CONVERSION OF OIL PALM EMPTY FRUIT BRUNCH (OPEFB) INTO HYDROCHAR VIA HYDROTHERMAL CARBONIZATION AND STUDY ON THE SUITABILITY FOR SOIL AMMENDMENT

LOGAN RAJ A/L RAMAN

UNIVERSITI SAINS MALAYSIA

2022

CONVERSION OF OIL PALM EMPTY FRUIT BRUNCH (OPEFB) INTO HYDROCHAR VIA HYDROTHERMAL CARBONIZATION AND STUDY ON THE SUITABILITY FOR SOIL AMMENDMENT

By

LOGAN RAJ A/L RAMAN

Thesis submitted in partial fulfilment of the requirement for degree of Bachelor of Chemical Engineering

July 2022

ACKNOWLEDGEMENT

This Final Year Project remarks the completion of degree of Bachelor of Chemical Engineering. Therefore, I would like to express my deepest gratitude and appreciation to everyone who contributed to the successful completion of my final year project.

First and foremost, I would like to deliver my deepest gratitude, towards my supervisor, Professor Dr Lee Keat Teong, who guided me since from the early stage of my final year project. I really appreciate his knowledge that shared to me that really helpful me to do this research. Besides, weekly discussion with him is really helpful for me and assist me in the completion of this Final Year Project.

Then. I would like to express my deepest gratitude to my co-supervisor, Mrs Vijayalecthumi who really helps to perform this research. I had gained a lot knowledge and experience that related to biomass carbonization. Moreover, I also had a lot discussion with her on the procedure to perform the hydrothermal carbonization was really helpful to me and provide me clear view on my outcome of my research. Besides, that she always assists me in performing the experiment and results analysis. Moreover, instant feedback from her was really assist me in improve my proposal and report/thesis writing. Therefore, my co-supervisor always concerns on my progress throughout this final year project and also this thesis writing.

Apart from, that I would like to extend my gratitude to lab technician who always concern about my safeness when in laboratory. Finally, I also want to appreciate my course mate, that involve is similar project scope with me. I'm as grateful as they are willing to share their idea and knowledge through this research and also during report or thesis writing. Last but not least, I'd want to thank everyone at the School of Chemical Engineering for their collaboration and willingness to share ideas, expertise, and skills. Thank you very much.

Logan Raj Raman

July 2022

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Symbol	**Description**	**Unit**
T	Temperature	◦C
S_{BET}	BET Surface Area	m^2/g
V_T	Total Pore Volume	cm^3/g
D_P	Pore Diameter	nm

Greek letter

α	Significance level

LIST OF ABBREVIATION

OPEFB	Oil Palm Empty Fruit Brunch
EFB	Empty Fruit Brunch
HTC	Hydrothermal Carbonization
HC	Hydrochar
MMT	Million Mretic Tonne
DI	Deionized Water
ANOVA	Analysis of Variance
GP	Germination Percentage
MGT	Mean Germination time
GRI	Germination Rate index
SL	Shoot Length
EP	Extractable Phosphorus
EC	Electrical Conductivity
CEC	Cation Exchange Capacity
SEM	Scanning electron microscope
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
DTA	Differential Thermogravimetric
BET	Brunauer, Emmett and Teller theory
PAH	Polycyclic Aromatic Hydrocarbon
HMF	Hydroxymethylfurfural
VC	Volatile Compound
AC	Activated carbon
KOH	Potassium Hydroxide
$\mathbf{N_2}$	Nitrogen Gas
C	Carbon
H	Hydrogen
S	Sulphur

PENGHASILAN HIDROCHAR DARIPADA OIL PALM EMPTY FRUIT BRUNCH (OPEFB) MELALUI PENGKARBONASI HIDROTHERMAL DAN MENGANALISIS KESESUAIAN HIDROCHAR UNTUK FUNGSI PIANDAAN TANAH

ABSTRAK

Sejak kebelakangan ini penghasilan hidrochar daripada sisa – sisa peratanian mendapat sambutan yang tinggi and padahal pemprosesan hidrochar daripada bahan sebegini dapat membantu untuk mengendalikan sisa – sisa pertanian yang terlampau banyak dan sekali gus dapat menghasil produk yang bermutu tinggi daripada bahan bunagan sebegini. Kajian ini menfokuskan kepada penghasilan hidrochar daripada oil palm empty fruit brunch (OPEFB) melalui pengkarbonisasi hidrothermal. Pengkarbonisasi Hidrothermal (HTC) merupakan salah satu teknologi ynay amat efektif di mana, ia boleh memproses pelbagai biomass yang lembap tanpa keperluan untuk pra pengeringan. Manakala, hidrochar merupakan salah satu produk yang nilai amat tinggi dan boleh digunakan untuk pelbagai aplikasi, Dalam kajian ini reaksi HTC telah dijalankan dengan mengunakan 2 faktor iaitu suhu (180 and 220 ◦C) dan masa bertindak (0.5 jam, 1 jam, 2 jam) and pada masa yang sama, impak suhu and masa bertindak atas penghasilan hidrochar telah pun dianalisis. Daripada analisis tersebut, didapati bahawa kedua-dua faktor ini berkadat langusng kepada penghasil hidrochar di mana pada suhu dan masa bertindak yang tertinggi, penghasilan hidrochar ialah sebanyak. 65.7%. Manakala, apabila suhu diturunkan, penghasilan hidrochar berkurang kepada 48.22%. Apabila, masa bertindak telah dituran kepada 1 jam, penghasilan hidrochar berkurang juga. Jesteru itu, daripada hasil analisis ini didapati juga bahawa dalam reaksi HTC impak daripada faktor suhu lebih tinggi daripada impak yang dibawa oleh masa bertindak. Kemudian, selepas penghasilan hidrochar, untuk mengenali kriteria fizikal dan kimia hidrochar pelbagai analisis telah dijalankan seperti BET, SEM, FTIR and TGA -DTA. Analisis darpada BET and SEM, didapati

