Production of Solid Fuel through Hydrothermal Carbonization of Organic Solid Waste

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May 2023

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This thesis is submitted to National University

of Sciences and Technology in partial fulfillment

of requirements for the degree of

Bachelor in Environmental Engineering

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Approval Sheet

It is certified that the contents and form of the thesis entitled "**Production of Solid Fuel through Hydrothermal Carbonization of Organic Solid Waste**" submitted by Ms. Maryam Ayaz, Ms. Yashra Irfan, and Mr. Ahmad Jawad Sohail have been found satisfactory for the requirements of the degree of Bachelor of Environmental Engineering.

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Acknowledgment

We would like to express our deep appreciation to our Supervisor Dr. Musharib Khan, for his invaluable guidance, support, and encouragement throughout the entire process of conducting the project. We are grateful to him for his expertise, insights, feedback, and assistance in every step that helped us overcome the challenges and successfully complete our Final Year Design Project.

We would also extend our gratitude to the administration and professors of IESE for enabling us to acquire the skills required for the completion of this project. Special mention to Sir Basharat and wastewater lab staff who provided assistance and guidance whenever we needed it.

Lastly, we are extremely grateful to our families and friends who were a constant source of motivation and moral support that kept us going.

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Abstract

Lack of energy generation raw materials and lack of proper solid waste collection, management and disposal mechanism create a pressurizing need to tackle the issue. Keeping in mind the current global scenario a renewable and sustainable solution is required. Therefore, addressing two of the major problems in Pakistan i.e. energy crisis and solid waste mismanagement the project highlights an innovative way of energy generation. This project utilizes three major fruits abundantly cultivated and commonly used for juice extraction. The peels and pomaces of three fruits apple, pomegranate, orange, and a mixture of all three of them are processed using a Hydrothermal Carbonization process at 180 ^{o}C and a retention time of 2 hours to be used as fuel for energy generation. Hydrothermal carbonization is a thermochemical conversion process that can even convert wet feedstock into hydrochar. The product obtained from this process hydrochar is further analyzed using multiple tests to characterize the fuel properties. The hydrochar produced is analyzed over several characteristic tests to establish whether or not the fuel has potential for energy generation. The tests include higher heating vales, proximate analysis, ultimate analysis and fiber analysis. The applications of this project in industries is also discussed. The samples have high enough HHV values and since these values do not differ significantly the mix of all fruits can also be used in industries. While individual fruits give equally promising results.

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Chapter 1 Introduction

The motivation behind choosing the specific topic for the project lies in the changing global paradigm and the need for countries to shift towards renewable energy sources for their survival and progress. The world is increasingly recognizing the importance of transitioning to sustainable energy systems to mitigate climate change, reduce dependence on fossil fuels, and ensure a sustainable future for generations to come. In this context, the utilization of waste as a resource for energy generation is gaining significant attention. Waste management has emerged as a critical challenge, particularly in developing countries like Pakistan. Improper waste disposal leads to environmental pollution, health hazards, and strain on limited landfill space. Addressing this problem requires innovative and sustainable solutions that not only tackle waste management but also contribute to the broader concept of a circular economy. A process like Hydrothermal carbonization presents a viable and promising generating hydrochar, a carbon-rich solid fuel. This process not only provides a solution to the waste management problem but also offers several additional benefits. The utilization of waste for energy through hydrothermal carbonization supports the concept of a circular economy. Rather than treating waste as a burden to be disposed of, it transforms waste into a valuable resource, closing the loop and minimizing the extraction of new raw materials. This circular approach helps conserve resources, reduce environmental impacts, and promote a more sustainable and efficient use of resources. Furthermore, it can create employment opportunities, stimulate local economies, and enhance energy security by diversifying the energy mix.

1.1 Background

Pakistan has a huge gap between the demand and supply of electricity across all sectors. The heavy reliance of the country on fossil fuels for energy generation. In the fiscal year 2021- 2022, there was a rise of 75.34% increase in crude oil imports whereas 75 % of electricity generation that is 3960 of a total 5280 MW of electricity generated through coal was from imported coal. Natural gas imports are also increasing as the reserves in Pakistan are finishing up (Economic Survey, 2022). The continuous usage of fossil fuels results in the emission of greenhouse gases, which is the primary cause of climate change. In contrast, renewable energy sources generate electricity without emitting greenhouse gases and have a considerably smaller environmental footprint. In addition, the transition to renewable energy sources is a crucial step toward achieving energy security and independence. As fossil fuel reserves are depleted, countries that heavily rely on these resources for their energy needs may face supply disruptions and price volatility. On the other hand, renewable energy sources reduce dependence on foreign energy sources.

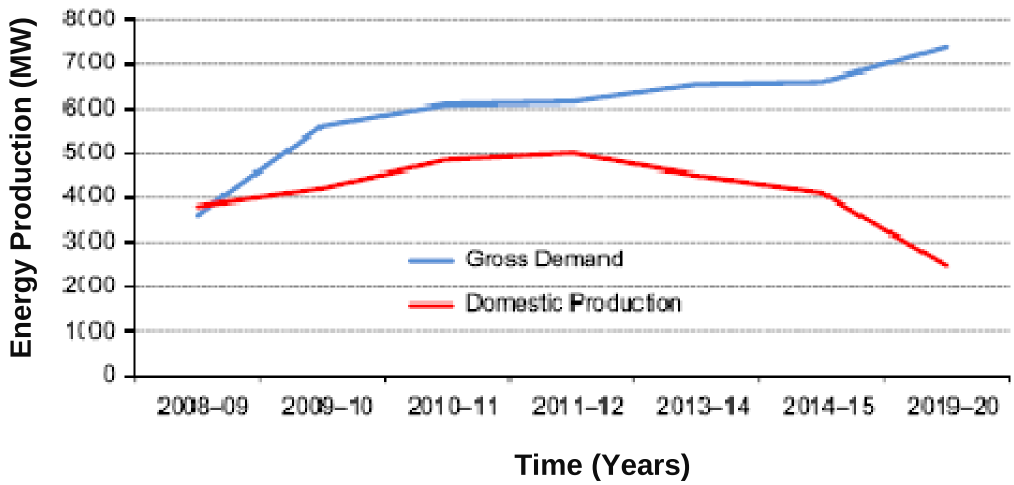

Figure 1.1 Energy Demand and Supply Gap Pakistan (Khan et al., 2014)

Solid waste mismanagement is another severe problem in Pakistan. With a rapidly growing population and urbanization, the amount of waste generated has increased significantly. Pakistan generates around 49.6 million tons of solid waste is generated annually (ADB Briefs, 2019).

One of the main issues is the absence of a proper waste collection and disposal system. In many urban areas, waste is either left uncollected or dumped in open spaces, creating unhygienic conditions and posing a risk to public health. The lack of segregation at source and proper sorting facilities also means that valuable materials are lost, and recyclable waste is often mixed with hazardous waste, posing a significant threat to the environment. The inadequate management practices have resulted in severe environmental and health consequences.

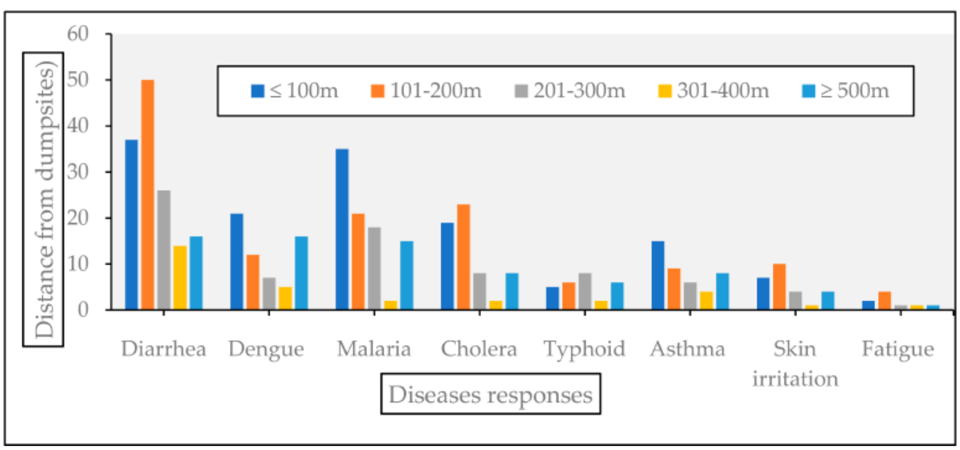

Figure 1.2 – Interrelation between diseases and distance from dumpsite (Akmal et al., 2021)

1.2 Theory

It is pertinent to utilize the mounting amount of solid waste into something useful. Considering the diminishing local energy generation resources, it is high time to utilize the waste into useful products. Commonly thermochemical processes are used for waste conversion. These processes include;

- Incineration,
- Pyrolysis,
- Hydrothermal Carbonization.

However, incineration is an energy intensive processes which require very high temperatures for operation. Incineration also contributes to huge amounts of air emissions of harmful pollutants including heavy metals (Saqib et al., 2019).

Pyrolysis is another thermochemical process which also requires high temperature and no studies exist to back the use of food waste for this process (Molino et al., 2016).

Hydrothermal carbonization has been widely used for conversion of food waste and this process also has various advantages as compares to the previously discussed methods.

1.2.1 Hydrothermal Carbonization

Hydrothermal carbonization is a thermochemical process that converts wet biomass into useful products. The products obtained from the process include;

- Solid – hydrochar
- Liquid – bio oil and water mixture
- Gas – CO_2 mainly

The focus of this project is the hydrochar which has calorific values as high as coal.

The major processes of hydrothermal carbonization are;

- Hydrolysis
- Dehydration
- Decarboxylation
- Polymerization
- Aromatization

1.2.2 Hydrothermal Carbonization Advantages

Hydrochar is a renewable energy source that offers multiple benefits including;

- Reduction of greenhouse gas emissions and compliance with regulations. It is an energy-efficient technology that operates at lower temperatures and has shorter processing times, making it well-suited for large-scale industrial applications.
- One of the advantages of hydrochar is its ability to process a wide range of feedstocks, including wet and high-moisture materials. This flexibility in feedstock selection allows for the utilization of various waste streams, making hydrochar a versatile technology.
- In addition to its energy production capabilities, hydrochar also produces valuable co-products such as bio-oil and biogas. These co-products have potential applications in fuel production, chemical synthesis, and heat generation. The utilization of these co-products can provide additional revenue streams, enhancing the economic viability of hydrochar technology.
- By leveraging hydrochar as a renewable energy source, industries can contribute to the reduction of greenhouse gas emissions and meet regulatory requirements. The energy-efficient nature of hydrochar, along with its ability to process diverse feedstocks, makes it an attractive option for large-scale industrial applications. The generation of valuable co-products further enhances its economic and environmental benefits, creating a sustainable energy solution.

1.2.3 Hydrothermal Carbonization Environmental Viability

- Hydrothermal carbonization converts organic materials into hydrochar through a combination of heat and pressure. This process significantly reduces the total organic carbon content in the feedstock, resulting in a decrease in organic carbon emissions upon its utilization as an energy source. By minimizing TOC emissions, hydrochar helps to mitigate the release of carbon dioxide and other organic compounds that contribute to climate change and air pollution.
- Unlike some conventional energy production methods or waste treatment processes that require the use of harsh chemicals, hydrochar production is typically carried out without the need for such chemicals. The hydrothermal carbonization process primarily utilizes water and heat, avoiding the use of chemical reagents that can be harmful to the

environment and human health. This reduces the potential environmental impact associated with the production of energy and the treatment of organic waste (Lachos-Perez et al, 2022).

- Hydrothermal carbonization allows for the utilization of a wide range of feedstocks, including organic waste materials such as agricultural residues, food waste, and sewage sludge. By processing these feedstocks into hydrochar, which can be used as a renewable energy source, hydrochar technology helps address the environmental problems that can arise from improper disposal of such waste materials. It enables the efficient and sustainable utilization of these feedstocks, diverting them from landfills or improper disposal methods, thus minimizing their potential negative environmental impacts.

1.2.4 Hydrothermal Carbonization Economic Viability

Hydrothermal carbonization as a renewable energy technology offers several advantages, including low heat consumption, no requirement for specific equipment, zero cost for industries using waste as raw material, low manufacturing costs, and the ability to use wet waste directly without the need for drying.

- Hydrothermal carbonization is an energy-efficient process that requires relatively low heat consumption compared to other thermal conversion technologies. The hydrothermal carbonization process operates at moderate temperatures and pressures, reducing the energy input required for the conversion of organic materials into hydrochar. This results in lower energy costs and contributes to the overall efficiency of the process.
- The process can be conducted using conventional equipment that is readily available in many industries. The process can be carried out in batch or continuous systems, and the required equipment is relatively simple and does not demand specialized infrastructure. This makes hydrothermal carbonization a cost-effective option as it eliminates the need for significant capital investments in specific equipment.
- Industries that generate food, fruit or vegetable waste can utilize hydrothermal carbonization as a means of converting those wastes into a valuable energy resource. Since the raw materials for electricity generation come from waste streams that would otherwise require disposal, the cost of acquiring feedstock for energy production is effectively zero. This reduces operational costs for industries and provides a sustainable solution for waste management.

