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BIOMASS PYROLYSIS PROCESS AND APPLICATION: AN APPROACH

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Abstract: *This review focuses on contrasting the information available for the two types of char in regards to the use of biomass residues and waste materials as feedstock's, the conversion processes and chemistry involved in their production, as well as potential applications. The pyrolysis of biomass to value the waste can enrich by producing the bio oil, bio char etc. The wet and dry processes of conversion are the method to produce the end product as per the need. A systematic review is formulated to overview the latest development in the area of pyrolysis of biomass.*

Keywords: *Pyrolysis, Process, Types, Product*



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INTRODUCTION

In pyrolysis the biomass is thermally decomposed in such a way that it is not exposed to the oxygen containing medium. It is an extremely complex process which involves so many different reactions in the reacting zone [1]. On heating the biomass, volatile biomolecules of biomass are cleaved which after condensation produce the bio-oil. Oxygen free atmosphere allows us to heat the biomass to a temperature above its limit of thermal stability, resulting in the formation of more stable products and solid residue. By making an oxygen free environment it is also ensured that on heating the biomass, combustion will not take place. Pyrolysis basically is composed of two stages known as primary pyrolysis and secondary pyrolysis.

Types of pyrolysis

Slow pyrolysis: Slow pyrolysis is having a long history of being used for the production of charcoal. It is the conventional type of pyrolysis which is characterized by slow heating rate and long residence time. In slow pyrolysis the biomass is pyrolyzed up to a temperature of the order of 400–500 °C with a heating rate of about 0.1 to 1 °C/s for a time ranging between 5 and 30 min. Slow pyrolysis favors the formation of char but liquid and gaseous products are also formed in a small quantity [2]. In slow pyrolysis, lower heating rate and longer vapor residence time provides a suitable ambience and sufficient time for the secondary reactions to complete.

Fast pyrolysis: In fast pyrolysis the biomass is heated upto a temperature of 850–1250 °C with a heating rate of 10–200 °C for a short span of time varying between 1 and 10 s. Fast pyrolysis is used for the production of bio-oil as the oil product yield in fast pyrolysis dominates to the char and gaseous product yield. A typical fast pyrolysis produces 60–75% of liquid product, 15–25% of biochar and 10–20% of non-condensable gaseous products [3].

Flash pyrolysis: Flash pyrolysis can be considered as an improved and modified form of pyrolysis. In fast pyrolysis the temperature required for the degradation of the components of biomass is achieved by heating it with a very high rate of the order of 1000 °C/s. or sometimes even higher than that. The temperature achieved in the flash pyrolysis is between 900 and 1200 °C and the heat pulse given to the biomass lasts for a very short amount of time which is 0.1–1 s [4]. Heat and mass transfer process along with chemical kinetics of these actions and phase transition behavior of the biomass plays a crucial role in the product distribution in flash pyrolysis.

Vacuum pyrolysis: It is the thermal degradation of biomass under low pressure and in the absence of oxygen. The pressure range during the vacuum pyrolysis is usually 0.05–0.20 MPa and the temperature is kept between 450 and 600 °C [5]. The heating rate in vacuum pyrolysis

is comparable to that of slow pyrolysis. Although few of the operating conditions of vacuum pyrolysis are similar to that of slow pyrolysis the method for removal of vapors from there action region provides a big difference between these.

Intermediate pyrolysis: This type of pyrolysis is generally utilized to make a balance between liquid and solid products. Slow pyrolysis produces high char yield but liquid products are relatively low while the fast pyrolysis produces high liquid yield but the char yield is reduced. Operating conditions for intermediate pyrolysis are in between slow and fast pyrolysis. Generally pressure remains 0.1MP during the process. Intermediate pyrolysis conditions inhibit the formation of high molecular tars and produce dry char which is suitable for the agricultural use or energy production along with good quality bio-oil [6]. Intermediate pyrolysis operates between 500 and 650 °C, with heating rate ranging between 0.1 and 10 °C/min with residence time of 300–1000s. The typical product contains 40–60% liquid, 20–30% non-condensable gases and 15–25% biochar [7].