bahawa anaysis ada sedikit perubahan pada permukaan EFB selepas proses HTC, dimana daripada analisis BET, mendedahkan bahawa menbandingkan luas permukaan EFB, keluasan bagi hidrochar meningkat daripada 1.26 m^2/g to 2.67 m^2/g , manakala analysis SEM menujukkan bahawa terdapat peningakatan dalam liang-liang pada permukaan hidrochar daripada yang terdapat dalam EFB. FTIR analisis pula menujukkan bahawa bahan funsdi *('functional group'*) bagi EFB dan hidrochar agak sama dan tiada perbezaan ketara. Serupa dengan analisis TGA-DTA, menyahkan bahawa kedua-dua hidrochar and EFB mempunyai kriteria pembakaran yang sama dimana membawa maksued yang kedua-dua sampel ini menpunyai komponents yang sama iaitu selulosa, hemiselulosa dan lignin. Perkara yang paling menarik dalam kajian ini ialah, hidrchar yang diporoses darpada HTC telah diaplikasikasn utuk kajian ujian percambahan biji benih untuk mengkaji kesesuaian hidrchar untik tujuan menbaiki tanah. Daripada ujian peecambahan biji benih Chilli (*Capsicum annum)* ia didapati bahawa, apabila menbandingkan pencambahan benih di dalam kedua-dua jenis medium tanah yang iaitu tabah yang menpunyai hidrochar dan medium tanah yang tiada hidrochar, tiada perbezaan besar yang dilihat. Kebanyakan, medium yang menpunyai kandungan hidrochar, merekodkan masa percambahan, kadar percambahan dan peratusan percambahan yang tidak menpunyai perbezaan ketara dengan yang percambahan benih yang tiada campuran hidrochar. Manakala, pada masa yang sama, keputusan negatif yang ketara telah dilihat pada ketinggan tumbuhan, di mana kesemua tumbahan yang membesar di medium tanah yang dicampuri hidrochar merekodkan ketinggiaan yang sangat rendah apabila dibandingkan dengan tumbuhan yang menbesar di tanah medium yang bebas dari hidrochar. Ia didapati bahawa pembesaran tumbuhan yang di dalam medium kandungan hidrochar telah terbantut, berpunca daripada proses HTC yang menghasilkan sebatian organik fitotoksik.

CONVERSION OF OIL PALM EMPTY FRUIT BRUNCH (OPEFB) INTO HYDROCHAR VIA HYDROTHERMAL CARBONIZATION AND STUDY ON THE SUITABLITY FOR SOIL AMMENDMENT

ABSTRACT

Recently, there is a high interest in the synthesis of hydrochar from agricultural waste/residue and therefore, this approach does not only eliminate the abundant agricultural waste, but also converts the wastes into valuable product. Therefore, this paper highlights on the synthesis of hydrochar from oil palm empty fruit brunch (OPEFB), via hydrothermal carbonization (HTC) reaction. Hydrothermal carbonization is found to be an attractive process, due to its ability to transform wet biomass into hydrochar without pre-drying. Meanwhile, hydrochar, has received attention because of its ability to be applied for many applications such as precursors of adsorbent for in wastewater treatment, solid fuels and also for soil amendment. In this paper, the HTC reaction was conducted at various temperature (180 and 220 ◦C) and residence times (0.5 hr, 1hr, 2 hr) and along with this, the effect of temperature and reaction time on yield of hydrochar was also investigated. From the investigation, it is found that reaction time and temperature is directly proportional to the hydrochar yields as at highest temperature and reaction time the yield produced was 65.7%. When the temperature reduced, the yield was reduced to 48.22%, while as the reaction time reduce to 1 hr the yield was reduced to 54.51%. However, as the effect of both parameters evaluated, the finding reveals that process was most influenced by temperature compared to reaction time. Then this study, also includes the physicochemical properties study of hydrochar, which were analysed by using various analysis namely BET, SEM, FTIR and TGA -DTA. The analysis of BET and SEM, reveals that surface morphology was improved such that in BET study the surface area of hydrochar improved from 1.26 m^2/g to 2.67 m^2/g in comparison to raw EFB, whereas SEM analysis indicates the minor pore development on the hydrochar surface compared to raw EFB Highly developed pores in the surface of hydrochar is key attributes for the hydrochar which enables it to be applied to many application, Further, FTIR results shows that functional group for raw EFB and hydrochar is mostly similar. The TGA-DTA confirmed that both hydrochar and raw EFB has similar thermal behavior which both sample tends to have similar components which is cellulose, hemicellulose and lignin. As for the most interesting part for this research, the synthesised hydrochar was analysed on its suitability as soil amendment via germination test. From germination test using Chilli (*Capsicum annum*), it is discovered that in comparison to the control medium there is not much significant difference observed in the hydrochar treated plant in terms of mean germination time, germination rate index and germination percentage. Whereby, with respect to the agricultural application of hydrochar, significant negative result was observed on the shoot length of hydrochar treated plants due to inhibition phytotoxic organic compounds produced during hydrothermal carbonization process.

CHAPTER 1

INTRODUCTION

Chapter 1 will be presenting the overview of this research and introduces on the OPEFB and its application. Moreover, in this section there also will be an introduction on the conversion technology that is used for the OPEFB conversion to hydrochar, which is hydrothermal carbonization. In general, this section will describe on the conversion process of the OPEFB into hydrochar, the problem statement and the objectives of this final year project.

1.1 Research Background

As an overview, Malaysia is one of the leading agricultural commodity producers in the Southeast Asian region. For the few past decades, Malaysia is found to be an emerging country in the oil palm industry, which also known as second largest after Indonesia which contributing more than 80% to global oil palm market. In Malaysia oil palm is the most cultivated plant, where approximately 5.4 million hectares of plantation area and 423 palm oil mills are in operation. Hence, active processing of oil palm causes Malaysia to become the world's top palm oil exporter for numerous palm oil products (Mohammad Padzil et al., 2020).

Oil palm biomass can be categorized as oil palm empty fruit bunch (EFB), mesocarp fiber (MF), palm kernel shell (PKS), palm oil mill effluent (POME) oil palm trunk (OPT) and oil palm frond (OPF). These are common solid lignocellulosic biomass generated from oil palm industries (Abu Sari et al., 2019). Based on Figure 1.*1*, an overview of the palm oil wastes that produced from oil palm processing mill is presented. According to the reports, approximately 15 million tons of OPEFB are generated annually and this amount is expected to increase because of high global demand on oil palm products. In 2019 alone, 151.2 MMT fresh fruit bunches were processed, producing solid and liquid biomass, with oil palm empty fruit bunch (OPEFB) as the largest fraction of solid biomass at about 33.3 MMT (Ibrahim et al., 2021a). But unfortunately, only approximately 10% the biomass had been used while rest are being discarded. OPEFB is a type of lignocellulosic material where it contains chemical blocks of lignin (> 20%), hemicellulose (> 25%) and lignocellulose (> 35%) (Rame, 2018), where all three components can be utilized collectively/separately for the production of biofuels, fertilizer, and compost. Hence, OPEFB has huge potential to be developed into high value-added products such as pulp, feedstuff, carbon briquette, and fillers, foods, and oleo chemicals. Furthermore, it possesses comparable properties to other woody plants which can be used as alternative main raw material to substitute woody plants (Mohammad Padzil et al., 2020). So, if the oil palm biomass remained unexploited, the number of generated wastes or feedstock from oil palm industries may outweigh the market demand.

