

**PRODUCTION OF HYDROCHAR-BASED CATALYST  
FROM OIL PALM TRUNK VIA HYDROTHERMAL  
CARBONIZATION**

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**PRODUCTION OF HYDROCHAR-BASED CATALYST FROM OIL PALM  
TRUNK VIA HYDROTHERMAL CARBONIZATION**

**by**

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## LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
C <sub>2</sub> H <sub>6</sub>	Ethane
C <sub>2</sub> H <sub>4</sub>	Ethylene
CH <sub>4</sub>	Methane
C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	Hemicellulose
DP	Degree of Polymerization
DTG	Derivative-Thermogravimetric Curve
EFB	Empty Fruit Bunches
FTIR	Fourier Transform Infra-Red
HHV	High Heating Value
HTC	Hydrothermal Carbonization
H <sub>3</sub> PO <sub>4</sub>	Phosphoric Acid
KOH	Potassium Hydroxide
K <sub>2</sub> CO <sub>3</sub>	Potassium Carbonate
LRS	Lignin-Rich Stream
MF	Mesocarp Fibres
NaOH	Sodium Hydroxide
OPF	Oil Palm Fronds
OPT	Oil Palm Trunk
PKS	Palm Kernel Shells
POME	Palm Oil Mill Effluent
SEM	Scanning Electron Microscope
TGA	Thermo-gravimetric Analysis
TOC	Total Organic Carbon
ZnCl <sub>2</sub>	Zinc Chloride

## ABSTRAK

Batang kelapa sawit adalah salah satu sisa yang paling banyak dihasilkan oleh ladang kelapa sawit. Bagi pengurusan batang kelapa sawit, ia boleh digunakan untuk menghasilkan produk dan bahan api berasaskan bio. Penggunaan batang kelapa sawit boleh dicapai melalui pelbagai proses penukaran termokimia. Antara proses penukaran termokimia, hidroterma karbonisasi adalah proses mesra alam yang merawat biojisim mentah pada suhu tinggi dengan menggunakan air. Melalui satu siri mekanisme tindak balas, termasuk hidrolisis, dehidrasi, dekarboksilasi, dekarbonilasi, pempolimeran dan pemeluwapan semula, hidroarang pepejal dijana. Objektif kajian ini adalah untuk menghasilkan hidroarang dan pemangkin-berasaskan-hidroarang daripada batang kelapa sawit melalui hidroterma karbonisasi. Kesan suhu dan masa tindakbalas proses hidroterma karbonisasi telah dikaji pada suhu berbeza 180 °C dan 220 °C dalam tiga keadaan masa tindakbalas; 0.5 jam, 1 jam dan 2 jam. Didapati bahawa suhu proses memberi kesan yang lebih ketara terhadap hasil hydrochar berbanding dengan masa tindakbalas proses. Kajian mendapati keadaan yang paling optimum untuk peratusan hasil hydrochar adalah pada 180 °C dengan 1 jam masa tindakbalas. Impregnasi hidroarang dengan kalium hidroksida telah dijalankan untuk mengkaji kemungkinan menggunakan hidroarang yang dihasilkan sebagai sokongan untuk pemangkin. Fourier Transform Infra-Red (FTIR), Brunauer-Emmett-Teller (BET), Analisis Thermo-gravimetrik (TGA) dan Mikroskop Elektron Pengimbasan (SEM) telah dilakukan untuk mencirikan batang kelapa sawit mentah, hidroarang dan pemangkin-berasaskan-hidroarang. Analisis SEM dalam kajian menunjukkan bahawa proses hidroterma karbonisasi telah mengubah struktur batang kelapa sawit dengan ketara sehingga permukaan hidroarang menjadi berliang, manakala impregnasi dengan kalium hidroksida telah mengubah permukaan hidroarang menjadi lebih tidak

rata dan tidak teratur. Selain itu, luas permukaan BET hidroarang meningkat selepas proses HTC. Tambahan pula, analisis FTIR menunjukkan bahawa bahan fungsi (*functional group*) untuk kedua-dua batang kelapa sawit mentah dan hidroarang adalah sama, tetapi sedikit berbeza daripada pemangkin-berasaskan-hidroarang. Analisis TGA mendedahkan bahawa kinetik penurunan berat badan mungkin serupa untuk ketiga-tiga bahan tersebut. Berdasarkan keputusan ini, sifat hidroarang berubah mengikut suhu, masa tindakbalas serta kaedah impregnasi. Oleh itu, suhu, masa tindakbalas dan kaedah impregnasi akan mempengaruhi hasil hidroarang dan aplikasi pemangkinnya.

## ABSTRACT

Oil palm trunk (OPT) is one of the most abundant wastes from the oil palm plantation. In order to manage the oil palm trunk, it can be utilized to produce biofuel or bio-based products. The utilization of oil palm trunk can be achieved by various thermochemical conversion process. Among the thermochemical conversion processes, hydrothermal carbonization (HTC) is eco-friendly process which treats raw biomass in the presence of water at elevated temperature. Through a series of reaction mechanisms, including hydrolysis, dehydration, decarboxylation, decarbonylation, polymerization and re-condensation, solid hydrochar is generated. The objective of this study is to produce hydrochar and hydrochar-based catalyst from oil palm trunk via hydrothermal carbonization (HTC). The temperature and residence time of HTC process were varied at 180 °C and 220 °C under three residence times; 0.5 hour, 1 hour and 2 hours and the effects on the yield of hydrochar were studied. It was observed that the reaction temperature has a greater effect on the hydrochar yield as compared to the residence time. The optimized condition for hydrochar yield (48.77 %) was found at 180 °C with the residence time of 1 hour. Impregnation of hydrochar with potassium hydroxide (KOH) was carried out to study the possibility of using the produced hydrochar as a support for catalyst. Fourier Transform Infra-Red (FTIR), Thermo-gravimetric (TGA) Analysis, Brunauer-Emmett-Teller (BET) and Scanning Electron Microscope (SEM) were carried out to characterize the raw OPT, hydrochar and hydrochar-based catalyst. SEM analysis revealed that the HTC process has altered the structure of oil palm trunk significantly to become hydrochar with a porous surface, while impregnation of KOH has altered the surface of hydrochar to become more uneven and irregular. Moreover, the BET surface area of hydrochar increased after HTC process. Besides, FTIR analysis shows that the functional groups for both raw

