Delft University of Technology

MSc Thesis in Sustainable Energy Technology

Biochar for horticultural and agricultural applications using high temperature torrefaction technology

Comparing the performance of different biochar materials for soil remediation and Carbon sequestration applications

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PERPETUAL NEXT

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Biochar for horticultural and agricultural applications using high temperature torrefaction technology

Comparing the performance of different biochar materials for soil remediation and Carbon sequestration applications

A thesis submitted to the Delft University of Technology in partial fulfilment
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This thesis is confidential and cannot be made public until September 28, 2022

Preface

This report was written in partial fulfilment of the requirement for the degree of MSc in Sustainable Energy Technology at Technical University of Delft. This project titled "Biochar for horticultural and agricultural applications using high temperature torrefaction technology" was performed from November 2020 till September 2021. This project was performed in collaboration with Perpetual Next technologies B.V and was undertaken to study alternative sustainable feedstocks suitable for horticulture and carbon sequestration applications.

While writing this report, it is assumed that the reader has basic knowledge about low-high temperature(300-800°C) biomass conversion technologies and understands the different parameters used in these operations. This research uses tools such as Harris profiling and regression analysis and a basic understanding of these methodologies will also help the reader in understanding the analysis performed.

Readers who are specifically interested in understanding the feedstock selection can find it in chapter 2.The results and the discussions for the biochars produced can be found in 4 and the conclusions and recommendations can be found in 5.

Delft, 28 September 2021
Pradeep Ravi

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Working on this research topic has been informative and fun from the get go. This research would not have been successful without the help, encouragement and support that I have had received in this time.

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I would also like to thank Mr.Jean-Michel Commandré and Mr.Laurent Martin from CIRAD, Montpellier for helping me better understand the torrefaction setup as well as for showing me around the facility. The high temperature gasification equipment as well as the vibrato torrefaction reactor looks really promising.The final set of experiments at the university was key to let me understand and interpret the data for the biochars. I would like to thank Mr.Hugo Veldhuizen for helping me out with the BET measurements and for all the feedbacks that I have received. It must have definitely taken a lot of hours out of your schedule but, you are always happy to help others and also learn in the process. A special note of thanks to Mr.Simone Asperati who helped me out with the pH calibrations and Ms.Ragnheiður Benónísdóttir and Ms.María Terol Sanchez for all the helpful training in the SEM-EDS labs. I am also really grateful to Dr.Jenny Jones from Leeds university for all her detailed insights and critcal feedbacks during our presentations.

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This has been a fairly perilous but entertaining journey and I can see the light at the end of the tunnel now.

Pradeep Ravi
September 28, 2021

Abstract

Biomass currently accounts for less than 10 percent of the world's renewable energy production. There is however an increasing trend in biomass consumption based on a variety of applications apart from combustion. The torrefaction process has been lauded consistently for being able to produce biochar even while operating under the low temperature regimes. With an increasing potential for biomass production coupled with an increased scrutiny on the use of biomass as a green fuel, the need for alternative clean applications for the biochar is the need of the hour. In this research ten different biomass materials are analysed and tested for potential horticultural applications with a specific focus on soil remediation.

Perpetual Next B.V. is a major technology provider and biochar pellet manufacturer using their patented HTT4 (High Temperature Torrefaction 4) technology. Currently the major global sustainability issue also stems from the sourcing of virgin wood chips from dense forests for pellet production. This project also specifically aims to remove the dependence on evergreen forests and wood chips by sourcing and experimenting primarily on alternative feedstocks from agricultural residues or other waste streams.

This research aims to provide a clear and useful analytical tool which will benefit the scientific community select suitable biomass materials based on material properties and end applications. The efficacy for the various torrefied biomass feedstocks on the soil and its stability are tested. The required torrefaction parameters and pre-processing and material handling are studied and documented in this research as well. Overall, about 50 different biomass feedstocks were identified and evaluated based on past performances from literature. The top 10 best performing feedstocks were sourced and subjected to various physical and chemical characterization tests. The selected materials were torrefied in a pilot reactor with operating conditions similar to the commercial HTT4 operation. A post characterization as well as targeted experimentation including the SEM-EDS, BET and pH measurements were performed on the biochar produced. Ultimately the feedstocks were scored and ranked from best to worst performing biochar for soil remediation and sequestration-based applications.

The analysis for the biomass feedstock spread across woody, grassy, and processed materials. A sequential filtering resulted in the selection of the following materials for biochar production-Bagasse, Rice husks, Maize residue, Grapevine stems, Washed roots, Miscanthus, Pinewood chips, Greenhouse tomato residue and Recycled wood. Forestry trimmings is taken as the current and comparative reference. The materials were mainly analysed for their Carbon and ash content, while the biochar was produced was analysed based on its surface area, porosity and degree of carbonization achieved through torrefaction. The surface area and porosity are also subjected to a regression modelling based on hundreds of data points from existing research. The soil permanence is a function of the H:C and O:C ratios which is also computed.

The results for eight out of the ten chars analysed show a stark improvement over the current reference with only the tomato residue and the rice husks showing little to no improvement. Overall, the washed shredded roots char, bagasse char and recycled wood char ranked top three in the analysis and are recommended for horticulture and carbon sequestration applications, while the tomato residue and rice husks show no improvements in properties using torrefaction and should be researched for alternative applications. Overall, the global nature of the feedstocks could influence its properties and care should be taken not to generalize the biomass materials based on this research.

Acronyms

S.No	Abbreviation	Expansion
1	HTT	High Temperature Torrefaction
2	FSM	FeedStock Matrix
3	Bi	Biot Number
4	Py	Pyrolysis Number
5	GS	Grape Stems
6	RH	Rice Husks
7	WS	Wheat Straw
8	BG	Bagasse
9	TW	Tomato Waste
10	MI	Miscanthus
11	PW	Pinewood chips
12	SR	Shredded Roots
13	VW	Virgin Woodchips
14	GAWW	Grade-A WasteWood
15	FW	Forestry Waste
16	ND	Not Detected
17	MDL	Minimum Detection Limit
18	EBC	European Biochar Certificate

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Chapter 1

Introduction

1.1 Introduction to biochar and the study

1.1.1 Biochar and horticulture

Horticulture agriculture are the backbones for a civilized society. The Dutch agriculture and horticulture ranks second on global food export list after the US generating sixty five billion Euros every year in revenue [111]. The sector that provides food for nourishment and development is plagued with issues pertaining to low crop yields, pests and inadequate rainfall[40]. A few of these issues can be resolved/ improved by the use of pesticides/ fertilizers, but these prove detrimental towards the health of the soil and may cause the food that is consumed to contain harmful amounts of chemicals[7]. There have been other commercial alternatives such as crop rotation or the use of organic compost as fertilizers to enhance the soil and boost it's productivity in the past with a degree of success[67][12][78].
The energy demanded by humans has been increasing continuously since the advent of the industrial age. The IEA reported that in just last decade, the worldwide energy demand has increased by 2.3% which is the highest ever increase in a decade[56]. Out of the 583 ExaJoules of energy demanded worldwide, more than 80% of our energy requirements is satisfied by non-renewable sources such as coal, oil and natural gas[2]. This 2020 split up of energy produced from each source is shown in figure 1.1.

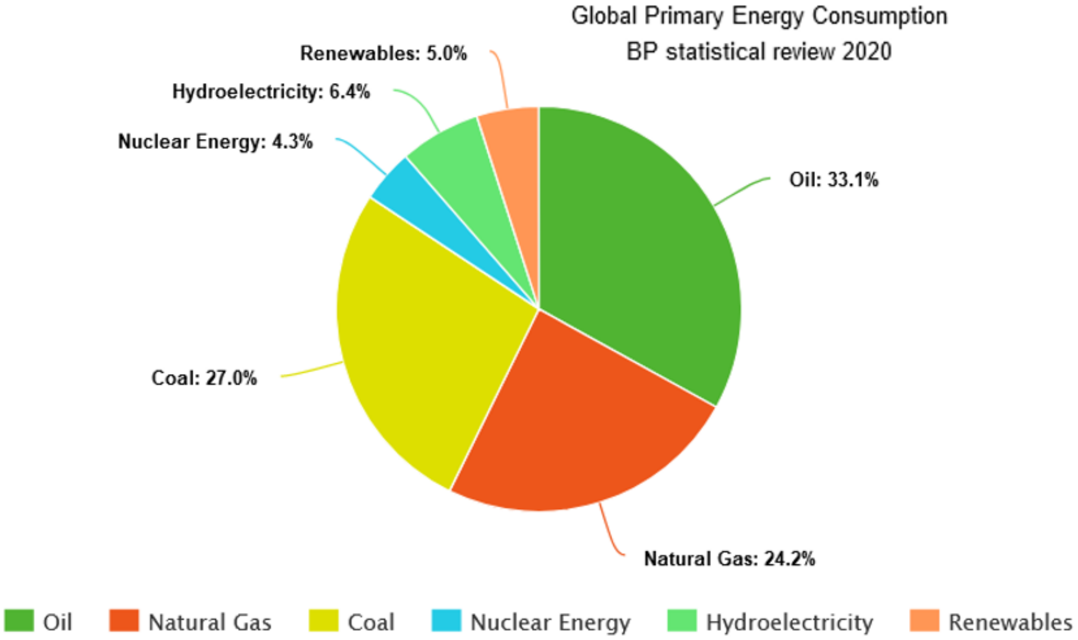


Figure 1.1: Energy consumption from different fuels

This incessant use of these polluting sources generate more than 38 Gt of Co2 globally every year[77]. To combat this increase in anthropogenic emissions as well as limited availability of coal, the world is slowly looking to increase the energy production from renewables while also looking for coal like alternative.

Biomass on a macro scale is the sum total mass of all the living organisms in a given space[19] . However, upon death and subsequent decomposition of the organism, only a portion of the organic matter remains in place. This remaining organic matter or biomass is useful primarily as a fuel due to its energy content and combustibility as a result of its inherent Carbon content[57].
Numerous feedstock sources, a high energy content and global availability facilitates biomass majorly as a coal substitute for combustion applications. Though this replacement helps in lowering emissions and helps preserve the remainder of the coal reserves, there are a few issues associated with the use of biomass for combustion or co-firing applications along with coal. Biomass primarily is classified into three generations namely the first,second and third depending on the feedstock in used for its production. While the feedstocks under the second and third generation are non-edible, the first generation feedstocks are basically starch based food materials and other edible seeds[55]. In this research only materials belonging to the second generation are investigated as the third generation feedstocks are algae based and are still in early stages of development[21].
The list of feedstocks under the second generation range from virgin wood chips to agricultural residues to energy crops. While the virgin wood chips and resulting pellets are make for a relatively cleaner material, the agricultural residues and other herbaceos biomass contain a high degree of contaminants owing to the presence of Suplhur and Chlorine in its organic structure. This results in fouling or slagging within the boiler and results in frequent cleaning requirements and lower boiler efficiency[58]. Secondly, most biomass feedstocks are sourced from perennial forests or agricultural fields and therefore contain a high percentage of moisture that is highly detrimental for combustion. Thirdly, the low volumetric and energy densities for certain herbaceous biomass results in an sharp increase in transport and handling costs[49]. Lastly, the land use pattern sharply changes with biomass feedstock requirements. This pattern of monoculture results in reduced nutrient availability and exchange within the soil while also enhancing the rate of attack by microbes and pests[52].As shown in figure 1.2 There is tremendous potential for biomass currently and the complete utilization of this source of energy can reduce the percentage of energy dependence from non-renewable sources of energy[46]. Figure 1.2 represents the current potential and future potential for biomass in 2030 based on a research performed by the ***planbureau voor de leefomgeving***, the Netherlands.

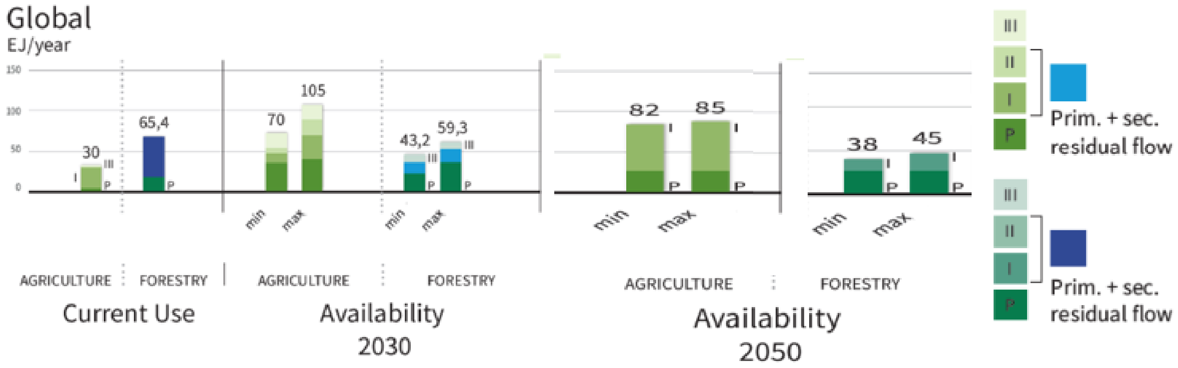


Figure 1.2: Current Biomass availability and 2030 potential[104]

It can be noted that though roughly 20% of the worlds energy demand can be satisfied through biomass incineration, careful identification of these feedstock sources as well as emission analysis needs to comprehensively calculated to ensure that this energy does not lead to deforestation and an increase in Carbon emissions[60].

These problems associated with biomass use can be resolved through its upgrading. Upgrading of biomass refers to the utilization of a thermochemical conversion of biomass which results in the converted material having many of its physical(grindability, hydrophocity,etc) and chemical properties(Carbon content, stability) improved. There are many common thermochemical conversion methods which involves the treatment of biomass to interact an elevated temperature and pressure. This results in enhanced combustion characteristics for the biomass after which the biomass properties become similar to coal forms such as Lignite and Peat. A few examples for such conversions include fractionation, liquefaction, pyrolysis, hydrolysis, fermentation, and gasification[22]. Pyrolysis is the process where biomass is allowed to degrade at an elevated temperature ranging from 250 degrees to 800 degrees in an oxygen free atmosphere. Low temperature pyrolysis(250-350 degrees) is called torrefaction which also occurs in an inert atmosphere in the presence of Nitrogen gas. In this research, we will only be discussing biomass upgrading through torrefaction producing a highly stable Carbonaceous charcoal like material which is high in energy content. This material is called biochar and has shown a great deal of potential not only for combustion, but also for horticultural and agricultural applications.

Biochar as a soil remediation agent is another great addition to help address the issues faced by the horticultural sector. There has been a great deal of research done on biochar and the benefits associated with its use to enhance the productivity from the soil and these results are shown in table 1.1.

Crop	**Soil**	**Biochar material**	**Application rate[t/ha]**	**Result**
Maize	Dark reddish-brown ferralsol	Salix spp	25	29% increase in yield over control[13]
Wheat	Ferrosol	Paper mill waste	10	250% yield increase over control[112]
Maize	Loamy silt soil	Mango wood	16	Increase in yield by 22% along with enhancements to pH,CEC, water retention and mineral availability.[90]
Peanut	Alfisol	Acacia	10	200% increase in yield, overall increase in N content.[118]
Meadow grass	Aqui-Entisol	Manure compost biochar	12	Increase in all nutrients (N,P,K,Mg,Ca)[66]
Cotton	Inceptisol	Corn straw	20	21% increase in yield over control[110]
Grape	Sandy clay loam	Orchard pruning	22	20%increase in yield over control[79]
Rice	Volcanic ash soil	Eucalyptus	30	294% increase in yield over control[79]
Radish	Vertosols	Poultry litter	100	96% increase in yield over control, overall increase in N content[31].

Table 1.1: Biochar results from various field studies.

Biochar is an enriched/upgraded form of biomass that is known for its high Carbon content and stability along with a slew of other characteristics that make it extremely attractive for horticultural applications. The blending of this biochar within the soil allows for successful Carbon sequestration for decades or even centuries. Traditionally, the upgrading to biochar involves a careful selection of the biomass feedstock from a specified geographic location. The place of sourcing as well as the season of harvest has a great impact on the properties of the resulting biochar.

Feedstocks sourced from different parts of the world need to be completely analysed chemically for any potential contaminants that could hamper the torrefaction process. The output quality of the biochar produced is closely tied with the input biomass quality and a cleaner feedstock can ensure higher lifetime of the reactor with minimal maintenance and downtime.

Commercially, virgin wood is preferred as a biomass feedstock owing to its high initial Energy content and homogeneous properties. The use of this wood for torrefaction has been heavily criticized as a coal alternative as it is attributed towards large scale deforestation across the world. The shift towards more sustainable feedstocks such as agricultural residue, food waste and tree trimmings are gathering more attention owing to their lower cost and higher circularity. This paper discusses torrefaction of nine such feedstocks sourced from various renewable channels and its application in horticulture and agriculture. These feedstocks will also be compared to the forestry wood chippings which is used as a baseline reference in this research

In general, biochar is an organic compound that exhibits high levels of stability due to its aromatic structure. The primary constituents of biomass are Cellulose, Hemicellulose and Lignin which are present in different amounts depending on the feedstock material and are depicted in 1.2. These structural compounds make up the biomass and they together constitute 85% of it. The remaining 15% consists of inorganics such as minerals and extracts.

Agricultural residue	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**
Hardwood	40–50	24–40	18–25
Softwood	45–50	25–35	25–35
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Wheat straw	33–40	20–25	15–20
Rice straw	40	18	5.5

Table 1.2: Cellulose, Hemicellulose and Lignin concentrations in common feedstock materials[25]

Cellulose is the major component of the lignocellulosic feedstocks with 50% cellulose content in woody materials and upto 90% in feedstocks such as cotton[41]. Cellulose primarily exists in the cell wall and ensures that the cell wall is stable and strong. Hemicellulose is another long chain polymer that coexists with cellulose within the cell wall. Owing to their long chain length and stronger linear chain, Cellulose is water insoluble and strong while hemicellulose which is composed of random amorphous structures is weaker[91]. Thus, hemicellulose is the first constituent compound to degrade at elevated temperature. The last component is Lignin which in addition to functions such as cell wall formation and water flow helps in maintaining the overall strength of wood. Lignin helps the various layers of the cell wall and the internal structure bind together and ensures that the mechanical strength of the plant is not compromised. Lignin is made up of cross linking polymers which give high degrees of thermal stability and is therefore the last compound to degrade at higher temperatures.

During high temperature torrefaction (also referred to as mild pyrolysis), the hemicellulose and cellulose deform from their initial branched structure into a more closed cyclic structure. This increases the strength in between the bonds of the compound making it resilient towards environmental decomposition within the soil. The surface of this biochar is covered with active sites and pores, thereby allowing nutrients, minerals and water to be exchanged between the soil and the plant root.

The biochar also can be incorporated with micronutrients such as Nitrogen, Potassium and Phosphorous which also helps boost the productivity of crops along with helping regulate the internal fixation cycles for the crops. This slow and timed release of minerals and water along with the presence of micronutrients in the required amount allows biochar to be an effective tool for boosting soil fertility and in turn leads to increased crop yields. A summary of all of biochar's beneficial properties are listed in figure 1.3

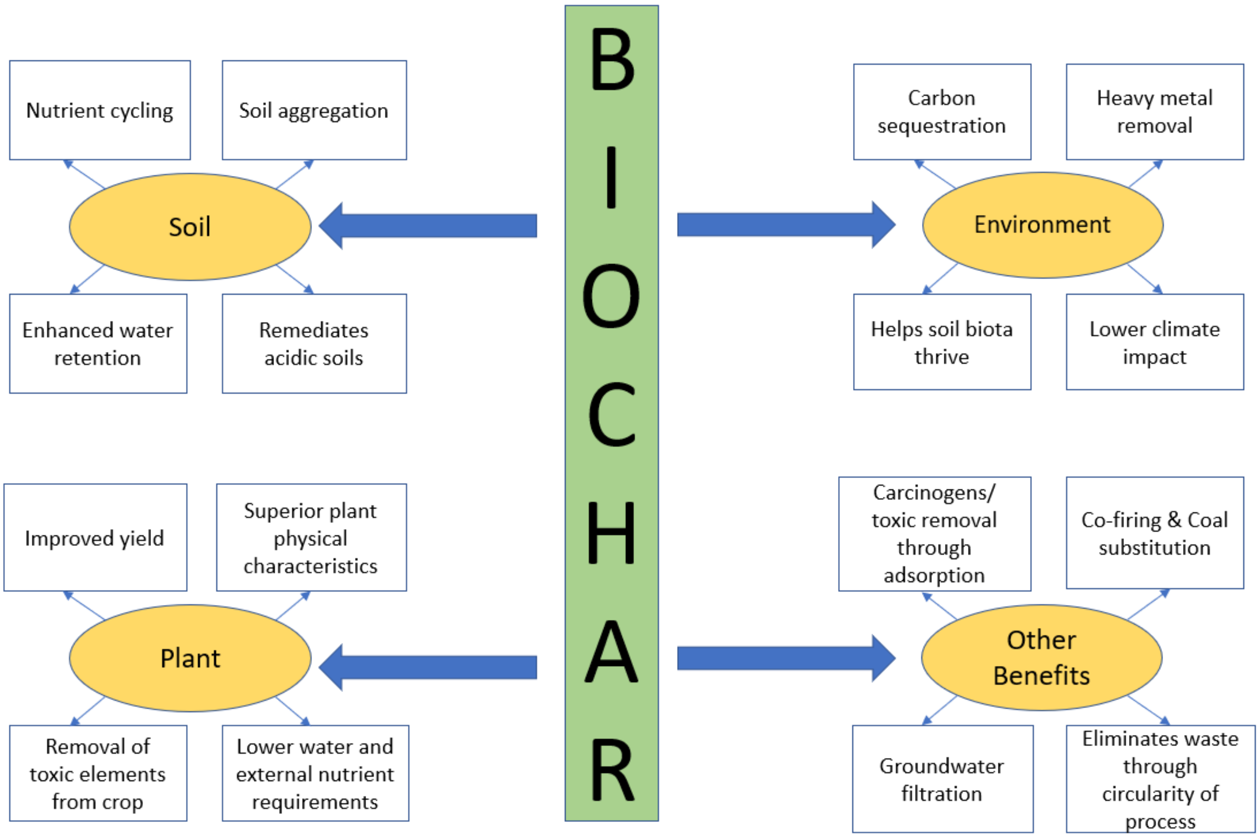


Figure 1.3: Biochar and its benefits

Currently a majority of biochar produced is being used as a coal replacement in co-firing or district heating applications. Biochar (or sometimes referred to as Biocoal) having a low ash and moisture content along with a high Carbon content is the perfect replacement for coal in the short term. With the plan on phasing out of coal powerplants and more stricter regulations pushing for clean energy from 100% renewable sources, a key application is the use of this biochar as a soil remediation. Keeping this in mind, a thorough investigation into forty different feedstocks was initially performed. Once the results from other torrefaction studies was performed and its efficacy as a soil additive was deemed good, the feedstock was shortlisted for extensive scrutiny.

The focus was mainly on keeping the overall costs low and to ensure that the feedstocks were circular. The torrefaction parameters were carefully studied and the results from the biochars were carefully analysed.. Through this study, the framed hypothesis is that feedstocks sourced from Agricultural or waste streams have higher potential for horticultural applications and lower overall costs compared to woody feedstocks and the baseline forestry waste biomass.

1.1.2 Aim of this study

The aim of this study is to maninly investigate lesser researched herbaceous feedstocks for the production of biochar using high temperature (350°C) torrefaction technology. The biochar produced is evaluated experimentally to determine the best feedstocks out of the ones that are selected from a performance and cost point of view. The feedstocks will be ranked based on criterias such as H/C and O/C ratios, pre and post treatments required and the microstructural analysis. The torrefaction of herbaceous (cellulosic) feedstocks such as tomato waste and grape stem is relatively new and this research also discusses the influence of the applied torrefaction conditions and relevance for horticulture for these newer feedstocks.

The important parameters which make the biochar useful for horticulture applications through soil remediation such as surface area and porosity will be researched and experimented. A modelling approach will also be utilized for the surface area and porosity to help ascertain if there are any discernible patterns through the different temperature regimes. Finally, the feedstocks will to tested and ranked on the basis of a set of key indicators. This in turn will help identify valuable feedstock and understand the torrefaction parameters required and better optimize the performance for biochar in horticulture and for other soil related applications.

1.1.3 Structure of the report

The report comprises of the following chapters: Introduction, Literature review, experimentation, observations and inferences. The introduction gives a brief overview of the topic and associated information related to the feedstocks and the torrefaction process. The literature review focuses on the different feedstocks types: Woody, agricultural residues and commercial waste and the understanding of pre and post treatments required along with the study of the torrefaction parameters for the different feedstocks.

The experimentation mainly deals with the torrefaction of the feedstocks and the associated surface analysis (SEM and Nitrogen adsorption) and chemical analysis (Proximate and ultimate analysis). The results from the initial chemical analysis determine the degree of pretreatment required and the expected values post torrefaction. The Results and discussion chapter gives an overview for the various results for the biomass and the biochar, while the conclusions and scope for further research is mentioned in the Conclusions and recommendations chapter.

Chapter 2

Literature review

This chapter contains the required prerequisite information crucial towards understanding the full scope for the raw materials, the process and the finished product. First, the report provides information on all the different feedstocks that were investigated and also the basis for selection of favorable feedstocks. Secondly, the most critical biomass and biochar properties are discussed. Thirdly, the different biomass conversion technologies are discussed with a specific focus on pyrolysis and the torrefaction process for these feedstocks . Fourthly, the different torrefaction reactors are discussed with the last part of the chapter dealing with the operating parameters for torrefaction.

2.1 Biomass Feedstocks

Any organic matter containing energy (which mainly comes from the carbon content) can be termed broadly as biomass. However, biomass comes in a lot of different types spread across the world. Historically, the most common form of biomass is wood owing to its abundance as well as its high carbon content. However, clearing acres of rainforests to satisfy our energy needs is not sustainable at all. Moreover, the high costs associated with woody feedstocks along with the negative connotation associated with the use of virgin wood chips is forcing biomass manufacturers to think about biomass from other waste streams. Since the last decade, there has been a considerable increase in agricultural feedstocks as well as materials that come from various waste streams that are deemed otherwise useless such as Chicken litter, food waste, etc. With the increase in environmental regulations as well as the government clamping down hard on the coal and coal-like materials, biomass which acts as a coal replacement is the way forward.

2.1.1 Feedstock selection

For this study, an initial study was performed on more than 25 different feedstocks based on existing literature. Specific focus was kept on those top produced feedstock residues and the ones that were circular. These feedstocks were then filtered through multiple layers of profiling and conditioning. The main strands revolved around the global production capacity, the pre-treatment required and how clean and sustainable the material was.
Figure 2.5 indicates that a variety of feedstocks ranging from woody to agricultural residues to waste streams were taken for analysis. Though our focus is on renewable feedstocks, it is important to take woody biomass as a reference. This initial selection was scrutinized further on the basis of transport logistics, level of pretreatment required and the quality of the torrefied material produced in the end. Though most agricultural feedstocks are relatively cheap or free to source, they require heavy pretreatment ranging from washing and drying to pelletization[108]. On the other hand, waste stream feedstocks such as grade A waste wood and foodwaste have a high degree of variability pertaining to the indicative quality of the raw material received.

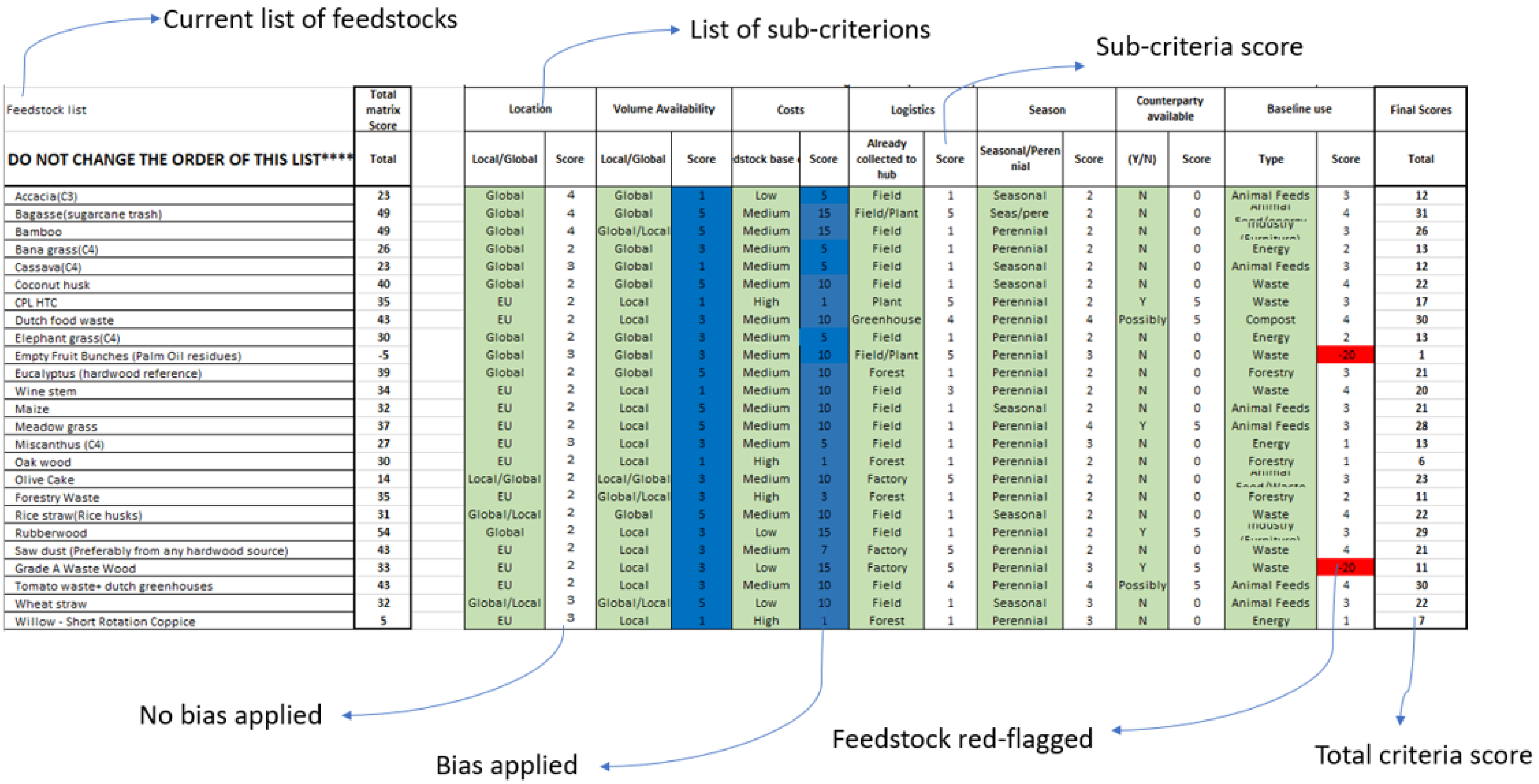
This complicates the pretreatment required as well as the final properties of the biochar that is produced. This problem can be minimized by including a sorting step prior to any other preprocessing steps or by placing strict requirement conditions from the supplier. Woody biomass though costly, should have a lower preprocessing cost as the only conditioning required is chipping to ensure that the feedstock and the output are of the required size and shape. This analysis is critical to determine on an overall level, which are the feedstocks that will be the best fit for horticultural and agricultural applications. The initial filtered list of 28 feedstocks is shown in figure2.5

Figure 2.1: Initial feedstock selection

Once the initial favorable feedstock selection is made, each of these materials needed to be assigned ranks. From an analytical perspective it was extremely difficult to properly identify those high performing feedstocks owing to various factors that inhibited the validation used. For instance, the severity of sourcing a feedstock that was not local to the EU and the added transportation costs and logistics could not be incorporated within the qualitative realms of measurement. For this, two tools were defined that helped us assign values for the various feedstocks on the basis of the different parameters used.

The first one was the Harris profiling which is an important tool prescribed by the industrial design guidelines. This tool was used as a preliminary investigation tool for 15 feedstocks and included elements such as costs, availability as well as expected increase in crop productivity through soil remediation. The results from this tool was analysed and the initial shortlist of feedstocks was made. A section of the Harris profiling is listed in appendix A.
The design guide also mentions that this tools is meant to provide indicative results that can help with getting an initial idea about the usefulness of a particular item ranked along different criterias. Therefore, the initial results from this profiling helped setup the next filtering tool the "Feedstock selection matrix"(FSM). The FSM is a designed to be a tool that ranks different feedstocks across three broad categories namely logistics, degree of pretreatment required and properties of the feedstocks specifically for horticultural applications.

Under each of these broad categories, there is a multi criteria analysis performed across each strand. For instance, the logistics section of the FSM deals with feedstock availability, the costs associated with sourcing these materials . The different criteria is then weighed according to the feedstock and then ranked from highest to lowest. The FSM consists of six different applications for the biochar produced including horticulture, co-firing and district heating. A section of the feedstock matrix is depicted in figure 2.2.



Feedstock list	Total matrix Score	Location		Volume Availability		Costs		Logistics		Season		Counterparty available		Baseline use		Final Scores
DO NOT CHANGE THE ORDER OF THIS LIST**	Total	Local/Global	Score	Local/Global	Score	dstock base	Score	Already collected to hub	Score	Seasonal/Perennial	Score	(Y/N)	Score	Type	Score	Total
Accacia(C3)	23	Global	4	Global	1	Low	5	Field	1	Seasonal	2	N	0	Animal Feeds	3	12
Bagasse(sugarcane trash)	49	Global	4	Global	5	Medium	15	Field/Plant	5	Seas/pere	2	N	0	Animal [illegible]	4	31
Bamboo	49	Global	4	Global/Local	5	Medium	15	Field	1	Perennial	2	N	0	industry [illegible]	3	26
Bana grass(C4)	26	Global	2	Global	3	Medium	5	Field	1	Perennial	2	N	0	Energy	2	13
Cassava(C4)	23	Global	3	Global	1	Medium	5	Field	1	Seasonal	2	N	0	Animal Feeds	3	12
Coconut husk	40	Global	2	Global	5	Medium	10	Field	1	Seasonal	2	N	0	Waste	4	22
CPL HTC	35	EU	2	Local	1	High	1	Plant	5	Perennial	2	Y	5	Waste	3	17
Dutch food waste	43	EU	2	Local	3	Medium	10	Greenhouse	4	Perennial	4	Possibly	5	Compost	4	30
Elephant grass(C4)	30	Global	2	Global	3	Medium	5	Field	1	Perennial	2	N	0	Energy	2	13
Empty Fruit Bunches (Palm Oil residues)	-5	Global	3	Global	3	Medium	10	Field/Plant	5	Perennial	3	N	0	Waste	-20	1
Eucalyptus (hardwood reference)	39	Global	2	Global	5	Medium	10	Forest	1	Perennial	2	N	0	Forestry	3	21
Wine stem	34	EU	2	Local	1	Medium	10	Field	3	Perennial	2	N	0	Waste	4	20
Maize	32	EU	2	Local	5	Medium	10	Field	1	Seasonal	2	N	0	Animal Feeds	3	21
Meadow grass	37	EU	2	Local	5	Medium	10	Field	1	Perennial	4	Y	5	Animal Feeds	3	28
Miscanthus (C4)	27	EU	3	Local	3	Medium	5	Field	1	Perennial	3	N	0	Energy	1	13
Oak wood	30	EU	2	Local	1	High	1	Forest	1	Perennial	2	N	0	Forestry	1	6
Olive Cake	14	Local/Global	2	Local/Global	3	Medium	10	Factory	5	Perennial	2	N	0	Animal [illegible]	3	23
Forestry Waste	35	EU	2	Global/Local	3	High	3	Forest	1	Perennial	2	N	0	Forestry	2	11
Rice straw(Rice husks)	31	Global/Local	2	Global	5	Medium	10	Field	1	Seasonal	2	N	0	Waste	4	22
Rubberwood	54	Global	2	Local	3	Low	15	Field	1	Perennial	2	Y	5	industry [illegible]	3	29
Saw dust (Preferably from any hardwood source)	43	EU	2	Local	3	Medium	7	Factory	5	Perennial	2	N	0	Waste	4	21
Grade A Waste Wood	33	EU	2	Local	3	Low	15	Factory	5	Perennial	3	Y	5	Waste	-20	11
Tomato waste+ dutch greenhouses	43	EU	2	Local	3	Medium	10	Field	4	Perennial	4	Possibly	5	Animal Feeds	4	30
Wheat straw	32	Global/Local	3	Global/Local	5	Low	10	Field	1	Seasonal	3	N	0	Animal Feeds	3	22
Willow - Short Rotation Coppice	5	EU	3	Local	1	High	1	Forest	1	Perennial	3	N	0	Energy	1	7

Figure 2.2: A part of the Feedstock Selection Matrix

The FSM is specifically designed to meet different scenario descriptions owing to the application of weighted biases for different portions of the FSM in accordance to application. For example, the presence of high inorganic ash in high quantities (>10%) is a deterrent for combustion based applications due to boiler slagging or fouling [122]. In the case of horticulture, this higher ash content actually helps with soil remediation due to higher concentrations of Potassium and Phosphorous within the biochar. Therefore, the weights had to adjusted accordingly for these two very different applications. Another example was to identify useful feedstocks for Asia-Pacific's (APAC) co-firing applications and district heating for EU countries. Again, the feedstocks that were globally in large volume was crucial for the APAC co-firing and the feedstocks that were locally available for a reasonable cost was critical for EU District heating.

This FSM can be tailored to simulate any real world application pertaining to the use of biochar for any number of feedstocks. The current limitation of this matrix is the lack of costs associated with each process and this will be added to the matrix in the future. This will help us give an indication of the feedstocks's sourcing and pretreatement cost v/s its performance.