- The low heat consumption as it operates at lower temperature, no requirement for specialized infrastructure, and the ability to use diverse feedstocks contribute to the reduction of manufacturing costs. This makes HTC an economically attractive option for industries seeking renewable energy solutions or waste treatment alternatives.
- Another advantage of hydrothermal carbonization is its ability to process wet waste materials directly, without the need for prior drying. This eliminates the cost and energy associated with drying the feedstock before conversion, reducing operational expenses. Additionally, the direct utilization of wet waste simplifies the overall process, making it more efficient and convenient (Román et al., 2018).

1.3 Problem Statement

Given the widening gap between energy supply and demand in the country, it is crucial to explore cost-effective and viable energy sources that can address this issue. These energy sources can help bridge the energy gap and provide a solution to the severe mismanagement of solid waste.

This project is offers to provide an alternative energy source to coal, which is currently being imported for electricity generation. However, the global scenario has changed significantly, especially with the post-COVID demand surge and the ongoing conflict in Russia, leading to a substantial increase in coal prices. The price of coal has skyrocketed to as high as 425 USD/ton (International Energy Agency, 2023). Considering the economic crisis in Pakistan, heavy reliance on coal imports is no longer feasible or sustainable.

Moreover, there is a pressing need to tackle the growing issue of food insecurity and develop effective mechanisms for waste management. Food waste is a significant global issue with serious economic, environmental, and social implications. The sensitivity surrounding food waste demands urgent action to ensure proper waste management practices are in place. By finding innovative and sustainable ways to utilize food waste, we can address these challenges. Around the globe 36% of the food is wasted (EPA, 2018) and 36 million tons of food are wasted every year in Pakistan only (The News International, 2021). The decomposition of food waste in landfills produces methane, which is a potent greenhouse gas that contributes significantly to the issue of climate change. Furthermore, the presence of waste in landfills poses various health risks and hazards.

1.4 Objectives

- To perform hydrothermal carbonization of selected fruit peels and pomace.
- Use solid waste to create a potential fuel i.e. hydrochar, thereby addressing the energy crisis and solid waste mismanagement issue.
- Characterization of fuel properties of the hydrochar generated for energy generation in Pakistan's context.

1.5 Sustainable Development Goals Mapping

In 2015, the United Nations adopted a set of 17 Sustainable Development Goals (SDGs) to be achieved by 2030. These goals serve as a blueprint for creating a more sustainable and inclusive world. They address a wide range of interconnected issues and aim to improve the well-being of all individuals while safeguarding the planet. Plethora of aspects are covered by these goals including education, sanitation, hunger, partnerships and much more.

1.5.1 Goal 3 - Target 3.9

"*By 2030 substantially reduce the number of deaths and illnesses from hazardous chemicals and air, water, and soil pollution and contamination."*

Open dumping of waste especially food waste leads to degradation of food at landfills and create unhygienic living conditions in the vicinity. Hydrothermal carbonization of food waste can help reduce this problem.

1.5.2 Goal 7 - Target 7.2

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

Hydrothermal carbonization presents a viable renewable energy generation option. This will be an environmentally clean energy option while an affordable source of energy in Pakistan.

1.5.3 Goal 12 - 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 losses in the supply chain that is rotten fruit during transportation and distribution process. Also, there is considerable fruit loss during the processing of fruit extraction the peels and pomaces are waste. These can be utilized as raw material for the hydrothermal carbonization process thereby reducing the losses.

1.5.4 Goal 13 – Target 13.2

“By 2030, integrate climate change measures into national policies, strategies and planning.”

Waste disposal at landfill sites lead to considerable emission of greenhouse gas emissions. Whereas the hydrothermal carbonization process is a carbon-neutral process curtailing GHGs emissions.

Chapter 2 Literature Review

Research is the foundation any good project and literature review provides that foundation. It sets base for future exploration and gathers current, relevant information on your chosen topic to ensure that the research is conducted appropriately.

2.1 Hydrothermal Carbonization Process Parameters

The primary factors that influence the properties of hydrochar are temperature, residence time, and the water-to-biomass ratio. The duration of the process and the temperature are the key determinants that impact the hydrothermal carbonization process and its extent of coalification. (Khan et al., 2021).

2.1.1 Temperature

Temperature plays a crucial role in hydrothermal carbonization and significantly affects both the process and the resulting hydrochar properties. As the temperature rises, there is a notable change in water viscosity, enabling it to penetrate the biomass structure more easily, thus facilitating degradation. Once the temperature surpasses the activation energy threshold, chemical bonds within the biomass start to break, triggering subsequent reactions like dehydration, decarboxylation, and condensation. Elevated temperatures tend to enhance the yield of hydrochar and contribute to its improved thermal stability. Additionally, higher temperatures promote an increase in the carbon content of the hydrochar (Khan et al., 2021). To ensure optimal hydrothermal carbonization, it is important to establish an ideal temperature range for the process. The hydrolysis rate of biomass is directly influenced by temperature, thus determining the suitable conditions. Based on our experiment, we conducted the process at a temperature of 180°C, which resulted in a notable yield of hydrochar across all samples. Moreover, the carbon content within the samples was also significantly satisfactory. It is worth noting that temperatures higher than this threshold would involve the participation of cellulose and lignin in the reaction, whereas at this temperature, only the degradation of hemicellulose takes place. (Heidari et al., 2019).

2.1.2 Residence Time

The duration of residence time during the hydrothermal carbonization process is a crucial factor to consider. Increasing the residence time, along with temperature, leads to a reduction in the yield of hydrochar produced. However, it should be noted that as the residence time and temperature are raised, the energy content of the resulting hydrochar increases. This is due to the higher energy density achieved as a result of the increased residence time and temperature. (Saqib et al., 2019).

In lignocellulosic biomass the residence time is important for the formation of secondary hydrochar produced from the extensive polymerization. It enhances the process by releasing on other products during the reaction. Shorter residence time was observed alters the morphology of the hydrochar (Naomon Khan et al., 2021) the residence of 2 hours/120 minutes were set so that a significant yield of the hydrochar from different samples could be obtained.

2.1.3 Water to Biomass Ratio

Biomass to water ratio is also an important parameter for the process. (Oktaviananda et al., 2017). Comparatively more water to feed in the reactor causes an increase in the energy so water to biomass ratio is also important to adjust to optimum ratio. Hydrothermal reactions are directly related to the amount of water being used in the reaction. The amount of water should be sufficient enough that heat and mass transfer are augmented for the reaction procedure (Khan et al., 2021).

The optimum ratio biomass to water was adjusted are 1:10 (Heidari et al., 2018). Higher water content to biomass ration will increase the morphology of the hydrochar by increasing the number of pores as well as the surface area.

2.2 Higher Heating Value (HHV) Determination

The higher heating value is a crucial parameter used to assess the quality of fuel. It represents the amount of heat released when a unit mass of the fuel undergoes combustion (Li et al., 2018).

The higher heating value (HHV) of a fuel is typically determined using a bomb calorimeter. An increase in the residence time during hydrothermal carbonization has been observed to correlate with an increase in the HHV value. The moisture content of the biomass also plays a role in affecting the HHV, with higher moisture content generally leading to a decrease in the higher heating value. Moreover, as the temperature rises, there is a corresponding increase in the HHV value (Czerwinska et al., 2022).

The combustibility of a fuel is influenced by its volatile combustible matter and fixed carbon content. Fuels with high volatile combustible matter tend to have lower combustion efficiency. Conversely, fuels with higher fixed carbon content tend to exhibit an increase in the higher heating value (HHV) (Missaoui et al., 2017).

2.3 Proximate Analysis

The properties of hydrochar are evaluated through several analytical methods, including proximate analysis, ultimate analysis, and determination of higher heating values. Proximate analysis involves assessing parameters such as ash content, volatile combustible matter, fixed carbon, and moisture content. To determine these parameters, specific ASTM methods were employed. For moisture content, ASTM-E871 was used, while ASTM-E1755 was utilized for ash content determination. The volatile combustible matter was determined using ASTM-E857. Fixed carbon content was calculated by subtracting the percentages of volatile combustible matter and ash content from 100% (Heidari et al , 2019).

Following the hydrothermal carbonization process, the moisture content and ash content of the hydrochar decreased compared to the raw biomass. The reduction in ash content contributes to an increase in the calorific value, while the decrease in moisture content enhances the energy densification process, leading to an increase in the fixed carbon value. Consequently, the heating value of the hydrochar is enhanced. Additionally, the volatile combustible matter is expected to decrease after the process due to the release of intermediate products (Oktaviananda et al., 2017).

2.4 Fiber Analysis

The lignocellulosic component within biomass affects the hydrochar properties. It includes lignin content, cellulose hemi-cellulose, ash content and extractives. It was done to analyze the behavior of these components during the reactions as the reaction temperature increases cellulose and the hemicellulose degrades while lignin tends to be more thermally stable. Also, that the calorific value of lignin is higher due to which the hydrochar formed has higher HHV value (Sharma et al., 2020).

A high level of lignin shows higher fixed carbon and lower volatile matter values resulting in a higher fuel ratio as well as higher heating values (Güleç et al., 2021).

The higher ash content values lead to reduction of the yield of hydrochar, and it subsequently affects the fuel quality. Volatile combustible matter values also reduced at comparatively higher temperatures because of degradation of the hemicellulose and the cellulose components and the release of volatiles at high temperature. Similarly, the increase in the carbon content causes increase in the higher heating values due to higher lignin content (Ghanim et al., 2016).

Chapter 3 Methodology

A proper step-wise procedure was followed for the completion of the project. The importance of proper methodology for any project cannot be overstated. A well-defined and structured methodology provides a systematic approach to project execution, ensuring its success. The project was completed using the following steps.

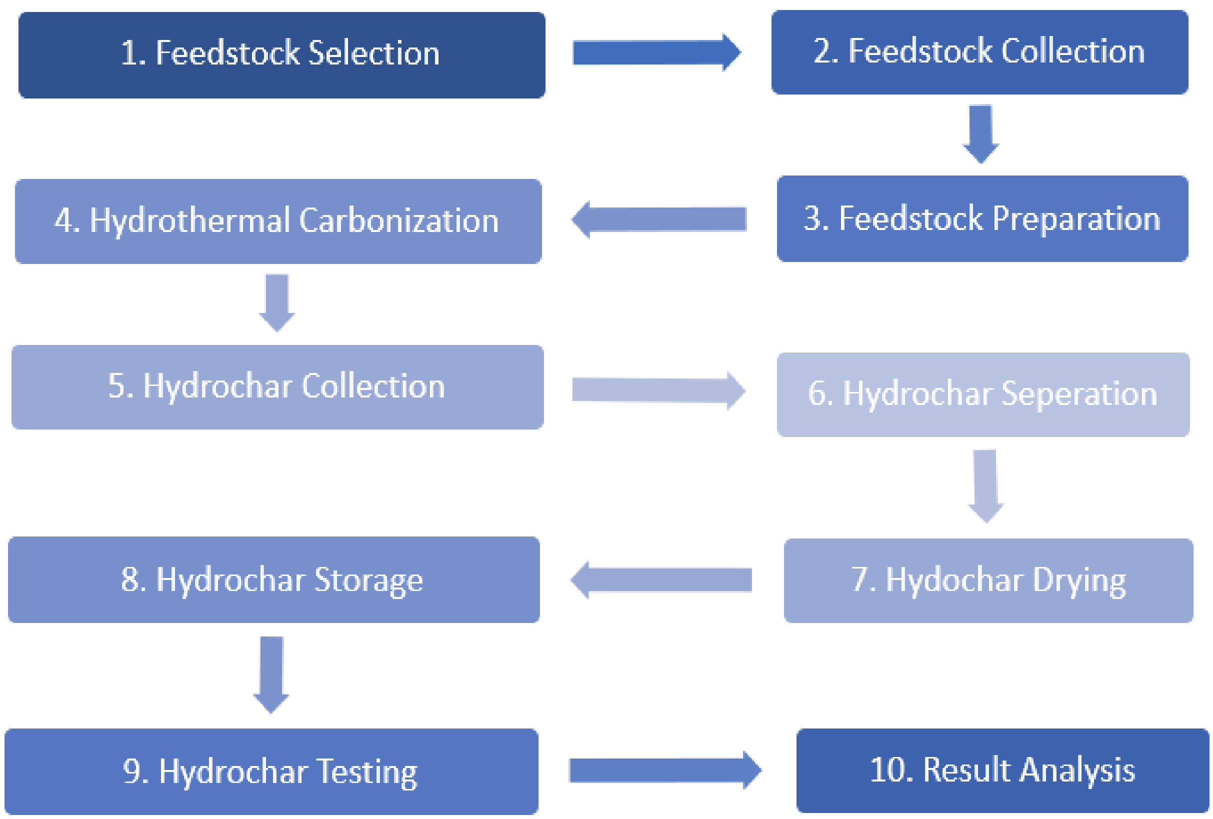

Figure 3.1 Steps followed through the course of the project

3.1 Apparatus Used

Figure 3.2 shows the apparatus used throughout the project (a) Hot air oven (b) Measuring Balance (c) Desiccator (d) Magnetic Stirrer (e) Filtration Assembly (f) Muffle Furnace (g) Teflon Lined Stainless Steel Autoclave (h) Tube Furnace

3.2 Fruit Selection

We selected three fruits apple, pomegranate and orange for the project. A mix of all three fruits was also studied to determine the need of segregating waste and if possible avoid that. The criteria for selecting fruits for this project were primarily based on two major factors: provincial fruit production and local fruit wastage resulting from their usage in industries. These criteria were considered to ensure a practical and locally relevant approach to addressing fruit waste and promoting sustainable resource utilization. Considering the provincial fruit production ensures that the chosen fruits align with the local context, considering factors such as availability, familiarity, and market demand. Industries that process fruits for various products such as juices, jams, or preserves often generate significant quantities of fruit waste during their manufacturing processes. This waste can include peels, pomace, pulp, or other by-products.