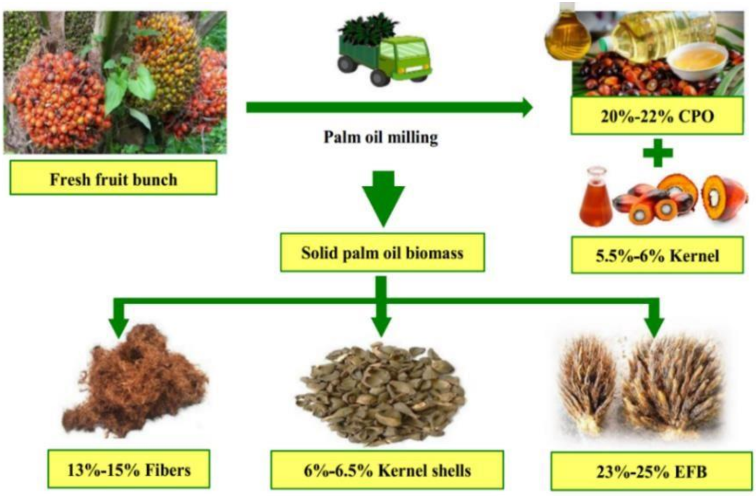

Figure 1.1 : Overview of Oil Palm Biomass or wastes that Generated from Oil Palm Processing (Yan et al., 2019a)

Conventionally, OPEFB were dumped and burnt in incinerator in palm oil mill and the produced ash would be used as a fertilizer for plantations which this method is widely applied in Indonesia (Rame, 2018). But the combustion of the OPEFB had been avoided due to environmental pollution. Practices such as reusing OPEFB as mulching and crude compost may results in leaching of the nutrient to the ground water (Ibrahim et al., 2021a). Hence, to ensure the environmental sustainability of the oil palm industry, the OPEFB must be transformed into high valued products where one of the potential products that would be synthesized and analyzed in this research is hydrochar.

Hydrochar has wider application in the various industry, especially in agricultural industry where it is utilized to improve the fertility of the soil. For example, utilizing hydrochar as soil amendment is a conventional and well-established method that is used in India, Europe, China, and America. Hydrochar based soil amendment, has the potential to improve the nutrient uptake and retention in the soil and provide habitats for symbiotic microorganisms in hydrochar pores (Tomczyk and Boguta, 2020). Thus, this feature will excellently improve soil fertility thus reduces dependency on chemical fertilizer (Gabhane et al., 2020). Furthermore, recent research is also reporting that, hydrochar has wider application in such way that to be used as universal adsorbent material for water and sewage treatment (Abu Sari et al., 2019). In addition, hydrochar could be upgraded to boost their sorption capacity by increasing their porous surface area and alter their functional groups via chemical activation, physical activation, and impregnation with mineral sorbents (Ibrahim et al., 2021; Vakros, 2018).

There are various thermo-chemical conversion techniques for conversion of lignocellulosic materials into hydrochar, for instances gasification, pyrolysis, torrefaction, and hydrothermal liquefaction (Low and Yee, 2021). Most common techniques that is used for hydrochar production is dry pyrolysis method (Yaashikaa et al., 2020). Pyrolysis involves biomass thermal decomposition without oxygen at range of 400 ◦C - 1200 ◦C. At zero exposure to oxygen, heated biomass would reach a temperature above its thermal stability limit hence produces hydrochar. However, for this research, hydrothermal carbonization (HTC) technology is preferred to produce hydrochar from OPEFB where it is found to be effective technology compared other existing methods. Hydrothermal carbonization (HTC) is a thermochemical conversion process that uses heat to convert biomass feedstocks to hydrochar regardless of their moisture content (Ohioline, 2021). This is in contrary to other processing technologies in which pre-treatment is required generally to minimize the moisture content of biomass feedstock.

In pyrolysis, before the conversion of biomass to carbonaceous materials, the moisture content needs to be reduced below 10%, to maintain the efficiency of the biomass processing. Thus, moisture content of biomass is always being a limiting factor for thermal conversion process due to high amount of energy is required in the pre-treatment of the wet biomass (Benavente and Fullana, 2015). Meanwhile, for HTC a variety of biomass can be used as feedstock regardless of their moisture content, and furthermore moisture itself can act as solvent to facilitate the carbonization process. Hence, energy and cost consumption for the pre-treatment or pre-drying can be avoided. Whereby, below Figure 1.2 shows the, overview of HTC reaction which involved various kind of biomass feedstock with different moisture content.

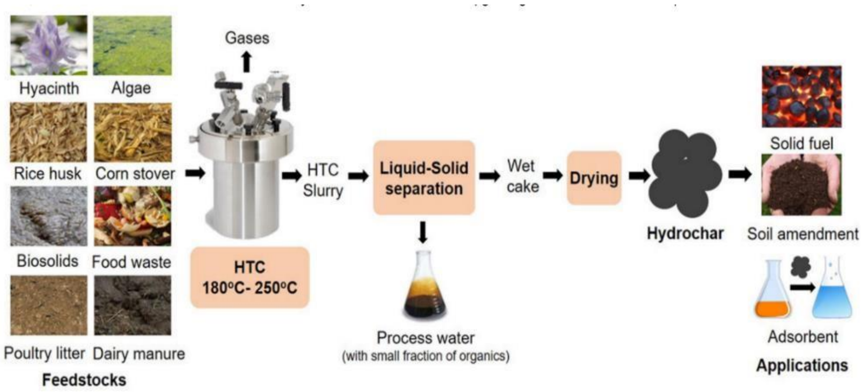

Figure 1.2: Overview of the hydrochar production from various feedstock via HTC. (Ohioline, 2021)

1.2 Research Objectives

The objectives of the project are listed as follows:

i. To study the effect of temperature and reaction time on the production of hydrochar of OPEFB from hydrothermal carbonization.

ii. To analyze the physiochemical properties of hydrochar from hydrothermal carbonization process.

iii. To study on the suitability of the hydrochar for soil amendment application via germination test.

1.3 Problem Statement

Palm oil industry is highly thriving industry in Malaysia, where product and byproducts from this oil palm industry is a key player in the biorefinery process, where it can be used in the production of various high value products. Along with that, huge amount oil palm wastes such as OPEFB are being produced annually. Now, these abundant biomass wastes are discarded by using them as soils compost or by combusting them in incinerator, that could cause negative impact to the environment. Thus, OPEFB is lignocellulosic material that has high potential to be used as feedstock to produce high value products.

Instead of discarding them as waste, in a more sustainable way, they can be utilized for the synthesis of hydrochar via hydrothermal carbonization. The conventional thermochemical method for hydrochar production is pyrolysis. However, pyrolysis method is a cost and energy consuming method because biomass feedstock used in pyrolysis should be pre-treated to reduce its moisture content. Hereby, hydrothermal carbonization (HTC) is found to be a more attractive process, because it could deal with variety of wet or high moisture feedstock without pre-treatment and water can be used to facilitates the thermal conversion reaction. Therefore, hydrothermal carbonization method is a cost and energy effective thermochemical process compared to conventional pyrolysis method.