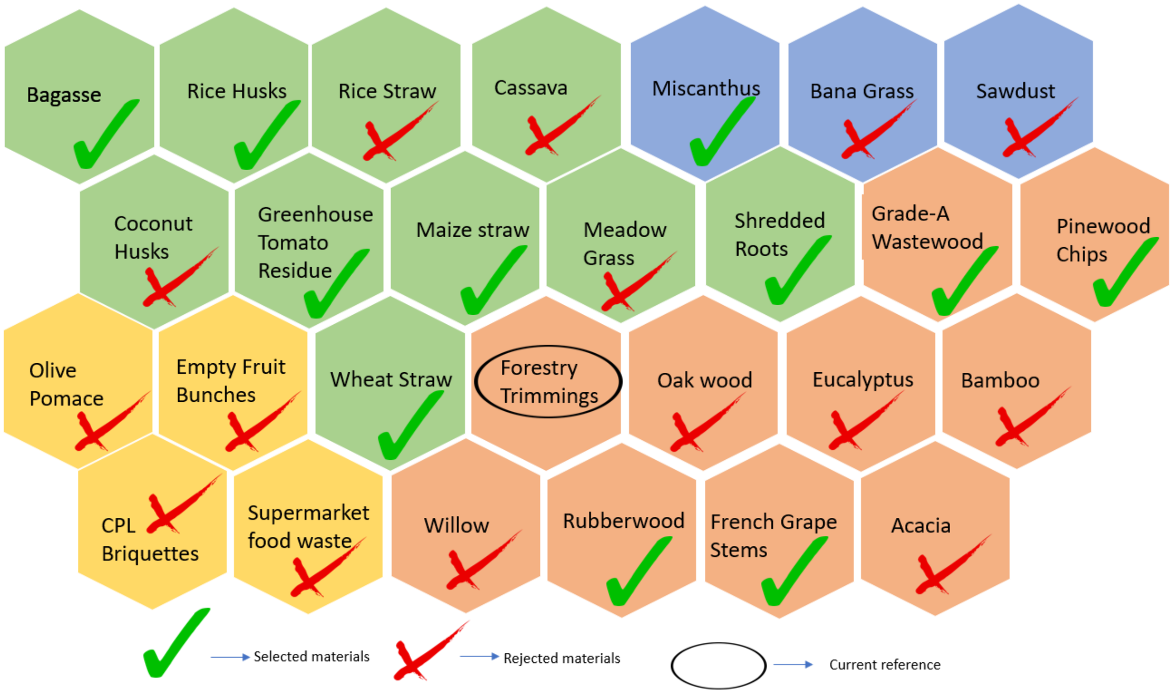


Figure 2.3: Feedstocks selected for further investigation

Through the FSM data, the list of feasible top feedstocks was populated as shown in figure 2.3. The top nine feedstocks were selected for further experimentation and to ensure that the claims made were validated. The selected feedstocks include (Bagasse , Miscanthus ,Wheat Straw, Grade-A Waste wood , Tomato residue ,Grape Stems and Rice Husks .) The virgin forestry wood chips currently in use is taken as a commercial hardwood reference in order to compare its efficacy against the feedstock from other sources.

2.2 Properties for biochar

Biochar for horticultural applications requires a specific set of physical and chemical properties for its commercial viability. A few properties such as Carbon content, H/C ratios and Pore structure are some of the most important properties for soil remediation. Most of these properties depend upon the type of biomass used and the torrefaction temperature and can be tailored according to our needs by carefully controlling them.These properties along with their units are represented in table 2.1 is further discussed in the following subsections.

Physical Property	Units	Observed Values from Literature
Particle Size	mm	Fine<1mm Chips: (1mm-10mm) Pellets (10mm- 25mm)
Bulk Density	kg/m^3	Herbaceous (50-150) Woody (200-300)
Surface Area	m2/g	Herbaceous (380-400) Woody (305-335)
Porosity	%	Grassy (75-85) Herbaceous (55-65)
Pore Size Distribution	%	Micropores (Majority) (12.0–58.0) Mesopores (18.9-31.7) Macropores (Minority) (5-10)

Table 2.1: Observed values for a few physical properties[68]

2.2.1 Physical properties

The physical properties of biochar include all the visually indicative parameters for the material. These properties determine the efficacy of the biochars use within the soil as well as its interaction with the roots, minerals and other microorganisms over time. These properties listed below will then be further tested to ensure that the biochars interaction with the soil will be positive.

Particle size

The biochar particle size can range from fine powder to large coarse chips. The biochar is filtered multiple times through a series of meshes in order to obtain the end product in the required size range. Commercially the mesh sizes in millimeters give an indicative size range for the biochar.To a large extent, the particle size of the initial biomass and that of the torrified biochar is similar except for a small percentage(1-2%) of extremely small particles that could have disintegrated from the parent biomass due to continuous vibrations at elevated temperatures inside the torrefaction reactor. Though the EBC does not specify any ranges for particle sized, the IBI indicates the following size distribution: Fine powder biochar (<0.5 mm), medium grained biochar (0.5mm-1.00 mm) and coarse grained biochar(>1.00 mm).

There are benefits and limitations for each of these size distributions and a careful analysis of the end application is crucial in determining the exact particle size of the biochar. The particle size of fine powder biochar is comparable with the sand particles (0.05-0.65mm) within the soil and therefore helps in uniform mixing and more effective interaction with the soil particles[71]. However, this amount of size reduction requires multiple cycles of milling post torrefaction and therefore increases the production costs during operation. Also, the biochar powder in this size range is extremely prone to losses during transport and application through wind/soil based erosion owing to its low density. The Medium and Coarse particles are relatively safe to these losses, but careful application within the soil is advised to ensure that there is uniformity in biochar-soil mixture. Although it seems that the finer the biochar the better the remediation properties, this is not the case as researched by Wenxi Liao et al[70] In this research, biomass feedstocks with a wide range of particle size distribution are studied.

Bulk Density

The bulk density of a material is defined as the total weight of a material confined in a given volume. Naturally, the particle size and the level of compaction is closely tied with the bulk density of the biochar. Higher values for bulk density indicate that more material is available within the same given physical space and therefore is crucial to obtain low values for transportation and fuel costs. The bulk density is higher for pelletized or fine powdered biochar and is the lower for coarse chips or irregular pellets.
At higher torrefaction temperatures, the volatile matter is removed from the biomass and a porous biochar that has usually lost more mass as compared to its loss in volume is obtained in the end.A few herbaceous feedstock materials which have a low inherent bulk density might require pelletization after torrefaction.The bulk density is an important factor for shipping and processing steps as these processes usually are factored

in on a volume basis. The bulk density of the material is the highest post the washing step owing to the extra weight of water and is subsequently reduced in the drying step. In this research, the bulk densities are calculated using a volumetric measuring flask and will be compared with pelletized forestry residue biochar. Owing to the pelletized nature of forestry residue, we expect it to have considerably higher value for bulk density in comparison with the other feedstocks.

Surface area

Biochar and other forms of activated carbon are known for its large surface areas. These large surface areas allow for maximum interaction with the nearby particles and therefore is an excellent tool for removal of undesirable chemicals and trace elements[65]. Biochar can also be used for the removal of heavy metals such as Cadmium, Arsenic and Lead [124] [54] [14] with a good degree of success. Similar to the bulk density, the surface area of the biomass is also increased through torrefaction of the material. The other parameters including residence time can be increased to further increase the surface area of the material to a certain degree[115]. The surface area of the material is one of the key parameter for numerous biochar applications as it has an influence on other parameters such as the Water Holding Capacity (WHC) and the ability of the biochar to interact and exchange minerals with the surroundings.

The surface area of the biochar is measured using a BET analysis (BET stands for Brunauer, Emmet, and Teller, the inventors for this measurement). In this method, a gas (usually Nitrogen) is allowed to be incident on the surface of the material and the amount of gas that is absorbed helps determine the surface area. However, the BET measurements can only detect pores within the pore sizes of 5 nm and 100 nm as represented in figure [26]. Therefore, the smaller micropores and macropores bigger than 100nm cannot be detected by this setup. The results from the BET analysis are discussed later on in the report.

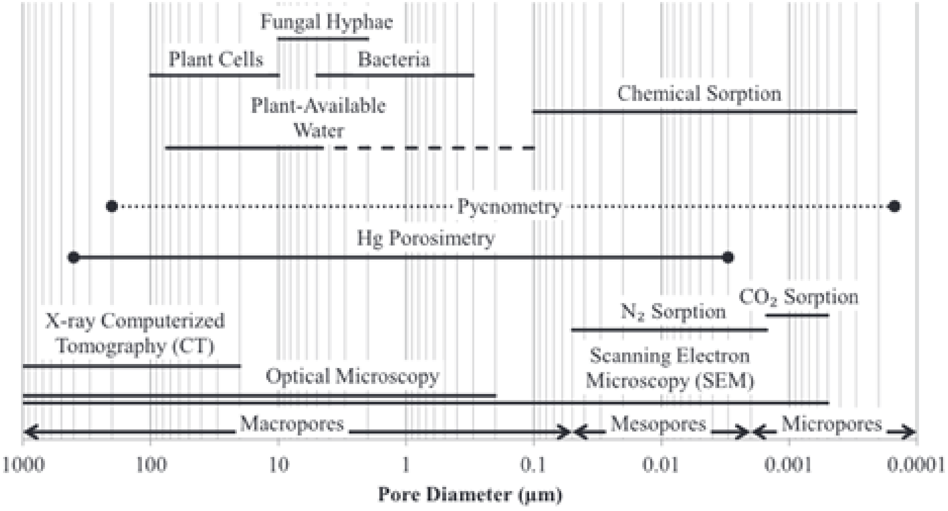


Figure 2.4: Pore size detection and measurement techniques and their ranges of operation[26] .

Porosity

Biochar is loosely defined as a highly enriched stable form of Carbon with an extensive network of pores within its microstructure. The presence of pores within biochar is attributed to the torrefaction process wherein the loss of volatiles within the parent biomass induces pores within the honeycomb structure of the biochar[95]. These pores are of critical importance with respect to other mechanisms of the biochar such as absorption and slow release of nutrients amongst others. The pores of the biochar also acts a tiny houses for microorganisms where they can fix nutrients and thrive[51].

The pores within biochar are spread over five different orders of magnitude from a few nanometer to pores with diameters that spread across tens of micrometers and are classified as Micropores, Mesopores and Macropores accordingly [24]. These pores sizes and their corresponding methods used for the pore size measurements are shown in 2.4 Micropores are pores having an internal diameter that is less than 2 nanometer. Mesopores are pores having internal width in between 2 and 50 nanometer, while macropores are pores where the internal width is greater than 50 nm [99]. Micropores and Mesopores contribute most to the surface area of biochars, with micropores mostly being responsible responsible for water uptake and other large gas uptakes. Mesopores having a much larger pore diameter is more suitable for slightly larger molecules including harmful colloidal silicates which can be effectively absorbed by the mesopores[83]. Macropores also allow for water and mineral transport within the soil and roots of the plant. These pores could also provide housing growth promoting microorganisms such as Rhizobacteria [92]. The split up for the pore sizes and their corresponding functions are shown in figure 2.5

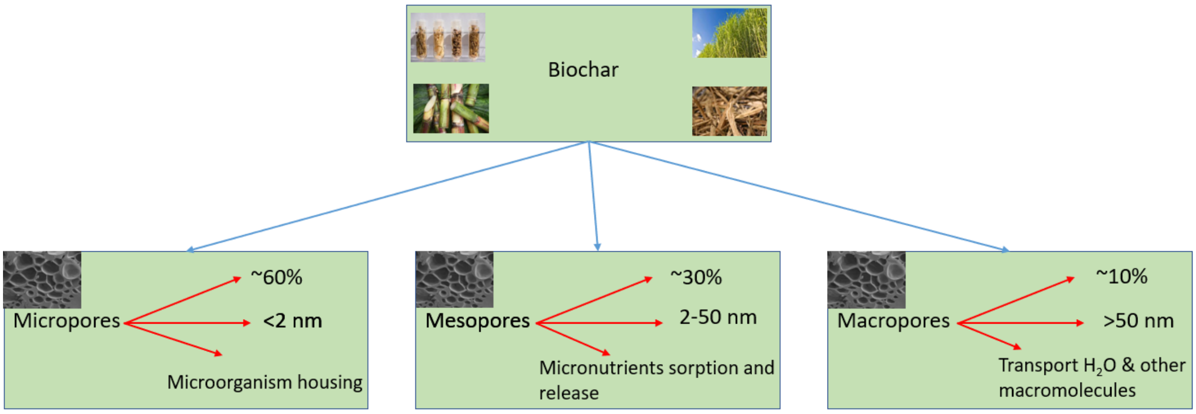


Figure 2.5: Pore size distribution in biochar and its functions.

Biochar from herbaceous biomass has a higher porosity compared to biochar from woody feedstocks[8]. This is due to the higher hemicellulose content in herbaceous biomass and the thermal degradation of hemicellulose within the torrefaction reactor gives rise to the pores within the biochar. Unlike surface area and the bulk density, porosity's dependence on temperature is not linear. Hemicellulose which is the first material to decompose within the biomass has a tendency to start degradation at 200 °C and fully devolatize at 350 °C. Therefore the maximum obtainable porosity happens in low temperature zones for pyrolysis at 350 °C and no considerable increase in porosity is noticed by increasing the temperature further[88].

The porosity for woody biomass is around 55% and increases to about 75% during high temperature pyrolysis (700 °C). Meanwhile, for herbaceous feedstock the initial porosity itself is high (80%) and it can go up to 85% post torrefaction. In High temperature torrefaction(300 °C), the porosity noticed is roughly around 60-65% and an increase in temperature is required to increase the porosity further. Higher ash content in the biomass causes low values for surface area and porosity [117]. The porosity within the biochar can be measured using Nitrogen gas adsorption or Mercury intrusion porosimetry though the latter is more accurate than the former as NGA can only detect micropores and mesopores but not macropores.

Water Holding capacity

The presence of the macro pores within the biochar helps with the trap and release of water molecules in the soil. The WHC is an essential element within the biochar which enables transport of water from the soil to the root of the plant. Typically to measure the WHC, a biochar sample is taken and immersed in water for 24 hours. Then, the biomass is weighed and then let to dry at 105 °C for 24 hours and weighed again. The difference in weight for the biochar indicates its water holding capacity. The particle size also has a big impact on the WHC with the ideal particle size being 2-4 mm for maximum WHC[50]. In this research, the WHC is not calculated but the values from literature are taken as an indicative reference.

Hydrophobicity

Hydrophobicity is the tendency of a material to repel moisture. The higher the hydrophobicity, the less is the material's affinity for moisture. Biochar is renowned for its ability to have high degrees of hydrophobicity. This in turn helps reduce transportation costs (Higher moisture content increases the weight of the material and thereby the fuel costs). The increased hydrophobicity also indicates that the material will inherently have a lower moisture content which increases its attractiveness in coal replacement co-firing applications.

Ironically, the increased hydrophobicity indicates that the WHC will be low and the hydrophobicity can be reduced by increasing the pyrolysis temperature to greater than 700 °C. This is due to the conversion of the aromatic HC to aliphatic HC at the increased temperature. This parameter is purely meant as a qualitative tool in this research and therefore will not be discussed further,

Grindability

Apart from substantially improving Calorific Value and hydrophobicity, another key parameter which benefits through torrefaction upgrading is the ability of the biochar particles to be milled according to requirements. This parameter also called "grindability" ensures that the bulky biochar produced is cut down in size to ensure uniformity of particles, lower transportation costs as well as increase the volumetric energy density by more than 200% [117]. This increase in other properties with an increase in grindability is taken as an indicative reference and will not be tested for within the scope of this research.

2.2.2 Chemical properties

The chemical properties of the biomass and biochar include all the constituent elements that make up the biomass as well as the effect of these elements on the various measurable properties for the biochar. These properties are important for soil applications as a majority of the chemical elements will be absorbed within the roots of the plant and ultimately in the food produced. Therefore, a careful inspection of the feedstock and the end product needs to be undertaken and the biochar produced must be within the toxic limits prescribed by the EBC. Many of the chemical properties are closely tied with the operating temperature and residence time and these parameters need to be closely monitored to obtain a product that matches the required specifications.

Proximate Analysis

The proximate analysis deals with the following measurements: Moisture percentage, Ash , Volatile Matter and Fixed Carbon content. This analysis is vital to estimate the combustion characteristics for the biochar produced. Normally, lignocellulosic feedstocks exhibit a higher percentage for moisture and ash with a lower fixed Carbon content.

Ultimate Analysis

The ultimate analysis of the sample is performed to get a better understanding of the elemental composition of the biomass and biochar. The elemental compostion differs depending on the biomass source and has a profound effect on the HHV of the biochar produced [30]. The commonly analysed elements as a part of the ultimate analysis include Carbon, Hydrogen, Nitrogen and Sulphur (also called the CHNS analysis). Oxygen and Sulphur can be measured too if they are present in measurable quantities.

H/C ratio

The H/C ratio is one of the most important parameters indicative of the biochar's stability within the soil. Biomass with its weak intrinsic aliphatic bonding has low levels of stability and can be easily decomposed into its constituent elements over time. However, when this biomass is upgraded through torrefaction, these aliphatic bonds reform to become cyclic aromatic bonds within a honeycomb framework of the biochar. This structure which is enriched in Carbon now exhibits high stability and requires a higher energy to break the bonds that hold the biochar together[116]. However, results surrounding poultry litter and woody biochar showed that they have similar H/C ratios despite woody biochar exhibiting much higher stability than poultry litter. This observation along with a few other anomalies indicated that H/C ratios are not the best fit to determine the overall stability of the biochar[44].

The H/C ratio is the fraction of elemental Hydrogen to that of elemental organic Carbon content(Corg). Traditionally, the fraction of inorganic Carbon content is calculated from the ash residue of the biochar and this is subtracted from total Carbon to give organic Carbon content Corg. However, in low ash biochar (<3%) this inorganic Carbon content can be deemed negligible and the whole Carbon can be considered to be organic Carbon [34].

O/C ratio

Similar to the H/C ratio, the percentage of Oxygen to that of Carbon is significant for the biochar's stability within the soil. As a thumb rule, an increase in the degree of torrefaction increases the percentage of Carbon available in the overall material. This in turn indicates that the material is more strong and stable. According to Spokas et al. biochar having O/C ratio < 0.2 indicates that the biochar will be stable within the soil for more than 1000 years and with values in between 0.2 and 0.4 indicating its stability for 100-1000 years[101]. Thus, the O/C ratio is a better tool for understanding and predicting the stability of the biochar within the soil. The H/C versus O/C is plotted for a few common feedstocks in figure 2.6

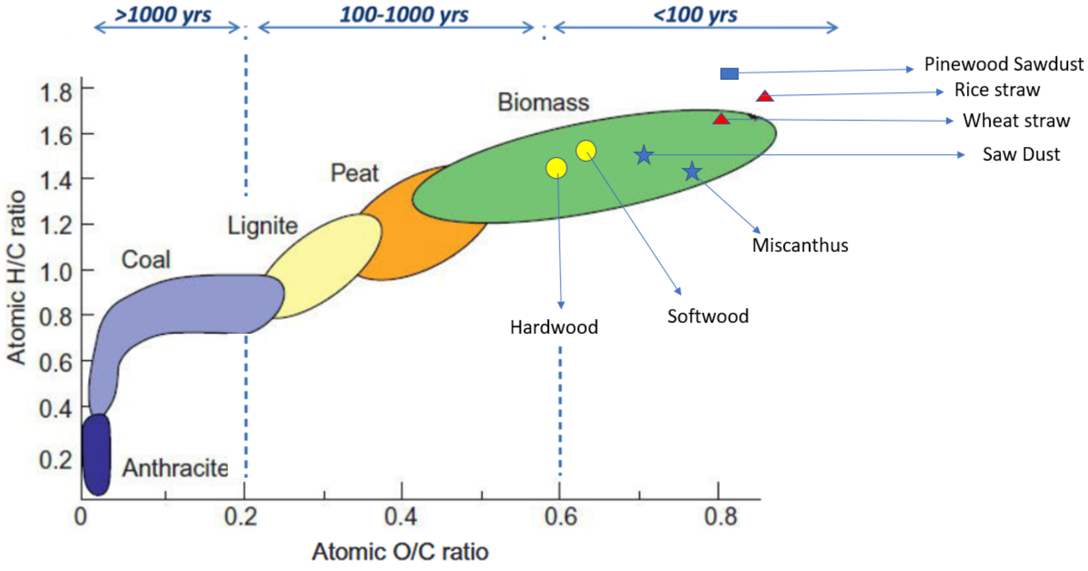


Figure 2.6: Van Krevelen diagram, inspired from Basu [5][18][27][73]

pH

One of the main issues with horticulture and agriculture is the fertility of the soil. Fields located close to industries or mining areas are prone to acidic leaching. Incessant use of chemical fertilizers can also lead to acidic soil which retards plant growth. When the pH of the soil drops below 5.5, the soil is deemed acidic and thus needs remediation. Biochar, when used to remedy acidic soil has a tendency to absorb the potentially toxic elements (PTEs) owing to its porous structure. Thus, biochar with pH above 9 can be mixed with the soil to increase the overall pH and counter the acidic characteristics through effective contaminant absorption[120].

Calorific Value

The Calorific value is representative of the energy content of the biochar. As expected, it increases with increase in the degree of torrefaction linearly with the increase of Carbon content. The calorific value is defined over two ranges namely the LHV, HHV (or) GCV depending on the water content within the biochar. The LHV is measured on a dry ash free basis for the feedstocks and is commercially preferred over HHV. The HHV and LHV are of higher importance for combustion applications over horticulture and agriculture. However, the EBC mentions that these values are a required parameter for biochar certification and therefore will be tested for.

Heavy metal concentration

In many studies biochar has been used as an effective absorbing tool against heavy metals such as Cd,As,Cr,Pb with varying degrees of success. Zhou et al and Suppadit et al managed to reduce Cadmium concentration through cotton stalk and quail litter biochar application respectively [123][105]. Other studies succeeded in removal of Chromium, Lead and Nickel over a period of time [14][45][85]. The presence of microscopic pores and a large surface area facilitates easy adsorption and prevents these heavy metals from leaching into the soil and ultimately into the food.

Macro and micro nutrients concentration

Nutrients are essential for plant growth and fertilizers in essence contain them in substantial quantities.Most compound fertilizers will contain three elements essential for growth, NPK which stands for Nitrogen (N) Phosphorus (P) and Potassium (K). Though Nitrogen, Phosphorus and Potassium, are the “Big 3” primary nutrients in commercial fertilizers, Sulphur (S) is also a major element that gets added in virtue of adding the NPK nutrients. These elements are called as the macronutrients and are required in small quantities for healthy plants over their lifetime. These elements help boost the various elements associated with plant growth as listed.

1.Nitrogen (N): Promotes leaf growth in early germination stage and also ensures that the plant does not wilt soon.
2.Phosphorus (P): Is highly important for the development of roots, flowers, seeds, fruits and is one of the most important minerals to sustain the plant’s health.
3.Potassium (K): Ensures strong stem growth, movement of water in plants, promotion of flowering and fruiting during initial germination as well as every subsequent harvest cycle.

These macronutrients though inherently present within the organic biochar, are available in insignificant quantities. Therefore additional calculated amounts of these macronutrients are blended along with the biochar to enhance the effects of these macronutrients.
Through elemental analysis, we find that there are a few other elements that are present in minuscule trace quantities. These elements such as iron (Fe), boron (B), chlorine (Cl), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni) are called micronutrients. Though the quantities of these elements extremely small in comparison to the macronutrients, they also important for the overall plant development. Trees and plants are able to adequately store these micronutrients and therefore no further addition of these elements are required by the biochar.

PAH and BTEX

During torrefaction a number of Polycyclic Aromatic Hydrocarbons(PAH) accumulate within the biochar. These PAH are highly toxic with many of them proven to be carcinogens. It is therefore imperative that these compounds be removed or within the limits specified by the EBC. All of these PAH compounds are however present in small traces(mg/kg) and are difficult to ascertain their degree of toxicity. Therefore the total of 16 fixed PAH are grouped into one unit for ease of understanding. The regulations set by EBC recommends that this sum total of the 16 PAH compounds be strictly lower than or equal to 12 mg/kg [119]. The compounds excluded in this list of 16 PAH include Benzene,Toluene, Ethyl Benzene and Xylene. These four compounds are extremely carcinogenic and therefore are classified separately called BTEX. These compounds are present in even smaller concentrations(μg/kg) and though there is no specific threshold for the BTEX limits, these values have to be indicated on the packaging of the biochar as per EBC norms [119].

2.3 Pretreatment techniques for biomass

The variability of feedstocks and the global nature of sourcing leads to a degree of non-homogeneity for torrefaction. The process of torrefaction is highly sensitive to these changes and it is essential that these parameters be controlled in order for the reactor to work optimally to get a uniform product output. Impurities or undesirables within the feedstock, non-uniform particle size and extremely low feedstock density are a few parameters that need to be rectified prior to the torrefaction step. A few common pretreatment techniques include Washing, drying, chipping, densification through pelletization. These techniques are discussed in brief below.

2.3.1 Washing

This pretreatment step is one the most rudimentary steps in biomass upgradation. Typically, all biomass except for those sourced from evergreen rainforests needs to be washed. This is due to external contaminants such as fertilizers, leachates or toxic uptake from the soil for other lignocellulosic feedstocks. Feedstocks such as Rice husks and Miscanthus contain a high ash and Chlorine percentage. This is an undesirable parameter within the torrefaction chamber and needs to be removed prior to torrefaction. Surprisingly, both these feedstocks react extremely well to simple washing reducing the ash content by up to 30% [36]. This technique is simple and effective for a wide range of feedstocks suffering from high ash content or external contamination, but requires large quantities of water over many cycles of washing. An alternative for simple water washing is Chemical cycling which uses highly reactive chemicals which displace the contaminants. This method requires lower chemical and water content but introduces new contaminants within the biomass [96].

2.3.2 Drying

Drying is usually the subsequent step after washing. Moisture present within the feedstock needs to be removed prior to its entry into the reactor. This removal of moisture is key in reducing the weight and size of the feedstock. This in turn leads to lower handling and storage costs [113]. This drying is done in two steps. The first step is called the pre-drying step and in this step the wet feedstock is initially taken to a temperature of 70 °C. This step removes all the superficial moisture through air drying. The next step is called the bone-drying step and in this step the air dried feedstock is elevated to a temperature of 140 °C. This is the last drying step and effectively removes all the water from within the feedstock[20]. Some feedstocks such as bagasse and food waste come with a high initial moisture content greater than 25%. Therefore a preliminary drying step is required even if the feedstock is completely clean.

2.3.3 Chipping

In the previous section we found out that the output biochar particle size is closely tied with the input biomass's particle size. Though there is a small size reduction owing to the devolatilization process, the input and output sizes are comparable. Chipping is a pre-processing step that is used to reduce the particle size of larger blocks of feedstock. In chipping, the particle size is considerably reduced by breaking them into smaller chips according to the required feedstock size. There is an optional milling step that follows chipping or as a standalone technique which is used to further reduce the particle size to the chips to get a fine powder. While chipping reduces the size of the particles to between 5 mm and 100 mm [84], milling can further bring down the particle size to 0.15-2.00 mm [94].

2.3.4 Screening

Screening is a pretreatment process (also used for post processing) which uses a series of sieves with reducing mesh size to filter out the biomass particles post milling. The feedstock materials that exit the sieve are sent to the reactor while the ones that are bigger than the mesh are sent back to the mill.

2.3.5 Densification

Feedstocks that are sourced from energy grasses or agricultural residues have considerably lower bulk densities compared to their woody counterparts. These feedstocks are unfit for torrefaction in their original form as most of the char produced from low density straws tend to become fine dust and float away with the flue gas. Therefore such low density feedstocks need to be densified. The process of densification is achieved by converting these feedstocks into their pellet form. This is achieved by using a binder and applying pressure and the process is called pelletization. Some lignocellulosic materials such as wheat straw and bagasse inherently have a high amount of natural binder called lignin. Therefore a very small percentage(<2%) of binder (or even water) is enough to fuse the particles together to pelletize it. But, other woody and grassy feedstocks require binders such as starch or lignin to help pelletize the raw material prior to torrefaction [103].

2.4 Biomass conversion technologies

There are numerous techniques that are used to convert the given biomass into a solid, liquid or a gaseous material depending on the final application. These techniques are referred to as thermochemical conversion or upgrading techniques as these processes usually results in the improvement of one or more physical and chemical properties. There are four important pathways to attain upgrading of biomass and these are discussed briefly in this section.

2.4.1 Combustion

The term combustion refers to chemical conversion of fuel in the presence of stoichiometric or excess Oxygen. The combustion of biomass at elevated temperatures (400-1200 °C) results in hot gases which can provide heat for steam generation at high pressure to spin the turbines in substations to generate electricity or direct heat. A simple depiction of a combustion process for biomass is shown in figure 2.7

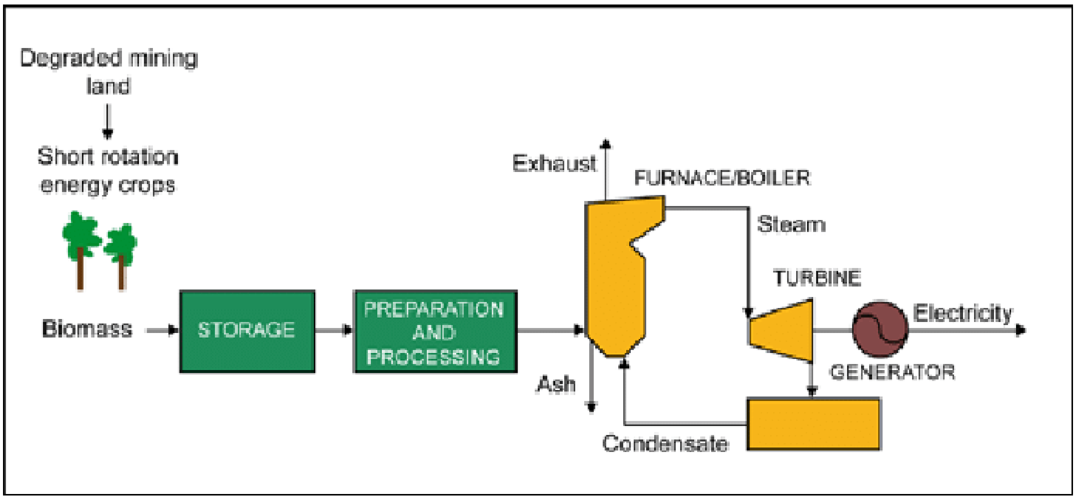


Figure 2.7: A simple combustion setup[108]

2.4.2 Gasification

Similar to combustion, gasification also chemically converts biomass to a product has at high temperatures (>700 degrees C). In substoichiometric conditions the producer gas consists of (CO+H2) along with a mixture of other gases. This technique requires that the biomass interacts with a "gasification agent" which is usually Oxygen (pure or in air) or steam which is circulated within the system in a controlled manner. These gasification agents enter the system at a high temperature and the interaction with biomass particles causes it to release a mixture of gases including nitrogen, carbon dioxide, carbon monoxide and hydrogen. The producer gas can be used directly as fuel for combustion or used in the production of synthetic fuels through the Fischer-Tropsch synthesis.A schematic diagram for the gasification setup is shown in 2.8

2.4.3 Liquefaction

In this conversion process, the biomass is converted into useful bio-oils and biochar. Though a small fraction of the output is biochar, the target product is bio-oil which is further utilized for combustion applications as well as in the preparation of a wide variety of cosmetic products. In this process, the biomass feedstock is made to interact with water in the presence of a water soluble inorganic compound such as sodium bicarbonate or potassium hydroxide. The key difference between the liquefaction process from the other conversion techniques is the lower temperature used (<500 °C) and Higher pressure applied within the reaction chamber (5-25 MPa). Since this technique involves mixing the feedstock with water during the process, feedstocks with a high initial moisture percentage are more suitable for liquefaction.

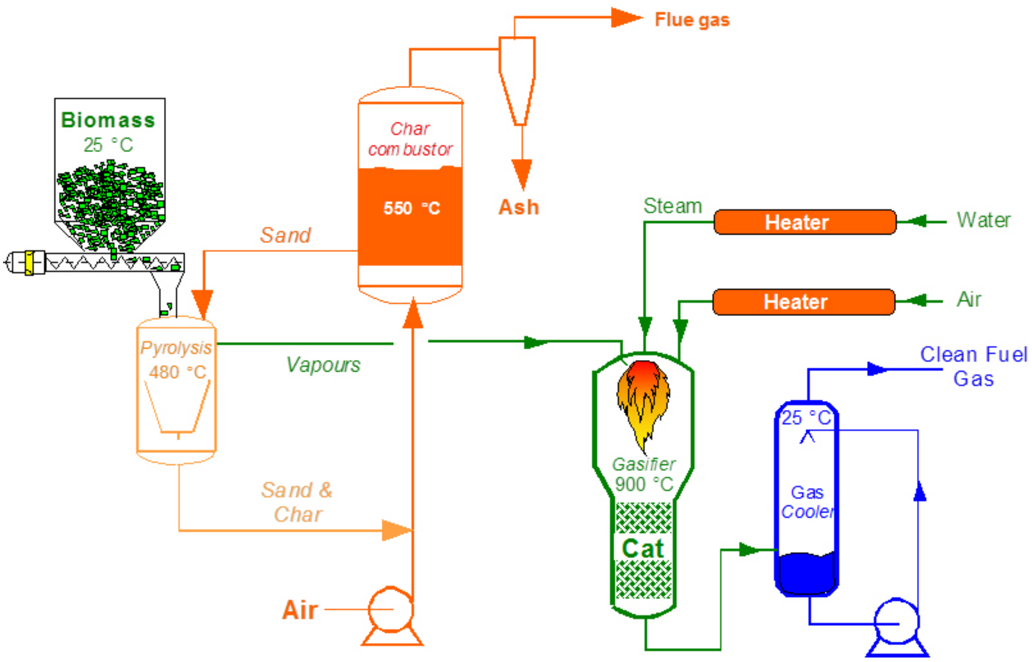


Figure 2.8: Gasification[71]

2.4.4 Pyrolysis

While both combustion and pyrolysis concern chemical conversion of a feedstock, the former occurs in an environment with excess oxygen while the latter occurs in a oxygen deficient environment[48]. Pyrolysis is one of the most common conversion techniques for biomass with pyrolysis usually being a side process within other main fuel conversion techniques. Pyrolysis falls under two categories namely fast and slow pyrolysis. In Fast pyrolysis, there is an increased heating rate(10-10000°C/min) and lower residence time of just a few seconds. Slow pyrolysis on the other hand utilizes slower heating rates(0.1-10°C/min) and a much longer residence time ranging from a few minutes to even hours. While slow pyrolysis results in the production of biochar, the fast pyrolysis mainly yields bio-oil[109]. temperature range for pyrolysis ranges from 250 to 1300 °C. Pyrolysis results in a mixture of components from solid Char to condensable liquids and volatile gases. Low temperature pyrolysis occurs at temperatures between 250 and 350 °C and is called torrefaction. This process is elaborated further since it is a key process for biochar production. A slow pyrolysis setup is depicted in figure2.9

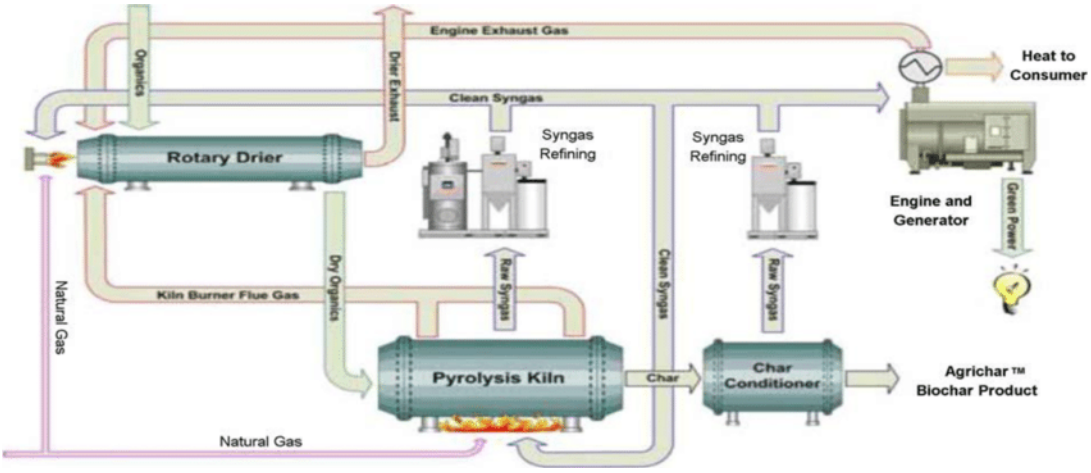


Figure 2.9: A slow pyrolysis setup[16]

2.4.5 Torrefaction

Torrefaction is a most decisive step biomass upgrading. It is in this step that many properties such as energy content, stability, etc are improved. Torrefaction is a thermal upgrading process wherein the biomass material is made to undergo a structural transformation under the influence of heating in an inert atmosphere, mostly consisting of nitrogen. The key characteristic of torrefaction is the fact that the entire process takes place in an oxygen limited environment that is hermetically sealed through airlocks.

In the rest of this work we denote by torrefaction the low temperature pyrolysis in the temperature range 250-320 °C. The process chemically consists of many smaller steps involving the sequential breakdown of the hemicellulose, cellulose and lignin in separate regimes, driving a devolatilization process (gas release). These regimes and the characteristic temperatures where the devolatilization peaks can be observed, are different for different biomass materials. Torrefaction in a wider sense can also denote a set of five separate process as shown in figure 2.10 namely the Initial heating, pre-drying, post-drying and intermediate heating, torrefaction and solids cooling.

1. Initial Heating-This is the beginning of the torrefaction process. The temperature is gradually increased from room temperature and the maximum temperature attained in this stage is 90 °C. This initial heating of the biomass sample causes the biomass humidity to evaporate and the material gets closer to its drying temperature.
2. Pre-Drying- At exactly 100 °C, the free water or moisture present in the biomass starts to evaporate. This region is marked by a constant temperature and is accompanied by minor mass loss.
3. Post drying and Intermediate heating- The torrefaction temperature is gradually increased from 100 to 200 °C. This increase in temperature causes the remaining chemically bound water molecules to evaporate along with other volatile matter. This region is marked by an increased mass loss as the material starts to lose its volatiles through initial torrefaction.
4. Torrefaction- The torrefaction step follows the intermediate heating step as the temperature continues to rise and then most of ten is kept at a high constant value for some time. The term "torrefaction temperature" refers to this value. The torrefaction phase is characterised by high mass loss. The amount of volatiles released within the torrefaction chamber depends on heating rate and residence time.
5. Solids Cooling- The feedstock material has completed torrefaction in the previous stage and has the right composition for commercial use. However, the material needs to be sufficiently cooled first to remove the possibility of auto ignition of the material. Commercially, woody materials are cooled to below 200 °C to prevent auto ignition while herbaceous feedstocks can tolerate slightly higher temperatures. This step marks the end of the torrefaction process and the upgraded biomass is ready for any suitable application.