oil palm trunk and hydrochar is basically the same, but slightly different from hydrochar-based catalyst. The TGA analysis revealed that weight loss kinetics was likely similar for all of them. Based on these results, properties of hydrochar varied according to temperatures, residence time as well as the impregnation of KOH. Therefore, the temperature, residence time and impregnation method significantly affect the production of hydrochar and its catalytic application.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Biomass is a viable potential source of renewable energy in the perspective of current energy scenarios. Due to the increasing of energy consumption and rapid depletion of fossil fuels, the current state of the world's energy supply has been receiving attention. As global energy demands increase exponentially over time, many researchers tend to develop alternative energy and chemicals by introducing green energy sources such as biofuel and bio-based products from biomass due to the versatility, plentiful availability and carbon-neutral property of biomass (Soh *et al.*, 2021a). Utilising biomass as a sustainable source for renewable energy and bio-based products also offers a holistic approach for managing the disposal of local biomass.

Oil palm industry is the largest agriculture sector, generating the most biomass residues which account for 85.5 % in Malaysia as shown in Figure 1. 1. It was estimated oil palm cultivation and palm oil production activities generate more than 83 million tons of dry solid biomass (Mohamed and Yusup, 2021; Soh *et al.*, 2021a), which includes oil palm trunks (OPT), palm kernel shells (PKS), empty fruit bunches (EFB), oil palm fronds (OPF), and mesocarp fibres (MF). Although some of the biomass is utilised, there is still a significant amount of oil palm biomass especially OPT that is not fully utilized as it is often left on the oil palm plantation for mulching process. As a result, the quantity of waste generated from the oil palm industry might outweigh the market demand. In this context, OPT represents a viable opportunity, not only because of its availability, but also its exploitation favours the reduction of fossil

fuel use, as well as development of new green markets by utilizing it as raw material for hydrochar production.

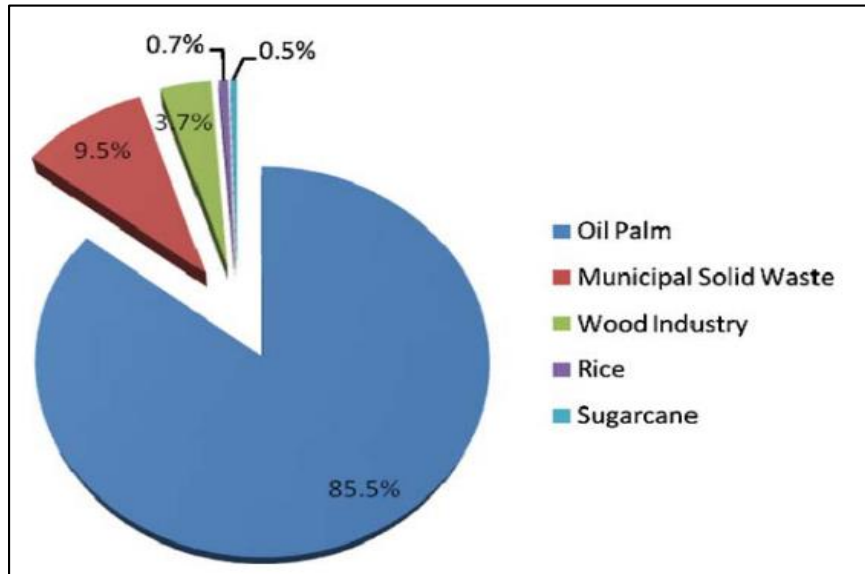


Figure 1. 1: Biomass Contributions from various industries in Malaysia (Ahmad, Kadir and Shafie, 2011)

Oil palm trunk, a solid waste that is available year-round in oil palm plantations. It is obtained in vast numbers after oil palm trees are cut down. Moreover, it is also generated from the upstream of palm-oil industry. Mohamed and Yusup, (2021) have characterized the chemical composition of oil palm trunk which is shown in Table 1.

1. Oil palm trunk is largely made up of parenchymatous tissues with countless vascular bundles and fibrous strands. Typically, OPT has a circular shape in lateral direction and it consists of two parts which are: 1) the major part of the trunk that contains three sections: outer, inner as well as middle and 2) the cortex with the bark (Rosli *et al.*, 2016) as shown in Figure 1. 2.