In addition, in HTC process various parameter may also affect the yield and quality of hydrochar, where the most common parameters is temperature and reaction time. Theoretically, at high temperature and reaction time, the yield of the hydrochar will be higher due to the high conversion rate of raw OPEFB to hydrochar. Therefore, since both parameters could affect the yield and quality of the hydrochar, the HTC process will be conducted with various reaction time and temperature in order to determine the parameter that has significant effect on the hydrochar production.

Furthermore, for the application, hydrochar that is produced from the HTC might be very useful to be used as soil amendments to improve the fertility of the soil. Some of the problems that rises in Malaysian agricultural industry is, excess use of chemical fertilizers. Generally, excess use of chemical fertilizers could cause negative impact to the environment such as eutrophication due to nutrient leaching from the soil. Basically, amending hydrochar to soil is effective practice that will improves the quality of marginalized agricultural land in impoverished regions and reduces environmental impacts. For instances, hydrochar amendment to soil might increases the cation exchange capacity (CEC). Because of the poor CEC in chemical fertilizers, water and nutrients are easily leached out of the soil, resulting in water and nutrient stress (Liang et al., 2006). Based on the reported studies, the use of hydrochar could improve soil physio-chemical properties of soil and increase agricultural crop yields (Manickam et al., 2015). Therefore, research also includes the study to determine the suitability of the hydrochar as soil amendment,

CHAPTER 2

LITIRATURE REVIEW

In previous chapter, an overview of OPEFB and hydrochar production from OPEFB via hydrothermal carbonization had been discussed. However, in this Chapter 2, a detailed literature review had been made, that presents the previous discoveries and reviews available from credible scientific records and references that are related to this research.

2.1 Oil Palm Empty Fruit Brunch (OPEFB) and Physiochemical Properties

Similar to other natural fibres, EFB fibres are naturally occurring composites consisting primarily of rigid, crystalline cellulose microfibrils which are embedded in a soft, amorphous matrix of hemicellulose and lignin. Rame (2018) stated that, the chemical composition of EFB fibres consist of cellulose (up to 65%) forms the bulk component of EFB fibres, followed by lignin (up to 29.2%), hemicellulose (up to 28.8%) and extractive (up to 3.7%). The Figure 2.1 below shows the structure and arrangement of OPEFB components.

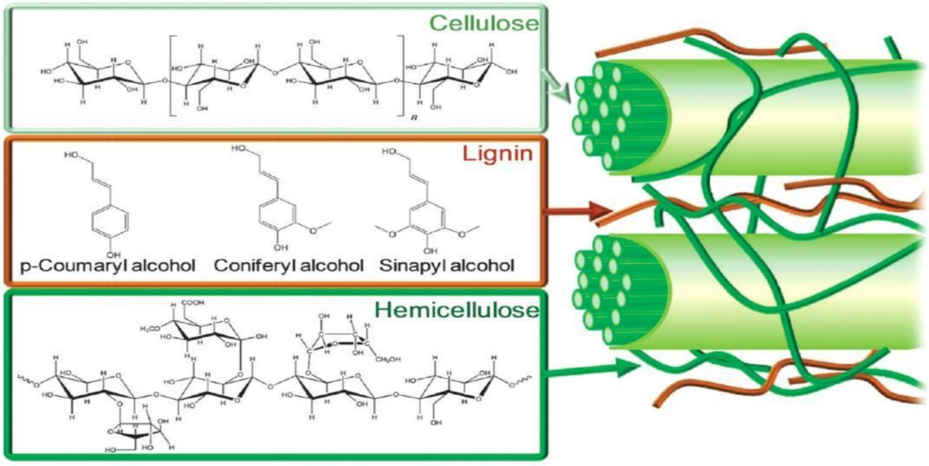

Figure 2.1: Structural representation of lignocellulosic biomass with cellulose, hemicellulose, and building blocks of lignin.

Moreover, in the year 2014 based on research made by Chang, a proximate analysis was made on the quantitative determination of moisture, volatile matter, fixed carbon, and ash contents within EFB fibers, whereas the ultimate analysis determines the amount of carbon, hydrogen, oxygen, nitrogen, and sulfur. According to the proximate analysis, EFB fibers are made up of volatile matter (up to 83.86 %), fixed carbon (up to 18.3 %), moisture (up to 14.28 %), and ash (up to 13.65 %). The high volatile matter concentration suggests that EFB fibres are easy to ignite, with an ignition temperature about 190 ◦C, and the large amount of fixed carbon implies that EFB fibres may generate a lot of heat when burned.

EFB fibres include significant proportions of volatile matter and fixed carbon, they have a high ratio of combustible to incombustible components and have a large high heating value (HHV) (17.02 - 19.35 MJ/kg), thus them a viable alternative to wood fuel. Ash, which is the solid residue of EFB that remains after combustion, consists mostly of metal oxides such as potassium oxide (2.4%), magnesium oxide (0.23%), silica (0.19%), phosphorus pentoxide (0.18%) and calcium oxide (0.13%).

Moreover, based on the performed literature review, in another research by Yan et al., (2019), a proximate and ultimate analysis was made on the raw EFB feedstock. Below Table 1.1 and Table 1.2 presents the average proximate and ultimate analysis respectively of the raw EFB feedstock.

Table 1.1: The Proximate analysis (air-dry basis, wt%) of the raw EFB biomass (Yan et al., 2019a)

Parameters	Value
Moisture content	7.86
Volatile matter	69.92
Fixed carbon	17.45
Ash	4.77

Table 1.2: Ultimate analysis (dry basis, wt%) of the raw EFB biomass feedstock (Yan et al., 2019a)

Parameters	Value
Carbon, C	46.72
Hydrogen, H	6.81
Oxygen, O	44.96
Nitrogen, N	1.26
Sulfur, S	0.25
Heating value, MJ/kg	17.78

Mosier (2005), also stated in his research that the soluble portion of an EFB fibre extract includes minerals (potassium (2.24 %), nitrogen (0.44 %), magnesium (0.36 %), calcium (0.36 %), phosphorus (0.144 %), proteins, pectic acids, fatty acids, phenols, oil, and wax. The hydrogen connections between distinct levels of cellulose chains, together with lignin crosslinking with both cellulose and hemicellulose, have generated a complex web of linkages that give EFB fibres their structural strength.

In another study, by Othaman, (2017), the author mentioned in his study that, complex matrix of three primary polymers, cellulose, hemicellulose, and lignin, makes up the building blocks of natural OPEFB fibre. Besides that, it was also reported that, OPEFB is composed 32.9% glucan, 22.4% xylan and 1.4% arabinan. Thus, OPEFB's lignocellulosic material has been touted as a great source of fermentable sugar for making value-added products. Cellulose and hemicellulose can be hydrolyzed chemically or enzymatically to yield glucose and other pentose and hexose sugars, which can then be fermented to produce bioethanol.