The schematic for the torrefaction process is listed in figure 2.11 and usually the process is a continuous one starting from raw biomass and ending with torrified biochar. Each of these processes are explained briefly to give an overview of the torrefaction setup. Finally, the parameters that govern torrefaction are described along with process specific parameters and tolerances.

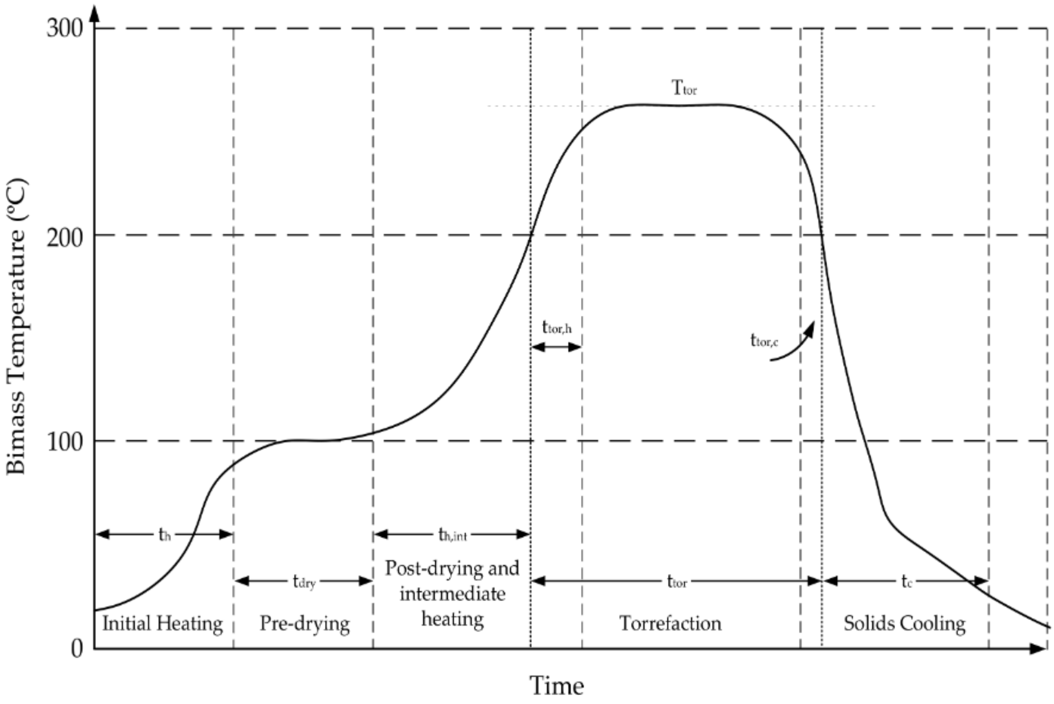


Figure 2.10: The different torrefaction stages[23]

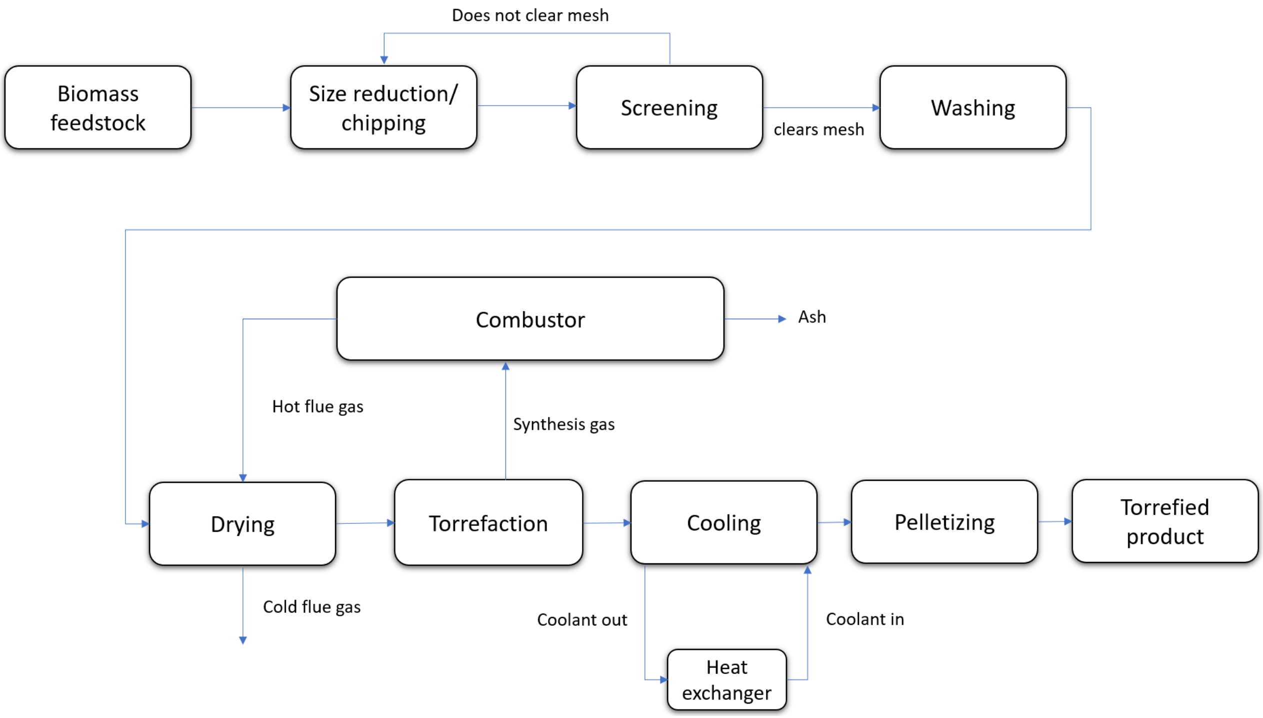


Figure 2.11: Schematic diagram showing the different torrefaction stages

2.4.6 Why Torrefaction?

Torrefaction is considered to be one of the most energy efficient pathways to improve existing properties or to filter out unwanted ones. The schematic shown in 2.12 is compiled by Jorge et al. [61] and highlights the most important changes to a material post torrefaction.

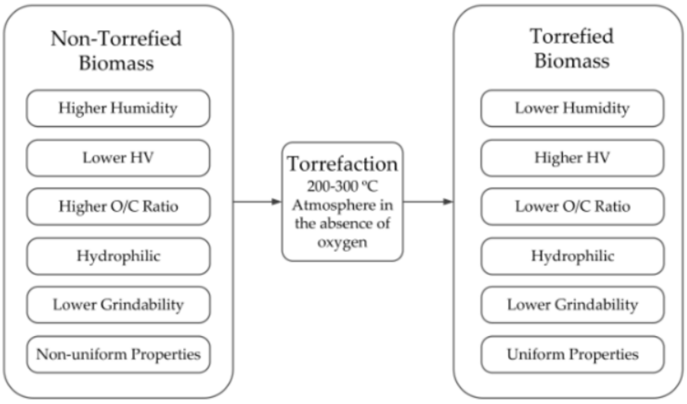


Figure 2.12: Biomass characteristics before and after torrefaction

2.4.7 Torrefaction product distribution

Once the feedstocks undergo the required amounts of preprocessing required, they are ready to enter the torrefaction reactor. Though the major yield material is the solid biochar (80%), there are still smaller fractions of condensable liquids(15%) and non-condensable gases(5%). The torrefaction product distribution and the exact compounds that are to be expected in each phase is shown in figure 3.1 .

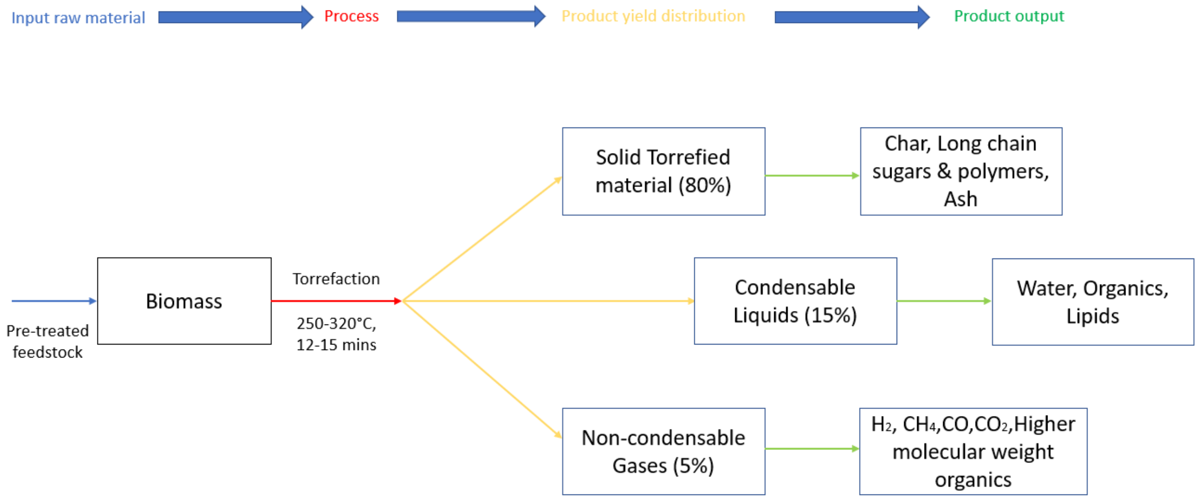


Figure 2.13: The products and yields from torrefaction

2.5 Torrefaction Reactors

The thermochemical conversion process from biomass to biochar through torrefaction can be realised using different reactors. Each torrefaction reactors has a distinct spatial setup and thermal operation regimes and this results in the biochars having varying properties. These properties include Mass and energy yields, split up of product yield distribution and particle sizes for the biochar produced. Though the torrefaction of the feedstocks were realized through the a fixed bench reactor with operating parameters based on the HTT4 , the other types of reactors are also explained in brief.

2.5.1 Fixed and Moving bed torrefaction reactor

The simplest kind of reactors are the fixed and the moving bed torrefaction reactor. The raw material is loaded onto a conveyor belt and heat is provided on either sides of the reactor bed through conduction. The fixed bed allows for intermittent operation while the moving bed reactor allows for continuous operation after a fixed residence time has been achieved. Both of these reactors operate on a counter-current flow.The advantage of this reactor is that it allows for a high degree of raw material filling within the reactor bed though this reactor suffers from high degrees of inhomogeneity with respect to heat transfer mechanisms.

2.5.2 Fluidized Bed Reactor

In the Fluidized bed reactor, the raw material is made to lie on a porous bed. Hot gases flow through these holes into the material with high gas velocities. The presence of these pores along with the fast moving gas particles enable the raw solid biomass particles to behave as a fluid. The material with a sufficient residence time and high gas temperatures will eventually torrefy and will get converted into biochar. This type of a reactor uses a dispersed multi-phase flow. The shortcoming of non-uniform heat transfer in the fixed/moving bed reactor is completely removed in the fluidized bed but the setup is more expensive and the a higher percentage of fine material gets lost in the process.

2.5.3 Microwave Reactor

This reactor utilizes high energy pulses in the form of microwaves. These microwaves are made to move across the cross section of the reactor. Other biomass conversion mechanisms used in fixed, moving or fluidized beds aim to achieve successful torrefaction through conduction or convection of heat over a period of time. In these mechanisms the heat first hits the outer walls of the reactors and which then subsequently moves inward towards the material. This however leads to a lot of thermal losses which can be overcome by using the microwave reactor. Owing to direct heating of the material inside the chamber, this technique has the highest degree of torrefaction homogeneity and a rapid heating rate. However, this technique is capital and energy intensive.

2.5.4 Rotary Drum Reactor

A much more commonly used more primitive technology is the rotary drum reactor. This reactor as the name suggests, contains a large cylindrical drums which rotates during its course of operation. The feedstock material is loaded into the stationary inner cylinder, while the outer ring is heated and made to rotate according to requirements. This process can be automated to make the operation continuous over a wide range of temperatures and long residence times for counter-current operations. Though this method leads to a greater degree of product control, the lower degree of filling and limitations arising from heat transfer limits often warrants the need for alternative reactors with higher heat transfer capabilities.

2.5.5 Screw reactor

The screw reactor consists of a long screw within the reaction chamber which helps move the material along the length of the reactor. This type of reactor makes use of hot sand like material to act as heat carriers or make use of heated screws itself to attain a suitable torrefaction temperature. This reactor similar to the rotary drum reactor suffers from heat transfer limitations and poor filling of raw materials within the reactor setup. These limitations however still do not limit the usage of screw reactors as it is still one of the most cost effective and proven torrefaction technology.[69]

2.5.6 The HTT4 Torrefaction reactor

Although there are plenty of torrefaction options available, this project was developed keeping the High Temperature Torrefaction 4 (HTT4) technology of CEG in mind. The sectional view of the torrefaction reactor is shown in figure 2.14. (1) is material infeed through which biomass is continously fed in to the reactor. Continuous operations on a large scale reactor can have an input feedrate of 20 tph while intermittent operations have a reduced loading/injection rate. (2) are the two frequency controlled oscillatos which are connected to a servo motors which can increase or decrease the vibrating frequency. The torrefaction chamber is shown in (3). Meanwhile, the synthesis gas is transported to the oxidiser(5) and sent back to the reactor via the fluegas duct(4) and is sent to the oxidiser (5) for combustion.The synthesis gas fan(6) helps in drawing out this gas from the reaction chamber. The torrefaction reaction chamber is hermetically sealed to prevent any flow of atmospheric gas inside. The torrefied char material exits the reactor as shown in (7) and (8) shows the cooling screws. The HTT4 consists of two separate heating zones, one located at the top and one located at the bottom of the reaction chamber. The infeed from the hopper falls on this vibrating bed which oscillates at a fixed frequency and consists of a top/bottom or top+bottom heated zones. The oscillation allows for the feed to jump up and down while the inclination provided ensures that the material traverses the length of the reactor. The torrefaction temperature is the measure of the core temperature the feedstocks experience within the torrefaction chamber. Though this temperature is around 250-300 °C, the top and bottom heated zones are at a much higher temperature which is evident from the flue gas temperature which is much higher than the biochar temperature. As the hemicellulose and cellulose start devolatizing, the char shrinks in size and hardens. The volatile gases escape out of the chamber through the channel provided to avoid any pressure build up within the chamber. This gas is termed as "flue gas" and still contains materials with good fuel properties such as CH4 and other combustible organic compounds. This flue gas is therefore sent to a combustion chamber and is used to provide the primary heat is sent to the torrefaction reactor and any remaining heat is sent to the external dryer thereby increasing the thermal efficiency of the overall process.

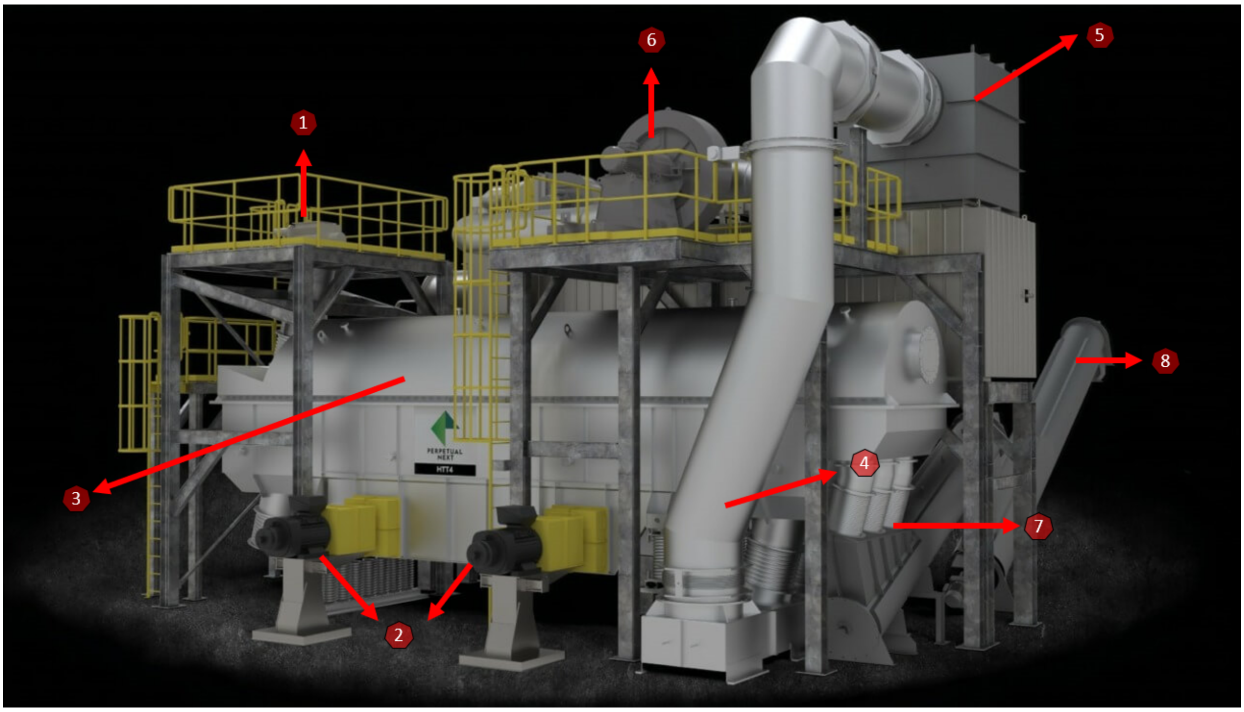


Figure 2.14: The HTT4 reactor from CEG

Once the material has gone through the length of the reactor it is sufficiently torrified and can be collected for further use. However, there is the issue of self heating of the biochar owing to the high degree of carbonization and high temperature at exit. To prevent the self ignition of biochar there is a conveyor that helps cool down the biochar to ambient or a sufficiently lower temperature. The biochar that exits this cooling belt reaches storage silos where the material is stored and is transported according to demand.

2.5.7 Torrefaction parameters

The torrefaction step is a multistep process with a number of critical parameters such as temperature, heating rate and residence time. Any changes to these parameters will result in a biochar with different physical and chemical properties. Therefore it is imperative that these parameters are first understood and then carefully studied to produce biochar of the required quality. These parameters are listed below. Although some of them have a considerably higher effect than other, it is important to know about the different parameters that govern the torrefaction process [29].

Temperature

Out of all the different torrefaction parameters, the temperature has the greatest effect with regard to product selection and specification. This is due to the temperature effect on the devolatilization of hemicellulose, cellulose and lignin. Increasing the temperature produces biochar with higher energy densities owing to a higher fraction of volatiles that get detached from the biomass surface [75]. However an increase in temperature leads to a decrease in mass and energy yields and thus a careful selection a torrefaction temperature is key. As we discussed before, the temperature inside a torrefaction reactor is higher at the top and bottom heating zones than at the conveyor. Thus, we will be normalizing the core temperature which is the actual temperature at the center of the torrefaction chamber, as the torrefaction temperature. This temperature for torrefaction is usually in the range 250-350 °C and studies have shown that the process tends to become exothermic above 280 °C owing to the exothermic breakdown of sugars within the biomass[32].

Residence time

The next crucial parameter after torrefaction temperature is residence time. The time that the material spends within the torrefaction chamber determines its energy content and degree of torrefaction [17]. Commercial reactors such as perpetual next's HTT4 reactor ensure a lower residence time(<15 min) for their torrefaction process to ensure higher throughput for the process. While longer residence time can ensure a higher energy density, similar to torrefaction temperature the mass and energy yield drops as the residence time increases. However this effect of lower mass loss is lost after a residence time of 1 hour owing to complete carbonization of the product [11].

Heating rate

The torrefaction chamber has a preset heating rate which ensures that the process requirements for heating and residence time are both factored in. Studies have shown that a small increase in the heating rate from 6 °C/hour to 10 °C/hour for bagasse torrified at 275 °C increases the mechanical durability of the pellet owing to a higher lignin percentage. Also a higher heating rate signifies that the biochar produced will be more hydrophobic [106].

Particle size

The effect of particle size is of moderate importance with regards to torrefaction. Primarily, the resulting particle size of the biochar depends on the provided particle size of the biomass at the start of the process. As discussed earlier, the grindability of the biochar improves with torrefaction therefore particle size reduction is preferably done after the torrefaction step as well[86]. Predominantly within the torrefaction chamber the process is controlled by two dimensionless numbers the Biot number(Bi) and the Pyrolysis(Py) number. Large particles have a large Biot Number and a small Pyrolysis number which leads to a higher core temperature within the core of the material. This in turn leads to a high value for thermal resistance and is a deterrent for effect heat transfer within the material [76]. Thus the particle size needs to be closely monitored to ensure high degree of thermal efficiency.

Sweep gas flow rate

Nitrogen gas is used within the chamber to maintain the required pressure and also keeps the torrefaction chamber inert. The amount of nitrogen gas used during the course of operation has to be set to control the temperature and to remove the released gases. A typical range used is from 10 to 30 L/min. A high nitrogen flow rate is used during peak operation to ensure that the gases evolved during the process do not react with the char or each other. In the research performed by Nabajit et al indicates that when the nitrogen flow rate is increased from 50 to 250 mL/min, the biochar yield decreases and there is a higher selectivity for the gas phase products.[37]

Angle of tilt

The HTT4 reactor as mentioned is slightly tilted at an entrance angle of 6 degrees. This angle ensures that the biomass particles move under the influence of gravity along the length of the reactor and leave the reactor when they are sufficiently torrefied. If this angle is too small, the residence time is getting longer and this will lead to unwanted mass and energy loss. If this angle is too large then this will lead to the material not getting torrified to the required degree. Therefore this angle needs to be carefully selected based on trial and error to arrive at the required optimum.

2.5.8 Post processing for the biochar obtained

Once the biomass is upgraded into biochar, the biomass is first cooled down to ambient temperature.The options for post processing are limited to pelletizing to improve bulk and energy density or grinding operations depending on the form factor of the char required.

Chapter 3

Methodology

This chapter discusses the methodology used in producing the biochar through torrefaction as well as the procedures for characterizing the biomass feedstock and the biochar produced post its upgradation. First, this chapter looks at all the different feedstock and the torrefaction technique used. Second, the apparatus and the techniques used for the different tests are explained. Thirdly, the rationale behind the economic and life cycle analysis are discussed in brief. Fourthly, the macronutrient requirements and costs associated with producing the biochar mixture along with the macronutrient blending is depicted.

3.1 Biomass preparation and analysis

A total of nine biomasses were sourced from various parts of the world owing to the global nature of the feedstocks and seasonality. The Pinewood chips,washed shredded roots and Tomato waste(4) were sourced from the Netherlands(52.3676° N, 4.9041° E) while the Rice husks(1) and Bagasse(2) were procured from Southern India(13.0827° N, 80.2707° E). The Grade-A Wastewood(6) originates from Sweden(60.1282° N, 18.6435° E) while the Grape stems(3) are from Bordeaux, France(44.8378° N, 0.5792° W). The Miscanthus(7) and Wheat straw(8) are from Derby, UK(52.9225° N, 1.4746° W). The Forestry waste(5) that is taken as a reference is from the evergreen forests of Estonia(58.5953° N, 25.0136° E). All of these feedstocks were procured in the range of 3-5 kilograms so as to have enough material for testing post torrefaction. Once the feedstocks were sourced, they needed to be bone-dried(initial moisture brought down to 15%) over a duration of 48 hours to remove any additional moisture within the feedstock. This was done in order to prevent any rotting of the material due to microbial action. The dried feedstock was then ready for the torrefaction and analysis. The overview of the feedstock materials in the raw form is shown in figure 3.2.

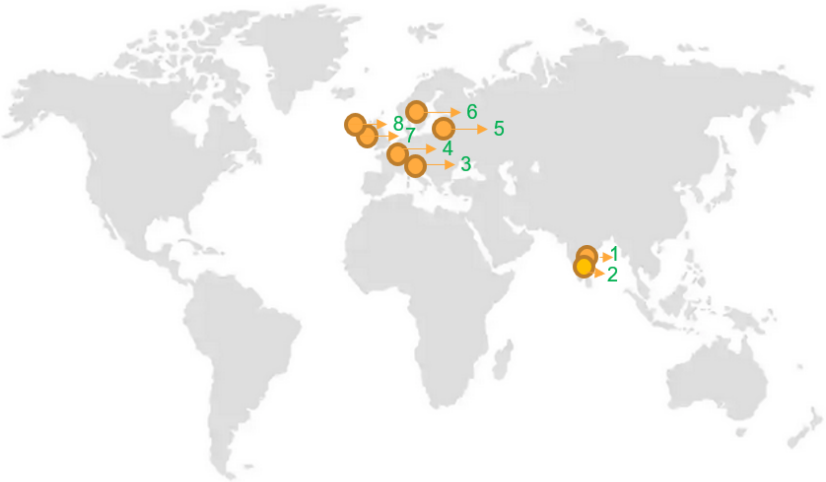


Figure 3.1: Feedstocks sourcing locations

Figure 3.2: All the feedstock materials in the raw form

3.1.1 Pre-torrefaction sample preparation

The sampling was performed according to BS EN ISO 14780:2017, around 100 gram of the material was separated and milled for over 24 hours in a ball mill to convert the bulk feedstock into powder [102]. This milling process also ensures proper mixing of the feedstock particles to ensure overall homogeneity of the mixture. A small portion (20%) of the powder was cold pressed to form pellets. The powder and pellet form for the feedstocks are shown in figure 3.3

3.1.2 Proximate Analysis

The proximate analysis contains numerous indicators such as the amounts of volatile matter, fixed carbon, ash and moisture content. For the same, the homogenized samples were sent to Socotec testing labs UK which adopts testing standards based on the United Kingdom Accredation Services (UKAS) to ensure results with a high degree of accuracy. The testing standards for the moisture content, ash content and volatile matter are DD CEN/TS 15414-1:2010,EN 15403:2011 and EN 15402:2011 respectively. The fixed carbon content is determined by subtracting the percentages of volatile matter, moisture, and ash content from the sample. The powdered and pelletized samples for a few feedstocks are shown below.

3.1.3 Ultimate Analysis

The elemental analysis of the percentages for Carbon, Hydrogen, Nitrogen and Sulphur constitute the ultimate analysis for the sample provided. The carbon and oxygen are the major elements(>85%) present and the hydrogen,nitrogen and sulphur make up the smaller fraction(<15%) of the biomass. The C-H-N analysis is performed according to the EN 15407:2011 standard while the Sulphur analysis is carried out based on the EN 15408:2011 standard.

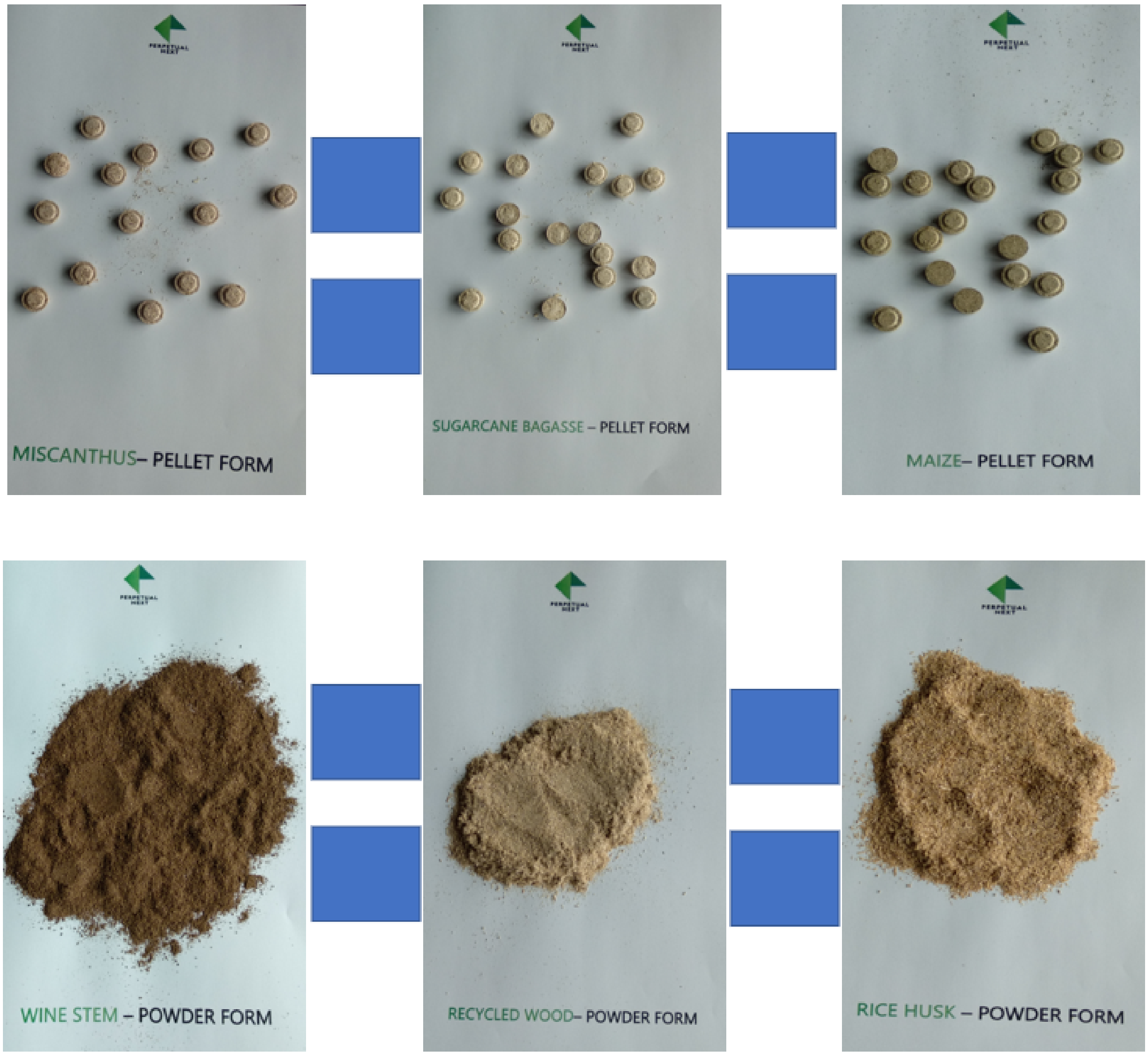


Figure 3.3: A few feedstock materials in the powder and pellet form

3.1.4 Calorimetry

The energy content of the biomass feedstock is determined through calorimetry. Using this technique the energy content in Joule(or megaJoule) per kg of the raw material is determined. There are two different types of heating values associated with calorimetry: the Lower Heating Value(LHV) and the Higher Heating Value(HHV). The HHV normally has a higher value compared to the LHV as the HHV includes the energy gained by condensation of the water vapour in the product gases into liquid (recovery of the latent heat of vaporization). The calorimetry is performed using the BS EN ISO 18125:2017 standard.

3.1.5 Particle size distribution

The particle size for the biomass is usually distributed over a range from coarse particles to fine powders depending on the type of material and the pre-processing method used. To get a clearer picture of the distribution within the various particle sizes, a series of sieves are used. The mesh size of the sieves decrease from one sieve to the next up until the last sieve which only allows powders to fall through. The resulting percentage of particles that are trapped in each layer is analysed. For the feedstocks selected, five different sieves are used namely the 25.00mm, 12.5mm, 6.30mm, 3.15mm, 2mm and 1mm. The material that is collected below the 1mm sieve is labelled as fine dust or powder. The BS EN ISO 17827-1:2016 and 17827-2:2016 standards are used in this technique.

3.1.6 Heavy metal analysis

Various heavy metals such as lead (Pb), arsenic (As), mercury (Hg) among others in their elemental or compound form are present in trace quantities within any organic matter. The determination of the amount of these elements is crucial to check if they fall within the guidelines set by the EBC and also to prevent the pollutants within the parent biomass from entering into the end applications. The heavy metals concentrations are observed through a gravimetric analysis in which the element or its ion shows different behavior depending on its molecular weight[4]. This technique is a reliable analytical method specifically for the heavy metals with their distinct molecular weight separating them from other elements. The following heavy metal concentrations are observed Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Vanadium and Zinc. The EN 15440:2011 standard is used for this analysis.

3.1.7 Ash analysis

Though biomass and biochar both inherently contain minerals such as Nitrogen, Phosphorous and Potassium essential for plant growth along with other alkaline earth metals, these are present in very small quantities insufficient for the holistic development of the crop. Thus the need to quantify the existing mineral content within the biomass feedstock and then ascertain the quantity of the nutrients needed to bolster the char which will in turn provides these macronutrient benefits to the soil and the crop. The Inductively Coupled Plasma (ICP) analysis of the ash is used to identify the following compounds : SiO_2,Al_2O_3,Fe_2O_3, TiO_2,CaO, MgO, Na_2O, K_2O,Mn_3O_4,P_2O_5 and SO_3. The BS EN ISO 18122:2015 standard is used for this analysis.

3.2 Torrefaction of the samples

The nine feedstock materials were torrefied at the facility at CIRAD, Montpellier (43.61° N, 3.87° E). The samples were weighed before and after torrefaction to get an understanding of the impact of torrefaction on the feedstock and the yield received post torrefaction. The overview of the torrefaction reactor, the parameters used and the post-cooling is mentioned in this section.

3.2.1 Torrefaction reactor

The torrefaction was performed in a lab-scale fixed bed reactor comprising of external heating zones. The schematic of the reactor used for the torrefaction of all the feedstocks is shown in figure **??**. This reactor comprises of ten trays that can be loaded up to a maximum of 100 gram for the different feedstocks in each tray. The reactor comprises of ten different thermocouples (t0-t9) which are positioned at different depths within the reactor chamber. Three thermocouples T9,T8 and T7 measure the outer heating zone temperature while the five thermocouples T1, T2, T3, T4, T5 measure the temperature surrounding the feedstock materials. The thermocouples T0 and T6 measures the entry and exit gas temperatures respectively.

The inert atmosphere is maintained by supplying nitrogen gas at a controlled rate (10-30 L/min). The heat required is supplied by externally heated hot air which enters from the bottom of the reactor. This air is made to be incident on the char through pores at the bottom of each loading tray. The chamber is hermetically sealed using screws along the top and the sides to prevent the mixing of atmospheric gases. The torrefaction gases produced inside the chamber is forced out through the top where it is then fed into an oxidiser and a scrubber which removes most of the particulate matter and emissions before being released into the atmosphere.

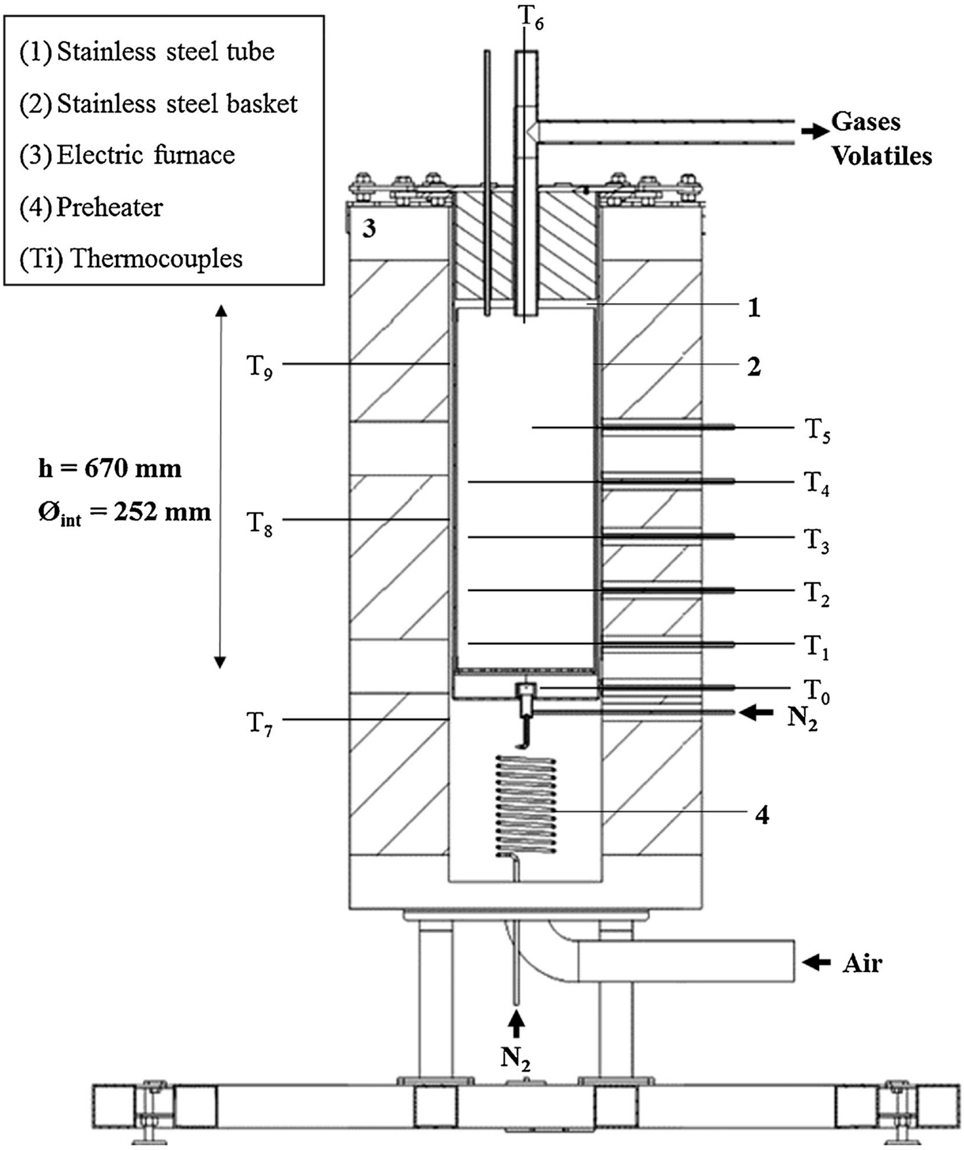


Figure 3.4: Schematic of the fixed bed reactor at CIRAD

3.2.2 Torrefaction parameters used

The torrefaction parameters were chosen in such a way so as to closely replicate the HTT4 operation conditions. The torrefaction parameters used are listed in table 3.1.

