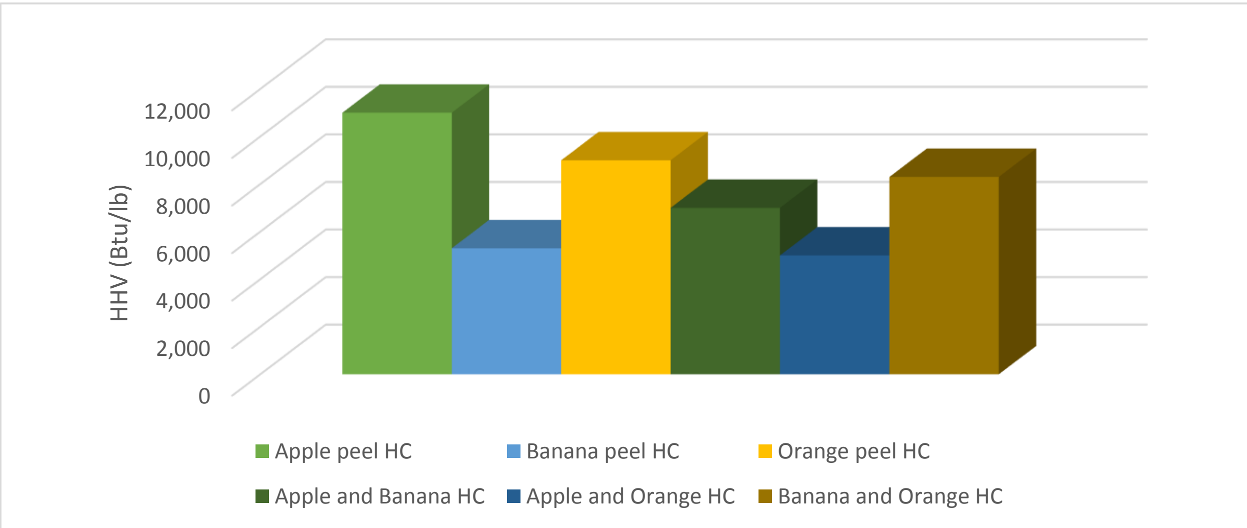


Figure4: Graph of calorific values of samples

4.3.2 Comparison of Calorific Values with Coal

Hydrochar can replace coal as a carbon-neutral solid fuel for combustion purposes in the industry. However, hydrochar would not be an attractive option if the energy yielded upon its combustion is lesser than that of coal. It is important to draw comparisons between the calorific values of the two to analyze if the hydrochar synthesized can be considered as a potential replacement.