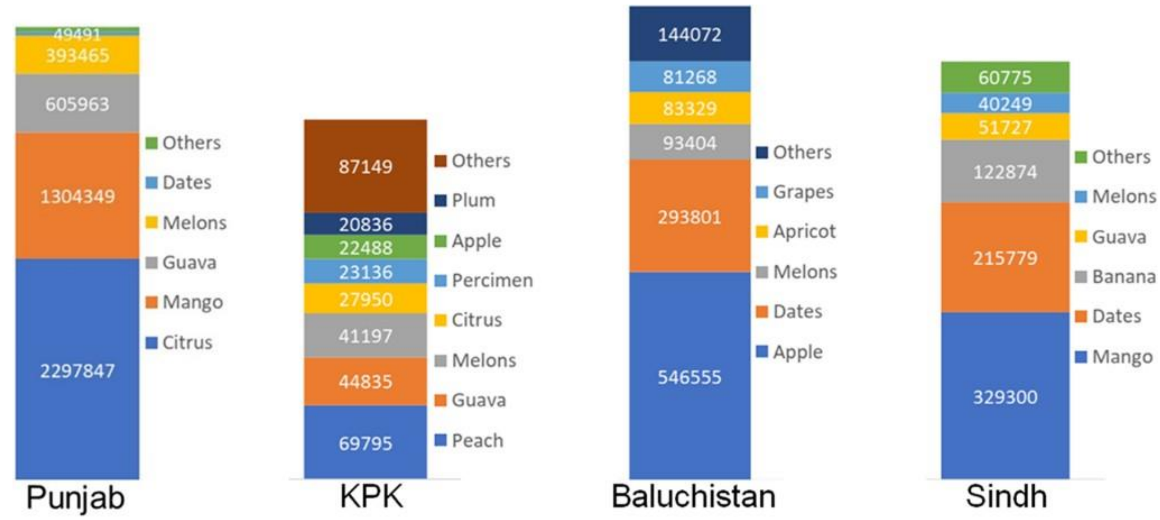

Figure 3.3 – Provincial production of individual fruits (*Fruit, Vegetables & Condiments Statistics, Ministry of National Food Security & Research. Government of Pakistan, 2019-2020)*

Another consideration while deciding the fruits was the research conducted on a fruit market. The research conducted on the fruit market involved quantifying the amount of waste generated during the transportation of fruits. This includes factors such as spoilage, rotting, bruising, or other forms of damage that occur during the handling and transit of fruits from farms or orchards to the market. The research on fruit waste in the market provides valuable information on the extent of waste generated within the market itself. This includes factors like unsold or unutilized fruits, spoilage due to inadequate storage or handling at the market, and consumer preferences that contribute to fruit waste. The final selection was based on season availability of the fruits.

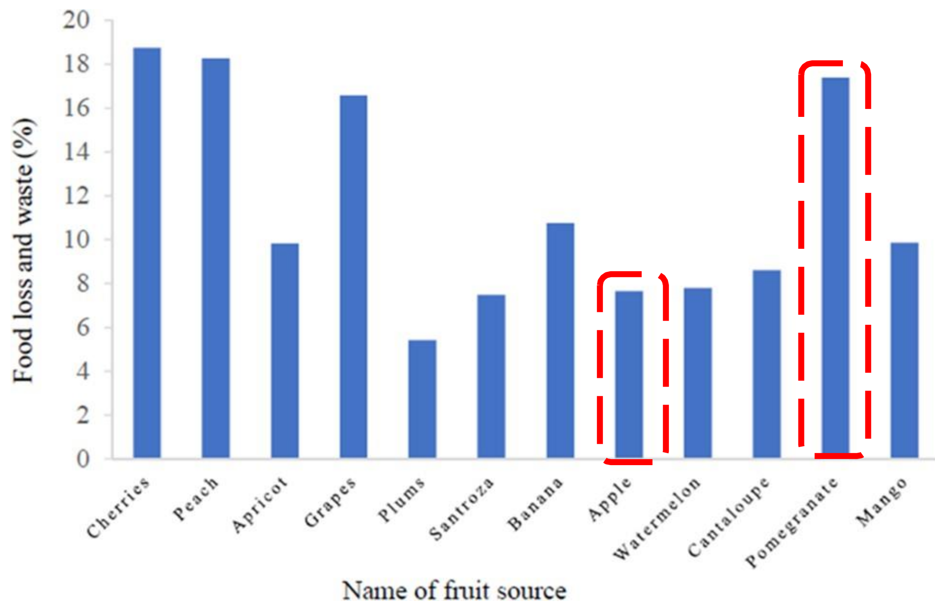

Figure 3.4 Fruit waste based on market survey (Khan et al., 2021)

3.3 Fruit Collection

The fruit peels and pomace were collected from a local shop in H-13 and from Concordia 2.

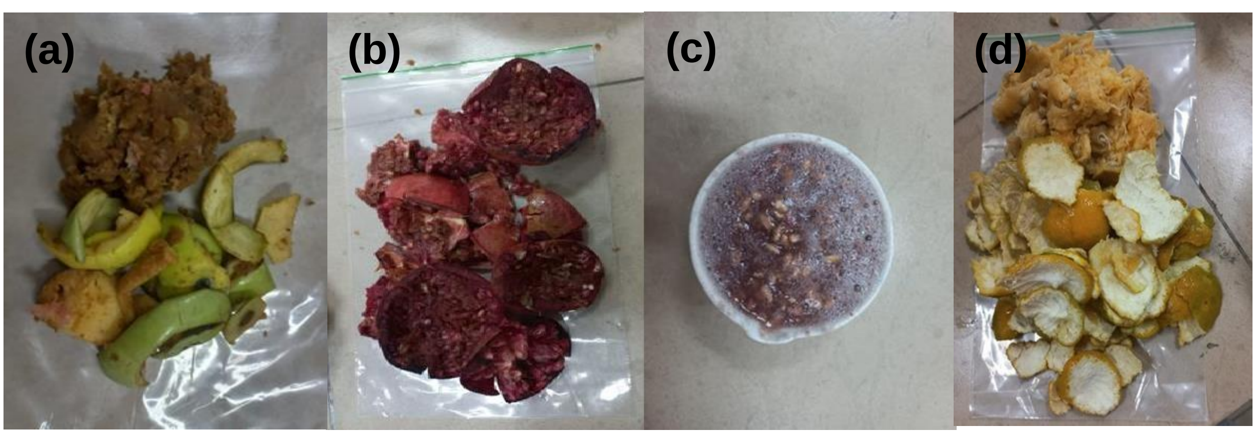

Figure 3.5 Raw peels and pomace (a) apple (b) pomegranate peels (c) pomegranate pomace (d) orange

3.3 Feedstock Preparation

Before starting the process, the feedstock needs to be prepared for it. The preparation involves the following steps;

3.3.1 Size Reduction:

To ensure efficient conversion with higher calorific values we need to reduce the size of the feedstock. This increases the feedstock's surface area and ensures expedited breakdown, better reaction mechanisms, and enhanced mass and heat transfers. Lignin, the most important component for HTC also breaks down faster when the feedstock is curtailed in size. However, reducing the size increases the energy costs of the overall process so an optimum size was selected. The mortar and pestle were used for size reduction.

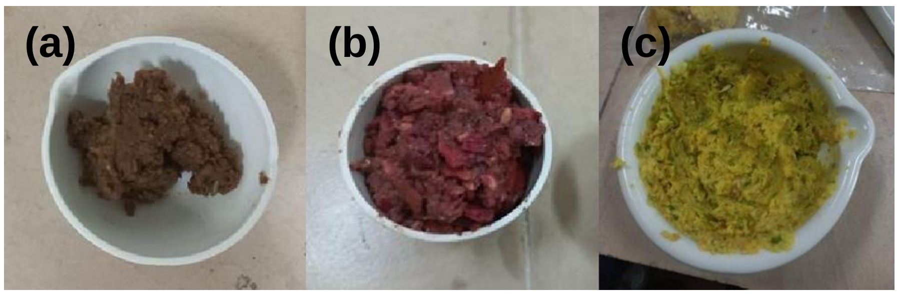

Figure 3.6 Crushed peels and pomace of raw fruits (a) apple (b) pomegranate (c) orange

3.3.2 Drying:

Through research, it has been established that the most ideal percentage of water to biomass ratio is 82-95 %. Though in our project we will use 90% in order to get the best results. As the moisture content in the selected feedstock is unknown, it must undergo a drying process. The sample will be placed in a china dish and then placed in the hot air oven at 65 ^oC for 12 hours. It was then removed from the oven using tongs, stored in zip-lock bags, and placed in the desiccator to prevent degradation (Basso et al., 2016).

Figure 3.7 Dried fruit peels and pomace (a) apple (b) pomegranate (c) orange

3.3.3 Slurry Preparation:

The feedstock stored in the desiccator is taken out and ground again if any clusters are formed to produce a powdered form. As the biomass-to-water ratio is 90% so for every 5 g feedstock mass 50 mL of water is taken. Distilled water is used in the process as it is free from any impurities that would hinder accurate results. Before the sample is placed in the autoclave a completely uniform feedstock and water mixture is prepared using a magnetic stirrer in the beaker. This mixing roughly takes place for 5-10 minutes. In the final run where the mixture of all three samples was taken equal amounts of each type are ensured i.e. 1g of each food item. They were mixed together to form a homogeneous mixture. Then slurry was prepared (Poomsawat et al., 2021).

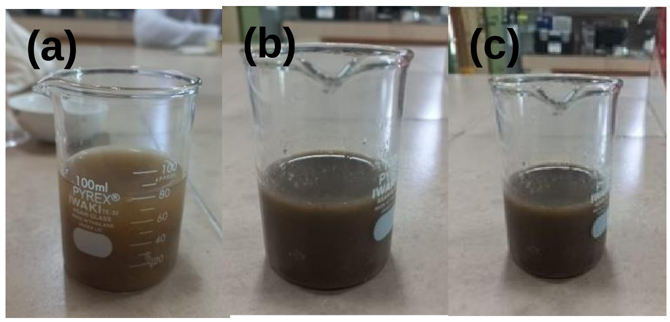

Figure 3.8 Homogeneous slurry of the dried waste (a) apple (b) pomegranate (c) orange

3.4 Hydrothermal Carbonization

The slurry is transferred to the stainless-steel autoclave. As established earlier the optimum temperature for the process is 180 ^oC. and a residence time of 2 hours was used. The autoclave is placed inside the muffle furnace. On the completion of the process time, the muffle furnace is turned off. The autoclave was cooled down for further two hours before continuing with subsequent steps (Czerwińska et al., 2022).

3.5 Hydrochar Collection

The products of the process are both solid hydrochar and liquid bio-oil. However, for this project we will only be dealing with the solid part and hence separation of the useful solid part is achieved through the subsequent steps.

3.5.1 Filtration

Vacuum-assisted filtration is used for required separation. The resulting mixture of hydrothermal carbonization is poured into the filtration assembly with filter paper of size 20 μm. The residue on filter paper is hydrochar whereas the liquid is obtained as filtrate (Zhang et al., 2018).

3.5.2 Washing

It is very important to ensure that the hydrochar obtained is free from any impurities. Washing is necessary to establish the former. Distilled water is used to wash the hydrochar at least three times.

