A Review On The Comparison Between Slow Pyrolysis And Fast Pyrolysis On The Quality Of Lignocellulosic And Lignin-Based Biochar

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Abstract. In recent years, biochar has attracted considerable attention due to its unique characteristics and wide applications in agricultural and environmental areas. Biochar is recognized for its potential role in carbon sequestration, reduction of greenhouse gas emissions, soil amendment, bioenergy production and waste mitigation. The current review discusses on the utilization of various lignocellulosic and lignin-based feedstocks for the biochar production. However, the quality of biochar varies among different thermo-conversion technologies due to the differences in their key process parameters and the feedstock composition. This article aims to review two production technologies for lignocellulosic and lignin-based biochar, namely, slow pyrolysis and fast pyrolysis. The effects of feedstock composition (cellulose, hemicellulose, lignin) and pyrolysis conditions such as temperature and heating rate on the quality of biochar are compared. The relationship between the feedstocks composition, temperature, heating rate of pyrolysis and the quality of biochar are also discussed. Future work would further correlate the effects of feedstock composition and process parameters on the quality of biochar such as surface area and functionality.

1. Introduction
The traditional treatment of biomass through landfill, composting or incineration may cause environmental pollution such as the emission of harmful gases, contamination of underground water, and etc [1]. These biomasses can be converted into biochar through pyrolysis process, which has attracted considerable attention in recent years. The positive effects of biochar amendment are attributed to their unique physicochemical properties such as high porosity, large surface area, abundant surface functional groups [2]. Biochar with specific selectivity and applicability [1] is recognized for its potential role in many environmental applications such as greenhouse gas emission reduction [3], carbon sequestration [4], heavy metal removal [5], salt mitigation [6] bioenergy production [7] and waste management [8]. Lignocellulosic and lignin-based biomass from agricultural and forestry wastes are the most common feedstocks. They are made up of three structural components such as cellulose, hemicellulose and lignin. The proportion of these components varies depending on the type of
feedstocks. They can be transformed into solid, liquid and gaseous products via two main technologies, namely, slow pyrolysis and fast pyrolysis. During the heating process, cross-linking, depolymerization, and decomposition occurs [9]. The chemical components of biomass will be converted into biochar, along with condensable liquid product known as bio-oil and non-condensable gaseous products such as carbon monoxide (CO), hydrogen (H₂) gas, light hydrocarbon and other compounds depending on the reaction conditions [9]. The resultant biochar is a porous carbonaceous residue exhibiting various surface functional groups and large surface area. However, the choice of feedstocks and operating conditions could alter the physical and chemical composition of biochar under oxygen deficit condition at a specific heating rate and residence time.

Different characteristics and quality of resultant biochar might lead to various potential applications in different fields. These will lead to difficulties in obtaining biochar with desirable quality such as high fixed carbon content, low volatile matter and low ash content. This paper aims to address such gaps by reviewing two biochar production methods, including slow pyrolysis and fast pyrolysis. This review contributes to better design on the operational condition to obtain high-quality biochar for desirable application. Research work to decipher the effects of feedstock compositions of lignocellulosic and lignin-based biomass and process parameters (temperature and heating rate) on the quality of biochar remained as an exciting research area for the advanced application of biochar.

2. Methods
The relevant data were collected from various scholarly databases such as Science Direct, Scopus and Google Scholar. The keywords used to obtain related information are biochar, pyrolysis, feedstock type and composition, temperature and heating rate. The data collected from the articles of interest were downloaded from Science Direct, Scopus or Google Scholar. In total, 35 papers were reviewed in this study, with publication years ranging from 2010 to 2020. The papers were arranged in chronological order to demonstrate the emerging trend of biochar utilization in solving the environmental issues. For instance, to remEDIATE heavy metal contaminated soil, greenhouse gas emission, soil salinization, removal of organic pollutants and etc. There were also papers summarising the properties of biochar produced through slow pyrolysis or fast pyrolysis. The comparison between the features of slow and fast pyrolysis are shown in Table 1. The feedstocks were separated into lignocellulosic and lignin-based biomass which undergone pyrolysis at different temperature and heating rates, as shown in Table 2. The selected biochar qualities were fixed carbon content, volatile matter and ash content.