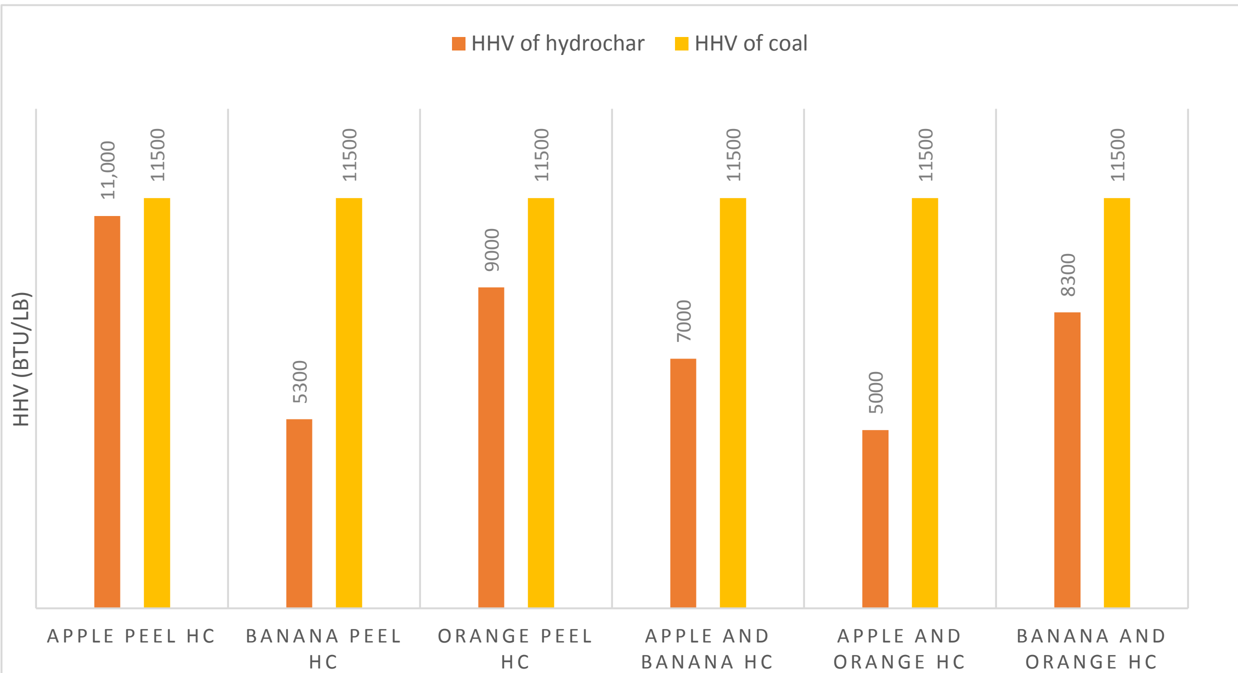


Figure5: Graph of comparison of calorific values of samples and coal

It can be seen that hydrochars synthesized from peel samples returned higher calorific values than those hydrochars synthesized from mixed biomass samples. This trend was followed in all of the six samples. Pure Apple peel hydrochar returned the highest calorific value and came very close to that of sub-bituminous to lignite coal (Kentucky Geological Survey, 2019).
Banana peel hydrochar yielded the least calorific value out of the three pure peel hydrochar samples while the apple and orange mixture of peels resulted in the least calorific value among the three mixed biomass samples.

4.4 Energy Yield and Energy Densification Ratio

The energy densification ratio refers to how many times the calorific value has been increased as compared to the calorific value of the raw waste. Waste valorization and energy conversion pathways should result in energy densification ratios equal to or higher than 1.

$$\frac{\text{HHV of hydrochar}}{\text{HHV of raw waste}} = \text{Energy densification ratio}$$

$$\text{Energy Yield \%} = \text{Energy densification ratio} * \text{\% yield}$$

The above-mentioned formulas were used to calculate the energy densification ratios and energy yields.

Sample	**% yield**	**Energy Densification Ratio**
Apple peel HC	65.7	1.27
Banana peel HC	68.53	0.75
Orange peel HC	65.35	1.2

Table5: Energy densification ratios of samples

Sample	**Energy Densification Ratio**	**Energy Yield %**
Apple peel HC	1.27	84.05
Banana peel HC	0.75	51.89
Orange peel HC	1.2	78.42

