**Pyrolysis: A Comprehensive study of its Subcategories and By-products**

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**Abstract**

The process of biomass pyrolysis presents a viable and sustainable approach for producing fuels and petrochemical alternatives. Various kinds of pyrolysis, along with its byproducts and applications, are explained in this chapter. Thus, it provides a comprehensive exploration of pyrolysis, a temperature-controlled process that thermally decomposes organic substances, yielding valuable by-products such as liquid bio-oil, solid biochar, and syngas in the absence of air or oxygen.

**Keywords:** Biomass, pyrolysis, biochar, bio-oil, syngas and agriculture

1. **Introduction**

Fossil fuels such as coal, natural gas, and petroleum products are becoming extinct worldwide. Due to the severe situation surrounding the next generation of energy and the need to reduce pollution from sources like landfills and greenhouse gas emissions, they may or may not be available in the future[1]. In order to reduce our reliance on fossil fuels, we need to find other energy sources and create green fuels from non-conventional energy sources like biomass[2]. Biomass is a renewable energy source that has drawn a lot of attention from around the world for a variety of applications, including combustion, due to its abundant availability, low nitrogen and sulphur content, and zero carbon emissions[1]. A significant renewable energy source, biomass energy has the potential to be used to provide alternative energy sources to replace fossil fuels and can be essential to the development of a biobased economy[3]. The three primary methods of converting biomass are thermochemical conversion, biochemical conversion, and direct burning. Thermochemical techniques such as gasification, Pyrolysis, liquification, and combustion are commonly used to convert biomass into fuels with higher heating values.

A temperature-controlled process that produces liquid (bio-oil), solid (biochar), and syngas when any organic substance is thermally decomposed in the absence of air or oxygen is known as pyrolysis[4]. Because of its widespread use as a biofuel and as a starting point for the synthesis of chemicals, bio-oil generated through the pyrolysis process and subsequently upgraded has garnered a lot of interest recently. Biomass can be heated above its thermal stability limit in the absence of oxygen, resulting in more permanent byproducts such solid residues. By creating an anaerobic atmosphere, it is further ensured that the combustion process will not occur when the biomass is heated[5]. It's a really complex process that includes many different kinds of special reactions in the reacting zone. Pyrolysis was discovered to take place at low temperatures, ranging from 250°C to 900°C, in another study. Agricultural biomass is composed of silica, lignin, cellulose, and hemicelluloses. While cellulose normally pyrolyzes at 350°C, lignin has a melting point that is substantially higher[6]. The pyrolysis process is diagrammatically illustrated in the figure1.



**Fig 1: Diagrammatic illustration of biomass pyrolysis**[7]

1. **Classification of pyrolysis**

Pyrolysis processes is classified into slow, fast, flash and advanced pyrolysis. Pyrolysis is an efficient process that may function under a variety of operating circumstances. The above indicated subclasses facilitate an environment in which different reaction mechanisms and circumstances can produce different kinds of goods[8][9].

* 1. **Slow Pyrolysis**

The production of biochar, an organic carbon-rich substance that can serve as a carbon sequester and enhance soil quality, is the primary result of the slow pyrolysis of biomass. Biochar is the main byproduct of slow pyrolysis because it is carried out at a moderate temperature, with a lengthy residence period and a low heating rate. Screw reactors, drum reactors, and rotary kilns are the reactor types most frequently employed for slow pyrolysis. In general, slow pyrolysis in the absence of air produces biochar when temperatures are maintained between 300 and 550 oC[10]. As accordingly, a long residence time (5–30 min) and a very low heating rate (0.1–0.8 oC/s) are needed for the entire reaction to occur. Longer residence period allows vapours created during the subsequent reaction to be expelled[11]. Biochar is produced as the primary product in the process (35–45%), along with intermediate products including bio-oil (25–35%) and syngas (20–30%)[12].