Table 1. 1: Chemical composition of oil palm trunk (Mohamed and Yusup, 2021)

Composition (wt % dry basis)	Cellulose	Hemicellulose	Lignin	Extractive	Ash
Oil Palm Trunk (OPT)	34.5	31.8	25.7	3.7	4.3

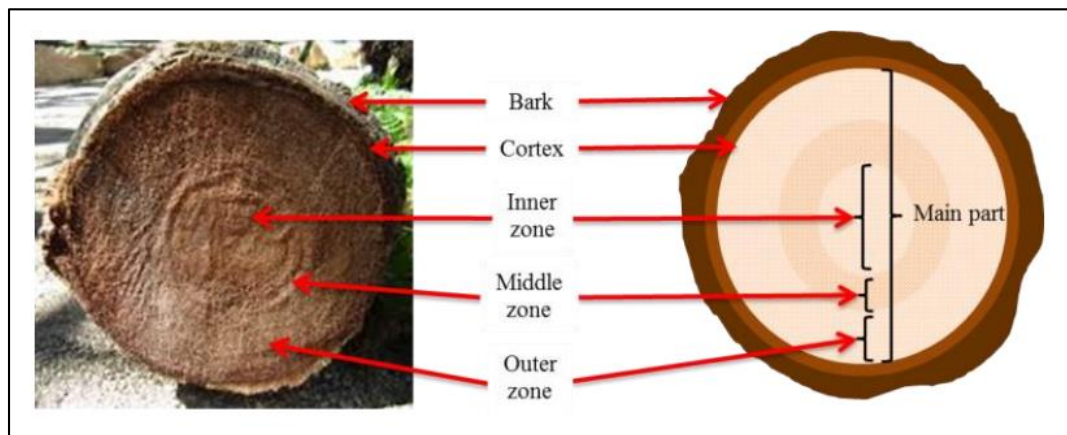


Figure 1. 2: Schematic illustration with an actual end of OPT crosscut (Rosli *et al.*, 2016)

A variety of biomass treatments such as mechanical treatment, biological treatment and their combination can be used for the conversion of biomass such as oil palm trunk into various bio-based products including biofuel. However, these treatments have some drawbacks such as long duration and formation of unpleasant smell (Sarwono, Tursiloadi and Sembiring, 2016). Among various types of biomass conversion processes, hydrothermal treatment is seen as a progressive technology to convert oil palm biomass into hydrochar with better properties and quality. The advantages of hydrothermal process included: (i) high flexibility on the feedstock selection (Sarwono, Tursiloadi and Sembiring, 2016), (ii) do not require costly and energy-consuming pre-drying process as the media is in the liquid phase (Román *et al.*, 2018), (iii) short duration with high reaction rate (Román *et al.*, 2018), and (iv)



simple and economical operation. Traditionally, pyrolysis of lignocellulosic biomass has been one of the primary alternatives for producing carbonaceous products. Lignocellulosic biomass will undergo thermal decomposition over a wide temperature range (300 °C - 1000 °C) under anaerobic conditions (Libra *et al.*, 2011; Alfredo Quevedo-Amador *et al.*, 2022). As the operating temperature for pyrolysis is comparatively high, more operational and investment cost are required for the high energy consumption. In contrary, hydrothermal carbonization process requires a lower reaction temperature (180 °C - 220 °C) compared to pyrolysis (Sarwono, Tursiloadi and Sembiring, 2016) which indicates that the production cost will be lower. Hydrothermal carbonization treats biomass in the presence of water under saturated pressure and high temperature for a few hours (Román *et al.*, 2018). The solvent properties of water will be improved and the hydrolysis of organic compounds will be facilitated by the presence of water in subcritical condition at elevated temperature. Through a series of reactions such as hydrolysis, dehydration, decarboxylation, decarbonylation, polymerization and recondensation, biomass is converted into char as the reaction proceeds. (Román *et al.*, 2018).

Hydrochar is the major product which has the properties of high carbon content, hydrophobicity and grindability. Liquid fraction is a by-product that contains a number of valuable organic chemicals such as hydroxymethylfurfural, furfural, lactic acid, acetic acid, formic acid, and levulinic acid (Nakason *et al.*, 2017). Hydrochar is a solid matrix resulted from the HTC of lignocellulosic biomass that is characterized by a carbon phase with high amount of oxygenated functional groups on its surface (Alfredo Quevedo-Amador *et al.*, 2022). Hydrochar has many potential applications such as carbon sequestration, soil amendments, bioenergy production, energy storage as well as wastewater pollution and environmental remediation (Zhang *et al.*, 2018).

One of the another important usage of hydrochar is to be used as a support for the production of hydrochar-based catalyst. The existence of these surface functionalities of hydrochar can be exploited to enhance the binding of catalytic species on the carbon-based solid. However, the hydrochar usually exhibits relatively low surface area and even non-porous, due to the formation of hydrocarbons on the surface, which limits its catalytic properties (Khodaverdian *et al.*, 2018). With the aid of activation treatments using a variety of activators such as KOH, ZnCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, and NaOH, hydrochar-based catalyst may have a better properties such as large pore volumes and surface area for catalytic application. The incorporation of activation methods expand the utilization of hydrochar as catalyst material for enzymatic and heterogeneous catalytic reaction. For instance, hydrochar-based catalyst can be used to catalyse the production of biofuel. By replacing conventional homogeneous catalyst with environmentally sustainable heterogeneous catalyst which is hydrochar-based catalyst seems to be essential for the advantage of lower costs of production and environmental concerns.

## 1.2 Problem Statement

The combination of rising energy consumption and continuous depletion of fossil fuel resources; together with the tremendously abundance of oil palm biomass without being completely utilised are among some of the main challenges facing mankind today. Therefore, there is a need for oil palm biomass to act as a renewable source for sustainable development of bio-products and green energy in order to minimize the dependence on fossil-based energy. Conversion of oil palm biomass using thermochemical methods such as dry pyrolysis, torrefaction and gasification have been studied by previous researchers. Unfortunately, these techniques possess a drawback in terms of economic viability mainly due to the high moisture content. Any feedstock with high moisture contents will need to undergo drying before processing. Due to the necessity of energy on the pre-drying of biomass, the more feasible choice would be eliminating any feedstock with high moisture content. Thus, this study emphasizes the significance of using hydrothermal carbonization for the utilization of high moisture feedstock. Oil palm trunk has been selected due to its vast amount produced from the local oil palm plantation industry. Apart from that, report on the use of oil palm trunk for hydrochar production using hydrothermal carbonization treatment is still very limited. In addition to that, the conversion of hydrochar derived from biomass into hydrochar-based catalyst that can catalyse transesterification reaction for biodiesel production is also rarely reported in the literature. Therefore, this study will focus on the production of hydrochar and also hydrochar-based catalyst from oil palm trunk via hydrothermal carbonization using different operational parameters.