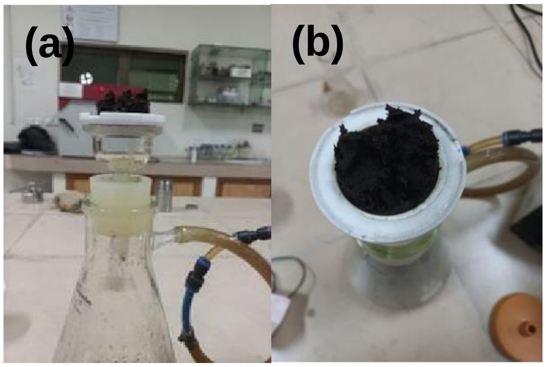

Figure 3.9 Filtration Assembly with hydrochar (a) front view of filtration assembly and hydrochar (b)) top view of filtration assembly and hydrochar

3.5.3 Drying and Storage

The hydrochar is poured into a porcelain dish/ china dish and placed in the muffle furnace for 24 hours at 105 ^{o}C. After 24 hours it is removed and again stored in a zip lock bag. This is placed in the desiccator to protect against any reaction with atmospheric moisture.

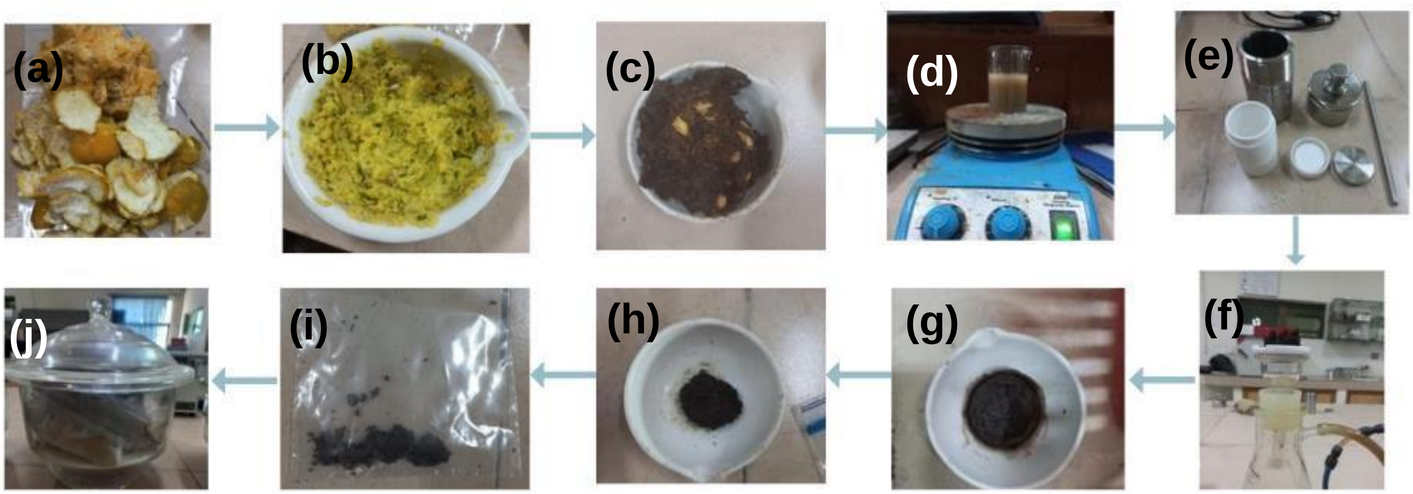

Figure 3.10 Step-wise methodology of the process(a) peels and pomace collection (b)size reduction (c) drying (d) slurry preparation (e) transfer to autoclave (f) hydrochar separation (g) hydrochar collection (h) hydrochar drying (i) hydrochar transfer to zip lock bag (j) hydrochar storage in dessicator.

3.6 Hydrochar Characteristics Analysis

This step is important for the characterization of the obtained hydrochar, especially for the next step of our research i.e. energy generation. The following tests will help us find the suitability of hydrochar and potential problems that can occur during combustion.

3.6.1 Higher Heating Value

The prepared hydrochar samples are taken to USP-CASE, NUST for Higher Heating value (HHV) or Gross Calorific value (GCV) analysis. The determination of calorific value takes place inside a bomb calorimeter. A mass of between 0.5 to 1.0 g of hydrochar inside a crucible with a pellet is introduced into the bomb that is filled with oxygen. The calorimeter filled with water is maintained at adiabatic conditions and is ignited electrically. The rise of water temperature can be used to determine the HHV (Friedl et al., 2005).

3.6.2 Proximate Analysis

Considering the sample obtained is dry basis we performed proximate analysis is used to find three important characteristic values of the hydrochar which are:

i. Volatile Combustible Matter

The next step is to determine the volatile organic matter content of hydrochar. The ASTM methods E857 are used for this purpose. The hydrochar is weighed and placed in the muffle furnace inside a covered crucible at 950 ^{o}C for 7 minutes. After seven minutes it is taken out and cooled down before reweighing it.

$$VM\ \% = \frac{v_i - v_f}{V1} \times 100 \quad \text{...eq 1}$$

v_i = initial mass of hydrochar before placing it in the furnace

v_f = final mass of hydrochar after taking it out of the furnace

However, the preliminary results obtained from the proximate analysis in the muffle furnace was not satisfactory. The process was repeated in a tube furnace which gave promising results (Cassel et al., 2012).

ii. Ash Content

Ash content determination is important to find as it reduces the HHV value of hydrochar. It also has a negative impact on combustion efficiency. Following the ASTM method, E1755 the remaining contents in the crucible are again placed in the muffle furnace but this time without cover and at about 750 ^{o}C. There is no set time limit for this step to continue the process until the mass becomes constant or turns grayish-white. Initially, it is placed for an hour, but the time can go as high as 4 hours. The sample is weighed at an interval of 30 minutes. After taking it out of the furnace it is placed in the desiccator to allow it to cool and then reweighed.

$$\text{Ash \%} = \frac{f_i - f_f}{v_i} \times 100 \qquad \text{eq 2}$$

Where, f_i = initial mass of hydrochar before placing it in the furnace the second time

f_f = final mass of hydrochar after taking it out of the furnace

iii. Fixed Carbon Content

Fixed carbon content is another important parameter as high fixed carbon content means high HHV value (Heidari et al., 2019).

$$\text{FC \%} = 100 - \text{\% VM} - \text{\% Ash} \qquad \text{eq 3}$$

3.6.3 Ultimate Analysis

The ultimate analysis was also done by determining the percentages of C, H, O, N. It can be determined by using the elemental analyzer as well as by using the following equations.

$$C = -35.9972 + 0.7698VM + 1.3269FC + 0.3250ASH \qquad \text{eq 4}$$

$$H = 55.3678 - 0.4830VM - 0.5319FC - 0.5600ASH \qquad \text{eq 5}$$

$$O = 223.6805 - 1.7226VM - 2.2296FC - 2.2463ASH \qquad \text{eq 6}$$

For the nitrogen content the percentages of C, H, O were subtracted from 100% (Poomsawat et al., 2021).

3.6.4 Fiber Component Analysis

This analysis is also very important to determine the lignocellulosic composition of the selected feedstock. It was performed through the following steps: (Li et al., 2004)

i. Extractives Determination

Both the hydrochar and the raw feedstock were leached in ethanol solution 2:1 water to ethanol ratio. They were leached for three hours at constant temperature. The samples were air dried overnight and then oven dried at 105 ^{o}C until the mass became constant. Readings for mass were taken every 30 minutes. After cooling, the samples are placed in zip lock bag and placed in desiccator until further use.

$$\text{Extractives \% } (W_1\ \%) = \frac{G_0 - G_1}{G_0} \times 100 \quad \text{eq 7}$$

Where, Go is the initial dried biomass sample,

G_1 = sample leached in ethanol in 3 h, air dried overnight and oven dried to constant weight.

ii. Hemicellulose Content Determination

1-gram sample from extractives determination process are taken from desiccator. They are placed in a flask and 150 mL NaOH is added along with distilled water. The sample is boiled for 3.5 hours. The residue is filtered using filtration assembly and washed until no more sodium ions are formed. This is determined using a pH meter. Once the pH is neutral there is no more sodium ions formation. The sample is then cooled and dried. It is reweighed to determine the hemicellulose content.

$$\text{Hemicellulose \% } (W_2\ \%) = \frac{G_2 - G_3}{G_0} \times 100 \quad \text{eq 8}$$

Where, G_2 is the sample used for hemicellulose analysis,

G_3 is the residue hemicellulose analysis.

iii. Lignin Content Determination

1-gram sample from the extractives determination is taken and mixed with 30 mL sulfuric acid. This mixture is stored in fridge at temperature between 8 to 15 ^{o}C for 24 hours. After 24 hours this sample is mixed with 300 mL distilled water and boiled for 1 hour. It is cooled for about 1 hour and filtered using filtration assembly. The residue is washed until no more sulfate formation. Sulfate ion formation is checked by addition of barium chloride into the filtrate. Barium sulfate forms white precipitate and so washing is continued till precipitates are formed.

Lignin % (W_3 %) = $\frac{G_5(1 - W_1)}{G_4}$ ×100...eq 9

Where, G_4 is the dried sample from extractives test used for lignin analysis,

G_5 is the residue lignin analysis,

W_1 is the percentage of extractives in the sample.

iv. Cellulose Determination

This is determined by subtracting rest of the component from 100 %.

Cellulose % (W_4) = 100 - (Ad + W1 + W2 + W3) ....eq 10

Where, W_1 is the percentage of extractives in the sample,

W_2 is the percentage of hemicellulose in the sample,

W_3 is the percentage of lignin in the sample,

A_d is the ash percentage of the sample.

Chapter 4 Results and Discussion

The results of all the tests conducted and the valuable information deduced through those tests are discussed in this chapter.

4.1 Mass Yield

Mass yield is a crucial factor to consider when evaluating and upscaling a project, particularly in the context of industrialization. It refers to the ratio of the mass of hydrochar produced to the mass of feedstock used during the process. In other words, it indicates the efficiency of converting the feedstock into hydrochar. When considering the industrialization of a project, achieving a good mass yield becomes paramount. A high mass yield implies that a larger proportion of the feedstock is successfully converted into hydrochar, maximizing the utilization of the input materials. This is desirable from both economic and environmental perspectives.

To improve mass yield, several factors should be considered during the project's development and upscaling. These factors include the selection of appropriate feedstock, process optimization, and the use of advanced technologies. The choice of feedstock plays a crucial role as different materials have varying composition and reactivity, which can affect the conversion efficiency. Process optimization involves fine-tuning various parameters such as temperature, residence time, and pressure to maximize the yield. Additionally, employing advanced technologies, such as catalysts or pre-treatment methods, can enhance the conversion process and increase the mass yield.

$$\text{Mass Yield \%} = \frac{\text{Mass of Hydrochar (g)}}{\text{Mass of Feedstock (g)}}$$

4.1.1 Results

Table 1 Tabular illustration mass yield results of four samples

Sr. No	Sample Name	Mass Yield Percentage
1.	Apple	24.93
2.	Pomegranate	42.72
3.	Orange	50.79
4.	Mixed	38.86

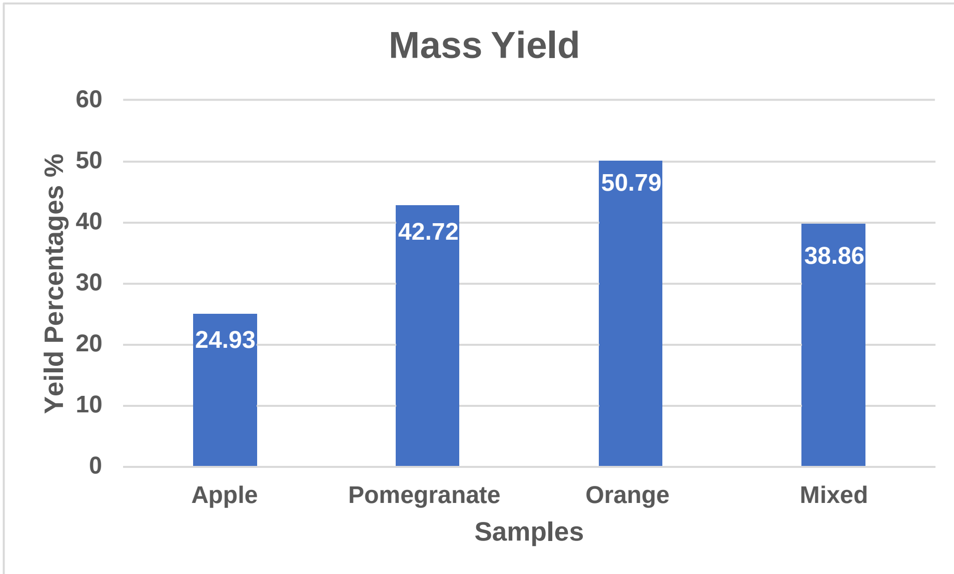

Figure 4.1 Graphical Representation of mass yield results of four samples

4.1.2 Discussion

The mass yield obtained from different fruits can vary due to differences in their composition. Each fruit contains unique combinations of carbohydrates, proteins, fats, and other organic compounds, which can influence the efficiency of hydrochar production. In the specific case mentioned, the highest yield was obtained from oranges, while the lowest yield was observed for apples.