Hydropyrolysis: Hydropyrolysis is a relatively new technique to convert the biomass into high quality bio-oil. In this process hydrogen/hydrogen based materials are also fed to the reactor along with the biomass at a pressure higher than the atmospheric pressure ranging between 5MPa and 20MPa [8]. The heating rate and, residence time and temperature are nearly same as that of the fast pyrolysis. So the hydropyrolysis can be considered to be a fast pyrolysis process under high pressure and in the presence of hydrogen/hydrogen based materials. As we know hydrogen is a reducing agent the presence of hydrogen at high pressure combined with high temperature reduces the oxygen content in the produced bio-oil as well as it inhibits the production of char. Besides, hydropyrolysis adds some amount of hydrogen to the liquid product also as soon as biomass gets devolatilized

Effect of biomass constituents

Lignin along with the cellulose is considered to be the main constituent of the biomass. Studies over the biomass structure revealed that cellulose, hemicellulose and lignin are the main ingredients of biomass which influence the product yield of pyrolysis. Generation of the char from lignin is the outcome of fracturing of relatively weak bonds and the consequent formation of more condensed solid structure [9]. Cellulose contributes mainly to the production of tar which eventually is a mixture of discrete ketones, aldehydes, organic liquids and char while Lignin primarily produces char and small amount of water on pyrolysis. Cellulose and hemicellulose component in biomass are liable to the volatile products and lignin for the char yield. Studies have suggested that more the presence of oxygen in the biomass more will be the reactivity [10]. Both cellulose and lignin present in the biomass enhance the formation of biochar but the biochar production is higher in the biomass which has more lignin as compared to cellulose.

Effect of operating parameters

Effect of residence time - Low temperature associated with long vapor residence time is required for higher biochar production . Increasing the vapor residence time helps the repolymerization of the biomass constituents by giving them sufficient time to react. While if the residence time is lesser, repolymerization of the biomass constituents does not get completed and biochar yield is reduced [11]. As light increase in the char yield on increasing the residence time was reported during the fast pyrolysis of poplar wood and yellow brown coal . The effect of residence time is often dominated by the temperature, heating rate and other parameters.

Effect of particle size – Particles size is a factor which should be taken care in the pyrolysis process as it can control the rate at which the heat is transferred to the input biomass. On increasing the particle size the distance between the surface of the input biomass and its core increases which retards the rapid heat flow from the hot to cold end. This temperature gradient favors the char yield [12]. Also on increasing the particle size the vapor formed during the thermal cracking of biomass has to cover more distance through the char layer causing more secondary reactions resulting in the formation of more amounts of char.

Effect of heating rate- Heating rate plays an important role in pyrolysis of biomass as the rate of change of heat influences the nature and composition of the final product upto a certain extent. At low heating rate the possibility of secondary pyrolysis reactions can be ruled out/reduced. Low heating rate also ensures that no thermal cracking of biomass takes place resulting in more biochar yield. High heating rate backs the fragmentation of biomass and increases the gaseous and liquid yield of limiting the possibility of formation of the biochar. The effect of heating rate on the biochar yield is more noticeable and potent at lower temperatures [13].

Effect of temperature- Increasing the temperature in pyrolysis affects the biochar yield in a negative way as the increase in the temperature allows the thermal cracking of heavy hydrocarbon materials, leading to the increase of liquid and gaseous and decreases in the biochar yield. At high temperatures, biochar formed during the primary pyrolysis reaction undergoes the secondary reactions and increases the liquid and gaseous products at the cost of solid char.

Effect of pyroliser bed height- Pyrolysis reactors can basically be classified into two categories: fixed bed reactor and moving bed reactor. The reactors with no movement of the biomass throughout the pyrolysis are termed as fixed bed reactor while the moving bed reactor are those in which the biomass is not stationary during the pyrolysis. The biomass can be moved during the pyrolysis using mechanical forces (rotary bed reactor) or by fluid flow (fluidized bed

reactor, entrained bed reactor, spouted bed reactor etc.) [14]. Heat in pyrolysis is transferred either by solid–solid heat transfer or by gas–solid heat transfer. Liquid and gas yield differs in fluidized and fixed bed reactors but the char yield in both types of reactors is same.