Table6: Energy Yield results for the samples

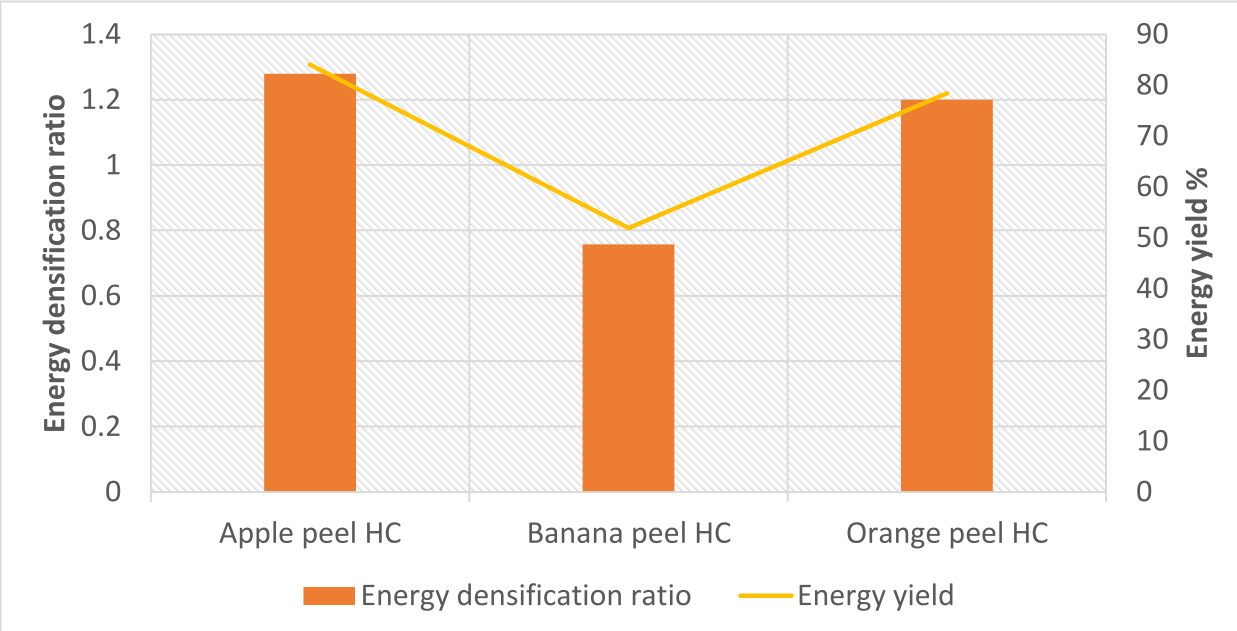


Figure6: Graph of energy densification and energy yield

Due to the lower calorific values of banana peel hydrochar, it is evident that it has also resulted in lower energy densification ratios. While apple and orange give similar energy densification ratios, banana peel hydrochar densification ratio is less than 1. This means that the banana peel hydrochar resulted in a lower calorific value than that of raw combustion of banana peel waste.

4.5 Proximate Analysis

Sample	Volatile Matter %	Fixed Carbon %	Ash %
Apple peel HC	75.1	24.88	0.02
Banana peel HC	74.3	24.21	1.49
Orange peel HC	76.3	22.02	1.68
Apple and Banana HC	77.8	24.2	2.00
Apple and Orange HC	74.6	23.87	1.53
Orange and Banana HC	74.3	24.33	1.37

Table 7: Proximate analysis results for samples

The proximate analysis results show that all hydrochars synthesized during the research from different combinations, resulted in ash content lesser than 3%. The volatile matter in all of the samples was greater than 70%.