Lab-scale experiments often involve smaller equipment and limited optimization compared to large-scale industrial processes. Consequently, the yield obtained in the lab might not fully reflect the potential yield achievable in an optimized industrial setting.

Temperature plays a crucial role in the conversion process. By adjusting the temperature, the reaction kinetics can be controlled, leading to improved conversion efficiency. Similarly, optimizing the residence time, which is the duration for which the feedstock is subjected to the conversion process, can contribute to increased yield. Finding the optimal balance between residence time and temperature is essential.

4.2 Higher Heating Value

Within the scope of the project, it is important to emphasize the significance of the higher heating value (HHV). This parameter quantifies the heat energy released during the complete combustion of a substance. It serves as a fundamental indicator of the energy content and the potential for energy generation.

The HHV is important because it provides valuable information about the energy-producing potential of the hydrochar produced from the project. By understanding the HHV, we can assess the amount of heat energy that can be obtained when the hydrochar is used as a fuel source. This is particularly significant for applications where energy generation or utilization is the primary objective.

A higher HHV indicates a greater energy content and, consequently, a higher potential for energy generation. It signifies that more heat energy can be released per unit mass of hydrochar when it undergoes combustion. Therefore, hydrochar with a higher HHV is considered more desirable, as it can contribute to increased energy efficiency and overall energy output.

By focusing on the HHV, the project can effectively evaluate the viability of the hydrochar as a potential energy source. It helps in assessing the energy-generating capacity and enables comparisons with other fuel sources or energy alternatives.

4.2.1 Results

Table 2 Tabular Illustration of Higher Heating Values of raw feedstocks and hydrochar produced

Sr. No	**Sample Name**	**HHV (MJ/kg)**
1.	Apple Raw	10.45
2.	Apple Hydrochar	21.61
3.	Pomegranate Raw	13.60
4.	Pomegranate Hydrochar	21.98
5.	Orange Raw	19.66
6.	Orange Hydrochar	21.93
7.	Mixed Raw	13.97
8.	Mixed Hydrochar	21.09

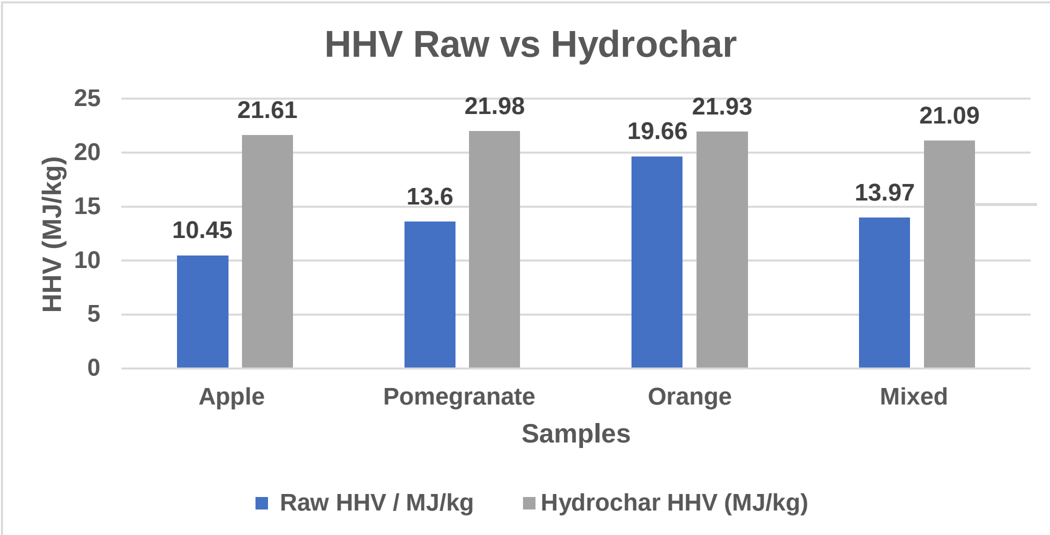

Figure 4.2 Graphical representation of HHV of raw and hydrochar of four samples

4.2.2 Comparison with Coal

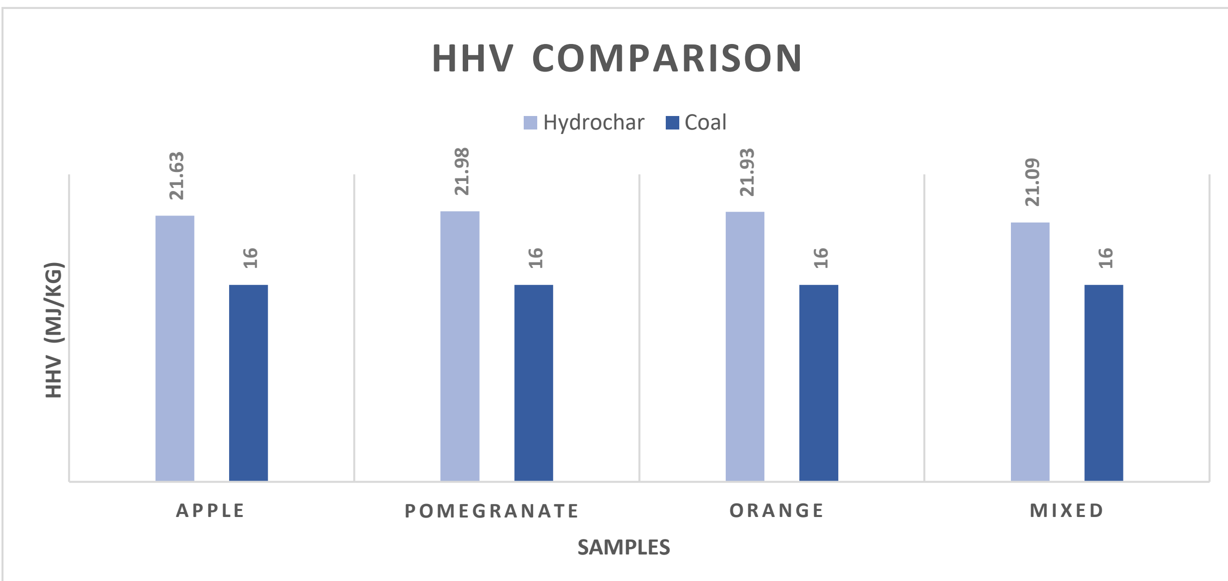

Figure 4.3 HHV of hydrochar of four samples compared to lignite coal found in Pakistan

4.2.3 Discussion

The hydrothermal carbonization process has shown significant improvements in the higher heating value (HHV) of the feedstocks used in the project. The observed increase in HHV after HTC indicates a notable enhancement in the energy content of the resulting hydrochar, potentially making it suitable for efficient energy generation.

By comparing the HHV values obtained from the HTC-treated feedstocks to the HHV values of lignite coal found in Pakistan, the project aims to provide further justification for the energy generation potential of the hydrochar. By comparing the HHV values of the hydrochar with those of lignite coal, the project can assess the viability of hydrochar as an alternative or complementary energy source.

If the HHV values of the hydrochar are found to be comparable or even higher than those of lignite coal, it provides a strong argument for the energy generation potential of the hydrochar. It suggests that the hydrochar can serve as a feasible substitute for or supplement to lignite coal, offering a more sustainable and environmentally friendly energy option.

4.3 Energy Yield and Energy Densification Ratio

Two important characterizations for the analysis of hydrochar produced are energy densification ratio and energy yield.

4.3.1 Energy Densification Ratio

The energy densification ratio measures the increase in energy content achieved through the hydrothermal carbonization (HTC) process. It quantifies the degree of energy concentration in the hydrochar compared to the original feedstock.

By calculating the energy densification ratio, it becomes possible to assess the efficiency of the HTC process in concentrating the energy content of the feedstock. A higher energy densification ratio indicates a more significant increase in energy content, implying that the HTC process has effectively enhanced the energy density of the hydrochar.

The energy densification ratio is determined by comparing the higher heating value (HHV) of the hydrochar to the HHV of the initial feedstock. The ratio is calculated as the ratio of the HHV of the hydrochar to the HHV of the feedstock.

$$\text{Energy Densification Ratio} = \frac{\text{HHV Hydrochar (MJ/kg)}}{\text{HHV Feedstock (MJ/kg}}$$

4.3.2 Results

Table 3 Tabular Illustration of energy densification ratios

Sr. No	Sample Name	HHV Hydrochar (MJ/kg)	HHV Raw Feedstock (MJ/kg)	Energy Densification
1.	Apple	10.45	21.61	2.07
2.	Pomegranate	13.60	21.93	1.61
3.	Orange	19.66	21.98	1.11
4.	Mixed	13.97	21.09	1.51

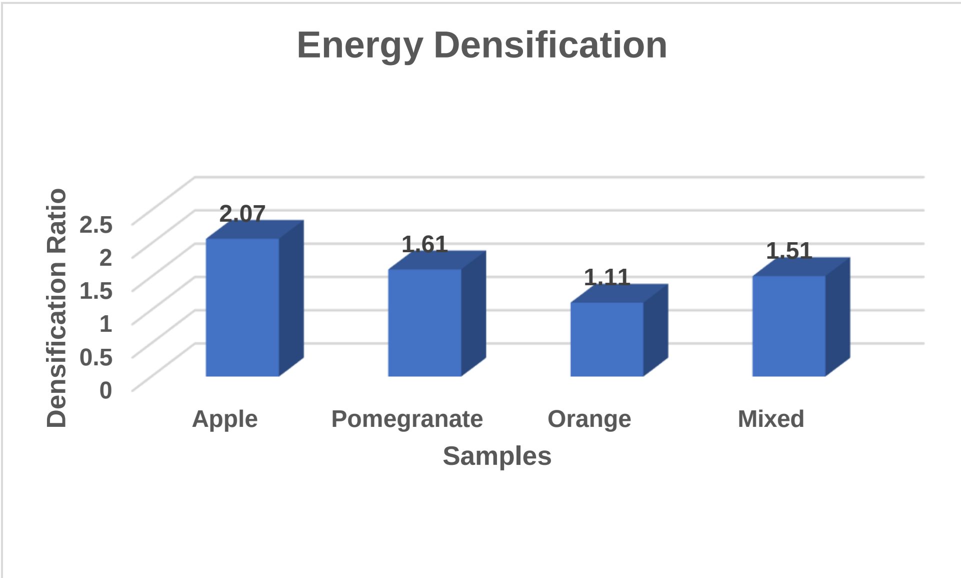

Figure 4.4 Graphical representation of energy densification ratios

4.3.3 Discussion

The energy densification results provided for different fruits apple, pomegranate, orange, and mixed, indicate the degree of energy concentration achieved through the hydrothermal carbonization (HTC) process. The energy densification ratio for apple is 2.07. This means that the energy content of the hydrochar produced from apple feedstock is approximately 2.07 times higher than the energy content of the initial apple feedstock. The HTC process has effectively concentrated the energy in the resulting hydrochar, resulting in a significant increase in energy density. Apple has the highest ratio of all the four samples.

The energy densification ratio for orange is 1.11. This implies that the energy content of the hydrochar obtained from orange feedstock is approximately 1.11 times higher than the energy content of the initial orange feedstock. The HTC process has contributed to an increase in energy density, albeit to a lesser extent compared to apple and pomegranate and mixed.

4.3.4 Energy Yield

Energy yield measures the amount of energy obtained from the HTC process relative to the initial energy content present in the feedstock. It quantifies the effectiveness of the process in extracting energy from the feedstock and converting it into usable energy in the form of hydrochar.

Energy yield is calculated by considering the mass of hydrochar produced and its corresponding HHV. The energy yield represents the proportion of energy present in the hydrochar compared to the energy content initially present in the feedstock.

Energy Yield = Mass Yield × Energy Densification

4.3.5 Result

Table 4 Tabular Illustration of energy yield percentages

Sr. No	Sample Name	Mass Yield (%)	Densification Ratio	Energy Yield
1.	Apple	24.93	2.07	51.61
2.	Pomegranate	42.72	1.61	68.78
3.	Orange	50.79	1.11	56.38
4.	Mixed	38.86	1.51	58.68

4.3.6 Discussion

The energy yield results provided for different feedstocks apple, pomegranate, orange, and mixed, indicate the proportion of energy obtained from the hydrothermal carbonization (HTC) process relative to the initial energy content present in the feedstock.

The energy yield for pomegranate is 68.78%. This indicates that around 68.78% of the energy content in the pomegranate feedstock has been effectively captured and converted into energy in the hydrochar form during the HTC process. This is the highest for all four samples. Whereas, the energy yield for apple is 51.61%. Apple has the lowest energy yield of all the samples.

These energy yield results indicate the efficiency of the HTC process in capturing and retaining energy from the feedstocks. Higher energy yield values signify a greater success in extracting and preserving energy during the conversion process.

