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Thermal conversion of biomass: a comparative review of different pyrolysis processes

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ABSTRACT Biomass has been worldwide seen as a promising solution for meeting the increasing energy demands of a growing population, replacing fossil fuels in whole or in part, and achieving sustainable development. The use of biomass as an energy source is done through various conversion routes such as combustion, gasification and pyrolysis. Pyrolysis is a simple and efficient thermochemical conversion process to obtain energy from biomass and generate high energy density products. These technologies used for energy utilization are distinguished according to the characteristics of the biomass and product, process efficiency, amount of oxidant used, temperature and rate of heating, among others. The technical and scientific knowledge of biomedical thermochemical conversion options is a fundamental step both for academic researchers who aim to investigate these technologies to improve and optimize these processes, and for entrepreneurs who aim to implement biorefineries in the market. In this context, this work aimed to review the latest pyrolysis technologies, discussing the characteristics and the main variables of this technology.

Keywords: Carbonization; wood energy, bioenergy, thermal conversion.

Conversão térmica da biomassa: uma revisão comparativa de diferentes processos de pirólise

RESUMO A biomassa tem sido vista mundialmente como uma solução promissora para atender à crescente demandas de energia da população, a substituição total ou em parte dos combustíveis fósseis pode alcançar o desenvolvimento sustentável. O uso da biomassa como fonte de energia é feito através de várias rotas de conversão como combustão, gaseificação e pirólise. A pirólise é um processo de conversão termoquímica simples e eficiente para obter energia a partir da biomassa e gerar produtos de alta densidade energética. Essas tecnologias utilizadas para utilização de energia são diferenciadas de acordo com as características da biomassa e do produto, eficiência do processo, quantidade de oxidante utilizado, temperatura e taxa de aquecimento, entre outras. O conhecimento técnico e científico das opções de conversão termoquímica biomédica é um passo fundamental tanto para pesquisadores acadêmicos que buscam investigar essas tecnologias para melhorar e otimizar esses processos, como para empreendedores que visam implementar biorrefinarias no mercado. Neste contexto, este trabalho teve como objetivo revisar as últimas tecnologias de pirólise, discutindo as características e as principais variáveis desta tecnologia.

Keywords: Carbonização; energia da madeira, bioenergia, conversão térmica.

Introduction

The United Nations (UN) forecasts that world population will reach 9.6 billion by 2025. As world population grows,

demand for energy will also. The urbanization may lead to higher emissions and energy consumption through industrialization, in this way as the shift from agriculture to

industry and services. Currently, this is fundamental for development of the one country (LIDDLE, 2014)

At present, the main energy sources are non-renewable and thus unsustainable over the long term, as well as, in the case of fossil fuels, being highly polluting. Consequently, concerns about environmental management and security of energy supplies are leading to increasing focus on renewable energy. Increase in the production and utilization of renewable fuels has become a major goal for many nations, especially signatories to the Paris Agreement on climate change, which commits countries to making efforts to limit global temperature rise to below 2 degrees Celsius. To attain this goal, the main challenges are improving the efficiency of currently used renewable energy sources and increasing exploitation of hitherto underutilized sources such as biomass, which can potentially have a much greater role in energy usage in industrial production. According to (JONES et al., 2014), estimated annual biomass availability potential is expected to reach 108000 Mtoe (tonne of oil equivalent), which is nearly ten times the world's current energy requirement.

Biomass has become a significant renewable energy source in recent years, as it can be used in thermochemical processes for the production of heat and electrical energy, and, importantly, the biomass is the only source of renewable energy capable of conversion into solid, liquid and gas fuels (KAN et al., 2016). This flexibility makes biomass based solutions suitable for integration into modern production systems. Currently, the main sources of biomass are (i) woody biomass; (ii) herbaceous and agricultural biomass; (iii) aquatic biomass; (iv) animal and human biomass residues (ANCA-COUCÉ, 2016).

Wood can be considered one of the most important source of renewable energy and this energy could satisfy 0–16% of global primary energy consumption in 2050 (Lauri et

al., 2014). The main challenges facing increased energy production from this type of biomass are possible land use competition with cropland for food production and competition from fossil energy, which in most situations is available at a lower price than biomass energy (HERBERT; KRISHNAN, 2016).

The use of biomass as source energy require conversions, that can be via thermal, biological or mechanical processes (GUEDES et al., 2018). Thermochemical conversion processes are a great promise to convert biomass efficiently and economically into energy, which can be used in different applications (BRIDGWATER, 2003). The processes are combustion, pyrolysis, and gasification.