Oil palm empty fruit brunch, which is considered as main agricultural waste, is found to be potential feedstock where it can be used as raw material in production of various biofuel and bioproducts through biorefinery approach. In addition, OPEFB is characterized as lignocellulosic biomass material (LBM) which is natural, non-toxic, abundant, sustainable, and renewable material. Generally, LBM obtained from either from woody or non-woody plants where more than 198 billion metric tons are produced annually. OPEFB has the similar properties as the LBM from woody plants, therefore it has a great advantage as a cheap and highly available feedstock for numerous applications (Mohammad Padzil et al., 2020).

2.2 Hydrochar and its Physiochemical Properties

It is undeniable that OPEFB has the unique characteristics or properties which enables it to be used as feedstock to produce various high valuable products where in our study hydrochar is one of the high value products developed from the OPEFB. Thus, physiochemical properties of the OPEFB will affect the quality or properties of the hydrochar yield from OPEFB. However, the criteria or the properties (physical and chemical) of the hydrochar is highly dependents on the processing conditions and feedstock composition (Vakros, 2018). As an overview, physical properties of hydrochar depend on size and its porosity whereby, the chemical properties of hydrochar on the percentage is based on the composition of the C, H, N, S, and O. The C, H, O, S, N etc., are present in the biomass as a complex biomolecule like hemicellulose, lignin, cellulose, etc. through C–C, C=C, –OH, –COOH, C–O–H, C=O, C–H linkages along with the inorganic anions like HCO3–, CO32– etc (Jeyasubramanian et al., 2021). Unlike the carbon found in most organic matter, the chemical environment of the carbon in hydrochar is altered during the heating process to produce aromatic structures that are highly resistant to microbial decomposition. Hence, Lehmann (2009) had reported that, the carbon compounds in hydrochar are stable for long periods of time, and effective for long-term C sequestration. For instances, according to Warnock et al., (2007), hydrochar is stable for 1000 to 10,000 years in soil, with an average of 5000 years, without any microbial decomposition. As for the processing condition, as per mentioned earlier Hydrothermal Carbonization (HTC) is a most promising technology for the conversion of the biomass into hydrochar. Therefore, operating parameters such as temperature and reaction time could also affect the properties of the hydrochar.

2.3 Hydrothermal Carbonization (HTC)

In a hydrothermal carbonization process, the biomass feedstock is heated in a high-pressure reactor at temperatures ranging 180 to 280°C (Reza et al., 2014). Thus, the biomass is decomposed by a series of simultaneous reaction in liquid phase, comprising of hydrolysis, dehydration, decarboxylation, aromatization, and recondensation. Therefore, this will reduce the hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios in biomass which in return increase the carbon-rich content in the hydrochar (Funke and Ziegler, 2010a). The product of the HTC is mainly consisting of wet solid hydrochar and liquid which consists of mainly water and solubilized organic products. At the same time, distribution of solid and liquid in products rely on the feedstock composition and process conditions, primarily temperature and residence time (Liu et al., 2013).

To describe in detail on the reaction chemistry of the hydrothermal reaction, initial reaction would be hydrolysis reaction, where water reacts with extractives, hemicellulose, or cellulose and breaks ester and ether bonds (mainly β-(1-4) glycosidic bonds), which will cause the formation of the wide range of products, including soluble oligomers like (oligo-) saccharides from cellulose and hemicellulose. Further, the hemicellulose will be hydrolysed at 180°C, but cellulose hydrolysis starts above 230°C. Cellulose can be broken down into oligomers, with some of the oligomers hydrolyzing into glucose and fructose. In hydrothermal process, other components such as extractives, which are monomeric sugars (mostly glucose and fructose) as well as different alditols, aliphatic acids, oligomeric sugars, and phenolic glycosides, are highly reactive.

Dehydration and decarboxylation of hydrolyzed products are most likely to occur simultaneously just after hydrolysis. The considerable decrease in oxygen content could be due to the reduction of carboxyl groups, primarily from extractives, hemicellulose, and cellulose. Hydrolyzed products degrade into furfurals such 5-HMF, erythrose, and aldehydes under hydrothermal conditions, which then dehydrate and decarboxylate into CO_2 and H_2O. Furthermore, the polymerization of hydrolyzed intermediates can result in the production of water. Retro-condensation of 5-HMF into aldol condensation or keto-enol condensation of n monomers, for example, produces n moles of water. As shown in the Figure 2.4 below, most of the intermediate molecules (5-HMF, anhydroglucose, furfural, erythrose, and 5methyl furfural) generated by dehydration and decarboxylation reactions of monomers undergo condensation, polymerization, and aromatization.

Bio-crude which is the product of simultaneous condensation, polymerization, and aromatization will further transform into a solid product which is hydrochar via sequential polymerization an aromatization. Hydrochar can be produced from a liquid-liquid (liquid biocrude), a liquid-solid (resulting from a liquid biocrude and solid lignin residue), or even a solid-solid reaction. The hydrochar is a cross-linked polymer, and has similar acid digestion properties as lignin, so it is almost impossible to distinguish from unreacted lignin fraction. Thus, a linear polymer like cellulose can convert into a cross-linked polymer similar to lignin. Among thermochemical conversion processes of biomass, HTC reactions in the liquid state is found to be different. The reaction chemistry of HTC reactions will determine the usage of HTC process streams.