4.3.7 Yield and Densification

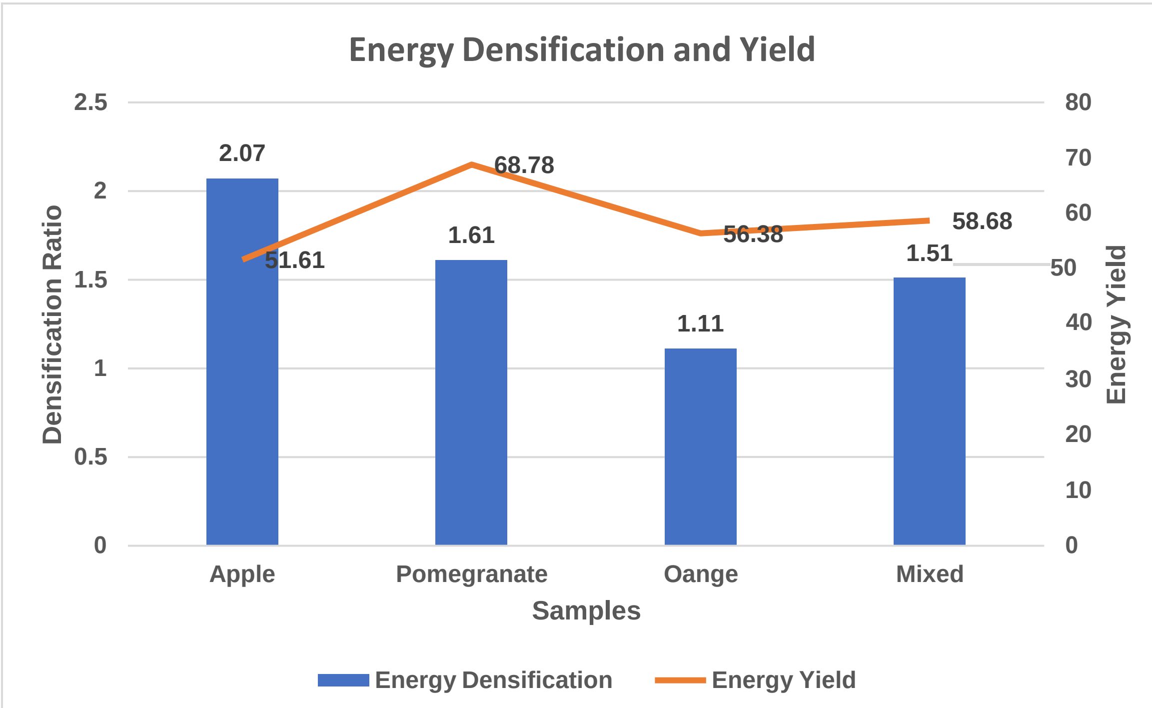

Figure 4.5 Graphical representation of relationship of energy yield and energy densification ratio

4.4 Proximate Analysis

Proximate analysis results play a crucial role in determining the important compositions and properties of hydrochar. While they do not directly contribute to the calculation of the higher heating value (HHV) of hydrochar, they provide valuable information regarding its composition and can highlight potential issues that may arise during combustion.

4.4.1 Preliminary Results

Table 5.1 Tabular Illustration of Preliminary Proximate Analysis Results

Sr. No	Samples	Moisture Content %	Volatile Combustible Matter Content %	Ash Content %	Fixed Carbon Content %
1.	Raw Apple	19.07	80.64	0.16	0.13
2.	Apple Hydrochar	0.04	96.46	0.49	3.01
3.	Raw Pomegranate	33.94	65.85	0.058	1.12
4.	Pomegranate Hydrochar	0.12	93.85	2.95	3.08
5.	Raw Orange	48.97	47.91	0.81	2.32
6.	Orange Hydrochar	0.18	87.68	3.16	8.97
7.	Mixed Raw	22.62	75.13	0.97	1.28
8.	Mixed Hydrochar	0.093	96.14	2.54	1.23

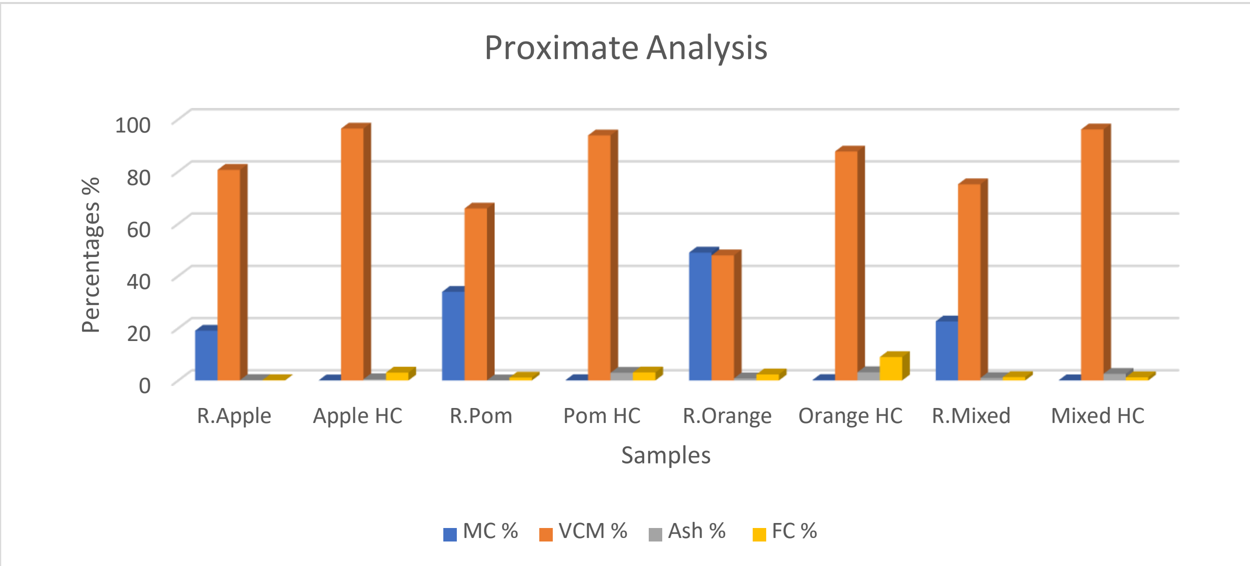

Figure 4.6 Graphical representation of proximate analysis

4.4.2 Final Results

Table 5.2 Tabular Illustration of Final Proximate Analysis Results

Sr. No	Samples	Volatile Combustible Matter Content	Ash Content	Fixed Carbon Content
1.	Raw Apple	91.57	2.22	6.22
2.	Apple Hydrochar	78.84	2.53	18.62
3.	Raw Pomegranate	81.83	4.12	16.41
4.	Pomegranate Hydrochar	63.57	3.25	33.19
5.	Raw Orange	79.68	4.03	16.29
6.	Orange Hydrochar	64.00	3.07	32.48
7.	Mixed Raw	72.76	3.21	24.03
8.	Mixed Hydrochar	56.59	2.70	40.71

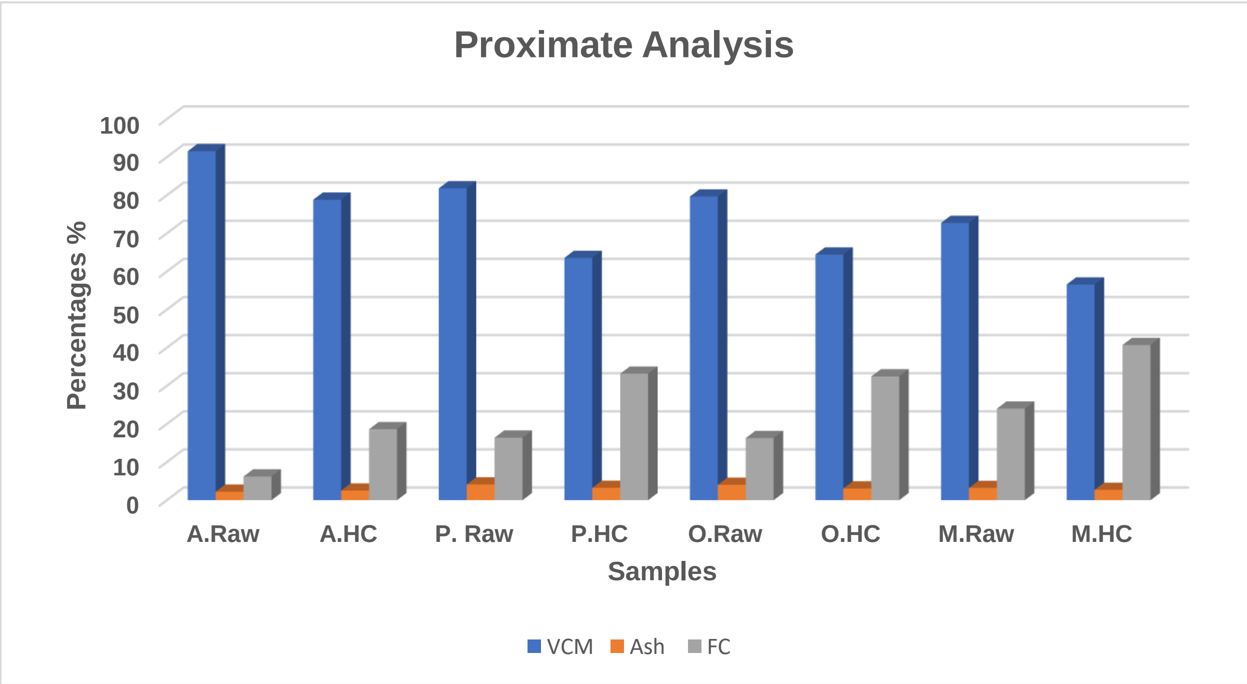

Figure 4.7 Graphical representation of proximate analysis

4.4.3 Discussion

Preliminary results for the proximate analysis were obtained by conducting tests for volatile combustible matter (VM) analysis in a muffle furnace. However, these results were found to be unsatisfactory. To address this issue, a thorough literature review was conducted to identify potential sources of errors.

One of the first findings from the literature was that the VM analysis must be performed in an oxygen-free environment. Initially, during the VM analysis in the muffle furnace, precautions were taken to ensure an oxygen-free atmosphere by placing the sample in a covered crucible. However, it was discovered that some oxygen managed to penetrate the crucible, resulting in undesirable effects. Specifically, when the samples were placed in the muffle furnace at 950 degrees Celsius, they turned grayish-white. This discoloration was not supposed to occur until the ash determination stage of the analysis (ASTM-E857, ASTM-E1755).

To rectify this issue and obtain more accurate results, the decision was made to repeat the tests using a tube furnace. A tube furnace provides better control over the environment and ensures a more effective oxygen-free atmosphere. By conducting the VM analysis in the tube furnace, the results improved significantly.

It is important to emphasize that the measures taken to address the sources of error, including switching to a tube furnace, were based on findings from the literature review. This approach ensured that the VM analysis was performed under more appropriate conditions, resulting in improved and reliable results (Cassel et al., 2012).

Secondly, during the preliminary analysis was an unexpected increase in the volatile combustible matter (VCM) content after the process. In the case of raw biomass, the VCM content should ideally decrease during the analysis. High VCM content can lead to low efficiency and emission problems, making it crucial to accurately measure and control the VCM levels.

The observed increase in VCM during the preliminary analysis raised concerns about the reliability of the results and the potential negative implications for efficiency and emissions. To address this issue and obtain accurate measurements, a thorough investigation was conducted (Zhang et al., 2022).

Thirdly, the fixed carbon content of a fuel source plays a crucial role in determining its higher heating value (HHV). The higher heating value represents the maximum amount of heat energy released during the complete combustion of a substance. Typically, an increase in the fixed carbon content leads to higher HHV values, indicating greater energy potential.

However, if the fixed carbon content is significantly low, it would have a limited contribution to the overall HHV of the fuel. This means that the fuel's energy potential may be compromised due to the low fixed carbon content.

The fixed carbon content represents the portion of a fuel that remains as solid carbon residue after volatile matter has been driven off during combustion. It is composed mainly of carbonaceous materials such as carbon, coke, and charcoal. The fixed carbon content contributes to the energy output because it undergoes complete combustion, releasing heat energy. If the fixed carbon content is low, it implies that the fuel consists of a higher proportion of volatile matter, such as moisture, hydrogen, and other organic compounds. While these volatile components may contribute to the overall mass of the fuel, their energy release during combustion is generally lower compared to fixed carbon. Therefore, a low fixed carbon content can result in a reduced HHV for the fuel (Sirisomboon et al., 2020).

So, the tests were repeated for VM analysis in tube furnace followed by ash determination in the muffle furnace. The VM results decreased from raw to hydrochar. The fixed carbon content was significantly after the hydrothermal carbonization process. Hence, satisfactory were obtained.

4.5 Ultimate Analysis

Elemental composition is important to determine because the higher the carbon content the greater the value of HHV.