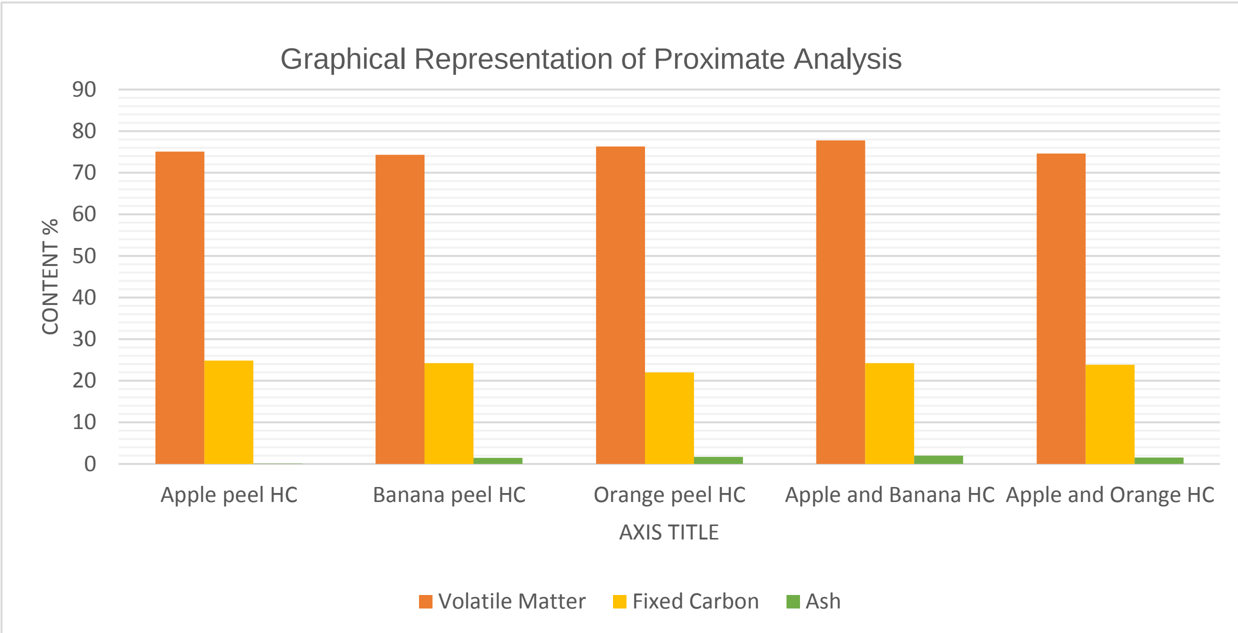


Figure7: Graphical representation of proximate analysis

Volatile matter can be seen as a dominant component of the resulting hydrochars while there is the least amount of ash present.

4.6 Ultimate Analysis

Sample	Carbon%	Hydrogen%	Oxygen%	Nitrogen %
Apple peel HC	54.83	5.84	38.79	0.51
Banana peel HC	53.80	5.76	38.36	2.05
Orange peel HC	52.50	5.86	39.376	2.25
Apple and Banana HC	56.65	3.79	31.21	8.33
Apple and Orange HC	53.60	5.78	38.51	2.09
Banana and Orange HC	54.83	5.84	38.79	0.51
Coal (lignite)	51.21	5.63	36.52	1.81

Table 8: Ultimate analysis results of samples

The obtained results are compared with the values of coal (lignite). It can be seen that all of the obtained hydrochars have higher carbon content than that of the quoted value. Carbon content is responsible for the calorific values of a substance. The higher the carbon content is of a hydrochar it would result in higher the calorific values (Kan, et al., 2016)

The pure apple peel hydrochar has the highest carbon content out of the three pure samples and that was reflected in the calorific values as well. Apple recorded the highest calorific value among the three pure samples.

4.7 The Economy of the Project

It is important to analyze if the technology being proposed is economically feasible or not. Pakistan is a developing country with a lack of financial resources and prevailing energy scarcity. The coal found in Pakistan is mostly sub-bituminous and lignite. To analyze the potential of hydrothermal carbonization, it is important to note how much money is used for the synthesis of hydrochar.