3. The effects of feedstocks composition and operating conditions of slow and fast pyrolysis on biochar quality
Biochar can be produced from various biomass through pyrolysis. Pyrolysis is the thermal decomposition of biomass at elevated temperature in the absence of oxygen. It is the fundamental chemical reaction that is the precursor of both gasification and combustion of solid fuels [10]. During pyrolysis, long-chain hydrocarbon in the biomass is broken down into simpler molecules in the form of solid charcoal known as biochar, and bio-oil produced through the condensation of volatile matter into the liquid phase. The non-condensable gasses such as CO, H₂ carbon dioxide (CO₂) and methane (CH₄) are formed as the co-products during pyrolysis. Pyrolysis processes are divided into two subgroups, i.e. slow pyrolysis and fast pyrolysis, which involve different operating conditions. The key differences between slow and fast pyrolysis are the maximum reaction temperature and heating rate. The different reaction temperature and heating rate are expected to affect the quality of biochar. Both pyrolysis processes are discussed in the following sections. Table 1 presents a comparison between the features of slow and fast pyrolysis.

The most common feedstock for biochar production is lignocellulosic and lignin biomass. Agricultural and forestry waste are the most economical and abundant renewable biomass in the world [11]. Lignocellulosic biomass contains 33% to 51% of cellulose, 19% to 34% of hemicellulose and 11% to 25% of lignin [12]. Lignin-based biomass generally contains a higher lignin content (>25%)
than the lignocellulosic biomass. Lignin is a complex heteropolymer mainly found in wood to form its secondary cell wall structure. Apart from the composition, the quality of biochar produced is also dependent on the thermo-chemical conversion platform.

The quality of biochar for industrial and domestic use is often based on carbon content (in %), volatile matter and ash content. These substances are the principal constituent of biochar. Carbon content is a crucial parameter in affecting the biochar quality because its skeletal structure is made up of approximately 70% of carbon [9]. During pyrolysis, the volatile matter is released when chemical bonds of biomass are broken down. At high pyrolysis temperature, more energy is supplied to the system, resulting in more broken bonds [13]. The high volatile content of biochar suggests that the biomass had not undergone a complete transition to char, which means the biomass is only partially pyrolyzed [13].

**Table 1.** Comparison of slow and fast pyrolysis for biomass

| Features            | Slow Pyrolysis          | Fast pyrolysis         |
|---------------------|-------------------------|------------------------|
| Temperature (°C)    | 300-700                 | 600-1000               |
| Heating rates (°Cmin⁻¹) | 0.1-10                | 10-10000               |
| Aeration            | Oxygen-free or limited  | Oxygen-free            |
| Residence Time      | Minutes-hours           | Seconds                |
| Target product      | Biochar                 | Bio-oil                |
| Reactors            | Fixed bed pyrolysis reactor, auger pyrolysis reactor | Bubbling fluidized bed, ablative reactor, rotary cone |
| Advantages          | -The highest yield of biochar. | -A higher yield of bio-oil. |
|                      | -Can accept a wide range of particle size. |                      |
| Disadvantages       | Further treatment of gases is needed due to high CO concentrations | -Low biochar yield. |
|                      |                         | -Fine particle of biomass feed (1-2mm) is required. |
|                      |                         | -Prefer biomass with low moisture content (<10%) |
| References          | Pandey *et al.* [14]    | Pecha and Garcia-Perez [15] |

Slow pyrolysis is a robust and energy-efficient process. The production of biochar is found to be the maximum as compared to the gaseous and liquid products during slow pyrolysis [16]. This method is widely used for farm-based or small-scale biochar production. The temperature range for slow pyrolysis is 300 °C to 700 °C, long residence time (minutes to hours) and low heating rate of 0.1-10 °C min⁻¹, which removes the vapours during the heating process [17]. Temperature and heating rate plays an important role in the quality of biochar. During slow pyrolysis, the low heating rate reduces secondary pyrolysis and thermal cracking process in both lignocellulosic and lignin biomasses, resulting in biochar as the main product [18]. At heating rate lower than 10°C min⁻¹, the chemical bonds are broken down, and the structure of biomass is affected, rearranging the structure into a more stable matrix which inhibits the formation of volatile matter [18]. Based on the studies conducted by Angım [19], the volatile matter of biochar decreases from 25.2 % to 11.6 % at a heating rate of 10 °C min⁻¹.