4.5.1 Results

Table 7 Tabular Illustration of Ultimate Analysis Results

Sr. No	Samples	Carbon %	Hydrogen %	Oxygen %	Nitrogen %
1.	Raw Apple	43.47	6.59	47.09	2.85
2.	Apple Hydrochar	50.08	6.06	41.00	2.86
3.	Raw Pomegranate	50.11	4.81	36.86	8.19
4.	Pomegranate Hydrochar	58.03	4.20	32.90	4.88
5.	Raw Orange	48.27	5.96	41.05	4.72
6.	Orange Hydrochar	57.37	5.46	34.12	3.05
7.	Mixed Raw	52.94	5.64	37.55	3.87
8.	Mixed Hydrochar	62.46	4.86	29.36	3.32

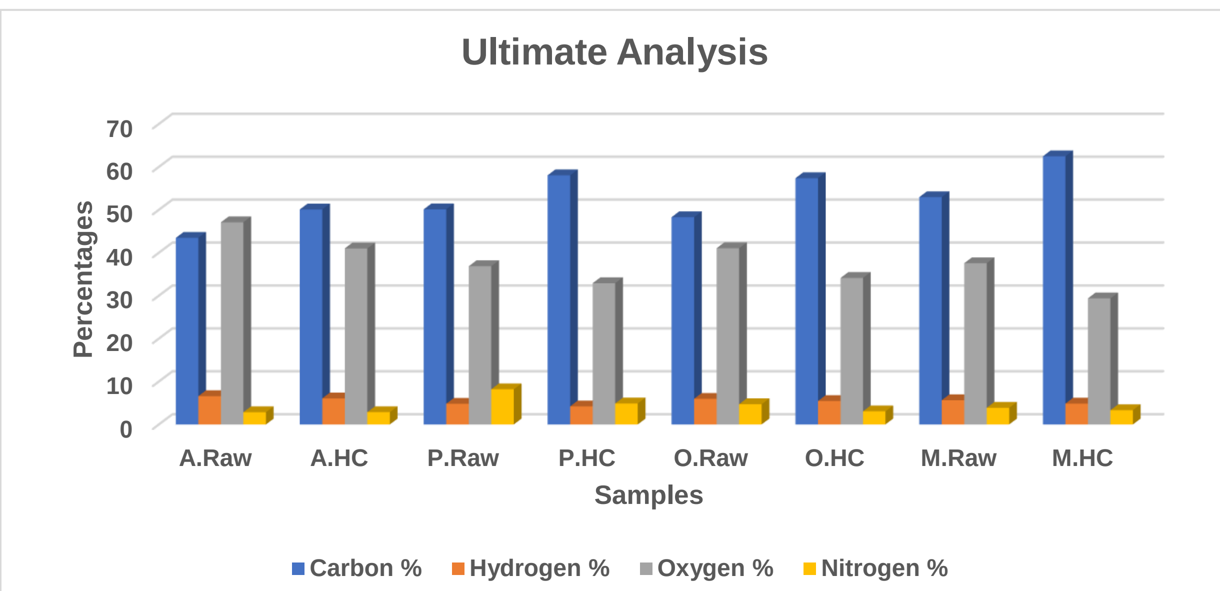

Figure 4.8 Graphical representation of ultimate analysis

4.5.2 Discussion

The hydrothermal carbonization (HTC) process is known to increase the carbon content of the feedstock. This increase occurs due to the structural and chemical transformations that take place during the HTC process, resulting in the concentration of carbonaceous materials.

During hydrothermal carbonization, organic feedstock, such as biomass or organic waste, is subjected to high temperature and pressure in the presence of water. Under these conditions, various reactions occur, including dehydration, polymerization, and decomposition of organic compounds.

One of the key transformations that take place during HTC is the removal of volatile components, such as water, oxygen, and other volatile organic compounds. This removal of volatile matter leads to a reduction in the overall mass of the feedstock, while the carbon content becomes more concentrated. The carbon enrichment in the hydrochar is attributed to the removal of oxygen-containing functional groups and the condensation of carbon atoms. These processes lead to a more stable and carbon-rich material with improved energy content and increased carbon content. This was the case in all the four samples tested.

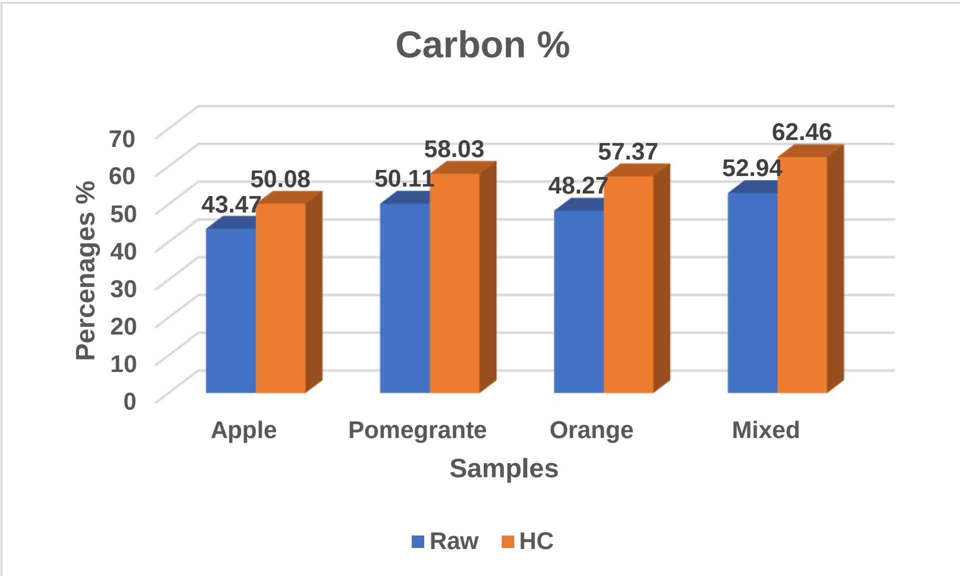

Figure 4.9 Change in carbon percentage

During the hydrothermal carbonization (HTC) process, the oxygen content of the feedstock generally decreases. This decrease in oxygen content is a result of the reactions that occur during HTC, leading to the removal of oxygen-containing functional groups and the conversion of oxygen-rich compounds into carbonaceous materials. Again, for all four samples the oxygen content decreases after the process.

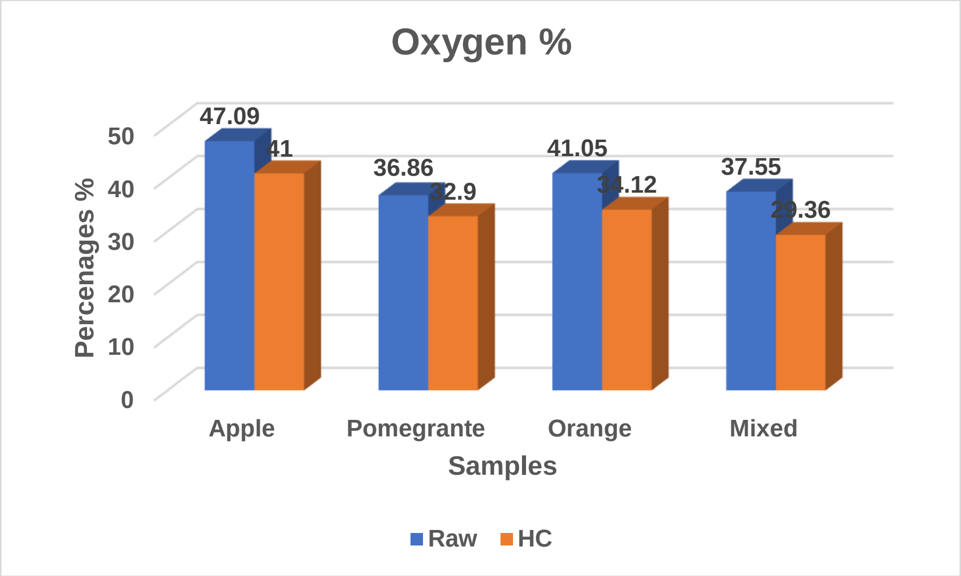

Figure 4.10 Change in oxygen percentage

Two other important parameters to be analyzed during the project through ultimate analysis are the O/C (oxygen-to-carbon) and H/C (hydrogen-to-carbon) ratios of the feedstock both of which typically decrease. This decrease in ratios is associated with several beneficial outcomes, including lower emissions, reduced moisture content, and minimized energy losses during combustion.

Lowering the H/C ratio is advantageous because hydrogen has a higher heating value compared to carbon. By reducing the hydrogen content and increasing the carbon content through HTC, the resulting hydrochar exhibits an improved energy content. This higher carbon concentration leads to increased fuel efficiency and reduced energy losses during combustion, ultimately maximizing the energy yield.

Similarly, decreasing the O/C ratio is beneficial in terms of emissions and combustion efficiency. By reducing the oxygen content through HTC, the hydrochar produced has a lower propensity for emission formation, resulting in cleaner and more environmentally friendly combustion processes.

Overall, lower H/C and O/C atomic ratios achieved through the HTC process offer several advantages. They contribute to lower emissions, including pollutants and greenhouse gases, leading to improved environmental performance. Additionally, the decreased moisture content enhances fuel quality by minimizing energy losses associated with water vaporization. Ultimately, these benefits contribute to increased combustion efficiency and energy utilization, making hydrochar derived from hydrothermal carbonization a promising fuel source for sustainable energy production (Zhang et al., 2022).

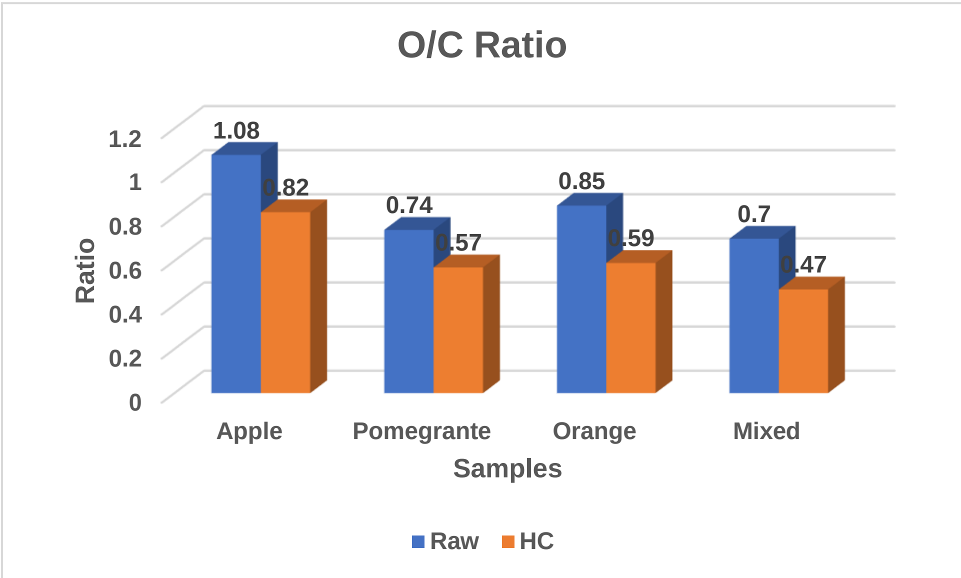

Figure 4.11 Change in O/C ratios

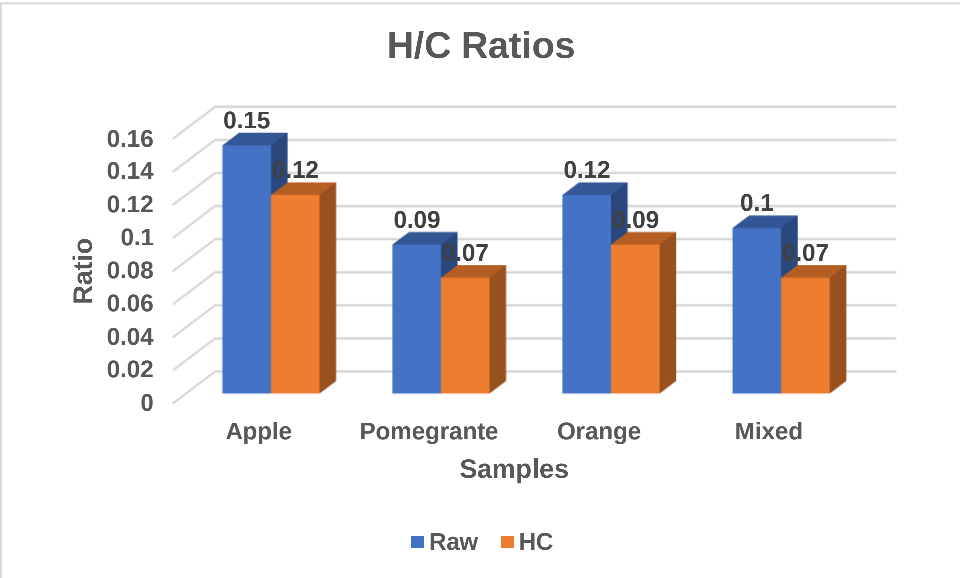

Figure 4.12 Change in H/C ratios

4.6 Fiber Analysis

The determination of lignin, hemicellulose, and cellulose content in biomass is crucial for estimating the higher heating value (HHV) and understanding the fuel properties. Fiber analysis is an important method used to quantify these components and assess their contribution to the overall energy content.