Key Parameter	Units	Value
Torrefaction inner heating zone temperature	°C	350
External heating zone temperature	°C	550-600
Residence time	Min	38
Heating rate	°C/min	15
Ambient temperature	°C	25
Nitrogen flow rate	L/min	10-30

Table 3.1: The torrefaction parameters

There is a noticeable gradient between temperature measured by the thermocouples at the outer and inner zones. The outer zone is much closer to the heat source and as a result is at a much higher temperature as compared to the inner zone which is shielded by a metallic layer and an air gap and is consequently at a lower temperature. This difference in temperature ensures that the the outer zone needs to be sufficiently heated to ensure that the core torrefaction temperature is maintained. The heating rate was fixed at 15 Degrees a minute and the outer initial temperature was measured to be 25 °C. This in turn ensured that the material had to reside for 38 minutes for the temperature to increase from ambient to 350 °C inside the reaction chamber. The Nitrogen flow rate was maintained at 10 L/min until the core temperature reached 100 °C and then increased to 30 L/min for the remainder of the torrefaction operation to ensure that the atmosphere remained inert even as the volatile compounds from torrefaction were evolving. Ultimately, the torrefaction process was stopped when t4 reached 350 °C and then the material was allowed to cool down.

3.2.3 Post cooling

The last step in the torrefaction process is to ensure that the char cools down to ambient temperature or lower. This char is a carbonaceous material and exits the reactor at temperatures exceeding 300 °C and it is important that the material be cooled down first to prevent auto ignition and maintain safety. This cooling is accomplished by forced convection of cooled air into the torrefaction chamber using a motor fan. The Nitrogen flow rate is brought down to 10 L/min and the material is cooled down until the core temperature reaches 50 °C. This method of cooling allows the solids to cool down more uniformly as compared to other rapid cooling methods such as water quenching or flash freezing which may could cause similar crystalline defects in the microstructure as commercial metals [10]. The materials are removed from the chamber post cooling and the weights are measured once again to ascertain the mass yield from the process.

3.3 Post torrefaction experiments

The biochar produced needs to be evaluated for its soil remediation and plant growth effectiveness. The char is subjected to similar characterization as the raw biomass including proximate and ultimate analysis, calorimetry, bulk density, heavy metal and ash analysis and particle size distribution. The methodology and standards used for these measurements and analysis are exactly the same as the ones used for the initial biomass characterization as previously explained. Additionally, the char is subjected to BET analysis, pH tests and SEM-EDS characterization to understand the material's surface behavior better. These tests are explained in this section and the results are discussed in the next chapter.

3.3.1 BET Analysis

The Brunauer-Emmett-Teller (BET) analysis gives an indication of the surface area and the porosity for a sample based on gas adsorption and the difference between the relative pressures (P/P0). The equipment used in this analysis is NOVAtouch™ which is the primary equipment which performs the initial analysis in terms of relative pressure and the TouchWin™ software which interprets the data provided into final values for surface area and porosity. The correlation between the weight of the gas adsorbed(W),weight of a gas monolayer(W_m) on the surface at the corresponding relative pressure(P0/P) gives the measure of the surface area and porosity. The variable C, is the BET constant and depends on the energy of adsorption of the first layer that is adsorbed on the surface [28]. The equation 3.3.1 governs the relationship for the sample BET isotherm as shown in 3.5.

$$1/W((P_o/P)-1) = 1/(W_m * C) + (C - 1/(W_m * C)) * (P/P_o) \tag{3.3.1}$$

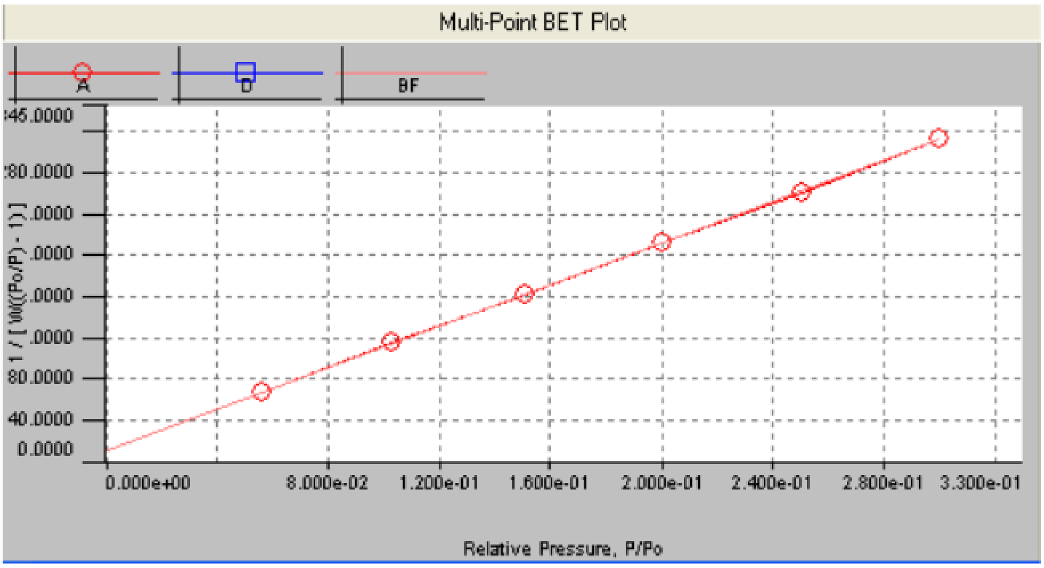


Figure 3.5: A sample BET plot [28]

The pore size is also determined by using a gas adsorption. Typically Nitrogen gas is used as the adsorbate owing to its inert nature. However, recent developments indicate that Carbon-di-Oxide is a much better alternative to Nitrogen for BET measurments as CO2 possesses better capability to activate the pores. In a study performed by Youkwan Kim et al., the BET and pore volume of oak wood biochar was only 231.2 m2/g and 53.1 cm3/g respectively when measured with N2 adsorption while, the BET and pore volume values for the same material almost doubled to 463.6 m2/g and 106.5cm3/g, respectively when CO2 was used as the adsorbate[8]. The study attributed this enhancement to CO2's ability to more effectively remove the volatile organic compounds (VOC's) from the surface of the material.However,CO2 is much less inert than N2 and therefore the resulting CO2 uptake and the resulting porosity could be tied to the interaction energies between the adsorbent and adsorbate. This indicates that further research into the merits and demerits for the carrier gases used in BET measurements is required.

The operation in NOVAtouch™ was performed with Nitrogen as the adsorbate and the reading reflect the surface area and porosity based on the amount of Nitrogen gas adsorbed on the surface of the char. The total pore volume is calculated from the amount of vapor adsorbed at a relative pressure close to one with the pores being filled in by the liquid adsorbate. The total pore volume is calculated by first evaluating the volume of liquid that is present in the pores (V_{liq}) in comparison to the total gaseous Nitrogen that is adsorbed(V_{ads}). The P_a and T are the ambient pressure and temperature, while R is the universal gas constant. 3.3.2 shows the correlation between these variables.

$$V_{liq} = \frac{P_a \times V_{ads} \times V_m}{R \times T} \tag{3.3.2}$$

The average pore radius(r_p) is related to V_{liq} and the BET surface area(S) according to the following equation 3.3.3.

$$r_p = \frac{2 \times V_{liq}}{S} \tag{3.3.3}$$

The NOVAtouch™ analyzer directly gives us the results for the BET surface area and the total pore volume on the basis of amount of Nitrogen absorbed per gram. Therefore these results will be directly used without the need for the intermediate formulas.

3.3.2 pH Analysis

The pH analysis is performed on the feedstock material to determine if the material is basic enough to remediate acidic soils. Normally, the pH of commercial biochars are in the range of 6-10. Industrial peat and other forms of coal are highly acidic with pH of 3-4 and therefore needs to be mixed with oxides or hydrides of lime to prevent acidic poisoning of the soil [87]. Acidity in soil occurs mainly due to effects of anthropogenic activities including acid rain (resulting from SOx and NOx emissions and atmoshperic chemical processes), industrial run-offs and excessive pesticide use. A few rare soil types including Acrisols, Alisols and Podzols which can be found in dense rainforests of Brazil and Australia have a high naturally occurring Aluminum percentage along with low Molybdenum levels. This causes them to have an acidic pH which needs remediation[1].

The apparatus used for the pH measurements is the Metrohm 914 pH meter which measures the change in Hydrogen ion activity as a function of the conductivity of the system. The pH meter consists of two electrodes, one reference electrode which is typically made of Silver/Mercury Chloride and the other pH-responsive electrode which is made out of glass. When the two electrodes are immersed in their respective solutions, the circuit is complete and a current starts to flow across which is measured by an inbuilt Voltmeter. The device converts this voltage measurement into a value for the pH of the solution.

As the char is solid, the liquid solution sample is prepared by first immersing around 3-5 gram of the biochar in a beaker with water for 48 hours prior to the first measurement. The device is calibrated by using IUPAC pH buffers of 4.01, 7.01 and 10.01 at room temperature to ensure a high degree of accuracy with the measurements.
To ensure there is minimal variability of the pH readings, the pH for the samples are measured once at 48 hours and once again at 72 hours after sample preparation. There is no need to take additional readings if the values at 48 hours and 72 hours are comparable. The values can then be averaged out to give the pH for the biochar samples.

3.3.3 SEM-EDS

SEM stands for Scanning Electron Microscopy and is a technique which is used to map the intricate surface morphology of materials. In SEM, high energy electrons are made to be incident on the surface of an object in a raster pattern. The signals sent back by the electrons bouncing off the surface of the material is collected by a receiver which translates this data into a high resolution outline of the cross sectional area[6]. EDS stands for Energy Dispersive Spectroscopy and is used to identify elements present within the sample. EDS analyses the intensity of the X-ray peaks generated as a result of the electrons interaction with the surface of the biochar. These peaks are then compared with known characteristic peaks for all elements and also measure the number of counts at one particular peak. This not only characterizes the elements present within the char, but also indicates the percentage composition of that particular element. This technique is most commonly used not only for general elemental charecterization but also to target specific hotspots in imaging. These hotspots could indicate the presence of various inorganic compounds or trace metals.

The JSM-IT100 InTouchScope™ SEM-EDS setup was used in this project. This powerful microscope is capable of producing high resolution images ranging from 50X-3000X magnification. The SEM apparatus is always kept in vacuum except during loading and unloading of the specimen. The biochar sample is degassed using a vacuum pump from 1 bar to 0.1 millibar and a high pressure air-spray was used to remove any fine particles which could be absorbed into the SEM system. The sample is observed at three different magnifications of 100X, 300X and 800X. For the EDS analysis, the entire area was first analysed at 100X magnification. The magnification was further increased to 300X and 800X where a 3 point analysis was performed at each of the said magnification to identify key inorganic compounds present in the biochar. The JSM-IT100 InTouchScope™ SEM-EDS setup is shown in figure 3.6 and the results from the area and point analysis are discussed in the next section.

Figure 3.6: The JSM-IT100 InTouchScope™ Scanning Electron Microscope

Chapter 4

Results and Discusssion

This chapter presents the results from the various torrefaction experiments conducted in this thesis.The different feedstocks are divided in two main groups: grassy agricultural feedstocks (bagasse, rice husks, maize, tomato waste,miscanthus,washed shredded roots) and woody feedstocks (pinewood chips,grape stems and recycled wood). The end result of the research is to identify those feedstocks which show great promise based on the properties they exhibit. Therefore, the results are depicted and discussed with regards to each feedstock and its performance with regards to forestry waste and other materials.

4.1 Pre-torrefaction test results

The whole project was divided into three phases: pre-torrefaction, the torrefaction and the post torrefaction. In this section, the tests performed on the raw feedstocks and the torrefied char are depicted, compared and discussed. All the results under this section are presented on a dry basis, except for the moisture content which is measured on an as received basis.

4.1.1 Proximate Analysis

The proximate analysis of the feedstock is critical to understand the fundamental makeup of the raw material. Here, the moisture content is separated from the proximate analysis to get a better understanding of the initial drying and cleaning requirements.The proximate analysis for the different feedstocks are listed in figure 4.1

Volatile Matter

Most biomass materials contain a high percentage (roughly 80%) of volatile matter and the remaining is split in between ash and fixed Carbon. This high percentage of volatiles consists of short and long chain aliphatic and aromatic hydrocarbons. There are traces of Sulphur and Chlorine as well which could result in fouling within the boiler/reactor which needs to be removed prior to torrefaction. In sharp contrast to common biomass materials, Grade-1 bituminous coal contains 50% of fixed Carbon and only 35% of volatile matter which makes coal a much more attractive option compared to biomass materials for combustion applications[42].

Usually, we observe that herbaceous materials have a lower volatile matter content in comparison with its woody counterparts. This decrease in the volatile matter is partly due to their chemical makeup and also results in much higher ash content[43]. However, here we notice that the percentage of volatile matter for the BG, MS are a little higherthan that of RW. This increase in volatile matter at the cost of lower ash might lower the usefulness of these two feedstocks for a soil based application. The other feedstocks including GAWW, GS, MS and TW are all within the expected range of 75-85% with only RH having a lower volatile content of 61%.

Fixed Carbon

The fixed Carbon content within the biomass determines the initial level of carbon saturation within the material. Through the course of torrefaction, the percentage of volatile matter continues to decrease over

time till the process is complete. While the VM continues to drop, the fixed Carbon continues to increase till the completion of the torrefaction process[44]. The initial fixed Carbon remains in the material and gets concentrated over the volume of the material post devolatilization and thus a steady increase in the carbon percentage can be observed. The FC of the different feedstock material is listed in the Fig. **??**.
The fixed Carbon content is higher in woody materials as seen from the higher values for GS, RW and GAWW. The fixed Carbon content for herbaceous materials is slightly lower than woody materials, except for TW which shows a FC content similar to other woody materials such as the GS and the GAWW. Also, the effect of fixed Carbon on torrefaction can be seen from the last two columns for PN-Estonia softwood and its corresponding biochar. There is a Carbon enrichment by approximately 200% from 14.3% to 27.4% post torrefaction.

Ash

The ash content of the biomass material is of critical importance in relation to the biochar's soil application. Key macro and micro nutrients including Calcium, potassium, manganese and phosphorus are present in considerable quantities within the ash content of a biomass material[80]. As observed in Table. 4.1, the ash content of herbaceous feedstocks is significantly higher in comparison to woody materials. This is due to the nutrient rich chemical makeup typically linked to the high ash content for these herbaceous materials to assist the growth and development. Rice husks had the highest percentage of ash with a majority of the ash occurring in the form of silica and calcium oxide. These nutrients are essential for plant growth and are found in large concentrations in the soil. The rice plant has a tendency to absorb close to 10-20% dry matter of the available Silica from the soil, while other plants only absorb 1-2% dry matter.[107]

Name of the feedstock	**Compounds present in the ash (%)**										
	SiO2	Al2O3	Fe2O3	TiO2	CaO	MgO	Na2O	K2O	Mn3O4	P2O5	SO3
Grape stems	9.6	1.3	0.7	0.1	40.8	4.6	0.8	7.8	0.1	2	1.9
Bagasse	50.9	1.4	1.1	0.1	3.9	2.6	2.3	19.5	0.1	6.8	3.5
Rice husks	92.2	0.1	0	0.1	0.8	0.4	0.2	2.5	0.1	0.5	0.4
Recycled Wood	21.3	5	4.1	7.3	24.8	4.2	4	5.5	0.8	1.4	6
Maize	36.7	1.2	1	0.2	9.6	4.5	0.3	19.5	0.1	10.1	2.4
Washed shredded roots	40.5	7.8	2.6	0.5	19.6	2.4	1.2	8.3	0.3	1.9	2.1
PN Estonia softwood	18.5	4.5	3.3	0.7	25.6	4.6	2.7	7.7	0.5	3.7	7.8
Pinewood chips	20.7	13.8	1.5	1	24.1	4.7	1.5	6.9	3.2	1.9	2.6

Table 4.1: Ash analysis for all the feedstocks

4.1.2 Moisture Content

The HTT4 operation requires that the moisture for the feedstock be within the range of 8-10% for optimal torrefaction output. The herbaceous feedstocks showed a considerably higher initial moisture content owing to rainfall or irrigation operations prior to harvest. Feedstocks including Bagasse, Maize, Tomato residue had a very high moisture content (above 60%) and thus will likely require significant amount of energy during the drying process. Post torrefaction of the feedstocks however, we can expect that the moisture content of the final biochar is much lower than the initial moisture content.

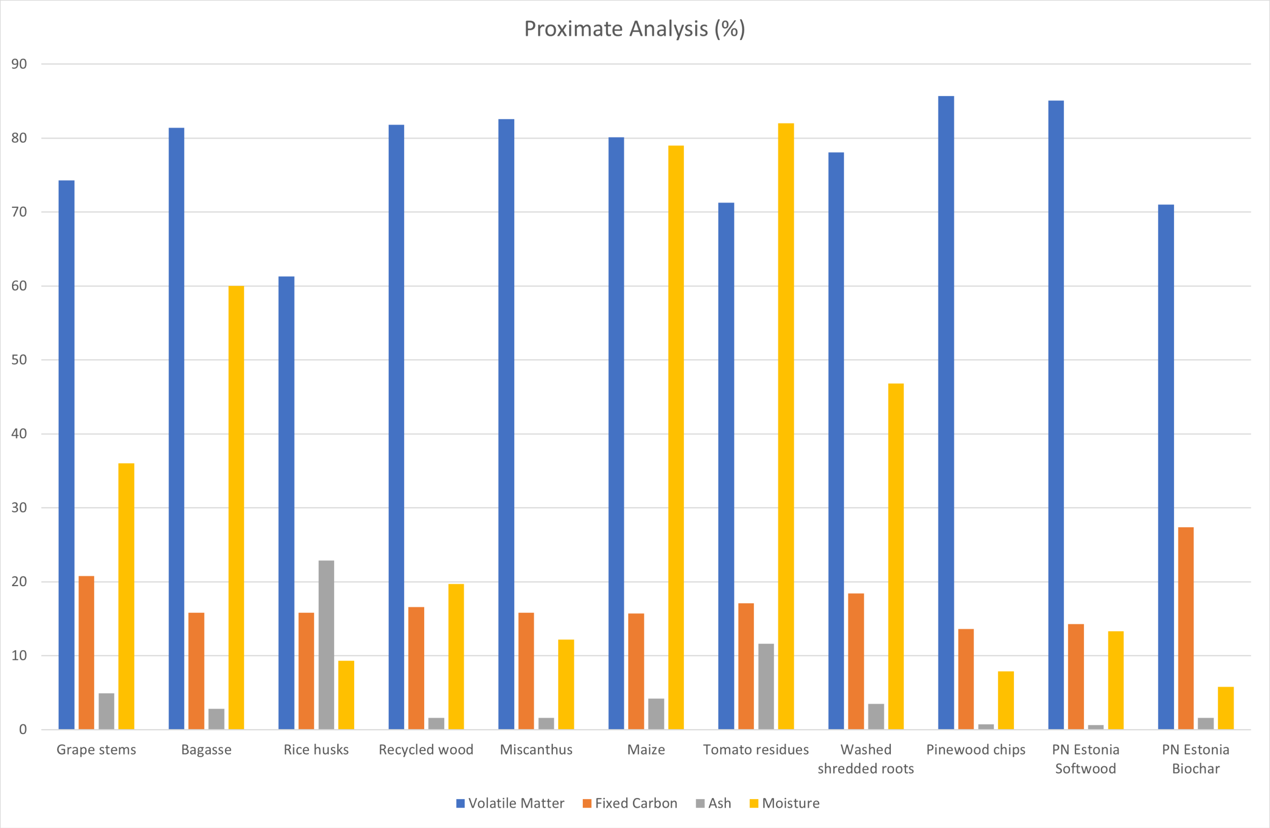


Figure 4.1: Proximate analysis for all the feedstocks

4.1.3 Ultimate Analysis

The chemical characterization for the different feedstock materials are discussed in this section. The elements Carbon(C), Hydrogen(H),Oxygen(O),Nitrogen(N) and Sulphur(S) are the primary constituents for all the woody and herbaceous materials. While Oxygen and Carbon are the major components(>90%), Nitrogen and Sulphur make up the remaining percentage of the material. The Ultimate analysis or the CHNS analysis usually pertains to the measurements of C,H,N and S as a percentage and the Oxygen content is calculated separately and is therefore excluded from the graph shown in figure 4.2.

C,H,N,O,S

The oxygen is determined through a suitable subtraction from the remaining components as according to 4.1.1

$$\%O = 100 - (\%C + \%H + \%N + \%S + \%Ash) \tag{4.1.1}$$

Name of the feedstock	Oxygen (%)
Wine stems	38.77
Bagasse	44.85
Rice husks	34.62
Rubber wood	40.29
Wood waste	41.1
Maize	41.38
Tomato waste	36.97
CEG-Estonia softwood	42.32
CEG Estonia Biochar	34.75

Table 4.2: Oxygen content in the feedstock materials

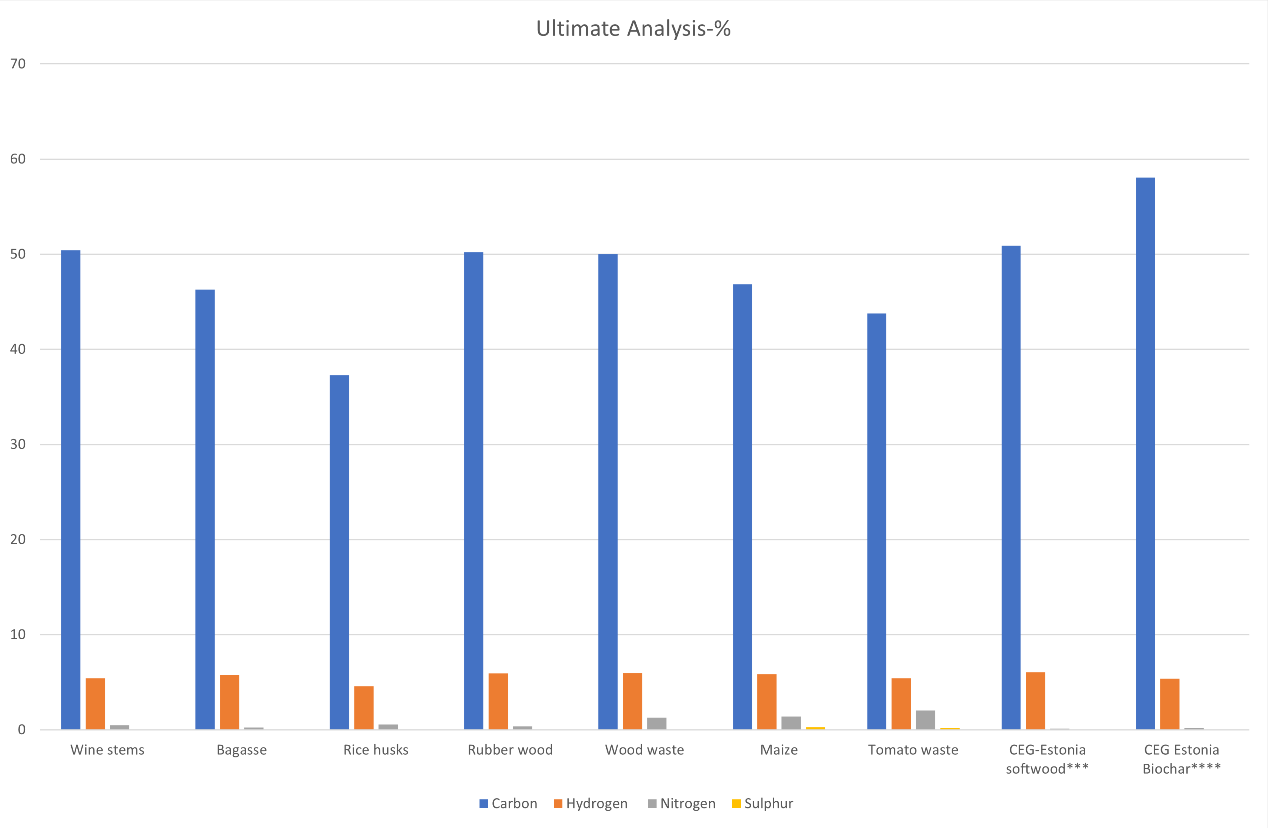


Figure 4.2: Ultimate analysis for all the feedstocks

The Carbon content for the feedstocks dominates the CHNS analysis with woody feedstocks showing a higher percentage of Carbon as compared to the herbaceous materials. The grape stems are still considered as a woody material due to the nature of the material received which was mostly small twigs and branches. Overall most of the feedstocks show a good overall carbon content which will prove crucial towards the stability of the char as this directly impacts the O/C ratios. The Smaller Nitrogen and Sulphur concentrations(<1%) are also in accordance with general observations. The Ultimate analysis comparison between the softwood raw material and the torrified char shows a noted increase in the Carbon percentage and this in essence is the process of Carbon enrichment through torrefaction.

4.1.4 Net Calorific Value

The LHV or Lower Heating Value(LHV) of the material determines its efficacy for combustion related applications. Primarily the higher the Carbon percentage, the higher the Net Calorific value. The LHV's obtained post Calorimetry is shown in table 4.3.

Name of the feedstock	Feedstock type	LHV (MJ/kg)
PN Estonia Biochar	Pelletized (biochar)	20.9
Pinewood chips	Woody	19.2
Recycled wood	Woody	18.7
Grape stems	Woody	18.5
Washed shredded roots	Grassy	18.5
Bagasse	Grassy	18.0
Miscanthus	Grassy	17.8
PN Estonia Softwood	Woody	16.6
Maize	Grassy	16.4
Tomato residues	Grassy	15.3
Rice husks	Grassy	14.8

Table 4.3: The lower heating values for the feedstock materials and the 21 MJ/kg char

The values for the LHV's of the feedstocks are cross checked based on their ultimate analysis. The LHV of the material is determined by removing the heat of vaporisation of water from it. This is done using equation 4.1.2 .

$$\textbf{LHV} = \textbf{HHV} - 24.44 * (9 * [\%H] + [\%MC])\,kJ/kg \tag{4.1.2}$$

Now, to determine the LHV, we need to first find the HHV for the material. There are three models used for this and are represented by equations 4.1.34.1.44.1.4.
1) **The Boie correlation**

$$\textbf{HHV} = 351.69 * [\%C] + 1162.46 * [\%H] - 110.95 * [\%O] + 104.67 * [\%S] - 62.8 * [\%N]\,kJ/kg \tag{4.1.3}$$

2) **The Milne equation**

$$\textbf{HHV} = 0.341 * [\%C] + 1.322 * [\%H] + 0.0686 * [\%S] - 0.12 * [\%O + \%N] - 0.0153 * [\%Ash]\,MJ/kg \tag{4.1.4}$$

3) **Friedl et al correlation**

$$\textbf{HHV} = 3.55 * [\%C^2] - 232 * [\%C] - 2230 * [\%H] + 51.2 * [\%C] * [\%H] + 131 * [\%N] + 20600\,kJ/kg \tag{4.1.5}$$

Jean-Michel Commandre et al,2019 found out that post torrefaction around 280 °C that the LHV(or LHV) will have 2.4-4.8 MJ/kg(12.3-28.6%) increase in comparison to the raw biomass material.The LHV of the biochar has an implicit correlation with the Carbon content, thus feedstock materials with a higher initial Carbon content(GS,RW,GAWW) will have a higher jump with regards to the final LHV of the biochar[62].

4.1.5 Bulk Density

The Bulk density of the raw material hugely depends on the form factor of the feedstock. Woody materials such as the grape stems, pinewood chips and recycled wood have a noticeably higher values for bulk density owing to their chip form and a higher mass. Lighter materials including bagasse, rice husks and maize show lower values for bulk density and thus require some form of densification through pelletization prior to torrefaction to reduce loss through fines and improve the overall mass yield. The torrefied Estonia biochar has the highest bulk density of 550 kg/m3 and this is due to the fact that the material has been pelletized post torrefaction. The bulk density for the feedstock materials along with the current biochar reference is shown in table 4.31

Name of the feedstock	Feedstock type	Bulk density (kg/m3)
PN Estonia Biochar	Pelletized (biochar)	550
Washed shredded roots	Grassy	496
Tomato residues	Grassy	399
Pinewood chips	Woody	313
Grape stems	Woody	292
Recycled wood	Woody	200
Miscanthus	Grassy	161
Rice husks	Grassy	153
PN Estonia Softwood	Woody	138
Maize	Grassy	133
Bagasse	Grassy	47

Table 4.4: The bulk densities for the feedstocks and the 21 Mj/kg biochar

4.1.6 Chlorine content

Chlorine was discussed partly under volatile matter in the proximate analysis. Though chlorine also falls under volatiles, the effect of this element is far more pronounced and has a severe impact on the torrefaction reactor and thus the amount of chlorine contained within various feedstocks needs to studied. The chlorine content in the raw feedstocks is shown in table 4.5

Name of the feedstock	Chlorine (%)
Grape stems	0.01
Pinewood chips	0.01
PN Estonia Biochar	0.01
Recycled wood	0.02
PN Estonia Softwood	0.02
Miscanthus	0.1
Rice husks	0.11
Maize	0.13
Bagasse	0.14
Washed shredded roots	0.15
Tomato residues	1.1

Table 4.5: Chlorine content in the feedstock materials

Traditionally, chlorine is categorized as a plant micro-nutrient meaning that a small fraction(0.2g/kg) of this element is crucial for the overall development. However, higher concentrations of this nutrient will cause to the plant leaves to become bleached, wilt and eventually die[114]. Apart from plant inhibitions, chlorine normally combines with elemental hydrogen and causes acidic corrosion of the interior lining of the reactor. This is commonly called as fouling or slagging within the reactor and the Chlorine release and activity increases with increasing temperature. Khazraie et al. discovered that while torrefaction of birch wood at 240 °C only released 25% Chlorine and 40% Sulphur, the same percentages increase to 85% and 55% respectively when the torrefaction temperature is increased to 280 °C [97]. The effective removal of this chlorine and other harmful volatiles are discussed under recommendations.

4.1.7 Particle size distribution

Commercially, the big chunks of the raw materials having higher bulk densities are chipped down to size while lighter feedstocks materials that tend to have lower bulk densities need to be pelletized. The chipping process does result in a fraction of material that is converted into fine dust or powder. This fine material does not torrefy and is usually carried out of reactor through the hot gas outlet. Thus, the particle size characterization is crucial for predicting the mass yield at the end of the torrefaction process and in understanding the homogeneity of the product received post torrefaction. Here, we will be looking at the individual particle size distribution across six ranges of distribution namely 25mm, 12.5mm, 6.3mm, 3.15mm, 2mm and 1mm. Any material that is lower than 1mm is classified as "fines". The overall particle size distribution is given in table 4.6.

Name of the feedstock	**Particle size distribution**						
	<25mm	<12.5mm	<6.3mm	<3.15mm	<2mm	<1mm	Fines
Wine stems	22.3	36.4	23.4	10.1	2.2	2.9	2.7
Bagasse	20.5	25.6	25.4	12	9.2	2.3	4
Rice husks	0	0	0.1	19.2	49.9	10.6	20.2
Wood waste	46.4	28	11.5	8.9	1.5	2	1.7
Miscanthus	93.5	0	0	1.5	1.9	2.3	0.8
Maize	0	0	18.1	62.5	7.8	7.2	4.4
Washed shredded roots	9.5	41.3	37.5	9.3	1.6	0.6	0.2
Pinewood chips	17.3	18.2	34.1	19.2	4.8	3.2	3.2
CEG Estonia Softwood	41	48.4	9.8	0.8	0	0	0
CEG Estonia Biochar	33.3	56.5	9.7	0.5	0	0	0

Table 4.6: Particle size distribution for the feedstocks

Grape stems

The particle size distribution for the grape stems is truly spread over the entire range with roughly 80% of the bulk material lying in the range of 6.3 mm-25 mm. The very small fraction of fines(<3%) along with other smaller particles is a good indication that the material will ensure that a majority of the bulk material is saved post torrefaction. As most of the particles have a discernible quantity in the usual chip range(10-25mm), no further chipping or pelletization is required for this feedstock.

Bagasse

Bagasse is truly an unique feedstock from the particle size perspective. Though close to 75% of the bulk material has a particle size of at least 6.3mm, the brittle nature of the feedstock will ensure that this raw material keeps disintegrating during transport and preprocessing handling. The initial percentage of fines in the bagasse is high and to ensure minimal loss of material, pelletization prior to torrefaction is recommended to ensure a higher torrefaction yield.

Rice Husks

Rice husks are one of the most smallest uniform feedstock material present for all the feedstocks compared. The husks covering a tiny grain of rice is therefore no bigger than 3.15mm with the majority(>80%) of the rice husks being smaller than 2mm. The need for pelletization is of the highest importance for the rice husks to greatly improve the physical char properties post torrefaction.

Recycled wood

Recycled wood residue that originates from construction and the timber industry has a great amount of variability with regards to the dimensions of the feedstock material. The sample material received as shown in figure 4.3 , represents the non-uniformity present within the raw feedstock. This is also evident from the particle size distribution analysis results where >75% of the material are larger pieces(>12.5mm) and the remainder of the sample material contains smaller wood chips and some(2%) fine saw dust as well. While the bigger chips may need chipping, the smaller fraction of the materials will need to be pelletized before torrefaction.

Figure 4.3: The Recycled wood received

Maize

Similar to the Rice husks, the maize residue contains a majority(>80%) of smaller particles less than 3.15mm. There are a few bigger pieces as well(3.15-6.3mm) roughly making up 18% of the entirety of the material owing to bigger pieces of the stalk that may not have been chipped properly. This feedstock material is encouraged to be pelletized prior to torrefaction to enhance the bulk density and increase the mass yield.

Miscanthus

Miscanthus giganteus the form of miscanthus used for biomass applications are harvested from the field for upgradation. Here, in the particle size analysis we see that 93% of the material is still larger than 25mm. This suggests that the material be chipped according to the torrefied char material required. The remaining small fraction(7%) of the fine material is from the silage during harvesting.

4.1.8 Pinewood chips and washed shredded roots

The pinewood chips and washed shredded roots had noticeable pieces ranging between 10-25 mm. The pinwood and the shredded roots have been pre-chipped and therefore show minimal fines or small chips.

PN-Estonia Softwood

The raw material for the Estonia softwood is a 60-40 mixture of spruce+oliver wood. This wood is chipped according to the particle size required for the char. This can be seen from the particle size distribution for the raw material. The lack of any fine material (6.3mm) shows that care has been taken to avoid any fine material and that the bulk materials are majorly in two size ranges 12.5 mm with 48% and 25 mm with 41%. Do note that these chips are pelletized post torrefaction to enhance the bulk density and lower transportation and handling costs.

PN-Estonia Biochar

A close comparison of the Estonia raw material and the corresponding char gives an interesting observation. There is a small percentage (8%) of material >25mm that has dropped post torrefaction. This is because of the vibratory nature of the torrefaction operation coupled with higher temperature within the reaction chamber that causes a small fraction of bulk material to disintegrate into smaller chips. The chips broken down have now fall under the 12.5mm-25.0mm range and thus shows an 8% increase.

4.1.9 Heavy metal concentration

Heavy metals such as Lead, Arsenic and Mercury are extremely harmful to human health. High levels of any form of these heavy metals will damage the brain, kidneys and will affect the next generations too[39].

Therefore, the EBC is very critical of these heavy metals within biochar specifically for soil and food related applications. The permissible limits for these toxic metals are shown in 4.7.

Heavy metals	Maximum Permissible Limit (mg/kg)
Lead (Pb)	150
Cadmium (Cd)	1.5
Copper (Cu)	100
Nickel (Ni)	50
Silver (Hg)	17
Zinc (Zn)	400
Chromium (Cr)	90

Table 4.7: Permissible levels for heavy metals in biochar

All the feedstocks on this list were tested for Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Vanadium and Zinc concentrations. Out of these heavy metals and contaminants, Mercury and Vanadium were not detected in any samples (except for waste wood which showed a small Mercury percentage(0.1%) and Tomato waste having 1.4% of Vanadium). The heavy metals Arsenic,Cadmium,Chromium and Lead are available in higher concentrations and are known to be the most toxic to humans and will therefore be discussed in more detail under this section. A value of ND indicates that the trace metal was not discovered or that its concentration was below the Minimum Detection Limit. The concentrations for these heavy metals are shown in 4.8

Name of the feedstock	Heavy Metal concentration (mg/kg)				
	Arsenic	Cadmium	Chromium	Lead	Nickel
Grape stems	0.8	ND	1.9	1.8	0.9
Bagasse	ND	0.2	2.3	1.2	1.9
Rice husks	ND	0.2	2.3	ND	3.8
Recycled wood	2.8	0.2	4.2	10.1	2.7
Miscanthus	ND	ND	3.4	1.3	1.5
Maize	0.4	0.2	3.7	6.5	1.4
Tomato residue	0.4	0.2	4	3.1	2.8
Washed shredded roots	ND	0.2	4.8	6.8	2.3
Pinewood chips	ND	0.2	1.6	1.8	1.7
PN Estonia Softwood	0.5	0.1	1	9.7	1.9
PN Estonia Biochar	0.4	0.1	2.3	3	1.3

Table 4.8: Heavy metal concentration in the raw feedstocks.

Arsenic Concentration

Arsenic ranks is one of the most lethal heavy metals even in extremely small doses(2-20 mg/kg) and thus has been classified as a group-A carcinogen[39]. Most of the Arsenic found in the earth occurs naturally from volcanic ash, weathering of rocks and in underwater sources. The WHO has a stringent regulation that the Arsenic concentration be lower than 10 parts per billion in drinking water as higher concentrations can lead to cancer, cardiovascular diseases and premature death. While the EBC does not have a limit for Arsenic,the International Biochar Initiative (IBI) recommends that the Arsenic concentrations when used for soil remediation applications strictly be within 100 mg/kg.

Cadmium Concentration

Cadmium is one the most active ingredients in battery production. Coupled with Nickel, this heavy metal is one the preferred electrode materials owing to a high voltage output during discharge operation. Cadmium exposure is common in Zinc extraction through mining as a small percentage of Cadmium naturally occurs in the Zinc ores. A small fraction of Cadmium is evolved during the purification of the ore to obtain pure Zinc.