Effect of pressure – Biochar yield has been found to be increased when the pyrolysis is completed under the influence of a pressure higher than the ambient pressure . Increase in the pressure elongates the residence time and as a result of this formation of secondary carbon by the decomposition of vapors on the carbonaceous takes place which adds upto the char formation [15].

Effect of catalyst - Presence of catalyst affects the pyrolysis product distribution among liquid, gaseous and solid phases. Presence of metals in the ash of raw biomass material partially eliminates the formation of char. Similar type of effect is visualized in the presence of acidic and basic catalysts. Catalysts used for the pyrolysis can be classified into two groups primary catalysts and secondary catalysts.

Dry pyrolysis

The main process for char production with significant yields is the dry pyrolysis process. It has been used by mankind for millennia to produce charcoal and tar-like substances, although it can be operated to produce multiple products (e.g., oil and gas) besides char. The so called ‘dry distillation’ of wood also yields methanol, acetic acid, acetone and many more base chemicals. Moderate heating rates with long residence times (slow or intermediate pyrolysis) yield high amounts of gases and vapors (30–35%) and approximately 20–40% as char . In industrial applications, these processes are operated in closed kilns where the non condensable gases are used to fire the reactors. Fast pyrolysis processes are operated in special reactors allowing for high heating rates and good mixing conditions [16].

Wet Pyrolysis

In hydrothermal processes, the solid material is surrounded by water during the reaction, which is kept in a liquid state by allowing the pressure to rise with the steam pressure in (high)-pressure reactors. As in dry pyrolysis, reaction temperature (and pressure) determines the product distribution. With process temperatures of up to 220°C and corresponding pressures up to approximately 20 bar, very little gas (1–5%) is generated, and most organics remain as or are transformed into solids. At higher temperatures, up to approximately 400°C, and with the use of catalysts, more liquid hydrocarbons are formed and more gas is produced. This so called ‘hydrothermal liquefaction’ has drawn some interest, although most liquefaction work is performed using organic solvents instead of water [17]. If the temperature and pressure are increased further, the supercritical state for water is reached and the primary product is gaseous (hydrothermal gasification) [18].

Feedstocks

Conversion to char via dry pyrolysis has been traditionally restricted to biomass with low water content, such as wood and crop residues, because of the high energy requirements associated with the inevitable drying prior and/or during the reaction by the evaporation of water. Potential feedstocks for wet hydrolysis span a variety of nontraditional, continuously generated and renewable biomass streams: wet animal manures, human waste, sewage sludges, MSW, as well as aquaculture residues and algae.

Products

Products from pyrolysis are solids, liquids and gases. Compared with dry pyrolysis, HTC produces higher solid yields, more water soluble organic compounds and fewer gases, comprised mainly of CO₂. In addition, the composition and structure of the solid product (hydrochar) from HTC differs substantially from dry pyrolysis chars [19]. The chemical structure of hydrochar more closely resembles natural coal than charcoal, with respect to the type of chemical bonds and their relative quantity, as well as its elemental composition [20].

Application of chars in soil

Biochar application may possess additional carbon mitigation potential owing to indirect effects; for example, increases in soil organic carbon (SOC), and decreases in GHG emissions and fertilizer use should be considered in addition to the direct benefits of carbon sequestration. Biochar application can increase yields:

- In degraded or low-fertility soils rather than at already-fertile sites.
- In tropical soils rather than in temperate soils.
- In combination with NPK fertilizers or nutrient releasing substances rather than without extra nutrient supply.
- When the chars themselves were sources of nutrients (e.g., biochar from poultry litter).

CONCLUSIONS

Pyrolysis is relatively a thermochemical process to produce biochar and other value added products from biomass effectively. Biomass with different sizes, compositions and moisture contents can be treated by the pyrolysis to produce biochar. Hydrothermal char production processes require a water content that exceeds the one feasible in dry pyrolysis. Hydrochar has substantially different characteristics than char from dry pyrolysis. However, the characteristics of both products, depend highly on feedstock and process conditions. HTC usually achieves a higher solid yield than dry pyrolysis, but does not produce energy gases as in dry pyrolysis. Hydrochar may be more stable than normal soil organic matter, but less stable than biochar from dry pyrolysis.

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