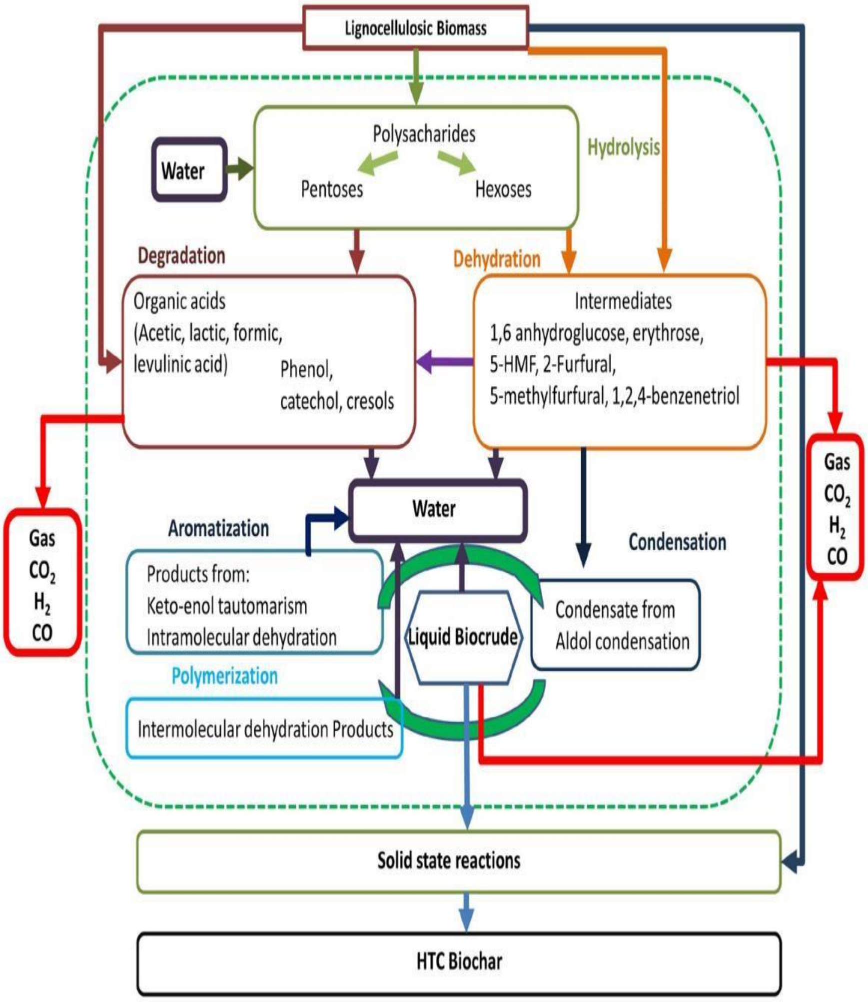

Figure 2.4: HTC Reaction Pathways for Lignocellulosic Biomass. (Reza et al., 2014)

Major benefits of HTC over other high temperature thermochemical conversion techniques is that HTC process allows wet biomass feedstocks for conversion process without pre-drying. As per stated in Ohioline, (2021), variety of feedstocks, including aquatic biomass, agricultural residues, and industrial and animal wastes, are feasible for HTC to carbonize moist biomass, without costly and energy consuming pre-drying step. Moreover, water in HTC will act as medium of heat transfer, and also facilitates the hydrolysis of the lignocellulosic structure of the biomass feedstock. Presence of water accelerates the carbonization process of biomass and simultaneously affects the product distribution (Ramsurn and Gupta, 2012).

HTC produces hydrochars with greater energy density and combustion reactivity, which showed that HTC appears as an energy efficient treatment for moist organic residues for the conversion of biomass into bio-energy feedstock (Liu et al., 2013; Benavente and Fullana, 2015). In addition, carbonization reactions and disruption of colloidal structures improves the dewaterability properties of the hydro-char as it helps release the bound water and thus is highly beneficial for biosolids management (Wang et al., 2018). Apart from that, there are also some drawbacks from the HTC technologies where, the mass transfer will be limited if, the feedstock particle size is inconsistent and reaction time is too short. Hence, the particle size should be homogeneous to ensure uniform heat and mass transfer (Ohioline, 2021).

2.4 Hydrochar Production from Oil Palm Empty Fruit Brunch

Pyrolysis process in the presence of sub-critical liquid water, at high temperature and pressure, is called wet pyrolysis or hydrothermal carbonization (HTC). Traditionally, pyrolysis method is widely used as carbonization method, but recently, hydrothermal process, had attracted much research, to develop it as most efficient technology for hydrochar production. Several research, are made on recent decades, on the hydrothermal carbonization method, to discover on its real potential over other carbonization technology.

Production of hydrochar from the OPEFB, has attracted many researchers as it is the most abundantly available biomass feedstock and it very much feasible for HTC due to its high moisture content. Basically, there are various research on the production method of the hydrochar from Empty Fruit Brunch (EFB). For instances, in 2016, Sarwono et al., has performed a hydrothermal carbonation of certain amount of EFB in reactor with 50 ml of water.

From the experiment, it could be found that the carbons content of the fixed carbon increased from 10% in raw material into 30% in the hydrochar and the HHV (MJ/Kg) had increased from 14.94 MJ/Kg in raw material to 20.15 MJ/Kg in biochar.

Yan et al., (2019) conducted research on hydrochar production from EFB using hydrothermal treatment. The process was carried out in a 500 mL hydrothermal reactor, at various temperature ranging from 120 – 220 °C with residence time of 60- and 120-min. Based on the results of the experiment, it is found that, hydrothermal treatment improved the physiological properties of raw EFB, in such way that improves the compositions od fixed carbon, lowers ash content, higher energy density and also high heating value of hydrochar increases to19.47 MJ/kg from 17.78 MJ/kg in EFB.

Most recently, research was made by, Kim et al., (2021), to specifically enhance fuel characteristics of the hydrochar that is synthesised from EFB. The experiment was carried out at temperatures ranging from 180°C to 250°C with a 10°C interval, with mass ratios of 1:8 and 1:16 between the dry sample and water content to ensure that the sample was adequately immersed. In addition, mass and energy yields, elemental analysis, proximate analysis, thermogravimetric analysis, derivative thermogravimetry, and Fourier transform infrared spectroscopy analysis of the reaction products were used to investigate the material properties of EFB under hydrothermal treatment conditions. It is identified that at high temperature, the fixed carbon content and heating value increased due to removal of the volatile matter, including oxygen initially. Carbon and oxygen make up 42.3 % and 36.4 % of the total content respectively, while the rest was estimated by subtracting carbon, hydrogen, nitrogen, and oxygen from the total. In the analysis for functional group, it is found that, the peaks of the O–H and C–H bonds of cellulose and hemicellulose hardly changed, but the peaks that represents lignin-based C=C and C=O stretching became more obvious compared to those of raw EFB after hydrothermal treatment.

2.5 Hydrochar derived from Oil Palm Empty Fruit Brunch

Apart from utilization of OPEFB for bioethanol production as a source of biofuel, another alternative for the usage of EFB is for the production of hydrochar. Hydrochar is a carbonaceous material or carbon rich material which is produced from the thermochemical process of the various biomass feedstock with absent or limited supply of oxygen (Kong et al., 2014). It is a highly carbon rich (65–90%) solid product that contains numerous pores and oxygen functional groups and aromatic surfaces (Qambrani et al., 2017). Hydrochar has high biodegradability, high contents of total and organic carbon, as well as optimal concentrations of micro- and macro elements (potassium, sodium, magnesium, calcium, copper, zinc, iron etc. Vakros, (2018), had mentioned that since EFB has high carbon content, rich in lignin and available abundantly, it has the potential as a precursor to produce hydrochar.

Hydrochar consists of large specific surface area, high content of surface functional groups, and exhibits high porosity, with longitudinal pores of sizes ranging from micro- to macropores (Tomczyk, Sokołowska and Boguta, 2020). Whereby, micropores are responsible for surface area and high absorptive capacity, while mesopores are important for liquid-solid adsorption processes. The size and pattern of pores in hydrochar depends on the composition of the feedstock materials and the temperature adopted during hydrochar formation (Qambrani et al., 2017).