* 1. **Fast Pyrolysis**

One of the most affordable conversion methods for producing renewable ethanol is the fast pyrolysis of biomass. Thermal decomposition of biomass occurs in the fast pyrolysis process at a moderate temperature (450-600 oC) with a very short residence period (< 2s) in the absence of air or oxygen[13]. The primary byproduct of rapid pyrolysis is a viscous liquid with a dark brown colour known as "bio-oil" or "pyrolytic oil," which is followed by syngas and biochar[14]. The fast pyrolysis technique yields the maximum amount of bio-oil—roughly 75% on a dry mass basis—and has the highest conversion efficiency. Fast pyrolysis-produced bio-oil is thought to be a more economical thermochemical conversion method than other biofuel production technologies. How profitable the fast pyrolysis process is depending on a variety of criteria, including feedstock cost, production volume, output yield, and quality. The yield of syngas has a negative impact on the yield of biochar and bio-oil in a fast pyrolysis process because the yield of these products abruptly decreases as the syngas yield rises. Because clean woody biomass has a high percentage of cellulose and hemicellulose, which is more favourable for bio-oil production, the bio-oil produced from woody biomass has a higher yield than agricultural by-products, forest leftovers, energy crops, etc. There have been several studies that have shown even greater temperatures, ranging from 850 to 1250 °C, with heating rates between 10 and 200 °C and brief stay periods of 1 to 10 s[15]. In a typical pyrolysis process, 15%–25% of biochar, 60%–75% of liquid products, and 10%–20% of non-condensable gaseous fuel products are produced[7]. Choosing the right feedstock particle size for a rapid pyrolysis process can have a negative impact on the yields of bio-oil, char, and syngas. This is because a larger particle size employed in the process produces a little decrease in heat transfer rate, which raises the yield of biochar while decreasing the yields of biooil and syngas. Therefore, tiny particle size feedstock should be utilized in order to produce the highest yield of bio-oil.

* 1. **Flash Pyrolysis**

The technique of flash pyrolysis involves heating biomass at a higher rate (from 103 to 104 oC/s) while maintaining a very short residence time (< 0.5 s)[16]. This leads to a greater output of bio-oil (between 75 and 80 weight percent). If the goal is to produce the most bio-oil possible, flash or fast pyrolysis is a more recognized procedure than others. A high output of bio-oil is the result of high heating rates, high temperatures, and short vapour residence periods[17]. The flash pyrolysis reaction typically occurs in a few seconds, however because it demands a higher heating rate, the size of the biomass particles should be small because of the instantaneous heating. The behaviour of biomass phase transition, reaction chemical kinetics, heat and mass transmission mechanisms, and reaction kinetics all affect how the products are distributed in flash pyrolysis[18]. The feedstock particle size should be less than 200 microns in order to get the greater bio-oil production (75%wt.) at a higher temperature range of 800 to 1000oC. For flash pyrolysis to be used commercially, it must run at a high temperature and a very fast heating rate due to the reactor's architecture. This can be achieved in a twin-screw mixing reactor or a fluidized bed reactor[19].

**2.4 Advanced Pyrolysis**

This includes hydro pyrolysis, intermediate pyrolysis and vacuum pyrolysis.

**2.4.1 Intermediate pyrolysis**

This is a blend of slow and fast pyrolysis processes, as the name suggests i.e. intermediate pyrolysis, and it is crucial for balancing liquid and solid products. This suggests that rapid pyrolysis yields more liquid products but is less successful at producing large amounts of char than slow pyrolysis[20]. Usually, pressure is kept constant at 1 bar during the process. Intermediate pyrolysis takes place at temperatures between 500 and 650°C with variable heating rates between 0.1 and 10°C/min and varying residence periods between 5 and 17 minutes[21]. Completed products typically consist of 40–60% liquid, 20–30% non-condensable gases, and 15–25% biochar. Instead of producing highly reactive tar, dry biochar can be produced by utilizing intermediate pyrolysis conditions. This biochar can be used in boilers and engines on its own or in combination with premium bio-oil[22].

**2.4.2 Hydro pyrolysis**

It is a relatively recent technique for converting biomass into high-quality products. It involves infusing hydrogen (H2) or a hydrogen-based material into the pyrolysis reactor at high pressure, between 50 bar and 200 bar above atmospheric pressure. There is no difference between rapid pyrolysis and the temperature range of 350–600°C, residence time of more than 15 seconds, and heating rate of 10–300°C/s[23]. Hydro pyrolysis can be understood as essentially a particular type of rapid pyrolysis that is exposed to high pressure in a hydrogen-rich environment or one that produces compounds produced from hydrogen. This method is not ideal for producing biochar because the high temperature and pressure of the hydrogen injection acts as a reducing agent, lowering the oxygen concentration in the produced bio-oils and so inhibiting the synthesis of biochar[24]. A catalyst is usually used in hydro pyrolysis to extract COx, water, and oxygen from the liquid product. Catalysts also reduce the processes of coking and depolymerization. But the difficulty of catalytic hydro pyrolysis is still evident in the process of developing the catalyst for this use[25].

* + 1. **Vacuum pyrolysis**

The thermal breakdown of biomass in a zero-oxygen environment while under vacuum or low pressure is known as vacuum pyrolysis. Pressure is routinely managed between 0.5 and 2 bar, while temperature is normally maintained between 450°C and 600°C[26]. Vacuum pyrolysis has relatively low heating rates, much like slow pyrolysis. Comparatively speaking, though, these two methods provide very different results. The rapid evacuation of organic vapours generated during primary pyrolysis not only significantly reduces the vapour residence period but also minimizes the occurrence of secondary reactions, which in turn guarantees a high yield of liquid products during secondary pyrolysis[27]. The quality and yield of the product are greatly affected by utilizing vacuum or low-pressure extraction alone since it prevents inorganic devolatilization[9].