### **1.3 Objective**

This study aims

- (i) To study the effect of different operational parameters towards the conversion of oil palm trunks into hydrochar via hydrothermal carbonization.
- (ii) To characterize the properties of synthesized hydrochar and hydrochar-based catalyst.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.0 Introduction**

This chapter comprises an overview and the background of the study which are important to the understanding of motivation leading to the scope of this study. Relevant findings and literature by other researchers are reviewed in this chapter.

#### **2.1 Lignocellulose-Based Biomass as Feedstock**

Lignocellulosic biomass is classified as a natural, non-toxic, abundant and sustainable biomass. It can be classified either as woody or non-woody type. Ash and water extractives are also present in lignocellulosic biomass. The components have strong chemical bonds and are highly associated with one another by non-covalent forces. Generally, they are cross-linked, bearing the plant's compositions and toughness (Safana, 2018). It is mainly made up of lignin, hemicellulose and cellulose. The proportion of these three components varies according to the type of biomass. Being one of the most significant agricultural countries in the world, Malaysia has been produced a huge amount of lignocellulosic agriculture waste. Malaysia generates roughly 168 million tons of biomass, which includes resources from rice straw, palm oil waste, coconut waste, forestry waste, sugar cane waste and municipal waste (Abdullah *et al.*, 2019). In Malaysia, lignocellulose biomass from agriculture sector is considered as the most potential feedstock to produce value-added products such as bioproducts and biofuel. The amount of waste produced from the palm oil, rubber, coconut, rice and forest sectors in Malaysia is illustrated in Figure 2. 1 (Gandahi and Hanafi, 2014). Palm oil sector contributes the largest quantity of waste in Malaysia,

hence, it has the highest potential for the production of value-added products through different conversion technologies.

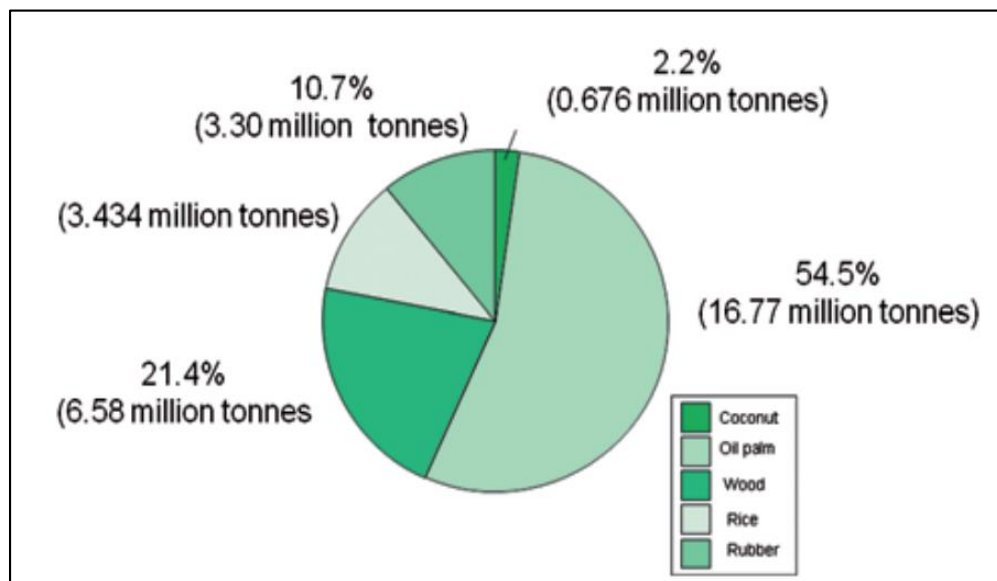


Figure 2. 1: Statistic analysis of waste in Malaysia (Gandahi and Hanafi, 2014)

### 2.1.1 Structure of Lignocellulosic Biomass

Cellulose is a crystalline biopolymer of D-glucose subunits linked by  $\beta$ -1,4 glycosidic bonds to form extended stable hydrogen-bonded chains. The molecular formula of cellulose is  $(C_6H_{10}O_5)_n$ , where n is a polymerisation degree. The major functional group of hemicellulose is the carboxyl group. The thermal stability of cellulose is considered stable due to its strong hydrogen bonds which make it crystalline and hard to depolymerize into glucose monomer units at low temperatures. However, some pre-treatments can be applied to reduce the degree of polymerization (DP) or the amount of glucose repeat units (Garba, 2016). The molecules that makeup cellulose polymers all share the same basic structure and lack side chains. Besides, cellulose is usually insoluble in water under normal circumstances. Nonetheless, it can hydrolyse in sub-critical water at around 180 °C and between 300 °C - 400 °C under normal conditions (Safana, 2018).

Hemicellulose ( $C_5H_{10}O_5$ ) is an amorphous organic polymer that comprises of both xylose, mannose, glucose, and galactose (Garba, 2016). Due to its amorphous shape, the thermal stability is comparatively simple. Under normal conditions, hemicellulose is hydrolysed at  $200\text{ }^\circ\text{C} - 300\text{ }^\circ\text{C}$  (Safana, 2018). The polymer chains of hemicellulose consist of small branches and numerous monosaccharide units. Basically, hemicellulose is less crystalline than cellulose, which makes it more reactive and soluble in water. However, the temperature range for polymerization is between  $50\text{ }^\circ\text{C} - 200\text{ }^\circ\text{C}$  (Safana, 2018).