Different pyrolysis processes

Pyrolysis is a simple and efficient thermochemical conversion process to obtain energy from biomass and generate high energy density products; it is the oldest technique for the production for the production of charcoal (HASAN et al., 2017).

In pyrolysis, thermal decomposition of the structural chemical components of the biomass, results in three products - charcoal, bio-oil and gas, whose yields vary depending on the operational conditions and feedstock. According to (TRIPATHI et al., 2016), no other biomass conversion method produces as many energetics products as pyrolysis does.

The efficiency of the pyrolysis process depends on the raw material (type of biomass, particle size, biomass pretreatment), reaction conditions (final temperature, pressure, heating rate, residence time), reactor type and variables such as the presence of catalysts and vapor condensation mechanisms (LU et al., 2009). Different types of pyrolysis exist and, dependent on the operating conditions, the pyrolysis is termed slow, flash, fast, intermediate or

vacuum (KAN et al., 2016). Also, the proportions and composition of the pyrolysis products also rely on the conditions used. Slow pyrolysis occurs at a lower process temperature, lower heating rate and longer residence times, which favors the production of charcoal. Flash pyrolysis is the process in which the reaction time is only several seconds, and the heating rate is very high. Due to the rapid heating, the particle size should be small. Fast pyrolysis favors the formation of bio-oil and occurs at a moderate temperature, the short residence time of the vapor and high heating rate, but not as high as in flash pyrolysis (GOYAL et al., 2008). Fast pyrolysis technology can have relatively low investment costs and high energy efficiencies compared to other processes, especially on a small scale, has minor capital investments, improved efficiency and environmental acceptability

(GUEDES et al., 2018). Intermediate pyrolysis is generally utilized to make a balance between liquid and solid products. The operating conditions for intermediate pyrolysis are in between slow and fast pyrolysis (TRIPATHI et al., 2016).

In light of the importance of the pyrolysis process and its obvious potential in greater utilization of renewable energy sources, this article aims to review the different types of pyrolysis of biomass currently available and the main products and applications of these processes (Table 1).

The work highlights recent advances and importance of this process for thermal conversion and energy efficiency. Understanding of the characteristics of the different types of pyrolysis and their respective products are critical to achieving high yields.

Table 1. Summary of key characteristics of pyrolysis process types.

| Pyrolysis | T (°C) | Time (s) | Heating rate (°C.s ⁻¹) | Principal product (%yield) | Co-products (%yield) | | Principal advantage | Main drawbacks |
|--------------|-------------|---------------|------------------------------------|----------------------------|----------------------|------------------|---|--|
| Slow | 350 to 700 | 300 to 126000 | 0.02 to 0.83 | Charcoal (30-35) | Bio-oil (18-20) | Gas (30-35) | Simple process | Long residence time |
| Intermediate | 400 to 650 | 60 to 900 | 1.67 to 5.00 | Bio-oil (40-60) | Gas (20-30) | Charcoal (15-25) | The moisture content of biomass is not the limiting factor | Bio-oil yield is lower compared to fast pyrolysis |
| Flash | 500 to 900 | < 1 | > 1000 | Bio-oil (60-80) | Gas (10-20) | Charcoal (15-25) | Bio-oils are unstable due to high heating rate | High and expensive technology |
| Fast | 450 to 1400 | 0.2 to 10 | 1000 to 10000 | Bio-oil (70-75) | Charcoal (12-25) | Gas (13-30) | Short residence time | The moisture content of biomass is the limiting factor |
| Vacuum | 300 to 600 | 0.001 to 1 | 6 to 60 | Bio-oil (45-50) | Charcoal (25-30) | Gas (15-20) | Lower reaction temperature which reduces energy consumption | Usually used at low pressure 0.05–0.20 MPa |

T= temperature.

Slow Pyrolysis

Charcoal is the main product of slow pyrolysis of biomass. Direct combustion as solid fuel, gasification for the production of synthesis gas and use in the steel industry as an alternative product to mineral coke in ore reduction are some examples of industrial applications of charcoal (SANTOS et al., 2016). Although long used, the process involves complex and still unknown physico-chemical reactions during the thermal decomposition, and it is difficult to guarantee and predict the quality of the final products: (i) charcoal or biochar, (ii) pyrolytic liquid, and (iii) non-condensable gases. At the industrial level, the quality of slow pyrolysis products is clearly a major challenge (VOLPE et al., 2017).