**3. Byproducts of pyrolysis**

**3.1 Biochar**

The solid byproduct of lignocellulosic biomass pyrolysis, known as biochar, has a carbon content ranging from 65 to 90 percent. The solid biochar's physicochemical properties are mostly determined by the feedstock type and process conditions, which in turn drives its widespread application. It was discovered that the biochar yield reached its maximum at low temperatures (<500 ◦C) when the bio-oil yield decreased[28]. The primary constituents of biochar are carbon, ash, volatile matter, and moisture. The percentage composition of each component is determined by the feedstock material and operating conditions[16][29]. Biochar derived from plant sources has a greater carbon content, ranging from 51 percent to a high proportion[30].

Recent research has looked into the use of biochar in agriculture on both a large and small scale in the field and in the lab. These applications include adding it to chemical fertilizers, encouraging microbial activity in the soil, adding it to soil as a soil supplement to boost crop output by making nutrients more available, and improving the soil's ability to retain water[31]. Biochar can enhance the levels of carbon, phosphorus, nitrogen, carbon mineralization, and other enzymatic activities in soil[32]. Furthermore, biochar has been demonstrated to have a limiting effect that aids in raising the pH of severely acidic soils and to decrease the release of heavy metals into the soil[33]. Biochar is produced using different methods than compost, even though it is a different type of soil conditioner. While organic substrates normally biodegrade to make compost in an aerobic environment by the microbial population, agricultural and other biomass is thermally degraded to form biochar in the absence of oxygen[34]. In addition, compost's advantages are not as long-lasting as those of biochar, which stays in the soil for longer. Another difference is the speed at which compost dissolves[35].

The issue of heavy metals/metalloids (HMS) and polycyclic aromatic hydrocarbons (PAHs) in soil and water has an adverse effect on all forms of life[36]. These contaminants lead to both poor farming practices and detrimental environmental effects. These pollutants can bioaccumulate and are persistent, toxic, and non-biodegradable[37]. The advantages of biochar make it one of the best bioremediation techniques for addressing the HMS and PAHs issue[38]. These advantages include sustainability, cost, and sequestration of carbon. The physical and chemical characteristics of biochar, such as its pore structure, specific surface area, and functional groups, have made it useful for the adsorption of a variety of pollutants[39].

**3.2 Bio-oil/ Pyrolytic oil**

The byproduct of pyrolysis is liquid oil, sometimes referred to as pyrolytic or bio-oil. It has a dark brown colour and can be used as a substitute fuel in a variety of ways. Organic materials such as phenol, amines, ketones, ethers, esters, furans, aromatic hydrocarbons, alcohols, and water constitute bio-oil, also known as pyrolytic oil[40]. Because of its high-water content (15–30%) and high composition of oxygenated compounds (35–60%), such as acids, aldehydes, ketones, and alcohols, bio-oil faces some technical challenges and limitations for use in the commercial sector, despite its many benefits, which include being eco-friendly, having a low-cost requirement, and having high conversion efficiency. Certain components in excess can have negative effects on the properties of bio-oil, such as a lower calorific value, which lowers the efficiency of burning and instability, which can occasionally be brought on by corrosion of oxygenated compounds.

**3.3 Syngas/Pyrolytic gases**

The main components of pyrolytic gases include H2, CO2, CO, H2S, and hydrocarbon gases (C1–C4). High temperatures, the inclusion of catalysts, and a prolonged residence period are the ideal circumstances for lignocellulosic biomass. pyrolysis to produce synthetic gas or gas high in hydrogen[40]. While CO2 is produced when carbonyl and carboxyl functional groups degrade thermally, CO is produced when C–O–C and C–O bonds separate. H2 is also formed when aromatic and C–H groups rupture. However, at low temperatures, the primary gaseous products are CO and CO2, whereas at high temperatures, the main gaseous product is CH4 due to lignin depolymerization[41].

1. **Conclusion**

Pyrolysis is a temperature-controlled process that, in the absence of air or oxygen, thermally breaks down organic materials to produce useful byproducts including liquid bio-oil, solid biochar, and syngas. Pyrolysis is an efficient process that may function under a variety of operating circumstances which are classified into different types like slow, fast, flash and advanced pyrolysis. Biochar is a byproduct of several processes that can improve nutrient availability and lower acidity. It has been used to improve soil fertility and restore contaminated agricultural soil. Therefore, adding biochar to soils is one of the best methods for lowering biotic stress in soil and increasing crop output, especially in the agricultural sector. The relationship between different waste management and energy production strategies varies in terms of constraints on the economy, society, and environment as well as in terms of parameters and production techniques. The most recent information that could be helpful in determining prospective directions for scientific advancement in the research of biochar was summarized in this chapter.

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