4.7.1 Cost of Hydrochar Synthesis

The power rating for hot air oven for drying = 1kW

Power of hot air oven for reaction= 1.60kW

Reaction time = 1hr

Time to dry the biomass= 12hrs

Total energy required for the energy =12kWh+ 1.60kWh = 13.60kWh

Price per unit of electricity = 17rupees/kWh

Price =231.2 pkr per sample

Price for hydrochar formation of all six samples = 1386.12 pkr

4.7.2 Pakistan and Coal Import

1 kg of coal costs 0.32 USD

17879*907.185*0.32

17879 short tons of coal would cost Pakistan

5,190,259 USD

This is equivalent to 1,001,216,531 PKR

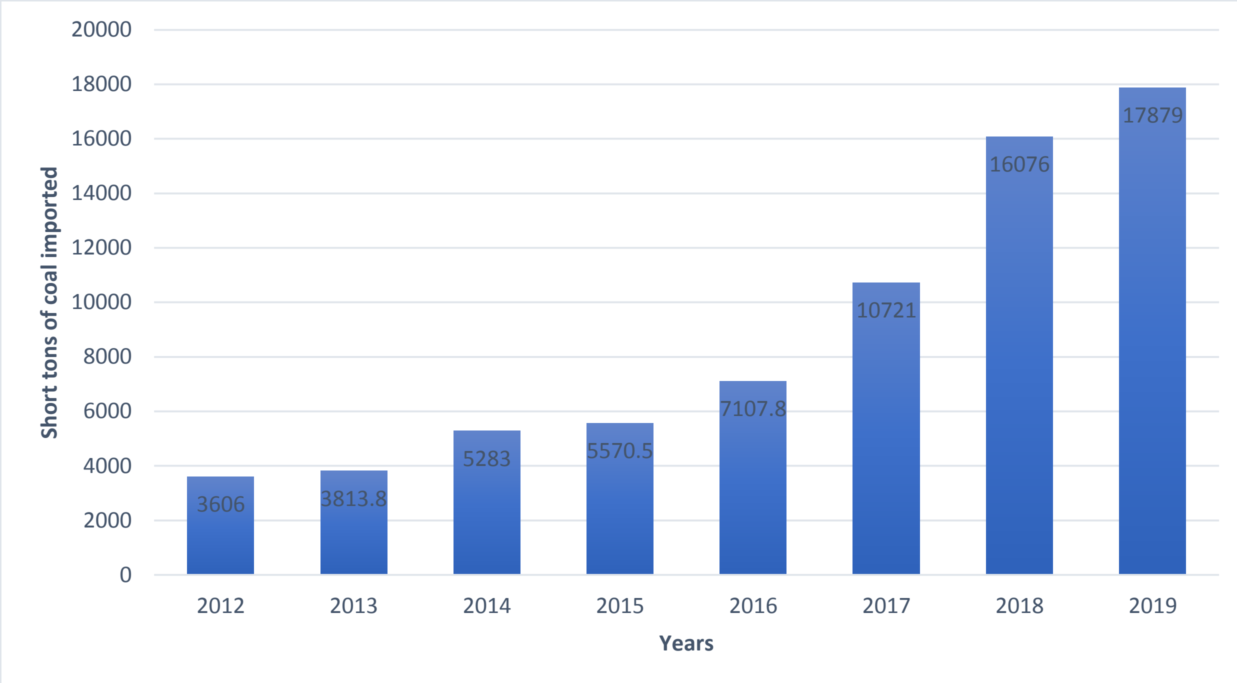


Figure8: Coal imports of Pakistan throughout the years (Globaleconomy.com)

The graph represents the coal imports of Pakistan. Over the course of years, our coal imports have started increasing exponentially. This is due to our ever-increasing energy demands and the lack of renewable options available in the market. As the demand for coal increases and so does its price in the international market, soon coal would become an expensive commodity for Pakistan to buy. It is important that Pakistan looks for inexpensive methods for energy harvesting from its renewable sources like food waste.

4.8 Substrate Concentration

Sample	Hemicellulose %	Cellulose %	Lignin %
Apple peel	18.12	12.5	14.32
Banana peel	41.38	9.90	8.91
Orange peel	10.53	9.21	12.74

Table9: Substrate concentrations of different fruit peels

Chapter 5

5 Conclusions and Recommendations

The conclusions of the research are divided into three categories according to the objectives mentioned in earlier chapters.

5.1 Microwave-Assisted Hydrothermal Carbonization vs. Ordinary Hydrothermal Carbonization

The first objective of the research was to analyze if there is any difference in the results of the two different modes of heating. The parameter that was used to judge the performance was the mass yield%. The microwave-assisted hydrothermal carbonization resulted in a higher fraction of the liquid part. This resulted in lower yields of the solid product, hydrochar. It is pertinent to have a higher yield of hydrochar because that is to be later used as a solid fuel. If there is a lesser yield of hydrochar through either of the processes, then it is disadvantageous in the efforts to popularize this energy conversion pathway.

Ordinary hydrothermal carbonization resulted in higher yields of hydrochar extracted from the same amount of mass of peels used in both cases.

Although ordinary hydrothermal carbonization is more time consuming because the ovens take time to reach the reaction temperature, the overall time taken for complete synthesis of hydrochar is greater than one hour.

After the results from the first objective were analyzed, the research proceeded forward with ordinary hydrothermal carbonization.

5.2 Mixed Biomass Effects on Hydrochar

The second objective of the research was to analyze how mixed biomass affects the synthesis of hydrochar and the properties of that synthesized hydrochar.

Mixed biomasses resulted in a higher mass yield of the synthesized hydrochar. This was seen in all three samples of the mixed biomass.

Mixed biomass samples resulted in lower calorific values than the highest possible calorific value possible individually by the fruit peel hydrochars.

This shows that food waste would have to be segregated before utilizing it for hydrothermal carbonization for energy harvesting.

5.3 Critical Analysis of Substrate Concentration

Banana has the highest component percentage for hemicellulose, followed by apple peels and orange peels. Banana with the least calorific value does not reflect the effect hemicellulose can have on the heating value of the hydrochar.

Banana has the least lignin content out of the three fruits that were used for the research. This reflects the calorific trend we established earlier in the results section of the reaction. This also corroborates the studies which have established that lignin content has the highest impact on the heating value of the hydrochar which are synthesized from biomass.