Lignin is a complex oxygen-containing organic polymer, consisting of aliphatic and aromatic structures. The lignin is formed by hydroxyls and methoxy-substituted phenyl-propane monomers and it is insoluble in water. The basic structure of lignin is  $[C_9H_{10}O_3 \cdot (OCH_3)_{0.9-1.7}]_m$ , where  $m$  is the polymerisation degree (Safana, 2018). In ambient temperatures, the hydrolysis of lignin in water begins at about  $600\text{ }^\circ\text{C}$  (Safana, 2018). Besides, the thermal decomposition of lignin occurs over a broad range of temperatures ( $150\text{ }^\circ\text{C} - 900\text{ }^\circ\text{C}$ ) due to the strong bond of the linkages in the lignin structure (Garba, 2016).

### **2.1.2 Oil Palm Biomass in Malaysia**

Malaysia, the second largest palm oil producer after Indonesia, generates a large amount of waste from the palm oil industry, which could potentially be used as feedstocks for bio-based products. It is a dependable resource due to its abundant availability, renewable nature and potential to produce renewable energy. As far as oil palm is concerned, there are around 15.4 million tonnes of production of palm oils in Malaysia from the year of 2016 to 2020 (Safana, 2018).

Common lignocellulosic biomass which is produced from the oil palm plantations are oil palm trunks (OPT), oil palm fronds (OPF) while from the palm oil mills are empty fruit bunches (EFB) and mesocarp fibre (MF), palm kernel shells (PKS), and palm oil mill effluent (POME). OPF is the leave that is obtained from the oil palm tree when oil palm bunch is being harvested whereas OPT is obtained at end of the lifecycle of oil palm tree. EFB is the solid residue after the removal of fruits from the fruit bunches. MF and PKS are derived from the pericarps and nuts of the oil palm fruits respectively during the extraction of crude palm oil from the fruits.

The oil palm wastes have caused a severe disposal crisis, yet in Malaysia, the main goal of waste management is to reduce and recycle the waste as well as to recover any potential energy resources. For instance, the pruned oil palm frond are largely used as animal feed, nutrient recycling, and soil conservation in the plantation (Mohamed and Yusup, 2021). One of the benefits of palm oil wastes is that palm oil mill is energy independent. The mill uses oil palm wastes such as shell and EFB as fuel to generate steam in waste fuel boilers for processing and power-generation using steam turbines (Safana, 2018).

If the exploitation of oil palm biomass remains untapped, the quantity of wastes produced from palm oil sector might overwhelm the market demand. Thus, utilizing oil palm biomass as a feedstock for the production of value-added products will increase the market demand for the resources.

## **2.2 Hydrochar**

Hydrochar is a carbonaceous component with remarkable physicochemical properties, including high carbon content and energy density as well as minimal



fibrous texture, formed by the thermal decomposition of biomass (Nizamuddin, 2015; Qureshi *et al.*, 2021). Production of hydrochar from industrial and agricultural waste serves the purposes of utilization of unwanted residues and production of hydrochar.

Hydrochar is the solid product from the HTC process. A series of complex reaction mechanisms has been occurred in the conversion of raw biomass to hydrochar during HTC process in different reaction conditions. In addition to this, the physicochemical properties might have changed during the process. Cui *et al.*, (2020) studied the hydrochar production from different wetland biomass wastes via HTC. Compared to raw biomass, the hydrochar was found to have a greater energy density, a moderate pH range (5.0–7.7), and more oxygen-containing groups. Qureshi *et al.*, (2021) reported that based on the results from elemental analysis, higher heating value (HHV), H/C and O/C atomic ratios and energy density of hydrochar, it was found that the HTC process has greatly converted oil palm trunk into better energy fuel. According to Masoumi *et al.*, (2021), the morphology of hydrochar is considered spherical shape and the total carbon content is approximately 58-64 wt.%.

### **2.3 Bio/ Hydrochar Production Method**

There are several thermochemical conversion methods for the production of bio/ hydrochar: pyrolysis and HTC. These thermochemical processes are being used to convert the biomass that consists of organic compounds into bio/ hydrochar together with other products such as non-condensable gases and bio-oil (Duku *et al.*, 2011; Khan *et al.*, 2019).

The difference between HTC and pyrolysis process is that pyrolysis requires dry biomass and emits volatile matter, which is not environmentally benign. Whereas,

the HTC can handle both wet and dry biomass, therefore, reducing the energy consumption, time consuming and cost required for pre-drying of feed material. Table 2. 1 shows the comparison of process conditions and char yield via different thermochemical conversion processes.