There are several studies, that analyses on the properties of the hydrochar from HTC process. For instances, Parshetti et al., (2013) had discovered from his research that, the hydrothermal carbonization of EFB provided carbonaceous solid products containing around 50–66% of the carbon originally present in the raw material, depending upon the process temperature used. Theoretically, both the H/C and O/C ratios decreased when the temperature was raised. Therefore, with increasing operating temperature, the carbon content of the hydrochar rises, while the hydrogen and oxygen contents decrease steadily. H/C and O/C atomic ratios, calculated for the initial biomass, and the resulting product, were displayed using a Van Krevelen diagram, as per shown in Figure 2.5, which is useful for representing the conversion of carbohydrate material to carbon-rich material. At higher operating temperatures, the dehydration trend became more obvious as compared to the one at the lower operating temperatures.

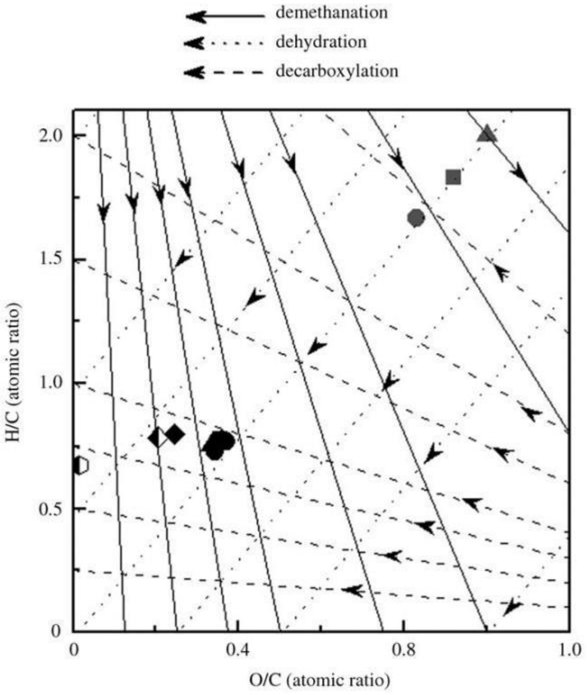

Figure 2.5: H/C versus O/C van Krevelen diagram of saccharides and the hydrochar products resulting from hydrothermal carbonization. (Marta Sevilla and Fuertes, 2009)

A shift in the O/C ratio suggests that decarboxylation also occurs during the HTC process (Marta Sevilla and Fuertes, 2009). Other than that, calorific value is an indication of the degree of coalification achieved. Higher HTC temperature promotes the dehydration, decarboxylation, and condensation reactions of the coalification process, thereby resulting in energy densification.

Furthermore, another study by (Nalaya et al, 2020) also made proximate analysis on the physiochemical properties of biochar, for instances pH of the biochar, at different carbonization temperature. It is discovered that, at lower temperature, the pH of the hydrochar is significantly lower. Based on the theory, the separation of alkaline salts from organic materials at the high pyrolysis temperature of the EFBB could explain the increase in pH values with increasing temperature.

2.6 Effect of the Operating Conditions for Hydrochar production

In the production of the hydrochar via Hydrothermal Carbonization Method, there are a lot of factors that possibly could affect the hydrochar yield. Based on the literature review, the most common parameters that have influence on the HTC process, is reaction temperature, reaction time, operating pressure, and biomass-water-ratio. Therefore, the effects of these parameter will be further discussed in the following section.

2.6.1 Reaction Temperature

Generally, temperature in considered as a key parameter in an HTC processing, which could cause a significant effect on the disintegration for fragmentation of the biomass bond. According, from a well-established literature by, (Nizamuddin et al., 2017a), it is stated that effectiveness of biomass conversion is directly proportional to an increase in temperature due to additional energy being delivered by the temperature to break the biomass bonds. Besides, in HTC, the solid production declines as the temperature rises, but conversely the liquid and gaseous products will increase. In general, solid products are prominent in the temperature ranges of 150 – 200 °C; liquid yields are larger in the moderate temperature ranges of 250 –

350 °C; and above 350 °C, gas formation yield leads to solid and liquid products. Carbonization at lower temperatures produces a higher amount of solid. At a higher temperature carbonization is greater resulting in the formation of more liquid and gaseous products along with lower solid products.

It is also found that, at higher temperatures during HTC process, the magnitude of aromatization of carbon structure increases. Furthermore, the fact that materials aromatize more at high temperatures can be related to the hydrochar and aromatic structures being arranged with fewer reactive sites, less abrupt disintegration, and therefore a well-organized hydrochar structure created under optimum conditions. Hence, temperature is found to be main operating condition that significantly affect the hydrochar yield.

Similarly, in another study (Jamari & Howse, 2012), well describes the effect of the temperature on solid fuel that produced from the HTC process of the empty fruit bunch (EFB). According, to the outcome of study, it is proven that the carbon value increased with increase in temperature in contrast to hydrogen and oxygen content. At higher temperatures, the oxygen and hydrogen contents decreased validating the removal of these substances with temperature.

Moreover, recently (Kim et al., 2021), had investigated on the effect of the hydrothermal temperature, on the production of carbon. It has been discovered that, as reaction temperature increases, both O/C and H/C ratios reduce and the characteristics of EFB to become gradually more similar to those of coal. Furthermore, the mass yield of hydrothermally treated EFB drops when oxygen-containing volatile compound (VM) was decomposed and eliminated, while the heating value increased as the fixed carbon content increased, according to the mass and energy analysis.

2.6.2 Reaction Time

Similarly, Nizamuddin et al., (2017), also stated that apart from temperature, reaction time is also one of the factors that affect the hydrochar properties and yields. Based on the review made by, Nizamuddin et al., (2017), was mentioned that residence time influences hydrolysis processes only up to a certain point in time, beyond which it does not have any specific impact on the process. Even though, reaction time as minimal effect on the process, however higher reaction durations yield a larger amount of solid output.

However, at a supercritical state, the hydrolysis rate and biomass degradation rate are both relatively fast. As a result, a shorter period is necessary to properly breakdown biomass. Moreover, according to Nizamuddin et al., (2017) there was also study made using a short run time. So, it is discovered that, solid fuels produced have higher heating values. This is due to the removal of oxygen present in biomass or by hydrolysis of hemicellulose. Besides that, when carried out at a lower run time (up to half of an hour) resulted in the production of HTC solid with a heating value equal or greater than lignin. During HTC process the higher the reaction time the greater the formation of defined structure porosity, pore volume and high BET surface area and vice versa.