The lesser lignin content of banana peels explains its lower calorific value which also explains why banana has the least energy densification ratio and energy yields.

The energy recovery potential for banana peels is lesser than that of orange and apple peels due to this reason.

5.4 Recommendations

There are some suggestions and recommendations for the future hydrochar synthesis in Pakistan

- The coming works can focus on the bottlenecks for the commercialization of the technology.
- Future works can focus on the synthesis of hydrochar and activation through different reagents for the use of hydrochar in supercapacitors.
- Our research solely focused on the hydrothermal carbonization of fruit waste peels for the energy recovery pathway, there are other applications of hydrochar which can be explored for comparative studies.

6 Bibliography

BP, 2016. *Statistical review of world energy,* s.l.: s.n.

Czerwińska, K., Śliz, M. & Wilk, M., 2022. Hydrothermal carbonization process: Fundamentals, main parameter characteristics and possible applications including an effective method of SARS-CoV-2 mitigation in sewage sludge. A review. *Renewable and Sustainable Energy Reviews.*

EPA, U., 2018. *Food Waste Report,* s.l.: s.n.

IEA, 2022. s.l.: s.n.

IPCC, 2018. *SR15 report on the impacts of global warming of 1.5 °C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change.,* s.l.: s.n.

IPCC, 2021. *AR6 WG1 Report,* s.l.: s.n.

Kan, R., Kaosol, T. & Tekasakul, P., 2016. Characterization and elemental composition of lignite and rubber wood sawdust pellets..

Li, X. et al., 2022. Biochar and Hydrochar from Agricultural Residues for Soil Conditioning: Life Cycle Assessment and Microbially Mediated C and N Cycles.

Masoumi, B. N. a. D., 2021. Hydrochar: A Review on Its hydrocharion Technologies and Applications.

Masoumi, S., Borugadda, V., Nanda, S. & Dalai, A., 2021. Hydrochar: A Review on Its hydrocharion Technologies and Applications. *Catalysts.*

Molino, A., Chianese, S. & Musmarra, D., 2016. Biomass gasification technology: The state of the art overview. *Journal of Energy Chemistry.*

Nasrollahzadeh, M., Nezafat, Z. & Shafiei, N., 2021. Chapter 5 - Lignin chemistry and valorization. In: *Biopolymer-Based Metal Nanoparticle Chemistry for Sustainable Applications.* s.l.:s.n.

Oktaviananda, C. et al., 2017. Effect of temperature and biomass-water ratio to yield and hydrochar characteristics of hydrothermal treatment of biomass..

Oktaviananda, C. R. R. P. A. P. C. Y. A. a. C. R., 2017. Effect of temperature and biomass-water ratio to yield and hydrochar characteristics of hydrothermal treatment of biomass..

ourworldindata.org, 2022. s.l.: s.n.

Prurapark, R. et al., 2020. Effect of Temperature on Pyrolysis Oil Using High-Density Polyethylene and Polyethylene Terephthalate Sources From Mobile Pyrolysis Plant. *Process and Energy Systems Engineering.*

Román, S. et al., 2018. Hydrothermal Carbonization: Modeling, Final. *Energies.*

Shi, J., Cui, H., Xu, J. & Yan, N., 2022. Carbon spheres synthesized from KHCO3 activation of glucose derived hydrochar with excellent CO2 capture capabilities at both low and high pressures. *Separation and Purification Technology.*

Soh, M. et al., 2022. Physicochemical and structural characterisation of oil palm trunks (OPT) hydrochar made via wet torrefaction. *Cleaner Engineering and Technology.*

The News International, 2021. *Food waste in Pakistan,* s.l.: s.n.

Tippayawong, N., Kantakanit, P. & Koonaphapdeelert, S., 2020. Characterization of hydrochar from hydrothermal carbonization of maize residues. *Energy Reports,* Volume 6, pp. 114-118.

US EPA, 2018. s.l.: s.n.

Yoganandham, T. S., Sathyamoorthy, G. & Remya, R. R., 2020. Chapter 8 - Emerging extraction techniques: Hydrothermal processing. In: *Sustainable Seaweed Technologies.* s.l.:s.n.