4.6.1 Results

Sr. No	Samples	Extractives %	Hemicellulose %	Lignin %	Cellulose %	Ash %
1.	Raw Apple	41.83	19.18	16.63	36.79	2.22
2.	Apple Hydrochar	0.12	10.82	46.85	33.01	2.53
3.	Raw Pomegranate	31.11	20.62	21.10	29.73	4.12
4.	Pomegranate Hydrochar	15.2	11.52	46.90	23.14	3.25
5.	Raw Orange	22.61	25.89	32.23	33.06	4.03
6.	Orange Hydrochar	15.18	13.65	46.83	23.87	3.07
7.	Mixed Raw	17.85	25.08	21.96	34.9	3.21
8.	Mixed Hydrochar	8.69	17.33	43.09	28.19	2.70

Table 8 Tabular Illustration of Fiber Analysis Results

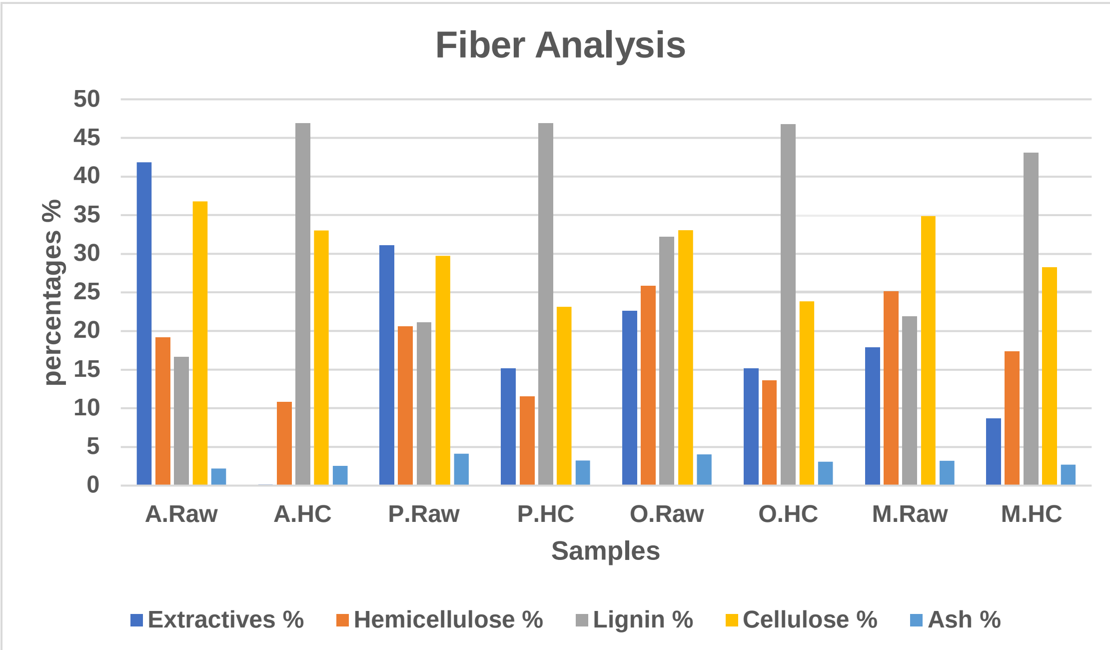

Figure 4.13 Fiber Analysis Results

4.6.2 Discussion

Lignin, hemicellulose, and cellulose are major constituents of biomass, and their individual proportions can significantly impact the HHV. Each component has distinct chemical properties and energy content, and their relative amounts determine the overall fuel characteristics.

The determination of lignin content helps estimate its contribution to the HHV. Biomass with high lignin content tends to have higher fixed carbon (FC) and lower volatile matter (VM) content, which can result in a higher fuel ratio and potentially higher heating value. This is due to the unique characteristics of lignin as a major component of biomass. Compared to other biomass components, lignin has a relatively higher resistance to thermal decomposition and a lower propensity to volatilize during combustion. As a result, biomass with higher lignin content tends to have a higher proportion of fixed carbon, which is the carbon remaining after volatile matter has been driven off. Fixed carbon is responsible for the release of heat energy during combustion and contributes to the higher heating value of the biomass. Therefore, biomass with higher lignin content can potentially exhibit a higher heating value due to its elevated fixed carbon content (Phang et al., 2023).

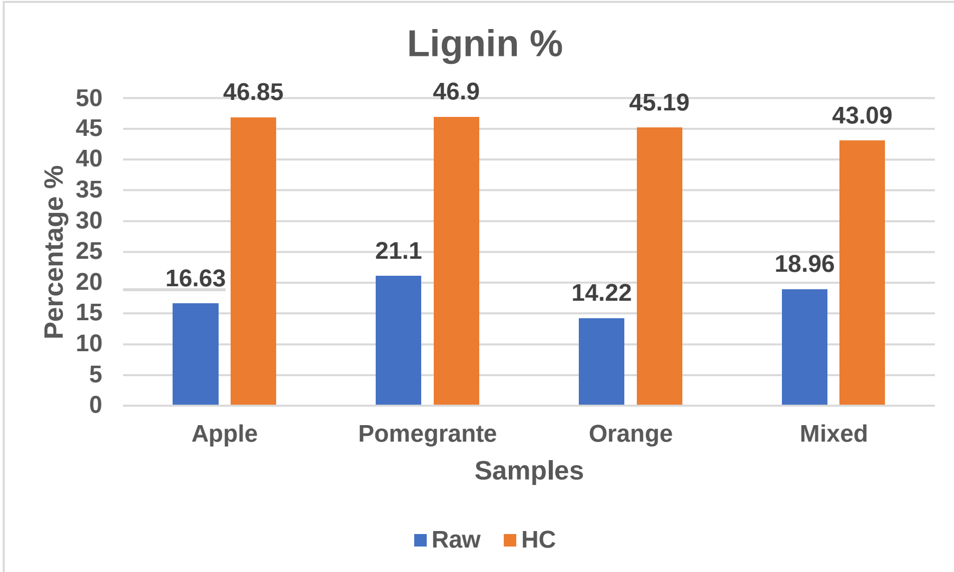

Figure 4.14 Fiber Analysis Results

In summary, biomass with high lignin content tends to have higher fixed carbon and lower volatile matter content, resulting in a higher fuel ratio and potentially higher heating value. The reduction in hemicellulose and cellulose content, along with the increase in lignin content, leads to a decrease in oxygen content and an improvement in fuel properties. These characteristics contribute to enhanced combustion efficiency, reduced emissions, and potentially higher energy yield when utilizing biomass with higher lignin content (Gulec et al., 2021).

Chapter 5 Scope

5.1 Applications

Fruit based hydrochar has several applications in Pakistan's context.

5.1.1 Fruit Processing Industries

In Pakistan, there are approximately 25 fruit processing companies involved in the production of various products such as jams and marmalades (Board of Investment, 2018).

These processing operations generate significant amounts of peels and pomace waste as byproducts. However, these waste materials can be effectively utilized for on-site electricity generation through the installation of a Hydrothermal Carbonization (HTC) plant.

By installing an HTC plant on-site, fruit processing companies can effectively convert their peels and pomace waste into hydrochar. The generated hydrochar can then be used for electricity generation. It can be utilized as a fuel in combustion systems such as boilers.

By utilizing peels and pomace waste through HTC for electricity generation, fruit processing companies can achieve multiple benefits. Firstly, it allows for the effective management of waste materials, reducing the environmental impact associated with their disposal. Instead of being discarded or sent to landfills, the waste is converted into a valuable energy resource.

Additionally, the on-site electricity generation using hydrochar can lead to energy cost savings for the fruit processing companies. By utilizing a renewable energy source derived from their own waste, they can reduce their dependence on conventional energy sources and potentially lower their energy expenses.

5.1.2 Juice Extraction Industries

In Pakistan, the juice extraction industry is thriving with over 50 operational juice extraction industries. These industries collectively generate a substantial amount of fruit waste, totaling approximately 2.16 million tons per annum (Jamil et al., 2018).

By applying HTC to the peels and pomace waste from the juice extraction industry, a valuable energy resource can be derived. The peels and pomace waste generated by the juice extraction industries are abundant in organic matter, including cellulose, hemicellulose, lignin, and other components. These organic materials make the waste ideal for HTC, as they have the potential to yield a significant amount of hydrochar with a high carbon content.

5.1.3 Curtailing Industrial Electricity Demand

During the fiscal year 2021-2022, the industrial sector in Pakistan accounted for a huge amount of the overall energy demand, representing approximately 28% of the total energy consumption (Economic Survey Report, 2022).

This made it the second-largest sector in terms of energy demand, following the domestic sector. However, a decrease in industrial demand can alleviate the burden on the energy supply and have various implications.

A decrease in industrial demand can have several positive effects on the energy system and the overall economy. Firstly, it can alleviate the burden on the energy supply and help maintain a more balanced energy distribution. By reducing the energy demand from the industrial sector, more resources can be allocated to other sectors, such as the residential and commercial sectors, ensuring a more stable and reliable energy supply.

Industries are often associated with significant greenhouse gas emissions and environmental impacts due to their energy-intensive processes. By reducing industrial energy demand, there can be a corresponding reduction in carbon emissions and other pollutants. This can contribute to environmental sustainability and help in achieving climate change mitigation goals. Also. It will help them meet their compliance rules easily.

5.2 Operational Hydrothermal Carbonization Plants

1. Pilot and commercial scale plants in Germany.
2. Pilot scale HTC plant at Swiss Federal Institute of Aquatic Science and Technology (Eawag), Switzerland.
3. Commercial scale plants in Ingelia, Spain.
4. Industrial scale HTC plant in China.

Chapter 6 Conclusions

- The project included a study being conducted to analyze the energy generation potential of three different fruits and their mixture. Various tests, including proximate analysis and biochemical analysis, were performed to evaluate the higher heating value (HHV) of the samples. The results of these tests justified the HHV values obtained.
- The study found that the lignin content and fixed carbon content were the primary factors contributing to the HHV values, and these factors were similar for all the fruit samples analyzed, as well as the fruit mixture. This suggests that there is no significant variation in the energy generation potential among different fruit wastes, and they can be used collectively without the need for segregation.
- The HHV values obtained from the analysis were promising, indicating that fruit waste can be effectively utilized for energy generation in Pakistan. This finding has important implications for addressing two major issues faced by the country:

  i. solid waste mismanagement,

  ii. energy crisis.
- Through conversion of, such as fruit waste, into solid fuel, Pakistan can tackle pressing issue of waste mismanagement. Fruit waste is an important component of total waste quantity in the country, and its proper management is crucial for maintaining environmental cleanliness and public health. Utilizing fruit waste for energy generation helps to divert it from landfills and reduces its environmental impact.
- Furthermore, utilizing fruit waste for energy generation contributes to addressing the energy crisis in Pakistan. The country faces challenges in meeting its energy demands, resulting in frequent power outages and energy shortages. By harnessing the energy potential of fruit waste, Pakistan can enhance its energy mix and reduce its reliance on conventional energy sources, thus mitigating the energy crisis.
- In summary, the analysis of different fruits and their mixture for energy generation revealed promising results. The similarity in lignin content and fixed carbon content among the fruit samples indicated that they can be collectively used without segregation. The HHV values obtained from the analysis reaffirmed the potential of fruit waste for energy generation in Pakistan. This approach not only helps in managing solid waste but also contributes to addressing the energy crisis, making it a valuable solution for Pakistan's challenges in solid waste management and energy availability.

Chapter 7 Recommendations

Considering the results of majority of the tests including the higher heating values were promising, there is a way forward for this project:

- There is a need for government assistance to encourage industries to utilize their waste on-site. Such measures can encourage industries to look for cheap and affordable measures and one where the benefits are two-fold can be easily adopted.
- Carrying out a techno-economic study of a pilot-scale hydrothermal carbonization plant is crucial to assess the feasibility and viability of its development. Such a study involves evaluating the technical aspects as well as the economic implications associated with implementing and operating the plant.
- The design and construction of a pilot-scale hydrothermal carbonization plant. This should be able to identify the following;
  - i. Optimizing the parameters that affect the process including temperature, pressure, process duration, and moisture content, to maximize the conversion of organic waste into hydrochar.
  - ii. Designing and selecting the appropriate reactor type and size for the pilot-scale plant. Factors such as reactor material, heat transfer mechanisms, agitation systems, and safety considerations are considered to ensure efficient and safe operation.
  - iii. Evaluating the energy requirements of the plant and identifying potential energy-saving measures are important aspects of the technical analysis. This includes exploring options for heat recovery, process integration, and optimizing energy consumption during various stages of the process.

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