Table 2. 1: Comparison of operational parameters and yield of product for thermochemical conversion processes

(Libra et al., 2011)

Methods/ Conditions	HTC	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Palm kernel shell				
Reaction temperature	200 – 380	600	430 - 540	-
Residence time	30	60	-	-
Reactor	Batch autoclave	Fixed bed	Fluidized bed	-
Char yield %	37.3 – 63.2	31.8	20 - 40	-
Empty fruit bunch				
Reaction temperature	250 – 350	350 – 650	400 – 600	425 - 550
Residence time	-	120	-	-
Reactor	Batch reactor	Large chamber muffle furnace	Fluidized bed	Fluidized bed
Char yield %	3.0 – 7.8	20.9 – 37.6	23.9 – 27.6	8 – 19
Fibres				
Reaction temperature	200 – 380	450 – 800	-	-
Residence time	30	60	-	-
Reactor	Batch autoclave	Laboratory scale	-	-
Char yield %	37.3 – 67.5	25.9 – 34.8	-	-
Fronds				
Reaction temperature	200 – 350	-	-	-
Residence time	30	-	-	-
Reactor	Batch reactor	-	-	-
Char yield %	35.1 – 58.3	-	-	-
Trunks				
Reaction temperature	200 – 350	400 – 550	400 – 550	-
Residence time	30	60 – 180	60 – 180	-
Reactor	Batch reactor	Lab-scale pyrolyser	Lab-scale pyrolyser	-
Char yield %	35.3 – 67.8	35.8 – 42.0	37.0 – 40.0	-

### 2.3.1 Pyrolysis

Pyrolysis is a thermal conversion method commonly used for producing biochar from biomass. It decomposes biomass under anaerobic conditions by rapid heating to produce solid, liquid and gaseous products. Biochar refers to the solid products, whereas bio-oil and syngas refer to the liquid and gaseous products, respectively. Pyrolysis is categorized into three types according to the temperature and heating rate: fast pyrolysis, slow pyrolysis, and pyrolytic gasification. Slow pyrolysis normally occurs within hours at temperatures less than 500 °C and heating rates less than 100 °C/min, while fast pyrolysis usually occurs at temperatures greater than 500 °C and heating rates greater than 1000 °C/min (Mohamed and Yusup, 2021).

In the production of biochar, operating condition, particularly temperature, plays an essential role in the quality and quantity of biochar. As the temperature rises, the percentage of biochar yield decreases. Besides, the biochar yield drops with the increased residence time due to the thermal degradation effect causing secondary decomposition of biochar (Hassan *et al.*, 2021). In 2011, Sukiran *et al.* studied the characterization of biochar from the pyrolysis of empty fruit bunches. The optimum condition for pyrolysis was varied from 300 °C – 700 °C which is considered higher compared to HTC. The lowest bio-char yield was 23 % obtained at the final temperature of 700 °C. In 2021, Hassan *et al.* also studied the yield of biochar derived from OPT using various pyrolysis temperatures and times. The experiments were carried out at temperature range between 300 °C to 600 °C and the residence times were 1, 2 and 3 hours. Overall, from the study, the yield percentage of biochar decreased from 47.52 % to 23.60 % when the temperature went up from 300 °C to 600 °C in 1 hour of residence time. The yield percentage of biochar decreased over

time, from 44.55 % to 21.95 % and 39.51 % to 18.16 % at residence times of 2 hours and 3 hours, respectively.

According to Kong *et al.*, (2014), the high moisture content of oil palm biomass necessitates the drying process to prevent loss of heating value and biodegradation. In addition to the normal pre-treatments of oil palm biomass waste, including chopping, grinding and shredding, an additional drying process before pyrolysis process also increases both the cost of production and the investment in equipment.

### **2.3.2 Hydrothermal Carbonization**

Hydrothermal carbonization (HTC) is a thermochemical process that utilise pressure and heat to transform raw material into carbonaceous biofuel using water as a solvent medium. This process generates three types of products which are solid hydrochar, gases and aqueous chemicals. The gas product consists mainly of carbon dioxide, while the aqueous extractive compounds can be simply removed from the reaction solution without engaging in complicated and expensive drying processes as well as isolation procedures. The hydrochar obtained consists 80 % - 90 % of the original feed's energy content and 55 % - 90 % mass of biomass's original bulk.

Bergius and Specht were the first to introduce HTC where they converted cellulosic material into a high carbonaceous material. The cellulose was mixed with water and heated in a closed vessel at 250 °C - 310 °C. Subsequently, a solid product with a higher C/O ratio was obtained, indicating that the HTC is a promising biomass conversion method (Tien, 2019). Although Bergius first discovered HTC in 1913, it has been re-discovered in recent years (Reza *et al.*, 2014). As biomass with high

moisture can be directly applied as feedstock, hydrothermal carbonization process broadens the field of char-producing feedstocks to a variety of non-traditional renewable and abundant wet biomass such as agricultural residues, animal manures, algae residues and municipal wastes (Libra *et al.*, 2011; Wang *et al.*, 2018). It is apparent that feedstocks can be more complicated and these renewable feedstocks represent a huge amount of organic matter that needs appropriate treatment to minimize the environmental contamination. Table 2. 2 shows the product yields distribution of HTC from various feedstock. HTC is usually carried out at temperatures ranging from 180 °C – 280 °C under an inert atmosphere and autogenous pressures of 2–10 MPa at subcritical conditions with the presence of water (Reza *et al.*, 2014; Tien, 2019; Alfredo Quevedo-Amador *et al.*, 2022). In a review journal, Khan *et al.* stipulated the importance of water in the HTC process, the production of carbon-rich materials or hydrochar and the proposed reaction mechanism of hydrothermal carbonization (HTC). Since water acts as a reactant to change the structure of biomass, it is believed that better quality of hydrochar can be achieved when water is used in subcritical condition during HTC process. Residence time has been reported is in the range of 1 min to several hours (Reza *et al.*, 2014).

Hydrothermal process causes the biomass to be thermally degraded, leading to disintegration of physical and chemical, which results in the synthesis of simple and small molecules by disrupting the massive and long-chain compounds like cellulose, hemicellulose and lignin. These results are obtained when some molecules dissolve into the liquid fraction, while others degrade into gaseous products, and the remaining are obtained in solid form.

The reaction mechanisms involved in HTC process include hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization.