Cadmium has a lower lethality as compared to Arsenic with lower concentrations of Cadmium causing brittle bones and kidney damage. The EBC recommends that the Cadmium concentration be lower than 1.5 mg/kg

Chromium Concentration

Chromium is one of a the most common elements found in the earths crust. However, continual exploitation of Chromium to bolster Iron over the past decades has led to its classification as a rare metal. Chromium, owing to its anti-corrosive properties is also the key ingredient in the production of stainless steel. This heavy metal exists in two forms, the trivalent form (+3) and the hexavalent form (+6). While the hexavalent form is toxic to humans, the trivalent form is an essential trace micronutrient for humans. The EBC specifies that the Chromium content be lower than 90 mg/kg for biochar used in soil applications.

Lead concentration

Lead is one of the most common heavy metals that is used in a plethora of modern applications. Some uses for Lead include batteries, ammunition and as barriers to prevent radiation or corrosive liquid leakage. More than 50% of the Lead produced today is used in the production of the Lead-acid battery. Lead exposure leads to a variety of issues such as anemia, weakness, and kidney and brain damage to humans and also unborn infants. Common lead exposure occurs from sniffing old paint residues or during construction and demolition work in various sectors. The EBC limits the Lead concentration to 150 mg/kg for commercial biochar.

4.1.10 Ash analysis

The importance of ash in supplying plant macro and micronutrients has already been established. Many essential elements such as Potassium, Silica, Magnesium, etc are present in their oxide form within the biomass material. It follows that the higher the ash percentage, the higher the concentration of these oxides within the feedstock. Out of these elemental oxides, the oxides of Silicon,Calcium and Potassium make up the majority(60%) of the ash, while the oxides of Aluminium,Iron,Titanium,Magnesium,Sodium,Manganese,Phosphorous and Sulphur constitute the remaining minority. The benefits of these elements are multi-fold from improvement in plant characteristics to lower water and fertilizer requirements. As these benefits have already been discussed in detail under the literature review chapter, the ash major and minor ash distribution percentage is listed in figures 4.4 and 4.5.

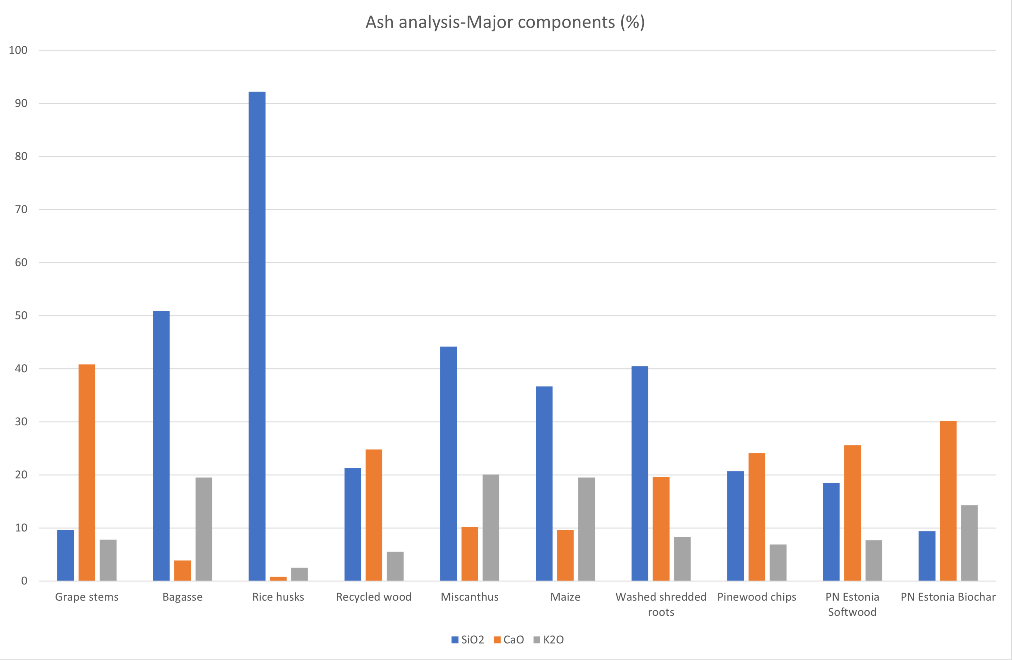


Figure 4.4: Major oxide concentrations in ash

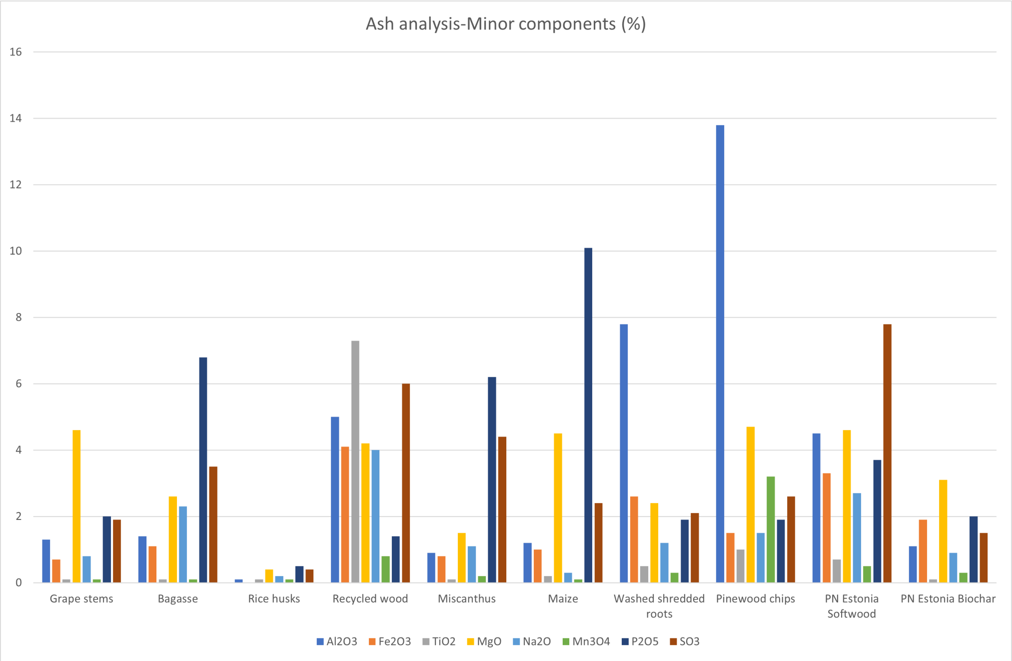


Figure 4.5: Minor oxide concentrations in ash

4.1.11 Economic analysis for the Plant Macronutrient requirements

The necessity of the plant macronutrients specifically Nitrogen, Potassium and Phosphorous for plant growth and overall development has been discussed with regards to specific macronutrient functions. However, this section aims to provide further knowledge on the terminologies involved as well as an initial financial estimate for the macronutrient addition to the biochars. Most compound fertilizers will contain three elements essential for growth, NPK which stands for Nitrogen (N) Phosphorus (P) and Potassium (K). Though Nitrogen, Phosphorus and Potassium, are the “Big 3” primary nutrients in commercial fertilizers, Sulphur (S) is also a major element that gets added in virtue of adding the NPK nutrients. As seen under the ash analysis, feedstock materials that contain higher ash percentage will ultimately have higher macronutrient concentrations. Therefore raw materials including RH, WS, BG and TW already contain a higher fraction of the required NPK’s and thus a smaller macronutrient addition will suffice.
Commercially, these nutrients are not added in their elemental form (N,P,K) as these elements are highly unstable on their own, but rather are mixed with an organic base in the form of its respective compounds (Oxides/Sulphides) which in turn ensures that these elemental nutrients reaches the roots of the plants.[89] These macronutrients are normally supplied by various fertilizers and growth stimulants by careful selection of these macronutrient in the required form. An overview of these macronutrients in commercial fertilizers in shown in table 4.9.

Understanding Fertilizers and NPK ratios

1. NPK ratios are listed as whole numbers separated by a hyphen (-). These numbers range anywhere from 0-100. In short, the three numbers on fertilizer represents the value of the three macro-nutrients Nitrogen (N), Phosphorus (P) and Potassium (K) or NPK for short. The higher the number, the more concentrated the nutrient is in the fertilizer.
2. First Number- (N value)- Is the percentage of elemental Nitrogen by weight in the fertilizer. Second Number- (P value)- Is the percentage of P2O5 by weight in the fertilizer. Third Number- (K value)- Is the percentage of K2O by weight in the fertilizer.
3. For example, a fertilizer having 15-13-20 fertilizer would contain 15% by weight of Nitrogen, and the same amounts of phosphorus and potassium as a mixture of 13% by weight of P2O5, 20% K2O, and 52% of some inert ingredient.
4. Since the values for Phosphorous and Potassium are linked to the weight of its compounds, the following expressions help us isolate the values for the elemental P and K.

5. Elemental P- 0.436 *P Value
Elemental K- 0.83 * K Value.
6. So, for example, an 185120 fertilizer contains by weight, • 18% elemental nitrogen, • 0.436 × 51 = 22% elemental phosphorus, and • 0.83 × 20 = 17% elemental potassium.
7. The UK scenario- In the U.K., fertilizer labelling regulations allow for reporting the elemental mass fractions of phosphorus and potassium. The regulations stipulate that this should be done in parentheses after the standard N-P-K values, as in "15-30-15 (15-13-13)”

So, what do these number mean for the nutritional requirements of different plants? It is fairly certain that different plant forms will require different concentrations of these plant macronutrients. Grassy turfs and fast growing grassy crops such as Miscanthus and Elephant grass will need higher concentrations of Nitrogen (N.P.K. (20-10-10)). Flowering fruits require higher Potassium and Phosphorous content to help flowers grow faster and reach a healthier maturity stage (NPK(5-10-10)).Flowering bulbs in Horticulture depend on phosphorus for deep and healthy roots (NPK(6-12-0/ 10-10-10)).In general, a perfect all-purpose blend for satisfactory results for most crops results from a balanced blending (15-15-15/20-20-20) and thus these are the most common blends in which fertilizers are available worldwide. A detailed overview of all possible crop and their NPK requirements are maintained by the agricultural department in the university of Georgia[35].

Final mixing ratios of the NPK minerals along with a generic biochar.

The overall mixing ratios for the individual constituents are described in this section. The biochar taken into consideration is sourced from forestry waste and a blending ratio of 20-20-20 and an application rate of 10 t/ha(Commercial blending ratio of the mix in the soil is of the range of 10 to 20 tonnes/hectare) is considered. The detailed breakdown for the other feedstock materials are discussed in the economics section. To make 1 Kilogram mixture of biochar NPK we require-
1)10 to 20% Perpetual biochar in the mix-Maximum of 200gms

2)2.66 gms of (20-20-20) fertilizer. (A good NPK application ratio is 1 part of NPK for every 75 parts of biochar applied, with the highest shown NPK value at 1 part for 45 parts of biochar[64])

3)The remaining must be a soil/organic substrate-797.34 gms of peat/ traditional potting soil.

This breakdown is shown in figure 4.6.

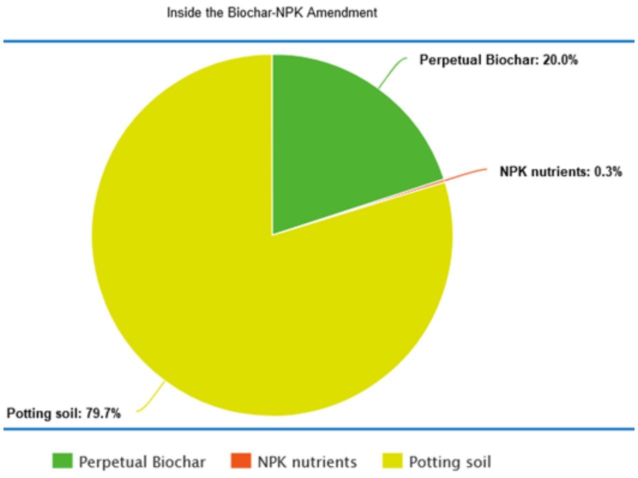


Figure 4.6: Mass based distribution of the biochar, substrate and macronutrients in the blended mixture

It is vital to create a baseline cost for realising this blended biochar as well to help us make a comparative analysis for all the other feedstocks. The NPK cost reference is taken from online e-commerce sites. The biochar costs are based on commercial research and are only meant as a indicative reference.
Overall Costs for making 1 kg Biochar+NPK mix.

The costs are computed in this section in sourcing and producing 1 kilogram of this blended biochar mix.
- Biochar cost- 300 Euro/tonne-6 cents per 200 gms.
- NPK cost - 21 Euro/kg- 5 cents for 2.66 gms.
- Soil cost-2 Euro/10 liters- 20 cents per 780 gms.

Total cost for making 1 kg of the blended NPK and Biochar is 26.08 Cents which in turn translates to 260.8 Euro/tonne. The distribution of costs is shown in figure **??** and it is interesting to see that though the macronutrients only account for 0.3% of the total fraction by weight, it takes up roughly around 36% of the total costs by value. This shows that these macronutrients are expensive and must be judiciously used.

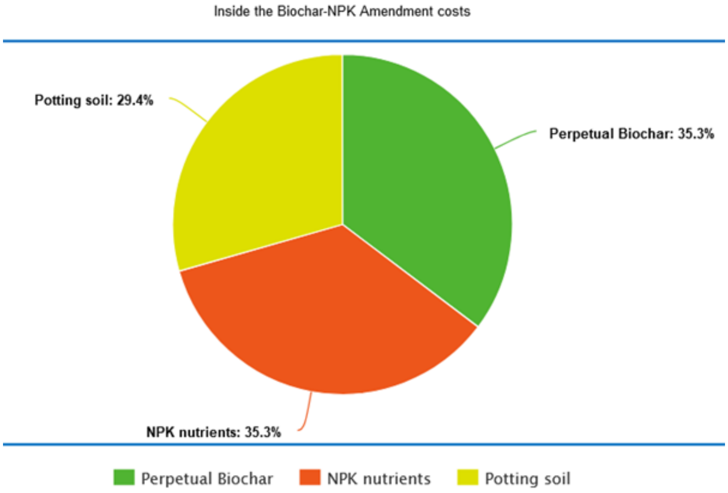


Figure 4.7: Cost distribution of the biochar, substrate and macronutrients per kg of blended mixture

Macro Nutrient	**Compound Form**	**Formula**	**Description**
Nitrogen	Ammonium Sulphate	$(NH_4)_2SO_4$	Contains 21% Nitrogen and 24% sulphur.Relatively cheap and very stable,but has lower Nitrogen content
	Ammonium Nitrate	NH_4NO_3	Contains 34% Nitrogen. Relatively expensive and has higher nitrogen content available for release, but it very unstable and tends to explode when in contact with heat. Also a major constituent in explosives.
	Urea	CH_4N_2O	Highest Nitrogen content of 46%. More expensive than Ammonium Nitrate and is the most commercially used component in modern fertilizers. The only problem is with the release of Nitrogen in the form of Ammonia through chemical reactions in the soil. This results in lower Nitrogen available for soil use.
Phosphorous	Triple Super Phospate	Na_3PO_4	Most used form of Phosphorous in fertilizer.Contains 46% of di-phosphorus pentoxide (P_2O_5)which is the main chemical which releases phosphorous into the soil.
	Mono Ammonium Phospate	$(NH_4)H_2PO_4$	Most preferred form of Phospate due to availability in the US and elsewhere. Contains 52 % Phosphorous in the form of P_2O_5 and also has 11% of Nitrogen.
Potassium	Muriate Of Potash	KCl	Unlike the other nutrients, Potassium is usually found in a variety of substances generally called Potash. The most commonly used form of Potash in fertilizer is Muriate Of Potash. Potassium is dissolved in salt form (KCl) of the range 95–99%

Table 4.9: Most common forms of NPKs

4.2 Regression Analysis for surface area and porosity

An important part of understanding a materials efficacy in its use as a soil enhancer is in its surface area and porosity measurement. A biochar exhibiting higher surface area shows that it can adsorb or desorb critical elements more effectively owing to a more available area to facilitate the process. Similarly, the presence of a higher degree of porosity also indicates its potential use to trap certain macronutrients allowing for its slow release over time. Commercially there are numerous techniques that can be used to measure the surface area and porosity for a given feedstock material including gas or liquid adsorption and pycnometry.

As is the case with most experiments, these techniques are quite expensive, time consuming and actually require the physical torrefied sample to complete the measurements. The surface area and the total pore volume are closely tied to the nature of the biochar feedstock and the torrefaction temperature. Therefore, a regression analysis was performed by analysing global research and isolating those feedstocks that are common and have a lot of data points available for analysis.

A total of 196 and 157 data points for Surface area and Porosity were isolated from research across the world with pyrolysis temperatures in the range of 200 to 800 °C. Biochars that have been activated or have had some special pre/post treatment done have not been included for this study. These data points were then averaged and made to fit a linear regression model that can then be used to approximately predict the surface area and the total pore volume of a feedstock material at a given temperature. The results from this regression analysis is depicted below and the database and calculations are included in the appendix.

4.2.1 Surface area regressions

A total of seven materials were selected for the surface area regression analysis. These materials include Wheat straw, Bagasse, Maize straw, Rice husks, Pinewood chips, Oak wood and Miscanthus. The intention behind the selection of the feedstocks is to check for the soundness of the model from the BET analysis for the feedstocks as well as to have an indication for agricultural residues and wood chips.

Traditionally, a high Carbon content and a low ash content promote a higher surface area post torrefaction and consequently, woody feedstocks exhibit a higher surface area as compared to grassy feedstocks, agricultural residues and other organic sludge [78]. The surface area has shown to increase with an increase in the torrefaction temperature and pH. Also, certain feedstocks do show a characteristic dip in surface area and porosity only at elevated temperatures (>450 °C). This is due to the decomposition of lignin over a wide range of temperatures (150-900 °C) in lignin rich feedstock materials [69]. This results in a slight decrease in the surface area and a departs from the usual behavior.

According to a research by Lijian Leng et al. the optimal pyrolysis conditions required for producing biochar of high specific surface area and porosity include using a moderate temperature in the range of 400-700 °C, a low heating rate in the range of 5-30 °C per minute and a long residence time in between 30 to 120 minutes. They also have identified that most common biochars have a surface area in between 8-132 m^2/g and a porosity of 0.016-0.083 cm^3/g with the micropores accounting for the majority of the pores under these operating conditions[78].

Bagasse, Rice husks

The surface area modelling predicts a low overall surface area for bagasse and rice husks. This is expected considering rice husks have the highest possible ash content of 23%. The low value for bagasse is inherent to the material and could be attributed a low fixed Carbon percentage of 15%.Similar to other materials that show a characteristic dip at elevated temperatures, bagasse and rice husks too shows a noticeable drop at temperatures above 600 °C owing to a high lignin content(17-20%). There has been some research done with regards to this lignin removal using Sodium chlorite with a good degree of success[100].

Maize, Micanthus, wheat straw

Maize, Miscanthus and wheat straw show a fluctuating trend at the lower temperature ranges of 200-400 °C with a steady increase in the moderate temperature range of 400-700 °C. There is a sharp and noticeable increase at temperatures above 700 °C. This steep increase in the surface area has also been exhibited by other materials and is attributed to the completion of the carbonization process to the maximum possible extent[38].

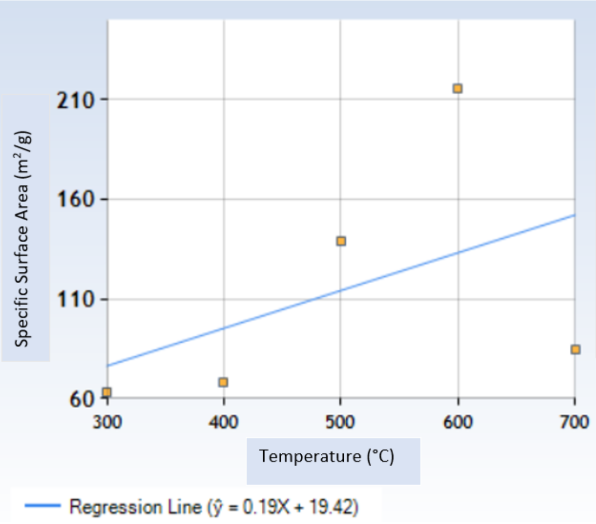


Figure 4.8: Surface area regression for bagasse biochar

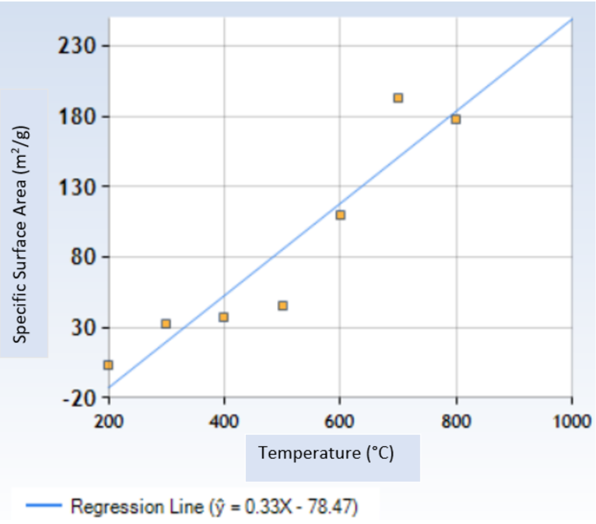


Figure 4.9: Surface area regression for rice husks biochar

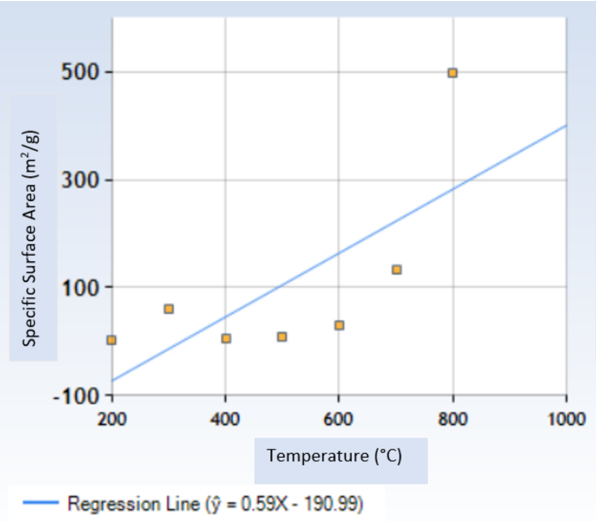


Figure 4.10: Surface area regression for maize biochar

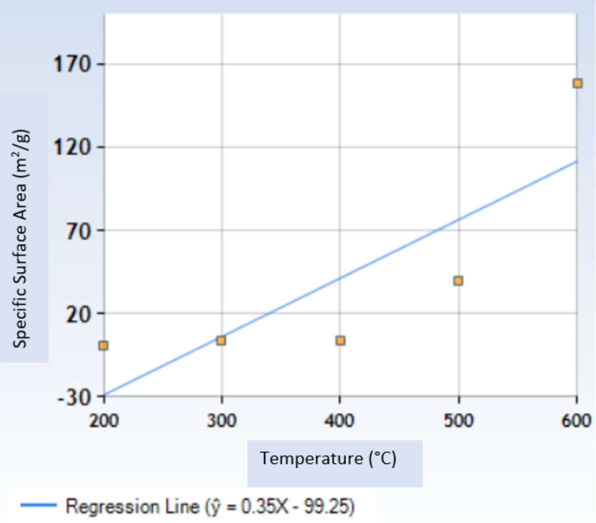


Figure 4.11: Surface area regression for miscanthus biochar

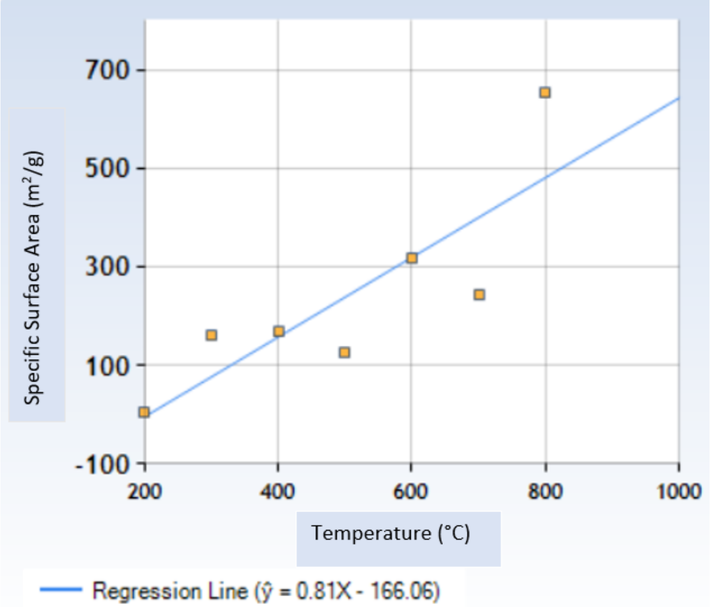


Figure 4.12: Surface area regression for wheat straw

Oak and pinewood chips

The highest values for the surface area belong to the woody feedstocks. These materials have a high Carbon percentage and a low ash percentage which in turn result in a much higher values for the surface area ranging from 60-400 m^2/g. These materials show a increasing-decreasing trend in the lower temperature regimes and a linear increase in surface area at elevated temperatures.

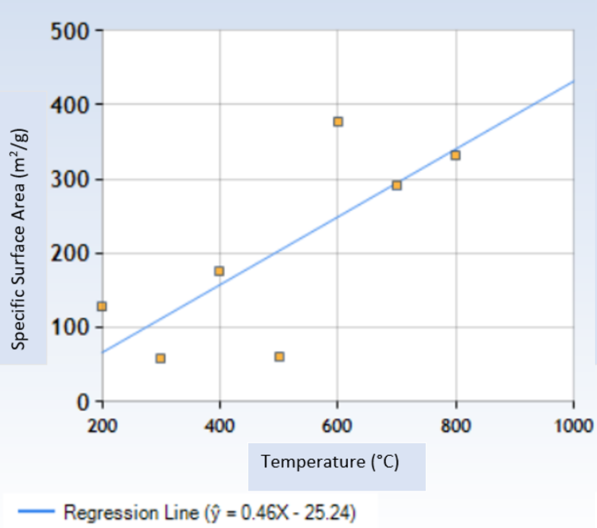


Figure 4.13: Surface area regression for oak wood biochar

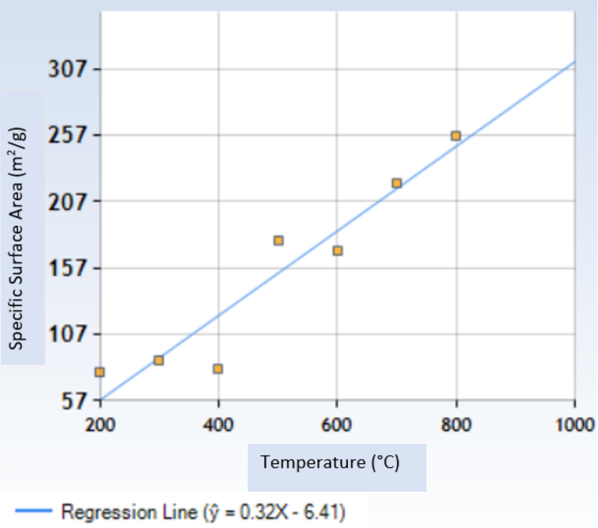


Figure 4.14: Surface area regression for pinewood biochar

4.2.2 Porosity modelling

The existence of a porous, honeycomb microstructure within biochar has been established by the scientific community. Just the presence of such a microstructure does not guarantee effective nutrient absorption and cycling. The size of these pores along with its distribution across the entire surface are the key parameters in helping us understand the biochar's impact on soil remediation and plant growth. Pores are evolved in biochar through dehydration of water molecules along with other volatile components at elevated temperatures which results in steam and other hot gases escaping the core of the substance by creating porous channels [15]. The porosity value is strongly interconnected to the surface area of a material and micropores make up the majority of the pores. Similar to the surface area, higher temperature leads to more porosity and a high ash percentage leads to pore blockage and acts as is detrimental for achieving a homogeneous microporous structure. Generally these pores have shown good promise for absorbing both organic (dyes, pesticides and other Volatile Organic Compounds) and inorganics (Phosphorous, Nitrogen and other heavy metals)[81].
The materials selected for the porosity modelling include Bagasse, Maize straw, Bamboo, Pinewood chips, commercial hardwoods, rice husks and coconut husks In this section, the total pore volume is subjected to regression analysis over a temperature range from 200-800 °C.

Porosity regression for Coconut husks, Rice husks,pinewood chips,commercial hard wood and bagasse

These materials are grouped together as they show similar behaviour at elevated temperatures. All the chars listed in this group including Coconut husks, Rice husks,pinewood chips and hard wood show a linear increase in porosity from 200-400 °C. There is a drop in porosity for these materials at the medium temperature range of 400-600 °C and this could be attributed to the complete release of volatiles within the 200-400 °C range. Therefore a further increase in porosity is not noted even though the temperatures are increasing [33]. There is a sharp increase in porosity in almost all the materials (except maize) and this could be attributed to the conversion of amorphous Carbon into crystalline Carbon through condensation. This in turn results in more volatile being removed creating interstitial gaps and cracks which result in a more porous structure [47].

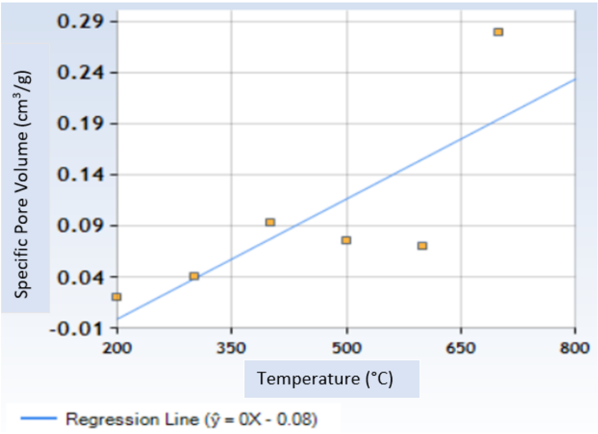


Figure 4.15: Surface area regression for maize biochar

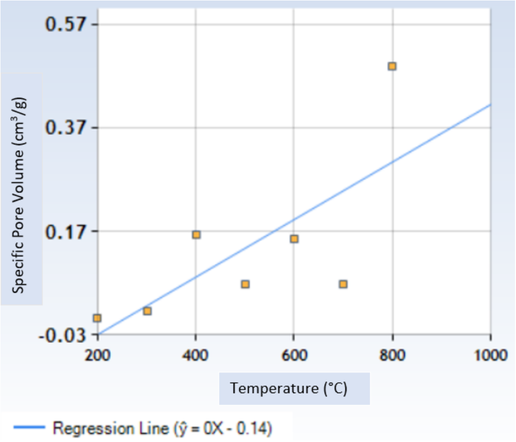


Figure 4.16: Surface area regression for miscanthus biochar

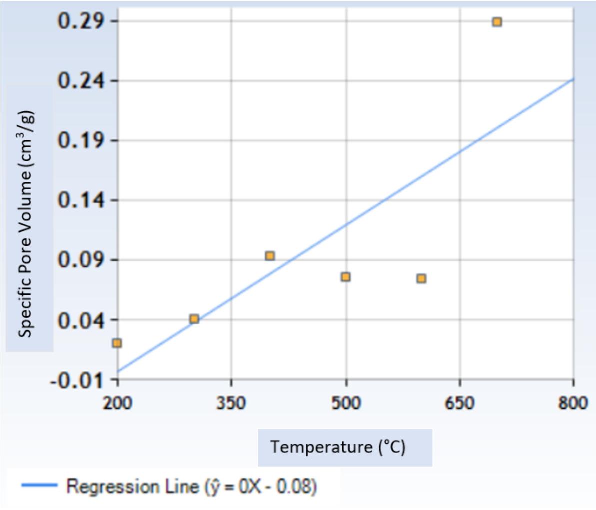


Figure 4.17: Surface area regression for maize biochar

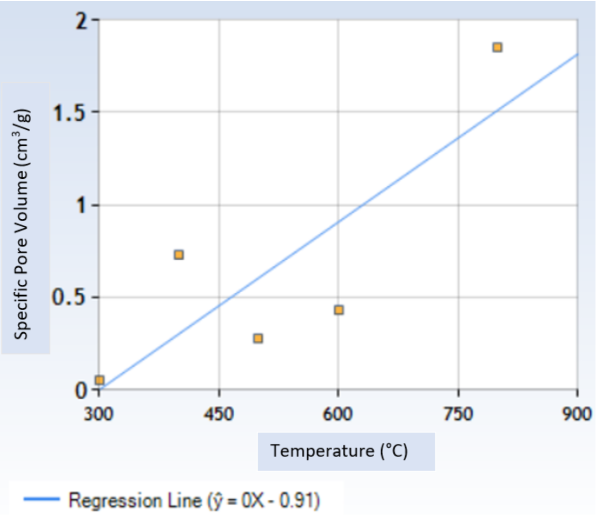


Figure 4.18: Surface area regression for miscanthus biochar

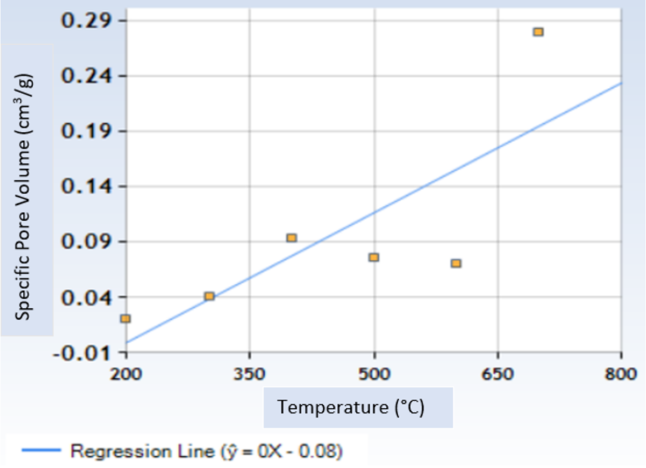


Figure 4.19: Porosity regression for Bagasse

Porosity regression for Bamboo and Maize

The char produced from Bamboo and maize show interesting trends with increasing temperature. While the Bamboo biochar shows a highly fluctuating trend at lower and higher temperatures, the Maize biochar shows a noticeable increase till 500 degrees and then a steep decrease at higher temperatures. Both of these feedstocks show a marked departure from expected porosity values. The Bamboo has most of its volatile constituents released in the range of 250 to 400 °C which can be seen from the increase in porosity for this temperature range. Further increase in temperature results in inorganic blocking the pores for an intermediate duration. Any further increase in temperature results in the formation of more pores through phase changes occurring in the Carbon microstructure. The maize biochar has a very high volatile matter content coupled with a extremely high initial moisture percentage. These factors could affect the pore developing mechanisms and result in a low micropore volume which does not increase with an increase in temperature.

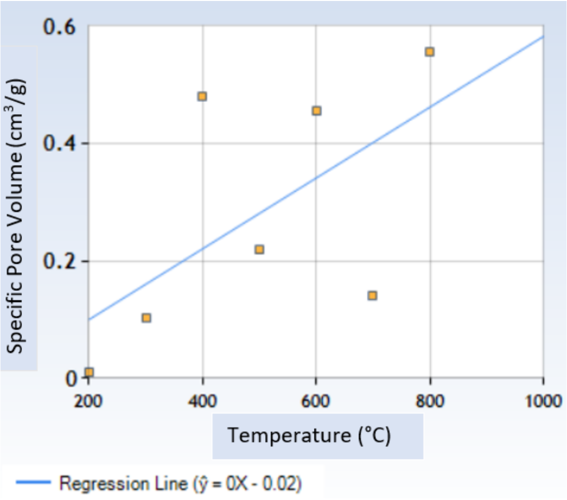


Figure 4.20: Surface area regression for maize biochar

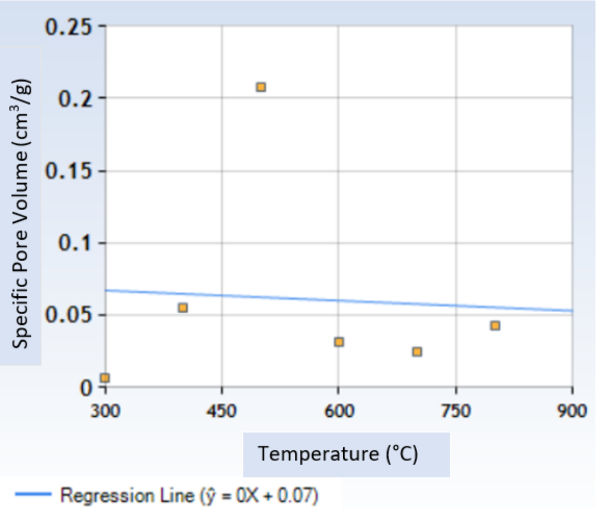


Figure 4.21: Surface area regression for miscanthus biochar

4.2.3 Inferences from the surface area modelling

For most of the materials subjected to regression analysis, there exists a striking trend that is visible for the surface area data points at lower temperature zones (200-400) and higher temperature zones (400-800). These zones will be separated into two distinct regions of operation and the results from the actual experimentation will be compared with lower temperature zone operation. Do note that for some materials (such as bagasse and oak wood char) this linear behaviour is only shown at higher temperature zones above 500 or 600 °C. The linear regression model will hold good in the higher temperature of operation owing to its linear nature at the higher temperature regimes. However, at lower temperature regimes, the linear model will only approximate the values with a significant deviation from normal observations. Therefore a different approach is taken for the lower temperature operation for comparison.

Impact of lower and higher temperature zone operations on surface area

The data points from the surface area modelling indicate that at lower temperature pyrolysis between 200 and 400 °C the values are close to each other and a drastic increase cannot be observed for most of the feedstock. This region will be termed as the plateau zone owing to the data points following an equation that closely represents a line that is parallel to the X-axis. A separate equation based on the observed Y-intercept will be recommended for this temperature and the same will also be used at a later stage to compare the experimental values with the regression model.