However, in a study by, Lu et al., (2013), it was revealed that the reaction time was found to be the crucial factor, which affects the yield of the hydrochar production. For instances, the study reports that the carbon distribution hydrochar changes with reaction time and provides insight to carbonization pathways/mechanisms. In the time ranges from 0 to 6–8 hr, a significant change in carbon distribution could occur. During this period and following an initial lag, a rapid decline in solid-phase carbon is observed, likely due to feedstock solubilization

Therefore, residence time or the reaction time, of the EFB, in the reactor also gives impact on the, hydrochar yield. Regarding this, a study was made by (Sarwono and Sembiring, 2016), but it is discovered that, 6-hour reaction time, has a greater conversion rate (about 62%) than 4-hour reaction time, even though the conversion rate is only slightly different. It is indicated that increasing the reaction time, did not result in a significant increase in EFB conversion. As a result, temperature appears to be the process parameter with the greatest impact on product qualities. Thus, temperature increases reaction rates, which has a significant impact on the quantity of biomass compounds that can be hydrolysed.

2.6.3 Operating Pressure

Apart from temperature and reaction time, operating pressure could significantly affect the conversion of the biomass into hydrochar. Related to this, a literature by (Funke & Ziegler, 2010b), gives an insight that, generally the carbonization process in the HTC reactor, is influenced by pressure based on Le Chatelier's principle. For instance, at high pressure condition the equilibrium shift from solid to liquid phase or vice versa are decided according to this principle. At the same time, it is a fact that the shift is towards the direction constituting a lesser number of moles. For example, both decarboxylation and dehydration reactions are depressed at higher pressure.

Similarly, in a separate study (Akhtar & Amin, 2011) discovered by maintaining the reactor pressure above the critical pressure of medium, rate of hydrolysis or degradation of the biomass feedstock can be controlled. This could greatly increase the number of acceptable reaction pathways that thermodynamically favour biomass conversion to valuable products. In addition, at high pressure condition, the density of solvent might increase, therefore, higher rate of extraction and disintegration of biomass is achieved by using high-density solvents.

As a result, the pressure in an HTC reactor can be increased, either by increasing the temperature directly or by adding fluids such as nitrogen. Besides, high pressure coupled with high temperature, will provide extreme environment where, the breaking of biomass composition occurs hastily and high quality of hydrochar is obtained in HTC process as final product Nizamuddin et al., (2017).

2.6.4 Biomass to Water Ratio

It is undeniable that, water that included in the HTC will act as catalyst or solvent under a supercritical condition where it facilitates the hydrolysis on the biomass feedstock and accelerates the carbonization process of biomass and affects the product distribution as well. There are also several research is proposed to identify the correlation between the biomass water ratio and hydrochar yield. In this case, from a literature reported by Oktaviananda et al., (2017), the hydrochar yields reported to have higher yield at higher ratio. Therefore, at the minimum ratio, low concentrations of solvent (water) were unable to dissolve the high concentration biomass possibly due to the decrease in dissolving power. Similarly, in another study, Mohammed et al., (2020), also supports that lower biomass/water ratios stimulate total disintegration biomass, resulting in a small amount of solid fuel.

2.7 Chemical Activation Solid EFB Hydrochar

Further, as an optional alternative, with aid of suitable physical and chemical treatments the physical and chemical properties of hydrochar could be improved. Based on the review by, Sajjadi et al., (2019), chemical activation is the process where, hydrochar is doped with a chemical agent to modify surface functional groups. In this process following to the thermal treatment, the precursor (hydrochar) would be impregnated with the chemical agent. For instances, chemical activation performed by soaking or suspending, the hydrochar in a chemical agent solution [at a ratio of up to 1:10] at temperature up to 120°C for a specific duration. Hereby, at high temperature a functional group-rich char would be produced and promote the formation new nanopores, and the subsequent enhancement in surface area (ElHendawy, 2009). At the same time, the application of various chemicals results in the formation of diverse surface functional groups. The Figure 2.6 below shows the pore development of empty fruit bunch (EFB) hydrochar, represented with A, B and C (Ukanwa et al., 2019).

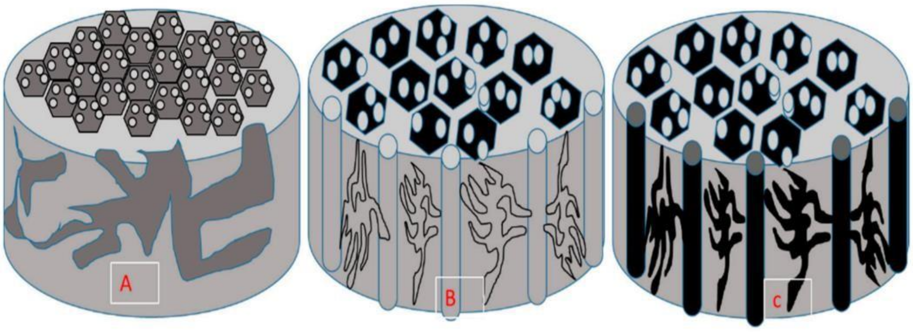

Figure 2.6: Activation effect on activated EFB hydrochar in pore development and morphology A: biomass structure; B: partially developed char structure; C: well-defined porous AC (Ukanwa et al., 2019)

There are several researches made on chemical activation EFB hydrochar, where one of them is recently made by Ibrahim et al., (2021), which is solely done to improve the adsorption activity of the EFB hydrochar. Hence, according to the study, 1.0 M of nitric acid solution was prepared by diluting the concentrated nitric acid with deionized water. Then, in a 500 mL Erlenmeyer flask, 5.0 g hydrochar was mixed with 100 mL of 1 M nitric acid solution and autoclaved for 60 minutes at 132°C and 35 psi. After cooling to roughly 60°C, the mixture was filtered and washed with distilled water until the pH of the rinsing water reached 6–7. The functionalized hydrochar was next dried in a desiccator for 24 hrs at 75 ◦C.

Similarly, in another research by Ketwong et al., (2022), washed hydrochar, was chemically impregnated in KOH solution at a ratio of 1:3 percent (w/w). The KOH impregnated hydrochar was agitated for 2 hours, then centrifuged and dried for 12 hours. Initially, a 2-step activation process was carried out by heating at 200 °C with the 1 hr reaction time and further the temperature was raised to 800 °C with similar reaction time. Further, the activated hydrochar was washed with deionized water and followed by 3 M of HCl solution to neutralize the hydrochar and lastly the activated carbon was dried overnight at 105 °C.

2.8 Soil Amendment

Basically, soil amendments are a well-known practice to improve the soil quality in terms of the soil structure and biochemical functionality. Basically, there are two basic type of soil amendments that are commonly utilized to enhance soil quality which are organic soil amendments and inorganic/mineral amendments. It has been discovered that adding soil amendments (organic and inorganic) will improves soil pH (3.2–7), lowering trace metal solubility by more than 80%, and assists in stabilizing the soil (Maiti and Ahirwal, 2019).

Organic amendments are composed of organic molecules derived from biomass and/or living beings. Usually, the organic amendments include, compost, wood chips, animal manure, straw, husk, sewage manure and as well as hydrochar. These substances are proven to have