Hydrolysis of biomass starts effectively at around 180 °C, at which hemicellulose is hydrolyzed, while cellulose and lignin begin to break down at 200 °C (Tien, 2019). For the cellulose which is not completely hydrolysed, it will form hydrochar by its own solid-solid reactions. At 200 °C - 260 °C, inorganic components are quite stable and likely to remain constant by HTC. Nevertheless, the degradation of polymeric components may cause inorganics to escape from the solid structure into the liquid (Reza *et al.*, 2014). Hydrolyzed products will decompose into furfurals, erythrose, and aldehydes under hydrothermal conditions, which subsequently dehydrate and decarboxylate into carbon dioxide and water, leading in a drop of oxygen values in the hydrochar. Furthermore, the polymerization of hydrolyzed intermediates will result in formation of water. After the dehydration and decarboxylation reactions of monomers, the majority of intermediate compounds formed undergo some mechanisms such as condensation, polymerization, and aromatization to become bio-crude. The liquid bio-crude is then converted into solid product which is part of the desired hydrochar with or without auto-nucleation.

Table 2. 2: Product yields distribution of HTC from various feedstock (Tien, 2019)

Product yield (%)			Feedstock
Solid	Liquid	Gas	
50 - 80	5 - 20	2 - 5	Biomass, waste materials
20 - 50	-	-	Municipal solid waste, food waste, paper
75 - 80	15 - 20	5	Various organic waste material
36 - 66	-	-	Cellulose, peat, wood
30 - 50	-	-	Cellulose
35 - 38	-	-	Corn stalk, forest waste

## 2.4 Factors Influencing HTC Process

HTC requires knowledge on the effect of parameters on the production of hydrochar. Reaction temperature and residence time are undoubtedly the major operational parameters. Reaction conditions may strongly influence the yield and characteristics of hydrochar and hydrochar-based catalyst. The effect of each parameter was further reviewed in the following section.

HTC is a comparatively slow reaction. The duration for the process may vary from a few hours to several days. Hydrothermal severity is a function of the combined effect of residence time and reaction temperature, based on the Equation 2.1. The severity increases with elevated temperature and/or longer residence time, resulting in a decrease in solid product yield. In earlier studies, different hydrothermal severities were used to treat the lignocellulosic biomass, and the corresponding solid hydrochar yields are presented in Table 2.3 (Wang *et al.*, 2018).

$$f = 50 \cdot t^{0.2} \cdot e^{\frac{-3500}{T}} \quad (2.1)$$

Where,  $f$  is the HTC conversion;

$t$  is the residence time;

$T$  is the reaction temperature



Table 2. 3: Hydrothermal severity and the corresponding yield of hydrochar from biomass (Wang et al., 2018)

Biomass	Temperature (°C)	Residence time (min)	Severity (log R <sub>0</sub> )	Hydrochar yield (%)
Corn stover	170	3	2.538	87.7±0.6
	210	10	4.239	63.0±0.4
Poplar	170	15	3.33	76.5
	200	15	4.12	60.0
Pine saw -dust	170	15	3.33	81.0
	220	15	4.69	66.0
Oil palm empty fruit bunch	150	60	3.3	85.4
	150	240	3.9	81.9
	190	20	4.0	72.2
Oil palm frond fibre	210	20	4.54	67.8
	250	20	5.72	52.7
Rapeseed straw	170	10	3.33	70.08
	190	30	4.19	57.47
	230	10	5.10	51.25

#### 2.4.1 Effect of Reaction Temperature

The reaction temperature has a significant influence on the hydrochar yield and physicochemical properties of hydrochar as the reaction temperature affects which reaction mechanism prevails. The reaction temperature serves the purpose of generating heat of disintegration to break the bond in biomass (Nizamuddin, 2015). The ability of temperature to breakdown the biomass is measured by variations in yield percentage. The efficiency of biomass conversion rises as temperature goes up. This

is because the bonds in the biomass are broken down using additional energy provided by temperature. As mentioned earlier before, the main products of HTC are solid, liquid and gas. In general, the temperature has heavily affected the distribution of products. In most cases, higher temperature favours gas and char products while medium temperature favours oil yield. This can be accomplished through secondary decomposition and the Bourdard gas reaction, which produces more gas, or through recombination of free radical processes, which produces more char (Nizamuddin, 2015). Results of a study conducted by Sugano *et al.*, (2008) proved that lower temperature favours the production of solid. With the increase in temperature, the formation of solid products may decrease gradually while the formation of liquid and gaseous rises. The solid product dominates at temperatures between 150 °C and 200 °C, whereas more liquid yield occurs at temperatures between 250 °C and 350 °C. At the temperature over 350°C, the gas formation will be the dominant product. Figure 2. 2 shows the distribution of product yield from the paper industry waste with respect to the temperature.

Higher temperature may decrease the solid product yield, however it tends to have a higher energy density, carbon content and heating value. Furthermore, it appears that the amount of inorganic and organic compounds in the liquid phase is decreasing (Hoekman *et al.*, 2011; Tien, 2019). Furthermore, more water and acetic acid are produced, which might be attributed to dehydration. It is associated with the promotion of decarboxylation, which results in more carbon dioxide being emitted. Hoekman et al. discovered that when the temperature increased from 215 °C to 255°C, the mass yield of hydrochar reduced from 69.1 % to 50.1 %, owing to the conversion to total organic carbon (TOC) comprising organic acids and sugars in the liquid products. Whereas, higher temperatures which is more than 295 °C would result in a

lower TOC with low content of sugar and a high content of organic acid. Wang *et al.*, (2018) conducted a study to investigate the process conditions towards the hydrochar formation. The yield of hydrochar decreased from 66.18 % to 53 % when the reaction temperature raised from 180 °C to 300 °C, indicating that increasing the temperature during the HTC process promoted the degree of condensation. This decrease is due to decarboxylation, dehydration and reduction of volatile matter; with the dropping of oxygen and hydrogen concentration during elevated temperatures of the process. Several studies have found that the hydrochar yield reduces with increasing temperature (Xiao *et al.*, 2012; Nizamuddin *et al.*, 2015; Qureshi *et al.*, 2021).