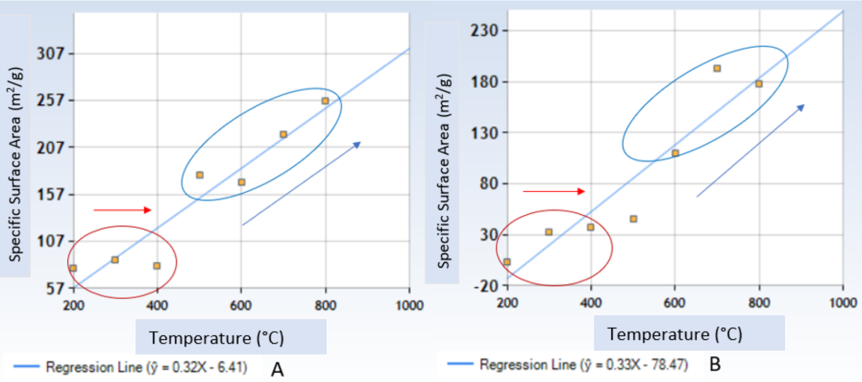


Figure 4.22: Trends observed in surface area regression for Rice husks(A) and pinewood chips(B)

Figure 4.22 represents the plateau (represented in red) and linear(represented in blue) zones observed in most materials. The exact rationale behind this behaviour has already been discussed in the regression analysis section, but the key proponent for this behaviour is attributed to the decomposition of cellulose, lignin and certain other volatiles only at elevated temperatures. The governing equations are therefore recalculated based on the average Y-axis intercept at this temperature range and are represented in table 4.10.

Biochar material	Low temperature pyrolysis (200-400°C)	High temperature pyrolysis (400-800°C)
Wheat straw	Y=50.3	Y = 0.80X - 166.05
Bagasse	Y=43.9	Y = 0.18X + 19.41
Maize straw	Y=3.6	Y = 0.59X - 190.98
Rice husks	Y=24.2	Y = 0.32X - 78.46
Pine wood chips	Y=3.5	Y = 0.31X - 6.41
Oak wood	Y=120.7	Y = 0.45X - 25.23
Miscanthus	Y=2.8	Y = 0.35X - 99.24

Table 4.10: Low and High temperature predictions by regression analysis

The results from the low temperature analysis are compared with actual measurements in the section on BET analysis.

4.3 Post torrefaction experiments

The torrefied biochars are characterized and subjected to a variety of tests to identify their strengths and evaluate their overall performance when specifically applied for horticulture. To this end, the base characterization similar to the raw material is performed as well as pH, BET and SEM-EDS analysis. The results from these characterizations are discussed in this section.

4.3.1 Proximate Analysis

Volatile matter

The torrefaction process leads to the release of moisture and light components as volatile matter which manifests itself as mass loss.

Name of the feedstock	Volatile matter (%)		Percentage Change
	Before torrefaction	After torrefaction	
Miscanthus	82.6	26.2	56.4
Washed shredded roots	78.1	22.9	55.2
Bagasse	81.4	27.6	53.8
Wood waste	81.8	28.1	53.7
Pinewood chips	85.7	32.2	53.5
Maize	80.1	28	52.1
Rice husks	61.3	16.3	45
Tomato waste	71.3	29	42.3
Wine stems	74.3	33.2	41.1

Table 4.11: Volatile matter for all the biochars

The feedstock materials lost about 41-56% of their initial volatiles, with the herbaceous feedstocks falling on the higher loss percentage side and the woody feedstocks falling on the lower loss percentage side. The torrefaction temperature is the key determinant for the amount of volatiles left over in the material post torrefaction. At higher torrefaction temperatures (350 °C and higher),there is a much more pronounced release of volatiles within all the feedstock materials.

Fixed Carbon

The fixed Carbon percentage is expected to increase in a material post torrefaction. This is due the volatile and other temperature sensitive materials leaving the material as opposed to extra Carbon getting added to the material. This is the intention of torrefaction and other similar Carbonization processes to develop a material with a significant Higher Heating Value.

Name of the feedstock	Fixed Carbon (%)		Percentage Change
	Before torrefaction	After torrefaction	
Miscanthus	15.8	69.3	53.5
Pinewood chips	13.6	67	53.4
Wood waste	16.6	68.6	52
Bagasse	15.8	67.2	51.4
Washed shredded roots	18.4	69.1	50.7
Maize	15.7	59.1	44
Wine stems	20.8	57	36.2
Rice husks	15.8	26.4	10.6
Tomato waste	17.1	12.2	-4.9

Table 4.12: Fixed Carbon for all the biochars

A quick comparison between the materials that lost the most volatiles and the materials that gained a siginificant percentage of fixed Carbon clearly shows the Carbon enrichment process.

Miscanthus	Miscanthus
Washed shredded roots	Pinewood chips
Bagasse	Recycled wood
Recycled wood	Bagasse
Pinewood chips	Washed shredded roots
Maize	Maize
Rice husks	Grape stems
Tomato residue	Rice husks
Grape stems	Tomato residue

Figure 4.23: Volatiles lost v/s Carbon enriched

While most of the chars show a significant improvement in the Carbon concentrations, the rice husks char shows only a slight increase and the tomato residue char shows a decrease in the overall fixed Carbon percentage. This is due to a high increase in its ash concentrations as discussed in the next sub-section.

Ash content

Similar to the fixed Carbon percentage, the ash content for the lignocellulosic biomass concentrates during the torrefaction process. The tomato residue char as well as the rice husk char had a significant increase (500% and 250% respectively) in ash concentrations. The low value for fixed Carbon coupled with high ash concentrations indicate that these chars should not be recommended for combustion applications.

Name of the feedstock	**Ash (%)**		**Percentage Change**
	Before torrefaction	After torrefaction	
Tomato waste	11.6	58.8	47.2
Rice husks	22.9	57.3	34.4
Maize	4.2	12.3	8.1
Wine stems	4.9	9.8	4.9
Washed shredded roots	3.5	8	4.5
Miscanthus	1.6	4.5	2.9
Bagasse	2.8	5.2	2.4
Wood waste	1.6	3.3	1.7
Pinewood chips	0.7	0.8	0.1

Table 4.13: Ash concentrations for all the chars

Moisture content

The majority of the free moisture present superficially on the surface of the feedstock is removed during the initial heating and pre-drying stages of torrefaction. Do note that though these torrefied materials are hydrophobic to a degree, they tend to absorb some moisture from the atmosphere and thus a few feedstocks show a slightly increased moisture percentage post torrefaction. Also, the moisture percentages reported in this table are on an as analysed form and have been pre-dried from their initial moisture content before they were tested.

Name of the feedstock	**Moisture (%)**		**Percentage Change**
	Before torrefaction	After torrefaction	
Wood waste	19.7	6.6	13.1
Bagasse	17	5.5	12.5
Tomato waste	15	7.4	7.6
Miscanthus	12.2	5.4	6.8
Rice husks	9.3	7.5	1.8
Pinewood chips	7.9	6.4	1.5
Maize	7.5	6.7	0.8
Washed shredded roots	5.5	6.3	-0.8
Grape stems	5.6	7.1	-1.5

Table 4.14: Moisture content for the feedstocks

4.3.2 Ultimate Analysis

The C, H, N, O, S percentages are measured and used in the Calorific prediction analyses. The ultimate analysis was also used to calculate the H/C, O/C, C/N molar ratios. These are plotted in van Krevelen diagram to indicate the stabilibty, aromaticity and polarity of the samples.

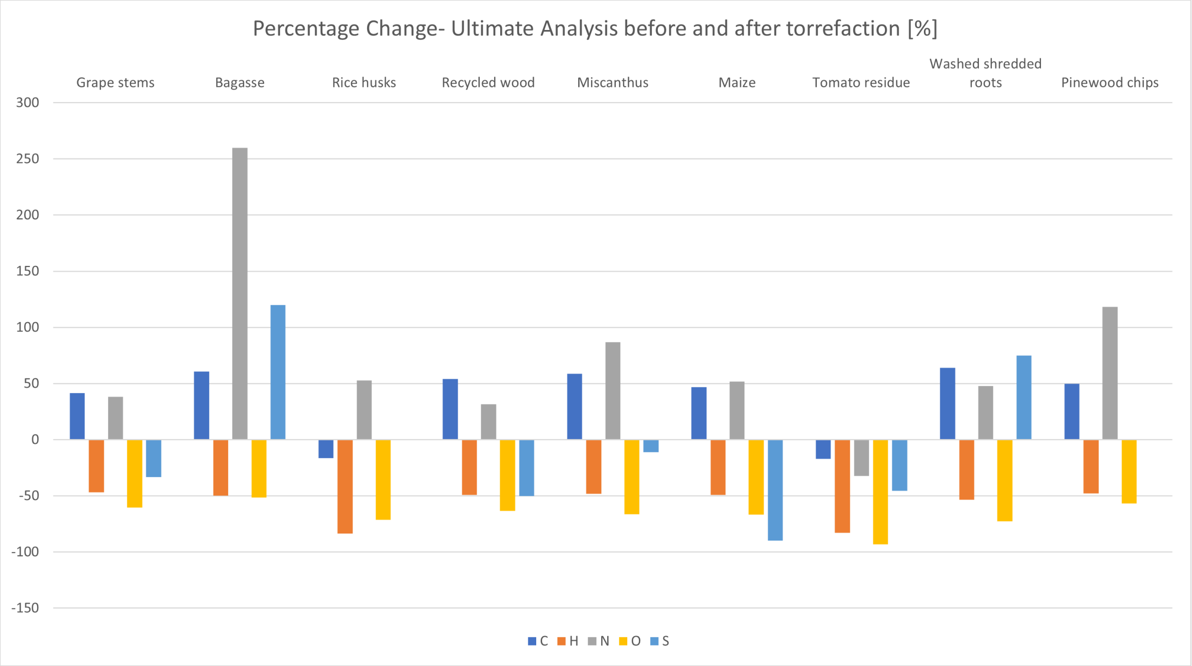


Figure 4.24: The percentage change in ultimate analysis before and after torrefaction.

Torrefaction results in a net increase in Carbon and Nitrogen with a net decrease in hydrogen and oxygen as the torrefaction severity increases.The highest increase(>60%) in Carbon content post torrefaction can be observed for the washed shredded roots and the bagasse biochar. This can be directly coupled with the relatively lower position in the Van-Krevelen diagram for feedstocks numbered 8 and 2. The Bagasse biochar showed a steep increase in the nitrogen concentration post torrefaction. This indicates that the bagasse biochar might have an affinity for the nitrogen gas which was used as the inert carrier gas within the torrefaction chamber.The expected Carbon and Nitrogen increase is showcased by almost all the biochars except for the rice husk which showed a net decrease in Carbon(-6%) and tomato residue which showed a net decrease in Carbon(-7.4%) and Nitrogen(-0.6%).

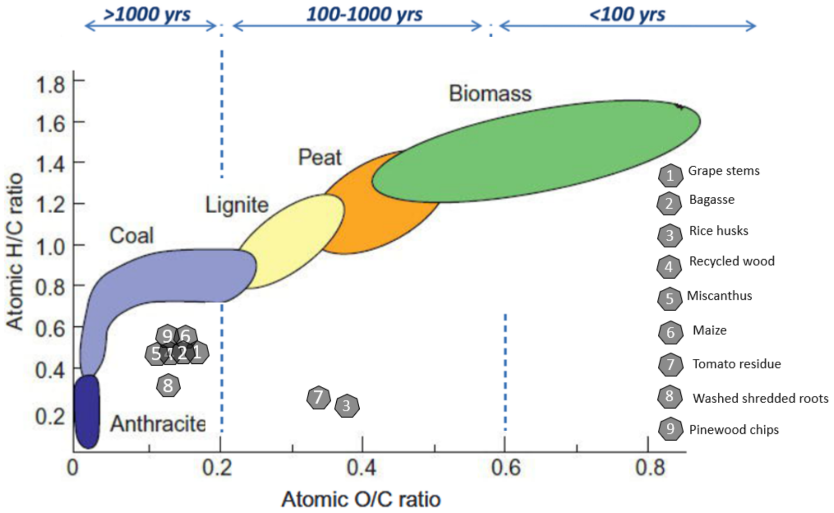


Figure 4.25: The H/C and O/C for the biochars plotted on the Van Krevelen diagram

4.3.3 Calorific Value

The Calorific values of the torrefied material depend on the initial calorific value as well as the torrefaction temperature. These CV measured using the bomb calorimeter along with the results from the modelling correlations according to Boie, Milne and Friedl et al. will be tested. The corresponding equations can be found under 4.1.2, 4.1.3, 4.1.4, 4.1.5.

Effect of torrefaction on the CV

The overall comparison between the raw feedstock and the torrefied feedstock is made to ascertain which feedstock gained a significant CV increase post torrefaction.

Biochar	**LHV (kJ/kg)**		**Total LHV increase (kJ/kg)**
	Before torrefaction	After torrefaction	
Bagasse	18049	29066	11017
Miscanthus	17812	28717	10905
Wood waste	18728	29228	10500
Washed shredded roots	18481	28448	9967
Pinewood chips	19240	29017	9777
Maize	16418	26045	9627
Wine stems	18537	26244	7707
Rice husks	14751	11854	-2897
Tomato waste	15324	12221	-3103

Table 4.15: LHV for the biomass feedstocks and the torrefied chars

As expected from the fixed Carbon and ash analysis, the rice husks and tomato residues had a net decrease in the LHV post torrefaction. This indicates that these materials do not respond well to torrefaction and might require higher operating temperature regimes. The highest gainers from the torrefaction process were the Bagasse, Miscanthus and recycled wood char with an overall CV increase of 10,500-11,000 kJ/kg. The other feedstocks too were not far behind with the shredded roots,pinewood chips, maize residues, the grape stems char showing a pronounced increase in the LHV too.
The HHV or the Gross CV is computed first for the different feedstocks. While the Boie and Friedl et al. correlation requires the Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur concentrations, the Milne equation requires an additional ash concentration as well as an input.

Biochar	**HHV (kJ/kg)**		
	Boie Correlation	Milne Equation	Friedl et al. Correlation
Wine stems	26708	26079	26307
Bagasse	27031	26365	27632
Rice husks	10701	9472	16453
Wood waste	28232	27792	28802
Miscanthus	29007	28430	29095
Maize	25999	25301	25565
Tomato waste	13495	12248	16697
Washed shredded roots	28550	27855	28053
Pinewood chips	29200	28692	29809

Table 4.16: The predicted HHV for the different chars

The LHV (or LHV) is computed using equation 4.1.2 and is compared with the LHV measured using the bomb calorimeter apparatus. The deviation is also measured to give an indication as to which model gives a better fit for the data obtained.

Biochar	**LHV (kJ/kg)**				**Error (%)**		
	Measured	Boie Correlation	Milne Equation	Friedl et al. Correlation	Boie Correlation	Milne Equation	Friedl et al. Correlation
Wine stems	26244	26082	25452	25681	0.62	3.02	2.15
Bagasse	29066	26401	25735	27002	9.17	11.46	7.10
Rice husks	11854	10543	9314	16295	11.06	21.43	37.47
Wood waste	29288	27352	26912	27922	6.61	8.10	4.66
Miscanthus	28717	28352	27776	28440	1.27	3.28	0.96
Maize	26045	25352	24655	24919	2.66	5.34	4.32
Tomato waste	12221	13300	12053	16502	8.83	1.38	35.03
Washed shredded roots	28448	28008	27314	27512	1.55	3.99	3.29
Pinewood chips	29017	28501	27992	29110	1.78	3.53	0.32

Table 4.17: The LHV predictions using the Boie, Milne and Friedl et al. correlations

4.3.4 Chlorine content

The Chlorine concentration within a material causes numerous boiler problems and adds to overhead maintenance costs. This Chlorine needs to be removed during the pre-processing step. Out of all the materials, only the tomato residue char and the washed shredded roots showed a net decrease in the Chlorine concentration. All the other chars reported a no net change while a few chars including maize, miscanthus and rice husks showed an increase in the Chlorine concentration.

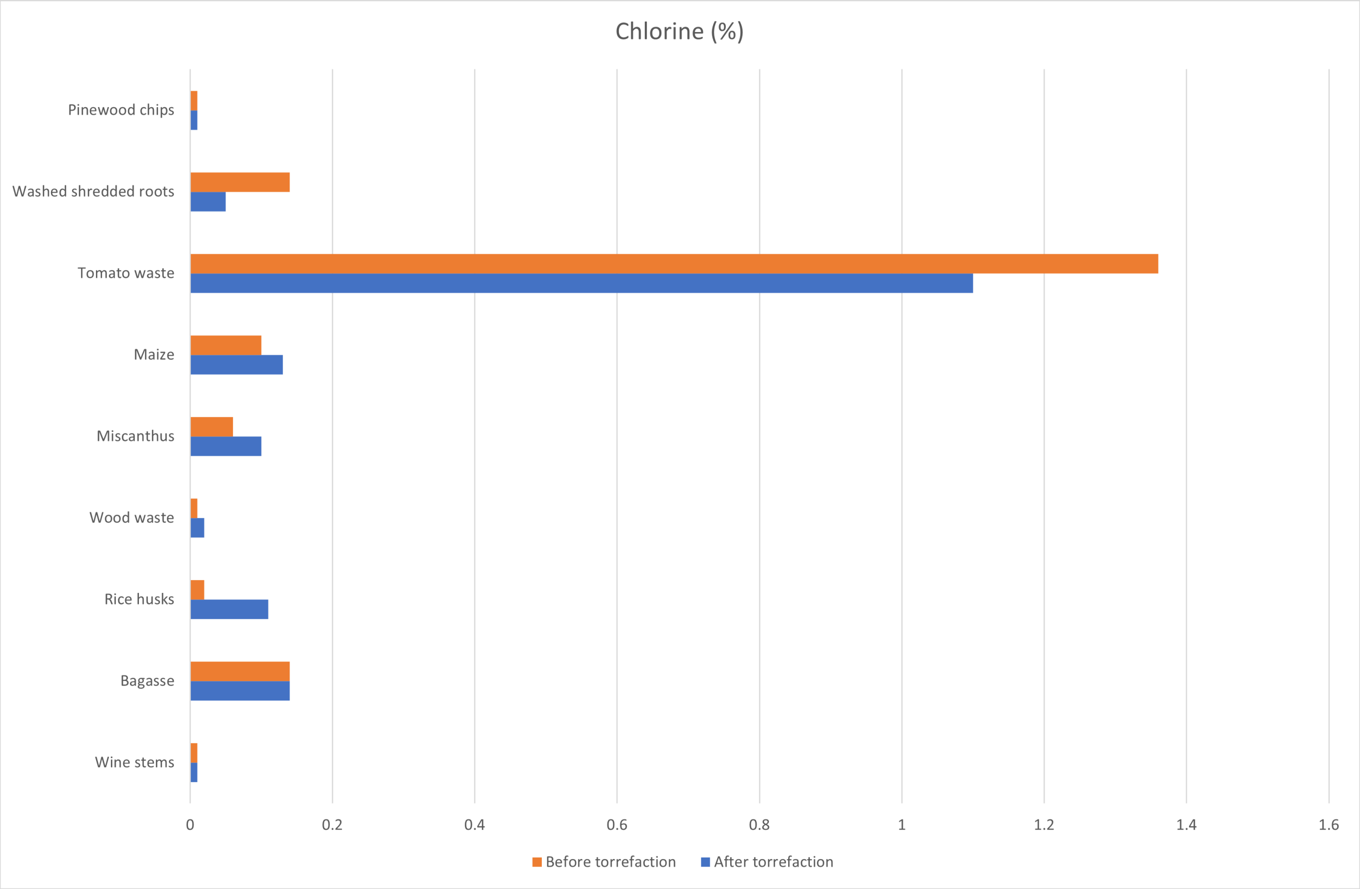


Figure 4.26: Chlorine concentration before and after torrefaction

4.3.5 pH

The results from the pH experimentation is shown in table 4.18 .

Material	**pH**				**Major Ash Oxide**	**Acidic/Basic Oxide**
	Initial	After 48 hours	After 72 hours	Average		
Tomato residue	6.98	10.41	10.81	10.61	K_2O	Basic
Recycled wood	6.98	9.36	9.57	9.42	CaO	Basic
Maize straw	6.98	8.93	9.47	9.2	CaO	Basic
Sugarcane bagasse	6.98	8.85	9.47	9.16	$SiO_2 + ZnO$	Basic
Grape stems	6.98	8.97	9.23	9.1	CaO	Basic
Washed shredded roots	6.98	8.86	8.80	8.83	ZnO	Basic
Miscanthus	6.98	8.58	9.01	8.8	SiO_2	Acidic
Rice husk	6.98	8.42	8.85	8.64	SiO_2	Acidic
Pinewood chips	6.98	8.25	8.85	8.55	$CaO+Al_2O_3$	Acidic

Table 4.18: pH for the feedstocks and the major oxide concentration in ash for the biochars

The base used to make the biochar solution was distilled water which had an initial pH of 6.98. As expected, feedstock materials sourced from agricultural and green house residues showed a much higher pH in comparison with woody materials owing to their higher mineral ash content. This higher pH value can be attributed to the higher ash content (4.1 which in turn leads to higher percentage of in-organics which makes the char basic and increases the pH value. All the nine biochars tested resulted in a high pH value pushing it in the regime of moderately basic to basic. The material with the highest pH is the tomato residue with an average pH of 10.61. This can be directly linked to its high ash percentage of 11.6 % of which Potassium Oxide makes up a high percentage(30%) thereby making the char extremely basic.

The recycled wood and the maize straw char ranked second and third in basicity with average pH values of 9.42 and 9.2 making these chars a good candidate for acidic soil remediation. Calcium Oxide is the dominant ash component(24.8%) in waste wood which is strongly basic and a combination of Calcium Oxide and Potassium oxide(29.1%) causes higher basicity in maize straw. According to a research by Mengyang et al., a biochar with a basic pH can increase the overall soil pH by 0.5-1 over a 28 day period[121]. The other feedstocks in comparison have a lower pH but are still basic enough to help neutralize acidic soil to a good degree. Interestingly, rice husks ranked second last in list of nine feedstocks despite having the highest ash content (22.9%) amongst all of them. A quick introspection into the ash analysis reveals that close to 95% of this ash is made up of Silica Oxide (SiO2) which is extremely acidic and even neutralize strong bases.

4.3.6 SEM analysis

The SEM analysis for all the biochars is used for investigation of the presence of a porous microstructure. The size and uniformity of these pores depend on the nature of the material specifically its biochemical constituents hemicellulose, cellulose and lignin. Though these pores could be observed for each material, they required different orders of magnifications for these porous structures to be identified clearly. This clearly indicates that certain substances are bound to be more porous than others. An example SEM image is shown in figure 4.29 in which the presence of a porous microstructure is indicated using the yellow circles and the presence of inorganics is shown using the red circle. These characteristic features can be observed in almost all the chars with a few chars not depicting any notable pores at all. The sample preparation of SEM required the crushing of the char into a fine powder and this results in the appearance of discontinuous and scattered pieces of the char. The goal of this analysis is to use it as a visual tool to compare the results of the BET-pore volume analysis. The EDS analysis for the obtained inorganic content is discussed in the next section.

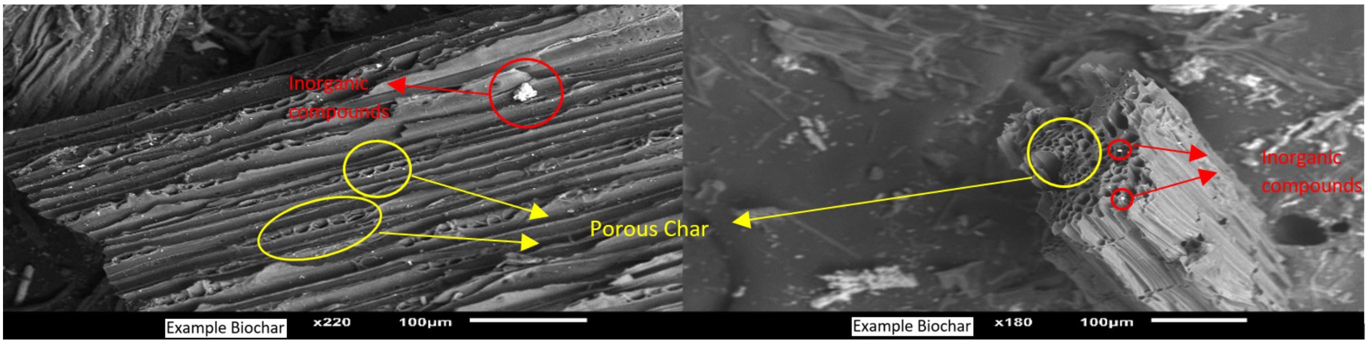


Figure 4.27: A sample SEM analysis

SEM-Bagasse

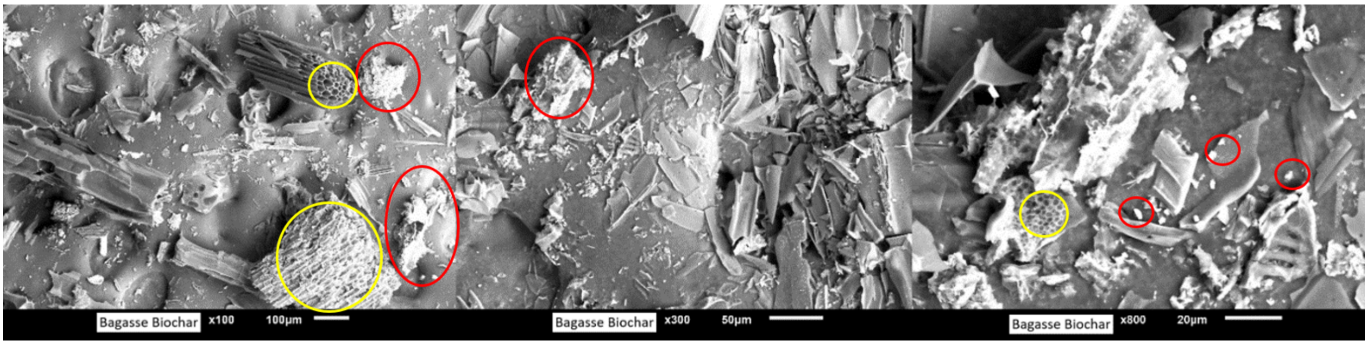


Figure 4.28: SEM analysis for the Bagasse biochar

Bagasse biochar shows a good porous microstructure at 100X magnification, further magnification reveals the presence of flaky crystals which confirm the existence of inorganic compounds. Bagasse biochar had a highly porous structure as identified from the BET analysis and this can be visually confirmed as well.
The higher volatile content (80%) for Bagasse biochar resulted in the formation of a majority of these pores. The higher pore presence could also be attributed to the low ash content(2.8%) as a high ash content leads to pore blockages.

Maize Biochar

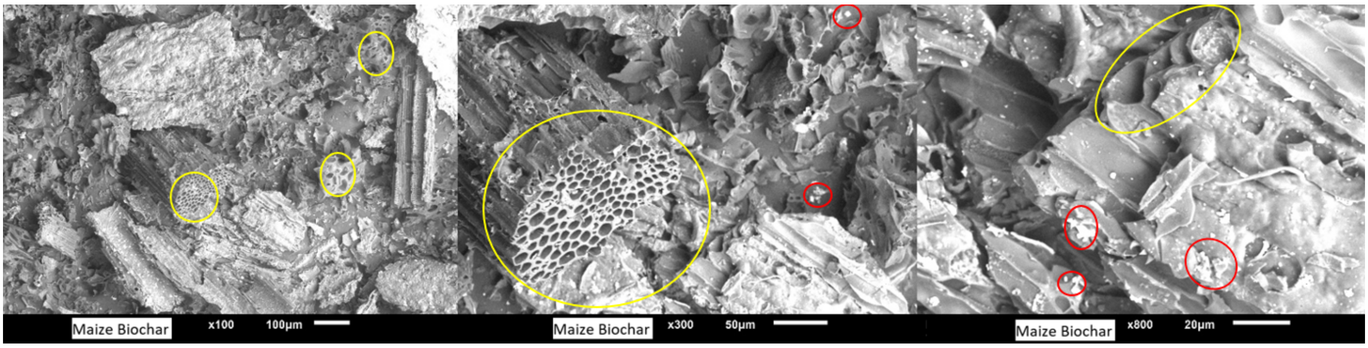


Figure 4.29: SEM analysis for the Maize biochar

Maize biochar similar to the Bagasse biochar shows a microporous structure at different orders of magnification. A quick look into the BET analysis shows that the char has a specific pore volume of 0.06 cm3/g which is four times the pore volume of its woody counterparts. The inorganic concentrations are visibly much fewer and this ties up with the low ash content of 4.2%.

Miscanthus Biochar

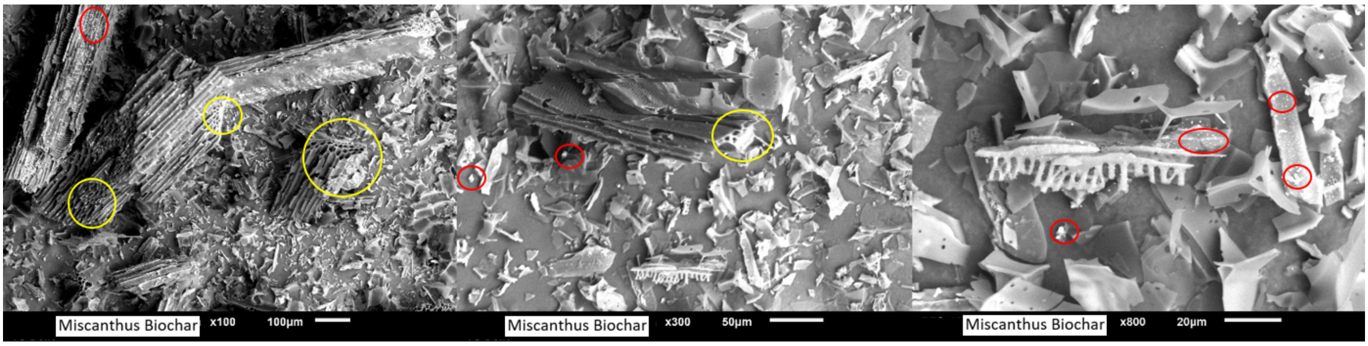


Figure 4.30: SEM analysis for the Miscanthus biochar

Miscanthus biochar shows glimpses of a porous microstructure. The porous char pieces are few and cannot be observed clearly at higher magnifications. The BET analysis tells a similar story with the miscanthus biochar ranking third and second to last in regard to its surface area and porosity respectively. This points to the fact that the volatiles within miscanthus where not release and ultimately it would require a higher torrefaction temperature to ensure more release of volatiles contributing to a increase in the porosity of the char.

Pinewood Biochar

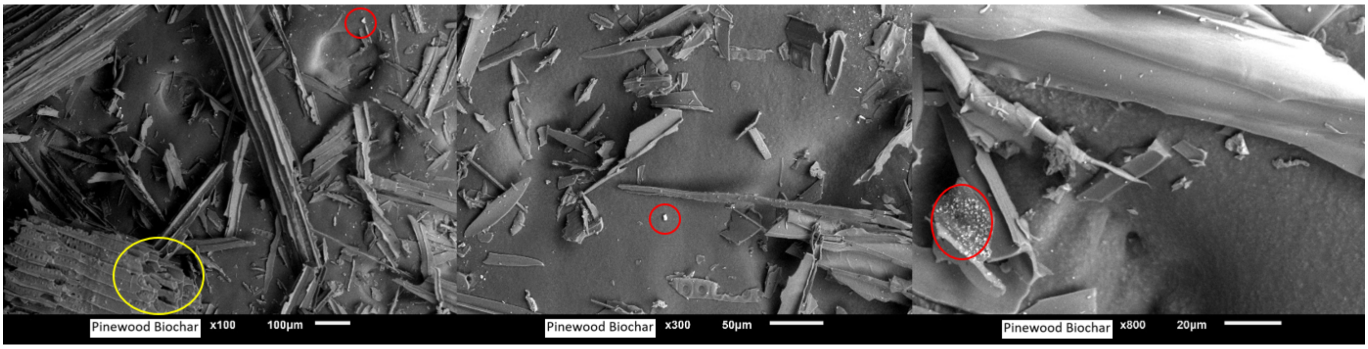


Figure 4.31: SEM analysis for the Pinewood biochar

Similar to the Miscanthus biochar, the Pinewood char has a sparse distribution of pores and inorganic content. The pinewood char was the second best performing woody char (after the Grapestems) with regards to its surface area and porosity measurements. The presence of a number of thin discontinuous strips of char indicates that the material could be sensitive to grinding resulting in the complete destruction of its porous microstructure.

Ricehusk Biochar

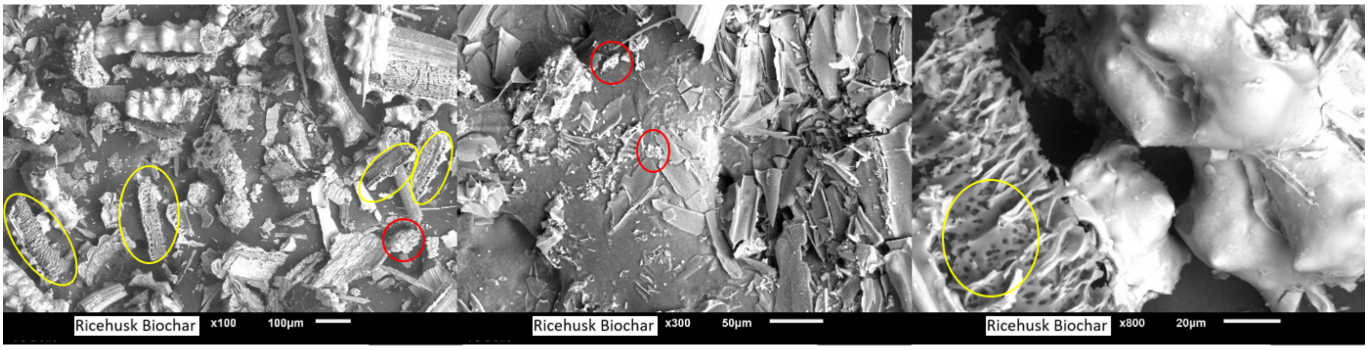


Figure 4.32: SEM analysis for the Rice-husk biochar

Ricehusk biochar was the only material that did not require size reduction before entering the SEM-EDS setup. This resulted in a truly unique microstructure where each torrefied husk particle was visible in the original form. The material showed a high degree of porosity at 100X and 800X which is corroborated by the findings using the BET setup. The Ricehusk biochar had the highest initial ash percentage of 23% and the lowest initial volatile percentage. The abnormality could be attributed to the composition of the volatiles and the nature of the material in itself. Increasing the temperature causes the highly reactive volatile to eject out of the material in a quick and sudden manner resulting in a porous structure without worrying about ash-pore blockage.

Tomato residue Biochar

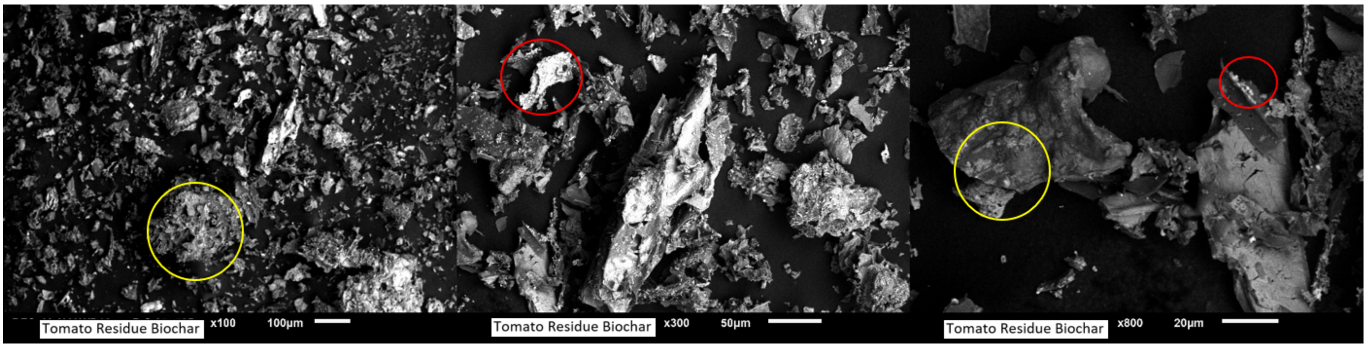


Figure 4.33: SEM analysis for the Tomato residue biochar

The Tomato residue char ranks the second lowest in comparison with other grassy agro feedstock materials. Only the washed roots had a lower measurements for surface area and porosity measurements. It was hard to identify the torrefied char pieces showing the presence of pores. The high ash content would predict the visual appearances of flaky inorganic substances in a good number, but the presence of inorganics is not clearly seen from the SEM images.

Washed Shredded roots Biochar

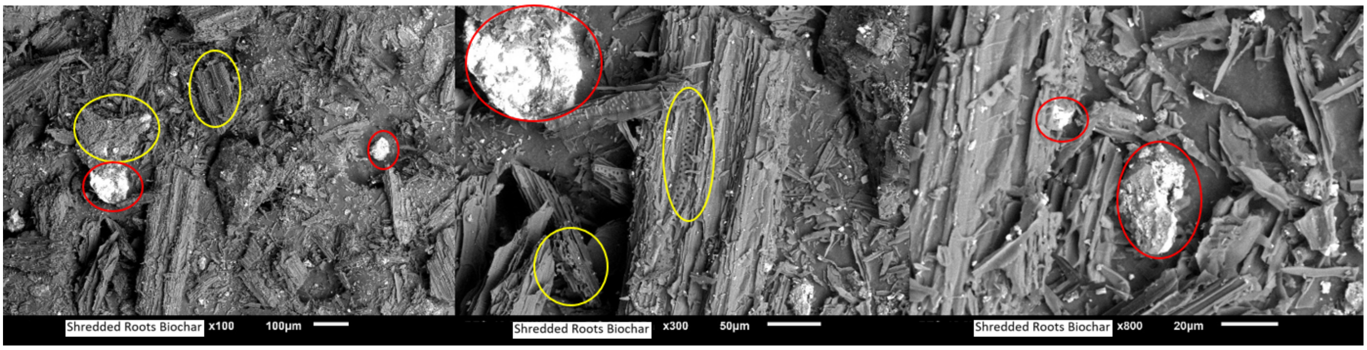


Figure 4.34: SEM analysis for the Washed shredded roots biochar

The Washed shredded roots biochar shows a distinct presence of inorganics on a macroscale. The availability of a porous structure from the torrefied char is limited and this shows that higher temperatures are required to remove a majority of the volatiles from the bulk of the material. The char was one of the worst performing materials with regards to surface area (third last) and porosity (second last) measurements.