Fast pyrolysis differs from slow pyrolysis in terms of their operating conditions, while different reaction conditions could produce different targeted products. In fast pyrolysis, the biomass is heated rapidly at 600-1000 °C under the oxygen-free condition to generate pyrolysis vapour and biochar. It employs fast heating rates (10-10000 °C min⁻¹) and short residence time (0.5-5 s) to maximize the bio-
It takes seconds to complete the process and yields approximately 60% of bio-oil, with biochar as the side products. With high pyrolysis temperature and heating rate, the yield of biochar is reduced while promoting the release of volatile gaseous matter. The biomass is heated rapidly and the pyrolysis vapour released are rapidly transported from the pyrolysis reactor [9]. These pyrolysis vapours have a shorter residence time in the high-temperature zone, which could reduce the amount of carbon deposition, decreasing the biochar yield [9].

Fast pyrolysis is a well-known technique for bio-oil production. In fast pyrolysis, it is essential to keep the vapour residence time in hot zones to the minimum (below a few seconds) to obtain high-quality bio-oil [20]. This process could hinder the decomposition of unwanted secondary vapour that could give rise to additional char and non-condensable gases, at the expense of bio-oil yield [20]. In fast pyrolysis with rapid heating rate, small size biomass of 1-2 mm is required to achieve high heat transfer from heat source to the biomass itself. Since biomass has low thermal conductivity, physical pretreatment is necessary to reduce the size of the biomass before fast pyrolysis. The moisture content of biomass plays an essential role in the fast pyrolysis process. The biomass with low moisture content (<10%) is preferable, as the high moisture content could lead to the formation of unwanted gas products, and increase the conversion of organic liquids [21]. According to Westerhof et al. [22], deep drying is an effective way to lower the moisture content in the biomass and to prevent the loss of organic vapours in the condenser.

Table 2. The feedstock composition, operating conditions and biochar quality of lignocellulosic and lignin-based feedstock

| Feedstock          | Chemical composition | Temperature (°C) | Heating rate (°C min⁻¹) | Biochar Quality |
|-------------------|----------------------|------------------|-------------------------|-----------------|
|                   | Cellulose (%)        | Hemicellulose (%)| Lignin (%)              | Fixed Carbon content (%) | Volatile matter (%) | Ash content (%) |
| Lignocellulose    |                      |                  |                         |                 |                 |                |
| Safflower seed press cake [19] | - | - | - | 600 | 10 | 79.20 | 11.60 | 9.2 |
| Rapeseed stem char [23] | 47.8 | 39.5 | 12.7 | 200-700 | 5 | 13.30-75.18 | 9.8-81.81 | 3.02-14.10 |
| Wheat Straw [24, 25] | 30-35 | 26-32 | 16-21 | 350-650 | 5 | 49.5-64.6 | 14.2-39.6 | 10.9-21.3 |
| Rice Husk [24] | 35 | 25 | 20 | 350-650 | 5 | 23.7-95.9 | 4.1-76.3 | 8.0-25.8 |
| Green waste [25] | 40-50 | 20-30 | 10-25 | 300-750 | 17 | 25.7-98.1 | 1.9-74.3 | - |
| Dried algae [25] | 7.1 | 16.3 | - | 300-750 | 17 | 30.0-96.1 | 3.9-70 | - |
| *Reed [26] | 61 | 27 | 12 | 550-850 | 100-500 | 42.78 | 72.12 | 8.47 |
| Lignin            |                      |                  |                         |                 |                 |                |
| Palm kernel shell [27] | 27.51 | 14.20 | 58.30 | 500 | 20-40 | 59.92 | 30.26 | 7.54 |
| Empty fruit bunch | 24.23 | 38.46 | 37.32 | 500 | 20-40 | 53.78 | 27.46 | 11.10 |
The fixed carbon content increased 59.92% of palm kernel shell biochar. Both 
properties as it increased from 105°C to 300°C. A higher temperature, 
more condensed carbon structure in biochar to 92.4% when the pyrolysis temperature increases. A higher 
proportion of cellulose, hemicellulose, 20% lignin and palm kernel shell has 27.51% cellulose, 14.20% hemicellulose, 58.30% lignin. The thermal decomposition of hemicellulose generally takes place at a temperature ranging from 250°C to 350°C, followed by cellulose decomposition (325°C to 400°C). Among all components, lignin is the most stable compound, and it requires a higher decomposition temperature of 300°C and up to 900°C. The biomass with a high proportion of cellulose and hemicellulose produces a high yield of tar while high lignin favours the formation of biochar, resulting in high biochar yield [18]. Li et al. [30] claimed that the raw materials with high lignin contents are conducive to pyrolysis process, generating biochar with high carbon content, fine aromatic structure and high surface area. According to Pandey et al. [14], the carbon content of biochar is directly proportional to the lignin content of biomass. Palm kernel shell has the highest lignin content of 58.30% among all the feedstocks. The fixed carbon content of palm kernel shell increased and volatile matter decreased after the slow pyrolysis process. The high fixed carbon content (59.92%) of palm kernel shell further supported it as a potential feedstocks in biochar production. Pyrolysis temperature is one of the critical parameters affecting the carbon content of biochar. This is an important property of biochar as biochar consists mainly of carbon along with other inorganic components. In Table 2, the rapeseed, wheat straw, green waste, dried algae and pinewood chip biochar showed great variation in their fixed carbon content. Both Ronsse et al. [25] and Zhao et al. [23] has reported that fixed carbon content is strongly dependent on the intensity of thermal treatment. When pyrolysis temperature increased from 200°C to 700°C for rapeseed biomass, 300°C to 750°C for wheat straw, green waste, dried algae and pinewood chip. The fixed carbon content increased significantly due to the release of volatile matter during the heating process [24]. This confirmed the observations of Tomczyk et al. [31] that the carbon content in biochar increases significantly from 62.2 to 92.4% when the pyrolysis temperature increases. A higher degree of polymerization could lead to a more condensed carbon structure in biochar [31]. Tag et al. [32] reported similar findings where the orange pomace biochar became more carbonaceous (56.8% to 68.1%) as temperature increases from 300°C to 600°C. The volatile matter of biochar follows a reverse pattern to fixed carbon content. Since the volatile matter is released at a higher temperature, micropores are being created, enlarging the specific surface area of biochar [33]. Similar findings were found in the experiment conducted by Sigmund et al. [34] where surface area and pore volumes of biochars increased 300% when temperature increased from 105°C to 300°C. The specific surface area of biochar is also one of the key biochar properties as it associated with its sorption ability for pollutant [34]. More volatile matter is being