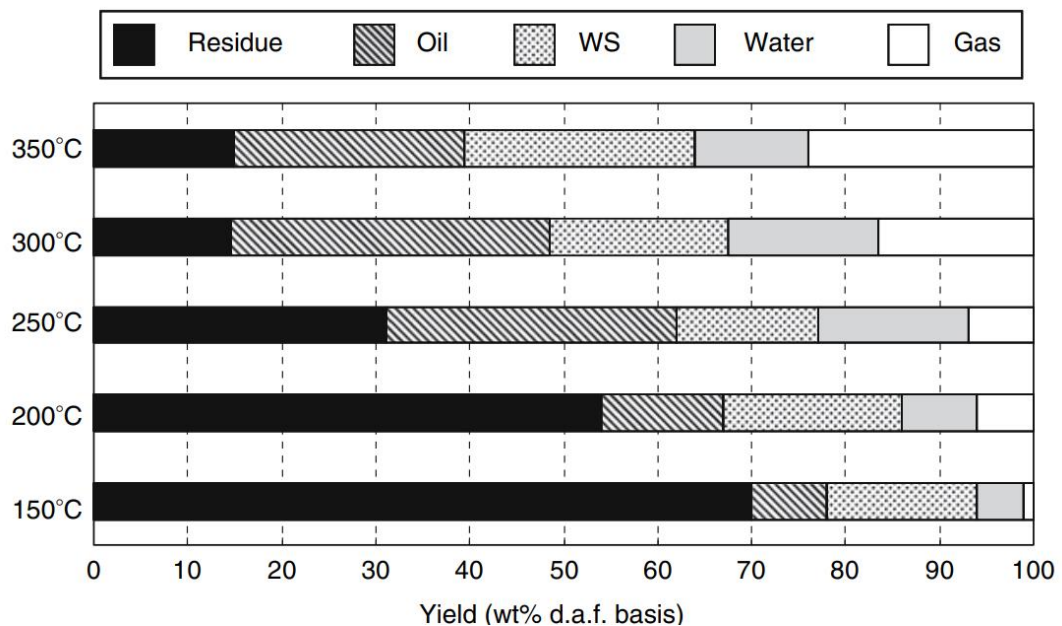


Figure 2. 2: Yield of product after liquefaction of eucalyptus with wastewater from paper regeneration (Sugano *et al.*, 2008)

#### 2.4.2 Effect of Residence Time

Residence time is one of the essential factors for hydrochar formation due to long residence time enhances reaction severity. It is reported that the residence time ranges from several hours to days, however the exact duration has yet to be determined.

Residence time is one of the key aspects in conversion of biomass and its quality. In comparison to temperature, the effect of residence time on the yield of solid product is almost the same but marginal. When the residence time is short, the yield of solid hydrochar is higher, while when the residence time is long, the yield of solid is lower (Khan *et al.*, 2019).

Residence time influences the HTC reaction until a certain time, after which it does not have any specific effect on the process. Under supercritical conditions, the rate of hydrolysis and biomass degradation is relatively fast, therefore, a short time duration is needed to crumble biomass effectively (Tien, 2019). Mahalik *et al.*, (2010) carried out a study that resulted that as the time increases, the rate of biomass conversion also increases.

Besides, residence time also determines the morphology of hydrochar such as formation of microspheres. Long residence time results in excessive polymerization and increment of size because of the stable oxygen groups formed from the surrounding oxygenated functional groups which may affect the formation of microsphere (Zhang *et al.*, 2018).

Romero-Anaya *et al.*, (2014) studied the morphology of hydrochar particles and the results showed that rising the residence time exhibits the same effect as elevated temperature by promoting the accumulation of microspheres on the hydrochar. In research by Gao *et al.*, (2013), hydrochar formed from water hyacinth via HTC process with the residence time of 30 min to 24 hours at 240 °C showed different surface characteristics. Results showed that hydrochar developed better structural characterization as time increased. A short residence time (less than 6 hours) results in trenches and fractures on the hydrochar surface, but no formation of

microspheres while a longer residence time (more than 24 hours), there is microsphere aggregations on the surface of hydrochar.

## **2.5 Modification of Hydrochar**

In the last few years, modification of hydrochar has received much interest and attention in order to increase its utilization. Although the porosity of hydrochar is improved by HTC, but further improvement is required as it has been demonstrated in the previous work that the porosity of hydrochars appeared to be limited due to the formation of secondary microspheres on the upper end of the primary chars (Qureshi *et al.*, 2021). In addition to poor porosity, the hydrochar obtained exhibits low surface area, which hinders the effective use of hydrochar in other applications. Thus, some post-activation approaches can be employed to improve the surface area and porosity which can be beneficial for hydrochar to be used as a catalyst material. Moreover, surface functional groups of hydrochar can be improved by some modification methods. Hydrochar has the potential to be used as a catalyst in a variety of applications due to its porous geometrical structure and functionalized/aromatic/reactive surfaces. For instance, hydrochar can be modified to act as a catalyst that can be used in production of biodiesel. Various hydrothermal technologies through different reaction conditions may result in different characteristics of hydrochar. However, the physicochemical properties of hydrochar can be altered and improved by various modifications such as physical or chemical activation and surface functionalization (Masoumi *et al.*, 2021). The most common activation methods are chemical activation and physical activation.