Recycled wood Biochar

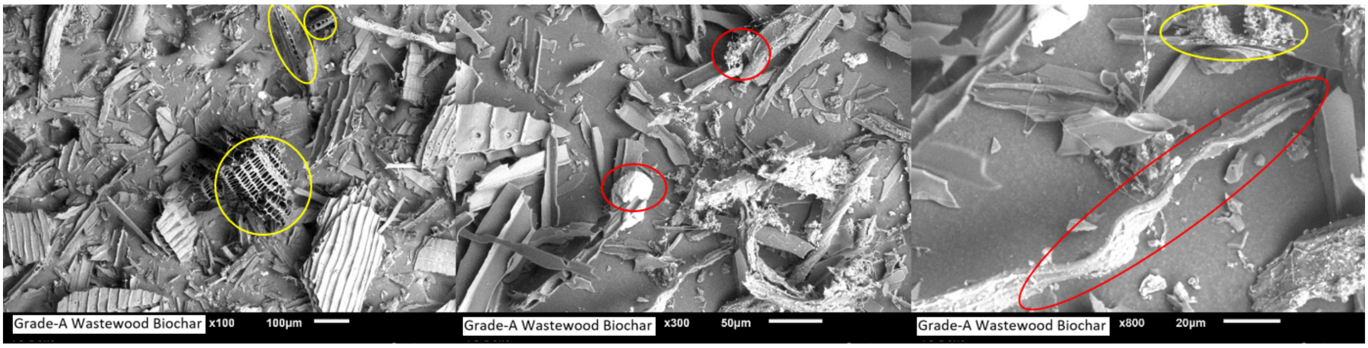


Figure 4.35: SEM analysis for the Recycled wood biochar

From the actual picture of the bulk material for the recycled wood feedstock, it is clear that the material is completely heterogenous and the same can be confirmed in the microstructure as well. Though a few well torrefied porous recycled wood char can be identified, the majority of the material consists of non-uniform pieces or flaky substances. The single sample for the recycled wood analysed under BET indicated that the surface area for the material was below the MDL and the porosity of 0.013 ties it up in the last place with Miscanthus char.

Grapestems Biochar

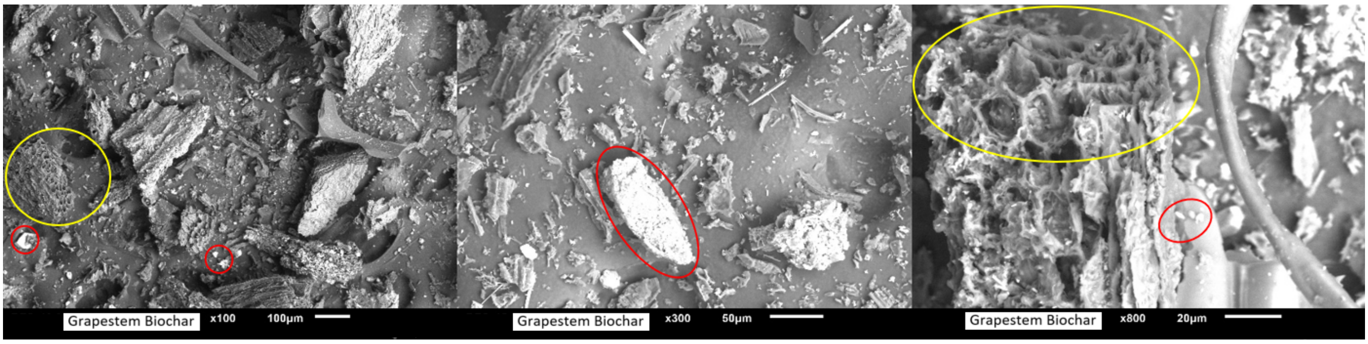


Figure 4.36: SEM analysis for the Grape stems biochar

The Grapestems biochar shows the presence of a comprehensive network of porous char coupled with a noticeable presence of inorganics. This microporosity can be observed under several orders of magnification and this is further substantiated by the BET measurements. The Grapestem biochar ranks third and fourth in porosity and surface area values respectively and promises to be a good replacement for commercial woody feedstocks.

4.3.7 EDS-Analysis

The EDS analysis was performed at three different magnifications: 100,300 and 800. At the 100X magnification, the area was selected to be scanned in a raster pattern and at 300X and 800X, three distinct points were selected to be analysed. These points were selected as they showed a distinct departure in the microstructure or had white spots which are characteristic of inorganics. For each of the material, one point at 300X and 800X respectively are represented here for a brief discussion. All the remaining EDS characterization is included in the appendix.

recycled wood

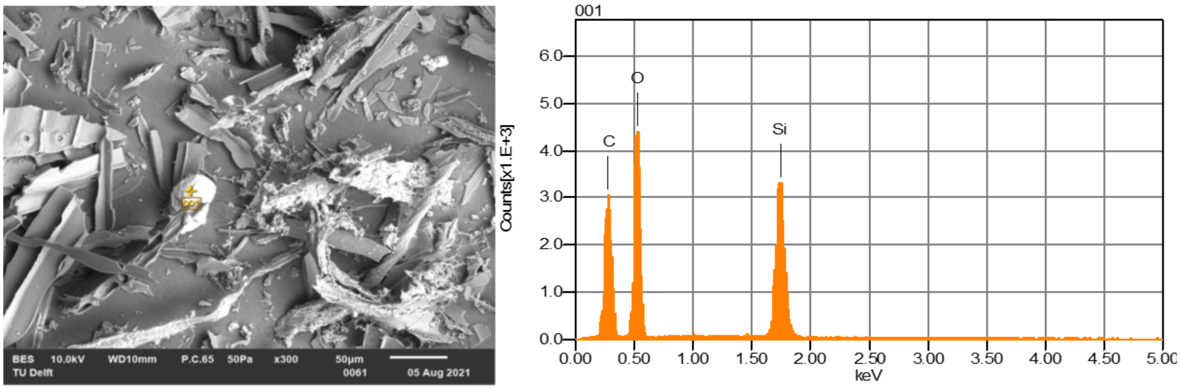


Figure 4.37: EDS analysis for the recycled wood biochar at 300X

Magnification	%C	%O	%Si	%Mg	%Ti	%K	%Ca	% Total
300X	40.38	41.74	17.88	-	-	-	-	100
800X	66.55	27.86	1.64	1.39	0.60	1.13	0.85	100

Table 4.19: Elemental analysis for recycled wood biochar

The EDS analysis for the recycled wood biochar indicates a high inorganic silicate presence at 300X magnification. Further magnification and analysis at 800X reveals traces of Titanium, Magnessium, Calcium and Potassium. These elements are a common occurrence in paints and wood laminates. The material is still relatively clean and carbonaceous but care has to be taken to separate out painted wooden pieces and nails from the mix.

Maize

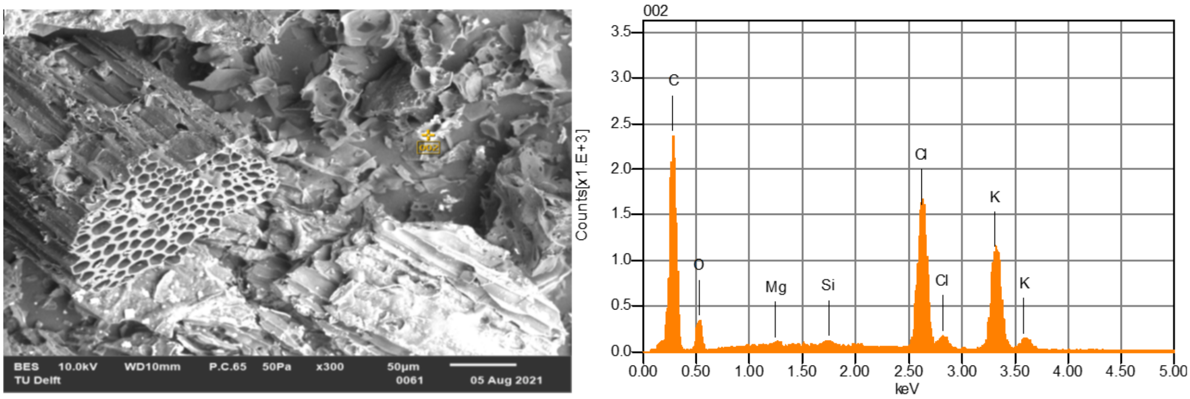


Figure 4.38: EDS analysis for the Maize biochar at 300X

Magnification	%C	%O	%Si	%Mg	%Cl	%K	%Ca	% Total
300X	47.41	46.58	0.27	0.23	20.59	24.92	-	100
800X	43.78	5.89	0.38	0.22	22.08	27.64	-	100

Table 4.20: Elemental analysis for Maize biochar

The Maize biochar shows characteristic peaks for Chlorine and Potassium apart from Carbon and Oxygen. Though the inorganic Chlorine content in the bulk material is low (0.13%), it is recommended to remove this Chlorine from the material before torrefaction either through washing or chemical treatments. The elemental distribution is similar at both magnifications with a higher percentage of inorganic crystals in the microstructure. There is a small fraction of elemental Magnesium and Silicon as well.

Grapestems

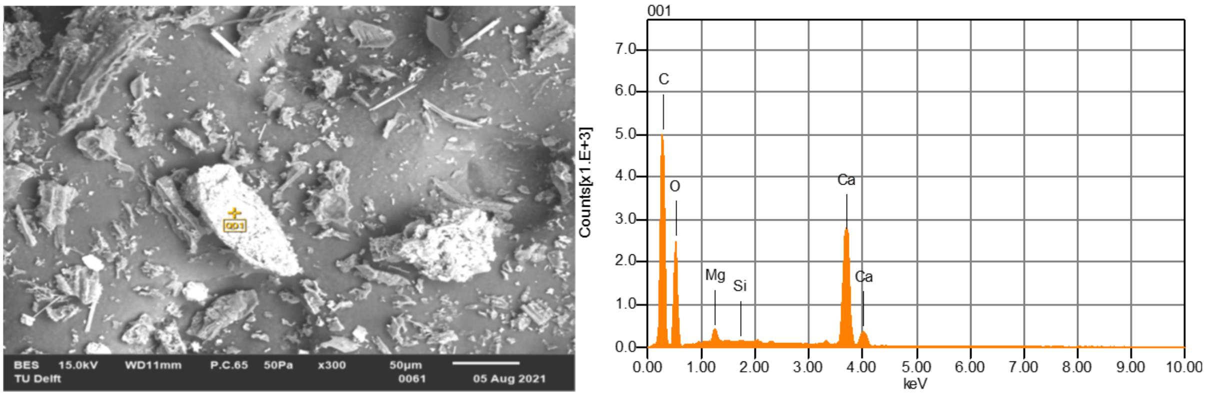


Figure 4.39: EDS analysis for the Grapestem biochar at 300X

Magnification	%C	%O	%Si	%Mg	%Cl	%K	%Ca	%Na	%S	% Total
300X	39.49	38.98	0.18	1.04	-	-	20.32	-	-	100
800X	64.31	32.23	0.14	0.22	0.76	0.25	1.07	0.82	0.42	100

Table 4.21: Elemental analysis for Grapestem biochar

The Grapestem biochar has the most diverse elemental distribution within the microstructure. Though a few of these elements such as Magnessium, Potassium, Calcium, Sodium and Sulphur are present in traces, the overall spread of these inorganic elements is diverse. As the grapestems were received right after the harvest of the grapes, it is speculated that these elements including Silica, Magnesium, Potassium, Calcium, Sodium and Sulphur are a result of fertilizer addition to the potting soil. These macronutrients are slowly absorbed and assimilated by the grape plant for various plant functions. The majority of the material is still highly carbonaceous and the trace elements are in a very small quantity that does not have to be removed or treated.

Bagasse

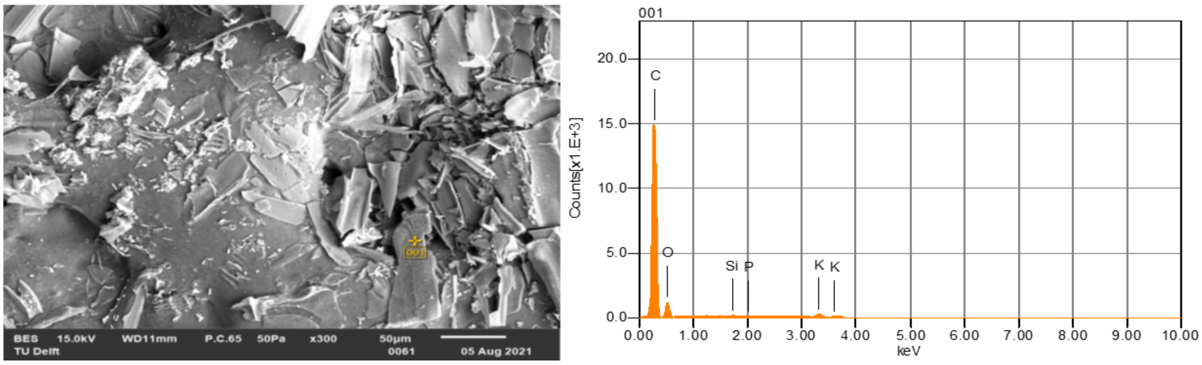


Figure 4.40: EDS analysis for the Bagasse biochar at 300X

Magnification	%C	%O	%Si	%Mg	%P	%K	%Ca	%Al	%S	% Total
300X	77.73	20.68	0.15	-	0.17	1.27	-	-	-	100
800X	73.64	23.04	0.81	0.17	0.30	0.85	0.75	0.43	-	100

Table 4.22: Elemental analysis for Bagasse biochar

The bagasse biochar is relatively clean and mostly comprises of Carbon and Oxygen as its major constituents. The lack of any distinct white spots or any odd shapes is another indication of the low concentration of inorganics. There are still traces of Silicon, Phosphorous, Potassium, Magnesium, Calcium and Aluminum all of which are in concentration ranges of less than 1%. The reason for such low concentrations of inorganics could be due to that the material is a byproduct of the sugar industry and the preprocessing techniques such as washing could result in a relatively cleaner feedstock post processing.

Tomato Residue

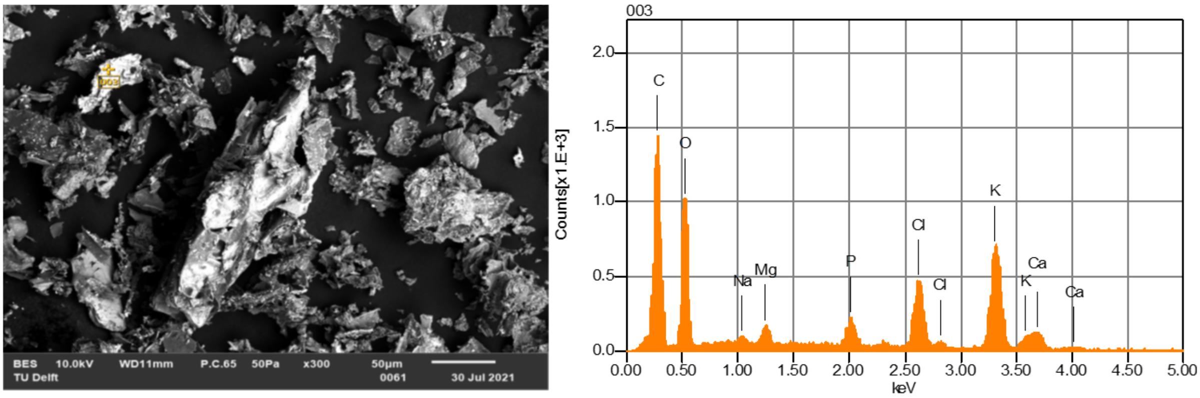


Figure 4.41: EDS analysis for the Tomato residue biochar at 300X

Magnification	%C	%O	%P	%Mg	%Cl	%K	%Na	%Ca	% Total
300X	32.27	25.28	2.69	1.07	9.12	24.61	0.49	4.48	100
800X	32.79	30.15	11.47	7.25	1.01	17.33	-	-	100

Table 4.23: Elemental analysis for Tomato residue biochar

The tomato residue has the highest concentration of inorganics in comparison to the other chars. The major inorganic concentration being Potassium at 300X and 800X. There is a considerable concentration of Phosphorous and Magnesium as well in the char which indicates that the source material needs to be treated for these constituents prior to torrefaction. These peculiar peaks for Magnesium, Phosphorous and Potassium are synonymous to the macronutrients required for plant growth. These macronutrients are fed to the plant via the soil during the growth phase for these tomatoes inside the greenhouses. Though these elements are required and essential during plant growth, they can quickly combine with sulphides and chlorides to cause fouling in the reactor.

Miscanthus

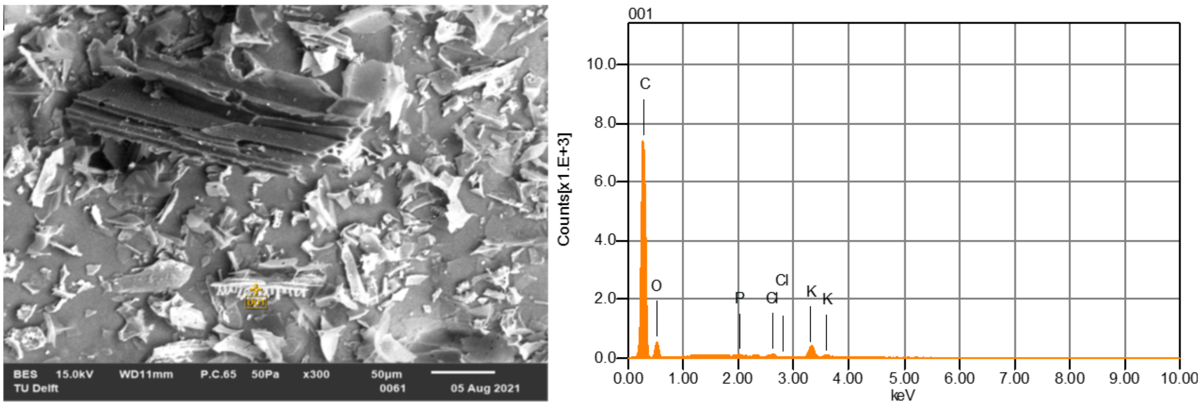


Figure 4.42: EDS analysis for the Miscanthus biochar at 300X

Magnification	%C	%O	%P	%Cl	%K	% Total
300X	76.04	19.17	0.37	0.59	3.83	100
800X	76.02	18.62	0.34	0.59	4.43	100

Table 4.24: Elemental analysis for Miscanthus biochar

Miscanthus is a relatively clean source of char consisting of higher Carbon content bolstered by a low inorganic presence. Zooming in onto the limited inorganic areas of the material revealed trace presence for Potassium, Chlorine and Phosphorous

Washed shredded roots

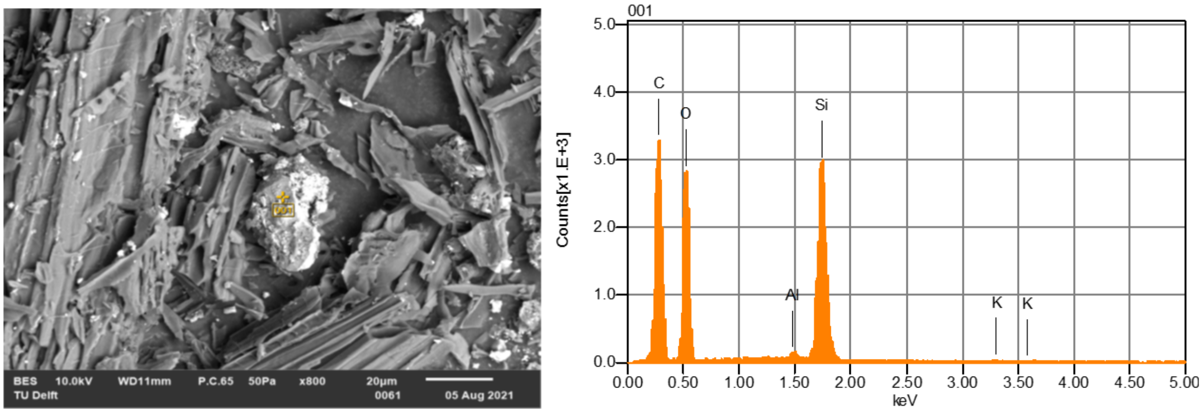


Figure 4.43: EDS analysis for washed shredded roots biochar at 800X

Magnification	%C	%O	%P	%Al	%K	%Si	%Ti	%Fe	%Ca	% Total
300X	50.13	19.17	0.52	1.24	1.11	3.63	16.41	7.03	0.75	100
800X	48.17	33.41	-	0.46	0.28	17.68	-	-	-	100

Table 4.25: Elemental analysis for washed shredded roots biochar

The washed shredded roots similar to the rice husks and shows a dominant Silicon peak coupled with a slew of other inorganics in moderately low concentrations. Interestingly, the washed shredded roots showed a distinct Titanium and Iron peak which was not observed in any other feedstock material. The other inorganics include Aluminum, Silicon, Phosphorous, Potassium and Calcium. As the roots are always transferring these nutrients from the soil to the shoots, it is possible for these elements to have been present in the soil as is the case with ferrosols and ferrallitic soils [9].

Pinewood chips

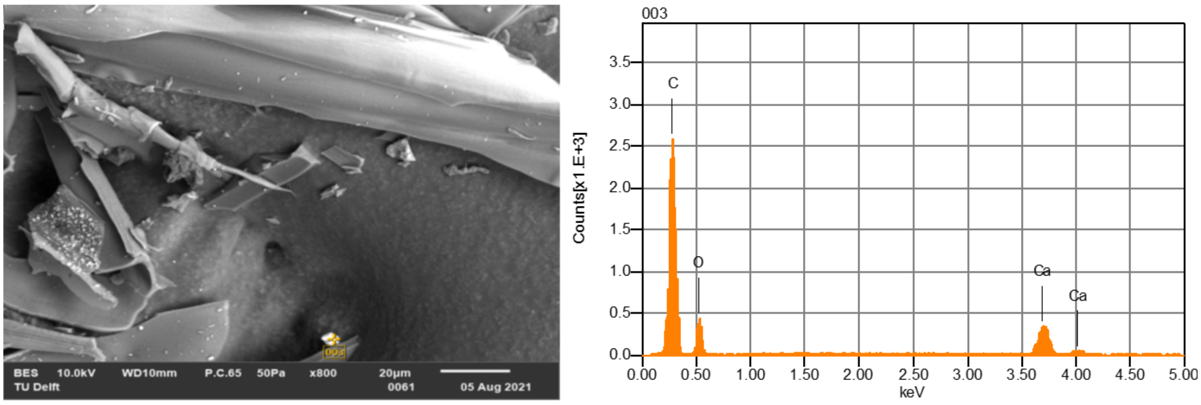


Figure 4.44: EDS analysis for Pinewood chips biochar at 800X

Magnification	%C	%O	%Ca	% Total
300X	74.85	25.15	-	100
800X	56.52	20.20	23.28	100

Table 4.26: Elemental analysis for Pinewood chips biochar

Pinewood chips char is similar to the miscanthus and bagasse char in the sense that the feedstock is very clean with minimal inorganic presence in the microstructure. The few inorganic points observed shows the scarce presence of Calcium. This feedstock therefore requires zero to minimal pretreatment.

Rice husks

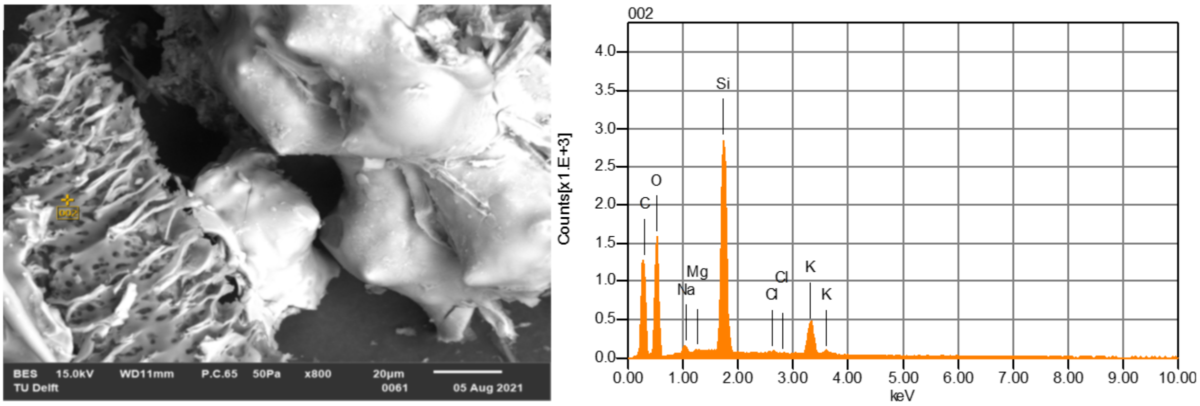


Figure 4.45: EDS analysis for Rice husk biochar at 800X

Magnification	%C	%O	%Si	%Mg	%Cl	%K	%Na	%Al	%S	% Total
300X	12.83	54.89	31.53	-	-	0.75	-	-	-	100
800X	38.37	38.39	15.96	0.21	0.37	5.87	0.83	-	-	100

Table 4.27: Elemental analysis for Rice husk biochar

The rice husks showed the most distinct presence of inorganics. Even thought this could be expected from the high ash content in the proximate analysis of the raw feedstock, the nature of the microstructure indicates an elevated concentrations of other undesirable constituents other than Carbon and Oxygen. The major inorganic constituent (80-90%) in rice husk ash analysis around the world is Silicon and this was first identified by Martin J.I in 1938[74]. Rice husks are still widely used to produce zeolites, carbides and nitrides of silicon for numerous applications[63][53][59]. This inorganic silica can be removed to an extent by using a mixture of KOH+HCl prior to torrefaction [72].

4.4 Surface area and porosity measurements

The data points and regression equations for the low temperature operations are now established. The BET apparatus gives a measurement of the nitrogen gas adsorbed in an isotherm and this can in turn be used to measured the available surface area for the biochars. The results from the BET measurements are listed in table 4.28 .

Biochar material	Measured surface area m2/g
Rice Husks	104
Bagasse	83
Maize	13
Wine stems	5
Pinewood chips	4
Tomato waste	3
Miscanthus	1
Washed roots	1
Recycled wood	Less than 1

Table 4.28: Measured BET surface area for the biochars

From the BET measurements it can be observed that both Rice husks and Bagasse have a high specific surface area while woody char including pinewood grape stems score poorly. Recycled wood char had a surface area less than 1 m2/g the minimum detection limit for the equipment. The highest initial moisture content for the bagasse (65%) could have potentially helped better carbonize the material under the operating temperature regime of 100 to 350 °C. The highest ash content for the rice husks(23%) can further be improved either by high temperature steam activation or chemically through KOH/K2CO3 reactions[93][98]. The results from BET measurements are compared with the regression model at the low and high temperature models in table 4.29.

Biochar Material	Torrefaction Temperature	Measured Surface area (m2/g)	Surface area prediction from low temperature regression. (m2/g)	Absolute deviation (m2/g)	Surface area prediction from high temperature regression. (m2/g)	Absolute deviation (m2/g)
Pinewood chips	350	4	3.5	0.5	105.2	101.2
Miscanthus	350	1	2.8	1.8	23.8	22.8
Maize	350	13	3.6	9.3	16.3	3.3
Bagasse	350	83	43.9	39	85.8	2.84
Rice Husks	350	104	24.2	79.8	36.24	67.76

Table 4.29: Comparison between the predictions from low and high temperature regressions

The BET surface area measurements and the observed data points from literature are plotted to give us a visual indication for the models accuracy. The yellow dot shows the measured surface areas and the other coloured dots in the background each represent an unique data point from literature.

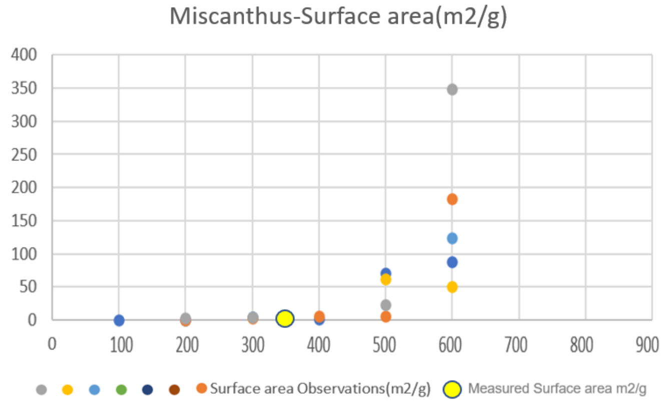


Figure 4.46: Surface area values for Miscanthus char from literature v/s measured

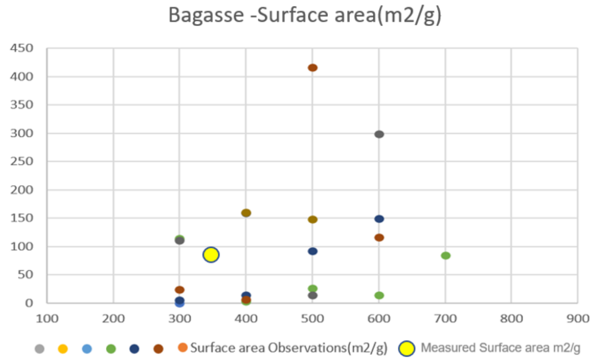


Figure 4.47: Surface area values for Bagasse char from literature v/s measured

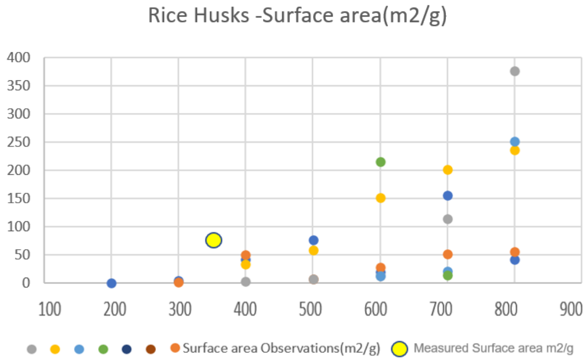


Figure 4.48: Surface area values for Rice husk char from literature v/s measured

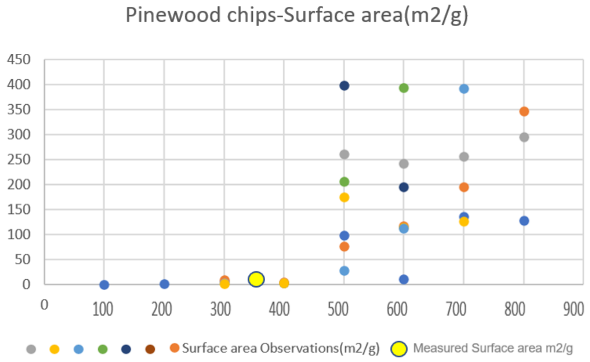


Figure 4.49: Surface area values for Pinewood char from literature v/s measured

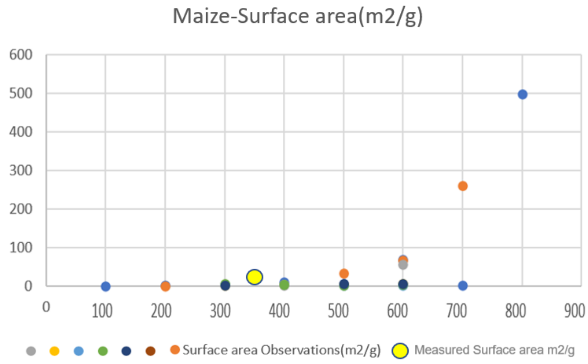


Figure 4.50: Surface area values for Maize char from literature v/s measured

4.4.1 Yield and Bulk density analysis

The raw and torrefied material are weighed before and after torrefaction to ensure that the char yield can be determined. The bed depth for the material holding plate was also measured to establish a correlation between bed depth, packing efficiency on the overall heat transfer mechanisms and the ultimate mass yield post torrefaction.

Biochar Material	Raw form Loading bed depth (cms)	Char Yield Raw form %	Powder form Loading bed depth (cms)	Char Yield Powder form %	Pellet form Loading bed depth (cms)	Char Yield Pellet form %
Miscanthus	2.8	36.20	1	33.67	1.2	31.11
Tomato Residue	2.1	46.99	-	-	-	-
Sugarcane Bagasse	1.7	24.90	2	47.19	1.2	35.26
Rice husks	1.6	41.95	0.5	61.61	1.2	54
Maize residue	1.1	28.18	1	62.73	1.2	47.14
Shredded roots	0.9	23.99	-	-	-	-
Recycled wood	0.8	32.32	0.8	37.76	1.2	33.21
Pinewood chips	0.7	33.47	-	-	-	-
Grape stems	0.4	39.16	0.4	41.17	1.2	32.95

Table 4.30: Biochar yield in the different form factors

Interestingly, it can be observed that torrefaction of agricultural residues and straw like materials resulted in higher yields as compared to its woody counterparts. This is in direct contradiction to the results obtained in literature which estimate a higher mass loss for herbaceous feedstocks[69]. A higher ash content will result in a much faster devolatilization of the parent material and consequently high ash herbaceous material react more vigorously inside the torrefaction chamber. Woody materials on the other hand have higher fixed Carbon percentage which gets concentrated over a smaller portion of the surface as torrefaction proceeds. This marked departure from normal observations can however be correlated to the loading bed-depth and the bulk density of the materials.

The loading of the feedstock is critical in understanding the ultimate yield of the material post torrefaction. The quantity of the material torrefied are roughly equal, however the bulk densities of the woody materials are orders of magnitude higher as compared to the herbaceous feedstock materials. This results in the herbaceous materials being packed tightly and occupying more space within the reaction chamber. The effectiveness of torrefaction process is largely determined by the heat transfer mechanisms and the intrinsic nature of the material. This heat transfer is unhindered in the pieces of woody materials that are few and loosely packed, thus resulting in a more carbonaceous product with an almost complete devolatization of the other components. Meanwhile, in the herbaceous feedstocks, the tight nature of packing does not allow for the heat to completely pass through the material as the top layer acts as an insulator for the intermediate layers and thus the bulk of the material is neither fully devolatilzed nor completely carbonized. This can be observed in the Miscanthus,Tomato residues and Rice husks which have the highest bed depths and consequently results in higher yields for these materials.

The maize residues as well as the sugarcane bagasse were extremely reactive inside the torrefaction chamber and suffered from a minor auto ignition even after cooling the material down to 50 °C. This post torrefaction combustion coupled with a high initial ash concentration and extremely low bulk density resulted in these two material having the lowest yield despite a moderately high loading depth. While the herbaceous feedstocks averaged about 33.7%, the woody feedstocks had a slightly higher average yield of 35% and the Grapestems had the best possible yield of 39.16% even though it had the lowest possible loading bed-depth.

The yields in the powder and pellet form were higher as compared to the the raw form and this is due the lower moisture percentage courtesy of an additional sample preparation step.This can be observed from table 4.30. The bulk densities for the materials are listed in table 4.31.

Material	**Bulk Density kg/m3**			
	Raw form		**Powder form**	**Pellet form**
	Before torrefaction	After torrefaction		
Washed roots	496	180	-	-
Rice husk	153	200	475	235
Maize	133	86.9	500	105
Recycled wood	200	140	350	140.6
Pine wood	313	145	-	-
Bagasse	47	64.2	420	95
Wine stem	292	140.9	520	318
Tomato waste	399	214.2	-	-
Miscanthus	161	80	350	100

Table 4.31: Bulk densities for the char

4.4.2 Specific pore size measurements

The BET analysis using Nitrogen sorption resulted in the identification of the specific pore volume for the different feedstocks. The amount of nitrogen absorbed at a particular partial pressure gives us the measure for the specific surface area as well as the indication for micro and meso pores present within the microstructure. The BET analysis performed is limited to measuring only meso and micropores(5-50 nm) within the material and cannot accurately detect the presence of macropores.(> 100 nm). Thus materials which show a very low specific pore size could in reality be rich in macropores and overall porosity. The Nitrogen sorption isotherms for the rice husks and the bagasse are shown in figures 4.51 and 4.52.

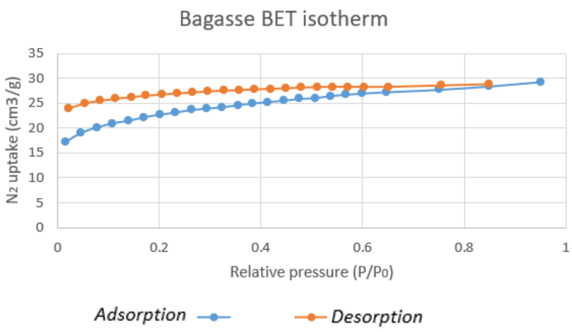


Figure 4.51: BET absorption-desorption isotherms for bagasse biochar

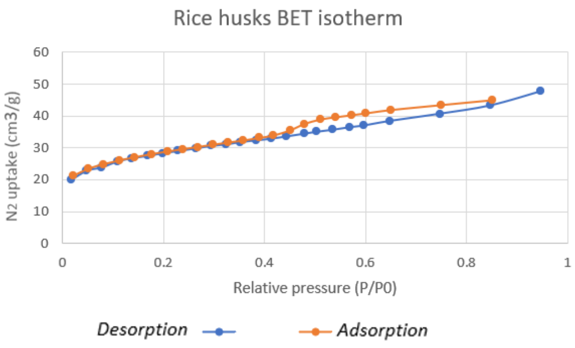


Figure 4.52: BET absorption-desorption isotherms for rice husks biochar

The BET isotherms for the bagasse and the rice husk biochars show an increasing Nitrogen uptake with increasing pressure. The bagasse biochar started at 15 cm3/g at the starting relative pressure of 0.05 during adsorption phase, but as the relative pressure was lowered back to 0.05 the desorption process still had a hysteresis of 10 cm3/g. This was however not the case with the rice husk biochar which showed a overlapping pattern during adsorption and desorption. It can be noted that the rice husks char managed to absorb almost double the volume of nitrogen as compared to the bagasse char and this can also be inferred from the specific pore volumes of the two biochars.