![Table 2](image-url)
removed from the biochar at high pyrolysis temperature, the quality of biochar could be further enhanced. Heating rate is a crucial parameter affecting the products produced from fast pyrolysis [35]. During slow pyrolysis, low heating rate (< 30 °Cmin⁻¹) provides sufficient heat conduction. Both cellulose and hemicellulose undergo thermal cracking separately, resulting in separate decomposition peaks [26]. During fast pyrolysis at a high heating rate, different types of chemical bonds in the structure of lignocellulose and lignin biomass are broken down at the same time [18]. The volatile matter is then released before the rearrangement reactions. The biochar produced at high heating rates has a low surface area, porosity and yield due to the rapid depolymerization at the surface of biochar [18]. The high heating rate also decreases the mass of the residue as a large amount of volatile content was released. The mass of Jerusalem artichoke stalks reduced by 1.63 % when the heating rate rises to 500 °C min⁻¹ [26]. In the experiment conducted by Zeng et al. [29], beech wood is utilized for bio-oil production since the pyrolysis process is conducted at a very high heating rate of 3000 °C min⁻¹.

**Conclusion**

Biochar is the main pyrolysis product, it is greatly affected by pyrolysis conditions and feedstock composition. This paper has reviewed the quality of biochar produced by various lignocellulosic and lignin-based biomass under slow and fast pyrolysis processes. The key differences between the two pyrolysis methods are the maximum reaction temperature and heating rate. The fixed carbon content of biochar obtained from slow pyrolysis mostly lies within the range of 30.0 % to 98.1 %. However, there is a wide variation in the range for several feedstocks such as wheat straw, green waste and pine woodchip. This is likely due to the difference in operating temperature and carbon content in the feedstock. The fixed carbon content of biochar from fast pyrolysis is about 44.07 %. The average value of fixed carbon content for fast pyrolysis is taken since the available data is limited. The fixed carbon content is an indicator of the recalcitrance of biochar. High fixed carbon gives the biochar higher stability and resistance to microbial decomposition, leading to longer shelf life. Biochar with high fixed carbon content also contributes to better carbon sequestration and higher proportion of biochar. The biomass with high cellulose and hemicellulose content produces a high yield of tar. A high proportion of lignin promotes carbonization and the formation of biochar. Lignin-based biomass exhibits higher fixed carbon content (45.36 % to 94.0 %) as compared to lignocellulosic biomass. Slow pyrolysis of lignin-based biomass is preferred to produce biochar with high fixed carbon content. Fast pyrolysis has low biochar mass recovery, resulting in low biochar yield. It is recommended when bio-oil is the product of interest. More information on the influence mechanisms of feedstock composition, temperature and heating rate on biochar quality, in terms of surface area and functionality is needed.

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