The specific pore size measurements is generalized in this research which measures the nitrogen sorption values for the biochars at a relative pressure of 0.95[68] and tabulated in 4.32 . The porosity modelling performed is compared with the calculated values to give the absolute deviation for the biochars as represented in table 4.33

Material	Specific Pore volume (cm3/g)
Rice husks	0.477
Bagasse	0.293
Wine stems	0.062
Maize	0.060
Tomato residue	0.037
Pinewood chips	0.021
Washed shredded roots	0.015
Miscanthus	0.013
Recycled wood	0.013

Table 4.32: Specific pore volume for the chars

Material	Specific Pore volume(cm3/g)		Absolute deviation (cm3/g)
	BET measurement	Regression prediction	
Pinewood chips	0.021	0.059	0.004
Maize	0.060	0.067	0.007
Recycled wood	0.013	0.152	0.139
Bagasse	0.293	0.476	0.180
Rice husks	0.477	0.056	0.421

Table 4.33: Pore volume regression analysis for the biochars

4.4.3 Correlation between Specific surface area and Total pore volume

The comparison between the surface area and porosity values results in some interesting observations. Literature evidence points towards a strong correlation between the two parameters[78] and the results from BET measurements is shown in figure 4.53.

Rice husks	Rice husks
Bagasse	Bagasse
Grapestems	Maize
Maize	Grapestems
Tomato residue	Pinewood chips
Pinewood chips	Tomato residue
Washed shredded roots	Miscanthus
Miscanthus	Washed shredded roots
Recycled wood	Recycled wood

Figure 4.53: Biochar ranked in decreasing order for surface area and pore volume

Ranking these feedstocks according to their pore volume and surface area immediately shows that these parameters are complementary to each other. Biochar materials such as Rice husks and Bagasse shows the highest values for both surface area and pore volume while Recycled wood ranks the lowest for these values. The surface area and pore size measurements were performed using Nitrogen adsorption and this correlation shows the presence of a higher available surface area densely populated with micropores and mesopores. However, the high silicate ash content for the rice husks and bagasse could lead further to pore blockages and this ash needs to be lowered or removed to increase the overall values for specific pore volume.

4.4.4 Stability of the biochars- the H/C, O/C and the C/N ratios

The EBC recommends that the H/C and O/C ratios for commercial biochars be lower than 0.7 and 0.4 respectively to ensure high degradation resistance and improve its soil permanence. The H/C and O/C ratios are computed and are plotted in the Van Krevelen diagram along with an indication of the biochar's stability over time.

Table 4.34: Stability indices for the biochars

(a) H/C ratios for all the biochars

Biochar	H/C
Rice husks	0.29
Tomato waste	0.30
Washed shredded roots	0.39
Miscanthus	0.47
Bagasse	0.47
Wood waste	0.47
Wine stems	0.48
Pinewood chips	0.49
Maize	0.52

(b) O/C ratios for all the biochars

Biochar	O/C
Washed shredded roots	0.14
Miscanthus	0.17
Wood waste	0.18
Maize	0.19
Pinewood chips	0.22
Wine stems	0.23
Bagasse	0.26
Tomato waste	0.39
Rice husks	0.39

(c) C/N ratios for all the biochars

Material	C:N
Tomato waste	25
Maize	39
Wood waste	46
Rice husks	79
Washed shredded roots	124
Wine stems	125
Bagasse	216
Miscanthus	247
Pinewood chips	552

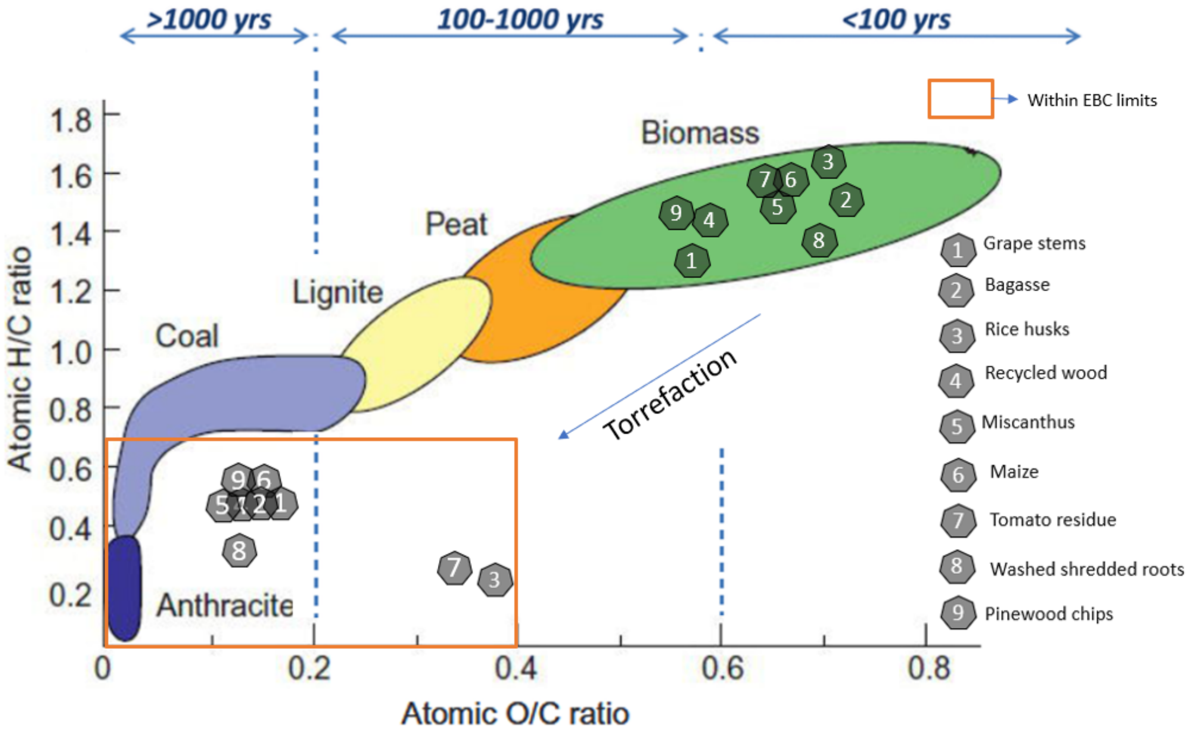


Figure 4.54: The Van-krevelen diagram with the biomasses and the biochars

From the Van-Krevelen diagram shown in 4.54, the tomato residue and the rice husks are the only two materials that cannot be sequestered for more than a thousand years. Although they have the lowest H/C ratios for all the chars, the high values for O/C ratio (0.4) shows that these materials have the lowest soil stability in comparision with all the other biochars. The washed shredded roots will have the highest resistance to degradation while ensuring efficient Carbon sequestration. The other char materials also show a remarkable stability potential(>1000 years) and fall very close to each other to be able to distinguish them individually.
Nitrogen is one of the essential micronutrients that is required for plant growth and development as well as for the upkeep of microorganisms within the soil. There exists a mutual relationship between these microorganisms and the soil with regards to nitrogen absoption and release. Research indicates that for a healthy

plant-microorganism coexistence, the C/N ratio has to at an optimal value of 24:1. At higher C/N ratios, there is more Carbon available for consumption as compared to Nitrogen and this leads to a deficit for both the plant as well as the microorganisms. While nitrogen rich materials such as manure and hay will lead to a lower C/N ratio, this will then lead to a surplus of nitrogen available for plant absorption after the assimilation by microorganisms. Straw based materials such as wheat,corn and rye have a very high C/N ratios(>100) and care should be taken to not continuously plant such crops with high C/N values. From the C/N computations, the biochar with the ideal C/N ratio is the tomato residue. All the other feedstocks have a higher than ideal C/N ratio especially the bagasse, miscanthus and pinewood chips biochars which had an incredibly high C/N ratios(>200) and should only be used for soil which contains a high initial nitrogen concentration[3].

4.4.5 Final ranking of the biochars

All the biochars are now tested for various physical and chemical properties and now they are compared with each other to identify the better performing biochar and the original parent material. The whole ranking was performed on three baseline categories, namely the raw feedstock properties, the effect of torrefaction on the feedstock and the post torrefaction properties specifically tailored for horticultural and sequestration applications. Under the raw feedstock properties, the global avaibility, the costs, the initial moisture and Chlorine content are scored upon. The Net changes associated with Carbon,volatiles, Calorific Value and yield are included in the effect of torrefaction, while the pH,Surface area, pore volume, Bulk density and the O/C ratios are a part of the post torrefaction biochar properties. The final rankings for the biochar along with the colour coding reference across the different property strands can be found in figure 4.36 . The detailed calculations are included in the appendix.
The overall scores for the feedstocks are listed in order of decreasing efficacy for horticultural and Carbon sequestration applications and is represented in figure 4.35.

Biochar	**Baseline score**	**Improvement over current reference (%)**
Washed shredded roots	48	29.17
Bagasse	43	20.93
Recycled wood	42	19.05
Grape stems	41	17.07
Miscanthus	40	15.00
Maize	40	15.00
Pinewood chips	37	8.11
Rice husks	36	5.56
Tomato waste	34	0.00
Forestry residue	34	0.00

Table 4.35: All the biochars ranked

Overall, the washed shredded roots, bagasse and recycled wood biochar ranked 1st,2nd and 3rd respectively and show the most improvement with regards to the current baseline forestry residue. The rice husks and tomato residue biochar are the least performing chars for horticultural applications and have insufficent Carbon to ensure effective Carbon sequestration.

Biochar	**Feedstock properties**				**Effect of torrefaction**					**Biochar properties**				
	Volume (%)	Costs (Eur)	Initial moisture content (%)	Initial Chlorine (%)	Net C increase (%)	LHV increase (kJ/kg)	Yield (%)	Chlorine (%)	Volatiles Change (%)	pH	Surface area (m2/g)	Porosity (cm3/g)	Bulk density (kg/m3)	O/C ratio
GS	🟨	🟨	🟨	🟩	🟨	🟨	🟨		🟥	🟨	🟨	🟩	🟨	🟨
BG	🟨	🟩	🟥	🟨	🟩	🟩	🟥		🟨	🟨	🟩	🟩	🟥	🟨
RH	🟨	🟩	🟩	🟨	🟥	🟦	🟨	🟦	🟥	🟥	🟩	🟩	🟩	🟥
GAWW	🟨	🟨	🟨	🟩	🟩	🟩	🟨	🟦	🟨	🟩	🟦	🟥	🟨	🟩
MI	🟥	🟨	🟩	🟨	🟩	🟩	🟨	🟦	🟩	🟨	🟥	🟥	🟥	🟩
MS	🟨	🟩	🟥	🟨	🟩	🟨	🟥	🟦	🟨	🟩	🟩	🟨	🟥	🟩
TW	🟩	🟩	🟥	🟥	🟥	🟦	🟨	🟥	🟥	🟩	🟨	🟨	🟩	🟥
WSR	🟨	🟨	🟩	🟩	🟩	🟨	🟥	🟥	🟩	🟨	🟥	🟨	🟩	🟩
PW	🟥	🟥	🟩	🟨	🟩	🟨	🟨		🟨	🟥	🟨	🟨	🟨	🟨
FR	🟥	🟥	🟩	🟨	🟥	🟥	🟩	🟥	🟥	🟨	🟨	🟨	🟩	🟥

Table 4.36: the scoring system for all the biochars

Chapter 5

Conclusions and recommendations

The work explained in this thesis outlines the analysis for a total of ten different biochars for potential horticultural and agricultural applications.These biochars were produced in accordance with the HTT4 operation conditions. A feedstock selection matrix (FSM) was developed to identify the best case feedstocks to produce torrefied biochar specifically focusing on horticulture and soil remediation. Overall, this research helps in the identification of useful feedstocks and also tests the efficacy of ten different biochars when specifically targeted for horticultural applications with an added focus on soil remediation and biochar permanence. The conclusions and recommendations are discussed in three broad categories, namely the feedstocks, the torrefaction process and the biochar.

5.1 Conclusions

5.1.1 Feedstock conclusions

The FSM indicates that the 5 best performing feedstocks for horticultural application for the EU regions are: Wheat straw, maize straw, meadow grass, tomato residue and supermarket food residues. However, the meadow grass and supermarket food residue had a lot of pre-treatment challenges which stem from an extremely high initial moisture content (>85%) and material characteristics and were not considered for this research.

A few selected feedstock materials including the tomato residue, bagasse and maize too had a high initial moisture percentage(>60%). Though they respond well to any drying techniques, these feedstocks will require an extra energy input during the pre-treatment stage which needs to be factored in.The recycled wood, washed shredded roots and rice husk biochar had the highest silicon concentration in its ash. Silica in the oxide form is very difficult to remove from the material and may cause issues such as higher ash,lower yield and low pore volume arising due to pore clogging.

5.1.2 Torrefaction conclusions

The average torrefaction yield for woody feedstocks (35%) was slightly higher as compared to herbaceous feedstocks (33.7%) at 350 °C. The yield analysis also gives a correlation with the loading and the bulk density of the material. The herbaceous feedstock materials had very low bulk densities and therefore were packed tightly within the same volume.The tighter the material is packed within the reactor, the lower will be the heat transfer through the bulk of the material and consequently result in higher yields with a lower degree of torrefaction. The yields were slightly higher for the powder and pellet form(10 and 15% respectively) and this can be attributed to their higher bulk densities.

5.1.3 Biochar conclusions

The enhancement of surface area and porosity is more pronounced at higher temperatures (>400 °C). This is evident from the non-linear regression behaviour at lower temperatures (200-400 °C) and a linear regression behaviour at higher temperatures(400-800°C).There exists a close relationship between the fraction of volatiles lost and the increase in fixed Carbon. Such a relationship can also be observed between an increase in surface area and an increase in the total pore volume for the biochar material as well. The increase or decrease in these parameters is however closely tied to the critical operating parameters such as torrefaction temperature residence time, etc.. The tomato residue, recycled wood and maize straw ranked top 3 in the order of basicity and will the most effective when used to remediate acidic soils.

The rice husks and the bagasse biochar had the highest surface area and total pore volume values in comparision with other biochars and could provide the most surface area to facilitate adsorption and desorption of water and nutrients. Except for the tomato residue and the rice husks, all the feedstocks had a noticeable increase in the LHV post torrefaction with grassy feedstock material showing a higher increase in LHV than the woody materials.The SEM analysis clearly shows the existence of a network of pores and the EDS analysis depicts the inorganics present within the microstructure.The EDS analysis of the microstructure reveals that the tomato residue and the maize biochar contain the most prominent inorganic peaks and are heavily contaminated while the pinewood chips and the bagasse biochars showing the smallest peaks for the inorganic concentrations. While the pinewood by nature is relatively clean, the bagasse is obtained from sugar extraction and undergoes multiple cycles of washing and therefore most of the inorganic contents are leached out during processing.

Only the washed shredded roots and the tomato residue showed a net decrease in chlorine concentration post torrefaction. The other biochars either show an increase in chlorine content or no net change post torrefaction.This could be attributed to the top two highest initial Chlorine concentrations for the tomato residue(1.3%) and the washed shredded roots(0.15%)The rice husk and the bagasse biochar show a net increase in bulk density after torrefaction which is usually not expected. This is due to a higher net decrease in the overall volume as compared to the decrease in weight post torrefaction. At higher temperatures, there is a higher vertical spread of the data points for the reported surface areas from various experiments. This variation indicates that the surface area is specifically sensitive to subtle temperature changes at higher temperatures. Out of the three models used to predict the LHV for the biochar post torrefaction, the Boie correlation has the lowest cumulative error percentage of 43.5 % and gives the best possible fit in comparison with the Milne and Friedl et al. correlation which give a cumulative error percentages of 61.5% and 94.7%.

All of the biochars with the exceptions of rice husk and tomato residue are stable within the soil for more than a thousand years. The most stable material amongst the ten biochars is the washed shredded roots owing to its lowest H/C and O/C ratios. Different crops required varying proportions of the growth nutrients or the NPK's. A careful blending of the biochar and nutrients is critical depending on the crop and soil requirements. Overall, the washed shredded roots, bagasse, recycled wood and grape stem char ranked the top four amongst the ten biochars and show a distinct increase(>15%) over forestry residue which is the current reference. Only the rice husks(5.6%) and tomato residue(0%) show little to increase over the current reference.

5.2 Recommendations

5.2.1 Feedstock recommendations

The feedstocks are sourced from across the world and this will definitely lead to variations in feedstock composition when sourced a different regions. Care should be taken to not generalize the analyses and subtle to noticeable changes should be expected depending on the location from which the feedstock was originally sourced from. Materials such as the recycled wood, food waste or processed residues show a high degree of material variability and inhomogeneity and sourcing of these materials should be done in a careful manner. For instance, highly painted/lacquered bits in the recycled wood will show a higher arsenic concentrations as compared to cleaner wooden pieces. Care must be taken to ensure that pieces containing nails, plastic wrapping and other contaminants do not enter into the reactor.

The FSM still contains a lot of scope for improvement. For instance, assigning actual costs for the raw material and operational costs could help identify those feedstocks which are the most economical to produce or to feedstocks that show the most improvement relative to costs invested can be identified.

Currently the FSM contains a total 29 different feedstocks that have been analysed. Expanding this list by adding more feedstocks will help improve the accuracy of this reporting tool by comparing and contrasting with other commercially viable feedstocks. Herbaceous materials will require extensive pre-treatement, more than commercial woodchips. This includes pre-drying, chipping (in the case of miscanthus) and washing (to remove inorganics such as chlorine, potassium,etc). These steps will require extra time and energy and have to be factored in prior to torrefaction.

Materials that have a high inorganic concentration such as the tomato residue, rice husk and maize such be washed or chemically treated prior to pre-drying and torrefaction.All the feedstocks safely fall within the EBC requirements for heavy metal concentrations, PAH and BTEX. The biochars produced from these materials are expected to be within the EBC requirements as well. The char analysis for these components are not performed owing to lack of material and are recommended for further studies.

5.2.2 Torrefaction recommendations

The torrefaction regimes of pre-drying, post-drying and torrefaction should be closely observed for each material. Feedstocks that have a lower moisture(<10%) content will enter the post-drying and torrefaction regime sooner than high moisture materials(>50%). This could lead to higher or lower carbonization than expected. The residual heat from the hot flue gases can be sent to the dryer or the oxidiser to enhance the thermal efficiency of the setup. Also ensure that there is a Carbon capture or an electrostatic precipitator setup to clean the exhaust gas before letting it into the atmosphere. The mass yield from the torrefaction run was extremely low (30%).To improve the yield of the torrefaction process, the temperature could be reduced to 300-320 °C. The same effect could also be achieved by reducing the residence time.

The HTT4 reactor consists of vibrating bed and a pre-heated chamber at 200 °C. These parameters could not be replicated within the lab-scale fixed reactor. Further experimentation or large scale trials should ensure that these parameters are incorporated to ensure that the process completely matches the commercial HTT4 operation.Though the shredded roots and sugarcane bagasse rank well across many categories, their yields are incredibly low (<25%). This indicates that the material is extremely sensitive to high temperature torrefaction and it is recommended that these materials be torrefied at lower temperatures of 280-300°C.

Ensure that the materials (especially the herbaceous feedstocks) cool down to ambient temperature or lower post torrefaction to reduce the chances of auto ignition. The biochars in this research have been carbonized to a great extent. This is due to the high operating temperature of 350°C and a long residence time of 38 minutes. The commercial biochars produced will have lower degree of carbonization and subsequently lower values are to be expected for the LHV and consequently higher values for the H/C and O/C ratios.

5.2.3 Biochar recommendations

It is recommended that the ICP ash analysis,PAH and BTEX analysis be performed for the feedstocks and the biochar material as well. In this research these tests were not performed for the biochar due to lack of material required for these tests.It is recommended that the tomato residue and rice husk be subjected to an intermediate temperature torrefaction (250-280°C) or be used for other applications such as anaerobic digestion or animal feed rather than high temperature torrefaction. The material properties for these chars degrade upon torrefaction to such an extent that biochar production does not justify the added energy input. The Recycled wood char has a high arsenic concentration of 2.8 mg/kg and care should be taken when using this material for soil/food related applications.

The tomato residue had the ideal C:N ratio of 25:1, the utilization of high C:N feedstocks(>60:1) continuously is not recommended as it will lead to the a complete depletion of soil nitrogen and will make the soil infertile.
Most of the calculations were performed to ensure that the biochar qualifies the EBC criterion. It is recommended that external studies refer to the guidelines set up by their local biochar governing bodies (The International biochar Initiative IBI, the Global Environment Facility GEF,etc..) The Maize, Bagasse and the Miscanthus biochar has a bulk density less than 100 kg/m3 and must be pelletized post torrefaction

to increase energy density and lower shipping costs. The regression analysis distinctly shows two regions each having different behaviours. The low temperature regression should be used for torrefaction up to 400 °C and the high temperature regression should be used for pyrolyis or gasification above 400 °C. The tomato residue shows a very high chlorine % and should be pre-treated to ensure minimal slagging and corrosion within the reactor. The BET equation is critical to the relative pressure at the point of reporting.

In this research the relative pressure (P/P0) is taken at 0.95. A comparative analysis between different researches at different relative pressure and different assumptions will lead to a wide disparities between the data sets [82]. The macropore limitation of the Nitrogen sorption measurements for specific pore volume calculation is mentioned. The use of other measurement such as Mercury Induced Porosimetry (MIP) could alleviate such limitations.The miscanthus, maize and pinewood chips are intermediary ranking biochars. The use of these biochars in horticulture and agriculture applications are encouraged if these materials can be converted into char in a sustainable manner.

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Appendices

Appendix A

Initial feedstock selection

In this appendix, the tools used for feedstock research and the initial feedstock selections are listed.

A.1 Harris Profiles

The overall scoring for 15 different feedstocks are listed in the table below.

Name of the feedstock	Harris profile score (Max-17)
Willow-Salix spp	7.5
Pinewood and spruce	9.5
Acacia	7
Portuguese wood-mix (Eucalyptus)	8.5
Russian wood-mix (Birchwood)	9.5
Wheat-straw	8.5
Maize/Corn-straw	6.5
Rice-straw	7
Chicken-manure & other organic wastes	11
Bamboo shoots	3.5
Sugarcane bagasse	-4
Coconut husks	-2
Cotton stalks	-0.5
Prosopis	3.5
Maize-Cow manure	0.5

Table A.1: Results from the Harris profiles

Harris profile weights	Multiplication factor
Increase in productivity	X2
Improves soil properties	X1.5
Unwanted heavy metal removal / wanted Mineral release	X1
Ease of production	X1.5
Acquisition cost	X1
Availability	X1

Table A.3: Weights assigned to the different categories

Criteria\concepts	**Willow-Salix spp**					**Pinewood and spruce**					**Acacia**					**Portuguese wood-mix (Eucalyptus)**			
	–	-	+	++		–	-	+	++		–	-	+	++		–	-	+	++
Increase in productivity			🟩					🟩				🟥					🟥		
Improves soil properties			🟩					🟩					🟩	🟩				🟩	
Unwanted heavy metal removal /wanted Mineral release		🟥						🟩					🟩					🟩	🟩
Ease of production			🟩	🟩				🟩	🟩				🟩	🟩				🟩	🟩
Acqusition cost			🟩					🟩					🟩	🟩				🟩	🟩
Availability			🟩					🟩					🟩	🟩				🟩	🟩
Total			**7.5**					**9.5**					**7**					**8.5**	

Table A.2: A section of the Harris profiles

A.2 The Feedstock selection matrix

The final scores for the feedstock selection matrix for the different scenarios are included here.

Master Matrix-No bias			**EU Bias**			**EU District Heating Bias**			**APAC Co Firing Bias**	
	Score			**Score**			**Score**			**Score**
Accacia(C3)	28		**Dutch food waste**	**63**		**Dutch food waste**	**66**		**Rubberwood**	**80**
Bagasse	50		**Tomato waste Dutch greenhouses**	**63**		**Saw dust**	**65**		**Bagasse**	**73**
Bamboo	54		**Meadow grass**	**57**		**Forestry Waste**	**62**		**Bamboo**	**72**
Bana grass(C4)	27		**CPL HTC**	**55**		**Rubberwood**	**60**		**Coconut husk**	**64**
Cassava(C4)	28		**Forestry Waste**	**55**		**Tomato waste Dutch greenhouses**	**60**		**Eucalyptus**	**58**
Coconut husk	**45**		Saw dust	55		CPL HTC	59		Elephant grass(C4)	55
CPL HTC	**40**		French wine stem	54		Meadow grass	58		Wheat straw	54
Dutch food waste	**44**		Rubberwood	54		Oak wood	57		Accacia(C3)	53
Elephant grass(C4)	**31**		Grade A Waste Wood	53		Wine stem	56		Cassava(C4)	53
Empty Fruit Bunches (Palm Oil residues)	**0**		Maize	52		Grade A Waste Wood	55		Rice straw (Rice husks)	53
Eucalyptus (hardwood reference)	**44**		Wheat straw	52		Wheat straw	54		Bana grass(C4)	51
Wine stem	**39**		Oak wood	50		Bagasse(sugarcane trash)	53		Dutch food waste	46
Maize	**33**		Bagasse	49		Maize	53		Saw dust	45
Meadow grass	**38**		Bamboo	49		Rice straw(Rice husks)	53		Foresty Waste	42
Miscanthus (C4)	**28**		Miscanthus (C4)	47		Bamboo	52		Tomato waste Dutch greenhouses	40
Oak wood	**35**		Coconut husk	40		Miscanthus (C4)	51		CPL HTC	39
Olive Cake	**15**		Eucalyptus (hardwood reference)	39		Eucalyptus	48		Meadow grass	38
Forestry Waste	**40**		Rice straw	36		Coconut husk	44		Oak wood	37
Rice straw(Rice husks)	**36**		Olive Cake	34		Elephant grass(C4)	35		Wine stem	36
Rubberwood	**59**		Elephant grass(C4)	30		Olive Cake	34		Grade A Waste Wood	35
Saw dust (from any hardwood source)	**48**		Bana grass(C4)	26		Willow - Short Rotation Coppice	33		Olive Cake	34
Grade A Waste wood	**38**		Willow - Short Rotation Coppice	25		Bana grass(C4)	31		Maize	33
Tomato waste+ Dutch greenhouses	**44**		Accacia(C3)	23		Accacia(C3)	24		Miscanthus (C4)	31
Wheat straw	**33**		Cassava(C4)	23		Cassava(C4)	24		Empty Fruit Bunches	16
Willow Short Rotation Coppice	**10**		Empty Fruit Bunches (Palm Oil residues)	-5		Empty Fruit Bunchess	-4		Willow - Short Rotation Coppice	13

Table A.4: Final scores for a part of the FSM

Appendix B

Modelling the surface area and porosity

A total of 14 materials have been modelled, 7 each for the surface area and porosity for the material. The averaged data points for the various materials are listed in this appendix.

B.1 Surface area modelling

Table B.1: Surface areas results at different temperatures

Torrefaction temperature (○C)	Mean surface area (m2/g)
200	3.59
300	159.03
400	166.98
500	126.19
600	316.28
700	243.92
800	652

(a) Wheat straw

Torrefaction temperature (○C)	Mean surface area (m2/g)
300	63.41
400	68.43
500	139.39
600	144.54
700	84.70

(b) Bagasse

Torrefaction temperature (○C)	Mean surface area (m2/g)
200	1.49
300	4.56
400	4.83
500	8.89
600	30.69
700	132.30
800	497.85

Table B.2: Maize straw

Torrefaction temperature (○C)	**Mean surface area (m2/g)**
200	3.07
300	32.33
400	37.18
500	45.23
600	109.36
700	192.68
800	178.00

(a) Rice husks

Torrefaction temperature (○C)	**Mean surface area (m2/g)**
200	1.60
300	5.20
400	3.68
500	177.94
600	169.81
700	221.20
800	256.86

(b) Pinewood chips

Torrefaction temperature (○C)	**Mean surface area (m2/g)**
200	127.68
300	58.54
400	175.80
500	60.60
600	377.21
700	292.26
800	331.43

(a) Oak wood

Torrefaction temperature (○C)	**Mean surface area (m2/g)**
200	1.18
300	3.73
400	3.48
500	39.99
600	158.94

(b) Miscanthus

B.2 Pore volume modelling

Torrefaction temperature (○C)	**Mean pore volume (cm3/g)**
300	0.02
400	0.08
500	0.07
600	0.14
800	0.28

Table B.5: coconut husks

Torrefaction temperature (○C)	**Mean pore volume (cm3/g)**
200	0.09
300	0.05
400	1.63
500	0.07
600	1.00
800	2.71

Table B.6: Bagasse

Torrefaction temperature (○C)	**Mean pore volume (cm3/g)**
300	0.01
400	0.05
500	0.21
600	0.03
700	0.03
800	0.04

Table B.7: Maize stover

Torrefaction temperature (○C)	**Mean pore volume (cm3/g)**
200	0.00
300	0.02
400	0.16
500	0.07
600	0.16
700	0.07
800	0.49

Table B.8: Rice husks

Torrefaction temperature (○C)	**Mean pore volume (cm3/g)**
200	0.02
300	0.04
400	0.09
500	0.08
600	0.07
700	0.29

Table B.9: Pinewood chips

Torrefaction temperature (○C)	**Mean pore volume (cm3/g)**
300	0.05
400	0.73
500	0.28
600	0.43
800	1.85

Table B.10: Oak wood

Torrefaction temperature (○C)	**Mean pore volume (cm3/g)**
300	0.05
400	0.73
500	0.28
600	0.43
800	1.85

Table B.11: Bamboo

B.3 References for the surface and pore volume modelling

Material	Name of the author	Title and date
Wheat straw	Jingkuan Sun et al.	Biochars derived from various crop straws: Characterization and Cd(II) removal potential, 2014
	Hongbo Li et al.	Mechanisms of metal sorption by biochars: Biochar characteristics and modifications, 2017
Bagasse	Vineet Vimal et al	Aqueous carbofuran removal using slow pyrolyzed sugarcane bagasse biochar: equilibrium and fixed-bed studies,2019
	Isabel Lima et al	Sugarcane bagasse and leaf residue biochars as soil amendment for increased sugar and cane yields,2017
	Mandu Inyang et al	Biochar from anaerobically digestedsugarcane bagasse,2010
	Estela M. C. C. Batista et al	Effect of surface and porosity of biochar on water holding capacity,2017
	M.M. Manyuchi et al.	Bio char Production from Sugar Cane Bagasse,2020
	Dan FENG et al	Preparation, Characterization of Bagasse-based Biochar and its adsorption performance in tropical soils,2014
Maize	Xiapu Gai et al	Effects of Feedstock and Pyrolysis Temperature on Biochar Adsorption of Ammonium and Nitrate,2014
	Muhammad Khalid Rafiq et al	nfluence of Pyrolysis Temperature on Physico-Chemical Properties of Corn Stover (Zea mays L.) Biochar and Feasibility for Carbon Capture and Energy Balance,2016
	Chunbun Guo et al.	Surface characterization of maize-straw-derived biochar and their sorption mechanism for Pb2+ and methylene blue,2020
Rice husks	Phuong T. M. Do et al.	Properties and potential use of biochars from residues of two rice varieties, Japanese Koshihikari and Vietnamese IR50404,2019
	Hua Wang et al.	Sorption of tetracycline on biochar derived from rice straw and swine manure,2018
	Caidi Yang et al.	Pyrolysis temperature affects pore characteristics of rice straw and canola stalk biochars and biochar-amended soils,2021
	Phuong et al.	Characterization of Biochar from Pyrolysis of Rice Husk and Rice Straw,2015
Pine wood	L. Lonappan et al.	Adsorption of methylene blue on biochar microparticles derived from different waste materials,2016
	Federico Masis Melendez et al.	Variability of Physical and Chemical Properties of TLUD Stove Derived Biochars,2020
	Shasha Jiang et al.	Characterization of hard- and softwood biochars pyrolyzed at high temperature,2017
Oak wood	Walelign Demisie et al.	Effect of biochar application on microbial biomass and enzymatic activities in degraded red soil,2015
	K. Jindo et al.	Physical and chemical characterization of biochars derived from different agricultural residues,2014
	C Trigo et al.	Influence of pyrolysis temperature and hardwood species on resulting biochar properties and their effect on azimsulfuron sorption as compared to other sorbents,2016
	Insha Wani et al.	Effect of pH, Volatile Content, and Pyrolysis Conditions on Surface Area and O/C and H/C Ratios of Biochar: Towards Understanding Performance of Biochar Using Simplified Approach,2020
Miscanthus	Alice Budai et al.	Surface Properties and Chemical Composition of Corncob and Miscanthus Biochars: Effects of Production Temperature and Method,2014
	Adam O'Toole et al.	Miscanthus Biochar had Limited Effects on Soil Physical Properties, Microbial Biomass, and Grain Yield in a Four-Year Field Experiment in Norway,2018
	W. Kwapinski et al.	Properties of Biochar Produced from Miscanthus x giganteus and its influence the Growth of Maize (Zea mays L.),2014

Table B.12: References for the surface area regressions

Material	Name of the author	Title and date
Coconut Husks	Tej Pratap et al.	A sustainable solution for agricultural and environmental applications,2021
	Mohd Hafif Samsudin et al.	A one-step self-sustained low temperature carbonization of coconut shell biomass produced a high specific surface area biochar-derived nano-adsorbent,2019
	Wanida Kajina et al.	Coupled effect of feedstock and pyrolysis temperature on biochar as soil amendment,2018
	Shagufta Gaffar et al.	Physiochemical Characterization of biochars from Six Feedstocks and their Effects on the sorption of Atrazine in an Organic Soil,2021
	Shivakumar et al.	Evaluation of Pore Size and Surface Morphology during Devolatilization of Coconut Fiber and Sugarcane Bagasse,2020
Bagasse	Liska Septiana et al.	Characteristics of Biochars from Plant Biomass Wastes at Low-Temperature Pyrolysis,2018
	Tej Pratap et al.	A sustainable solution for agricultural and environmental applications,2021
	Farzad Moradi-Choghamarani et al.	Physico-hydraulic properties of sugarcane bagasse-derived biochar: the role of pyrolysis temperature,2019
	Chittaranjan Raul et al.	Sugarcane bagasse biochar: Suitable amendment for inland aquaculture soils,2020
	Koji Kameyama et al.	The Preliminary Study of Water-Retention Related Properties of Biochar Produced from Various Feedstock at Different Pyrolysis Temperature,2019
	Mohammad Boshir Ahmed et al.	Insight into biochar properties and its cost analysis,2016
	Wanida Kajina et al.	Coupled effect of feedstock and pyrolysis temperature on biochar as soil amendment,2018

Table B.13: References for the pore volume regressions-1

Material	Name of the author	Title and date
Maize cob & stover	Eman A. Assirey et al.	Chemical analysis of corn cob-based biochar and its role as water decontaminants,2020
	Liska Septiana et al	Characteristics of Biochars from Plant Biomass Wastes at Low-Temperature Pyrolysis,2018
	Xiubin Wang et al	Maize biochar addition rate influences soil enzyme activity and microbial community composition in a fluvo-aquic soil,2015
	Alba Dieguez-Alonso et al.	Towards Biochar and Hydrochar Engineering—Influence of Process Conditions on Surface Physical and Chemical Properties, Thermal Stability, Nutrient Availability, Toxicity and Wettability,2018
	Mohammad Boshir Ahmed et al.	Insight into biochar properties and its cost analysis,2016
	Xu Yang et al.	Effects of maize stover and its biochar on soil CO2 emissions and labile organic carbon fractions in Northeast China,2017
	Tej Pratap et al.	Nanobiochar: A sustainable solution for agricultural and environmental applications,2021
Rice husks	Liska Septiana et al.	Characteristics of Biochars from Plant Biomass Wastes at Low-Temperature Pyrolysis,2018
	Zhongxin Tan et al.	Morphology, pore size distribution, and nutrient characteristics in biochars under different pyrolysis temperatures and atmospheres,2017
	Koji Kameyama et al.	The Preliminary Study of Water-Retention Related Properties of Biochar Produced from Various Feedstock at Different Pyrolysis Temperature,2019
	Tej Pratap et al.	Nanobiochar: A sustainable solution for agricultural and environmental applications,2021
	Mohammad Boshir Ahmed et al.	Insight into biochar properties and its cost analysis,2016
	Yuehui Jia	Study of the Effect of Pyrolysis Temperature on the Cd2+ Adsorption Characteristics of Biochar,2018
	Do Thi My Phuong et al.	PORE CHARACTERISTICS & ADSORPTION CAPACITIES OF BIOCHARS DERIVED FROM RICE RESIDUES AS AFFECTED BY VARIETY AND PYROLYSIS TEMPERATURE,2016

Table B.14: References for the pore volume regressions-2

Material	Name of the author	Title and date
Pinewood	Tej Pratap et al.	Nanobiochar: A sustainable solution for agricultural and environmental applications,2021
	Farzad Moradi-Choghamarani et al.	Physico-hydraulic properties of sugarcane bagasse-derived biochar: the role of pyrolysis temperature,2019
	Davide Bergna et al.	Comparison of the Properties of Activated Carbons Produced in One-Stage and Two-Stage Processes,2018
	Koji Kameyama et al.	The Preliminary Study of Water-Retention Related Properties of Biochar Produced from Various Feedstock at Different Pyrolysis Temperature,2019
	Zhengang Liu et al.	Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment,2010
	Mohammad Boshir Ahmed et al.	Insight into biochar properties and its cost analysis,2016
	Alba Dieguez-Alonso et al.	Towards Biochar and Hydrochar Engineering—Influence of Process Conditions on Surface Physical and Chemical Properties, Thermal Stability, Nutrient Availability, Toxicity and Wettability,2018
hardwood (Oak, Eucalyptus, willow)	Tej Pratap et al.	Nanobiochar: A sustainable solution for agricultural and environmental applications,2021
	Alba Dieguez-Alonso et al.	Towards Biochar and Hydrochar Engineering—Influence of Process Conditions on Surface Physical and Chemical Properties, Thermal Stability, Nutrient Availability, Toxicity and Wettability,2018
	Koji Kameyama et al.	The Preliminary Study of Water-Retention Related Properties of Biochar Produced from Various Feedstock at Different Pyrolysis Temperature,2019
	Wanida Kajina et al.	Coupled effect of feedstock and pyrolysis temperature on biochar as soil amendment,2018
	Mohammad Boshir Ahmed et al.	Insight into biochar properties and its cost analysis,2016
Bamboo	Tej Pratap et al.	Nanobiochar: A sustainable solution for agricultural and environmental applications,2021
	Deng et al	Characterization of Modified Biochars Derived from Bamboo Pyrolysis and Their Utilization for Target Component (Furfural) Adsorption,2015
	Gong et al	Bamboo biochar amendment improves the growth and reproduction of Eisenia fetida and the quality of green waste vermicompost,2017
	Aditya Rawal et al.	Mineral-biochar composites: molecular structure and porosity,2016

Table B.15: References for the pore volume regressions-3

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