Yields of products vary and depend on the process parameters and feedstock characteristics. Yields of 30-35 wt% biochar and 18-20 wt% bio-oil have been presented

(MAŠEK et al., 2013). The aqueous fraction varies greatly, from 30-35 wt%, because it depends on the gas fraction and the moisture content of the biomass (SCHROEDER et al., 2017), as shown in Table 2.

In this type of pyrolysis, the main operating conditions that directly influence the charcoal yield is the maximum temperature, which reaches levels between 200-500 °C (LEE et al., 2013) or 300-700 °C (CHATTERJEE et al., 2014). And the relatively low heating rates that reaches 1-10 °C or 10 -20 °C depending on the desired product (PRÖLL et al., 2017), with shows in the Table 3. The heating rate has a direct influence on the porosity of the charcoal. In general, micropores are favored by slow heating, while high rates benefit macroporosity, due to the rapid exit of volatiles (BRIDGWATER, 2012). At temperatures below 300 °C, changes occur in the matrix of the solid material due to the breakdown of aliphatic compounds. Significant changes in the structure of the material occur between 300 °C and 500

Table 2. Example yields of the principal products of slow pyrolysis.

| Biomass | T (°C) | Time (min.) | Bio-oil (wt%) | Biochar (wt%) | Gas (wt%) | Aqueous fraction (wt%) | Reference |
|------------------------|--------|-------------|---------------|---------------|-----------|------------------------|--------------------------|
| <i>Annona Muricata</i> | 400 | 25 | 18.60 | 32.20 | 17.70 | 31.50 | (SCHROEDER et al., 2017) |
| <i>Eucalyptus</i> | 400 | 25 | 20.52 | 31.18 | 48.30 | - | (HASAN et al., 2017) |
| <i>Oklahoma</i> | 450 | 20 | 35.90 | 31.40 | 32.70 | - | (YANG et al., 2016) |
| <i>Eucalyptus</i> | 500 | 180 | 42.00 | 30.2 | 27.7 | - | (JESUS et al. 2018) |

T= temperature.

Table 3. Principal parameters of the slow pyrolysis process.

| Reactor type | T (°C) | Heating rate (°C.min ⁻¹) | Main product | Reference |
|----------------|---------|--------------------------------------|--------------|---------------------------|
| Muffle furnace | 450 | 1.07 | Charcoal | (DOS SANTOS et al., 2016) |
| Muffle furnace | 450 | 1.67 | Charcoal | (SOARES et al., 2015) |
| Muffle furnace | 250-450 | - | Biochar | (PENG et al., 2011) |
| Tube furnace | 300-700 | 5 | Biochar | (WU et al., 2012) |
| Fixed bed | 500 | 10 | Biochar | (LEE et al., 2013) |

°C. These changes are characterized by the predominance of the secondary reactions. Above 500 °C there is a rearrangement of the structure of the carbonized material, characterized by the coalescence of the carbon core within the

structure, which makes it progressively less reactive (ZHAO et al., 2016).

In slow pyrolysis operations, the residence time of the material in the reactor can range from 5-10 minutes to 25-35

hours (ROY; DIAS, 2017). It is interesting to note that increasing the residence time of the gas phase in the reactor can improve carbon fixation and charcoal yield (TRAN et al., 2017). According to Alonso et al. (2017), longer residence time of the gaseous compounds results in more secondary reactions, which contributes to maximization of carbon and yields.

Although wood is the predominant raw material currently used for slow pyrolysis (CARNEIRO et al., 2017), other raw materials such as sugarcane bagasse, cashew nuts, rice hulls, palm trees and forest residues have also been used (PROTÁSIO et al., 2014). Varma and Mondal (2017) worked with two heating rates (10 and 50 °C·min⁻¹) and different final temperatures (350-650 °C) observed that in the pyrolysis of sugarcane bagasse the charcoal produced has potential for use as solid fuel or for production of activated charcoal. Several authors have found that the pyrolysis of the residual biomasses presents great potential to be used in bioenergy production (LEE et al., 2013; MONTOYA et al., 2015). He et al. (2018) also found that in slow pyrolysis of biomass the yield of charcoal decreases and the yield of gases increases with increase in temperature from 300 °C to 600 °C. It was further noted that the maximum yield of oil tar was reached already at temperatures between 450-500 °C.

Intermediate pyrolysis

Intermediate pyrolysis is performed with intermediate heating rates between slow and fast pyrolysis (MOHAMMED et al., 2016a). Slow pyrolysis produces high yields of solid material, while yields of liquid products are relatively low. The opposite tendency is observed for fast pyrolysis, which produces high yields of liquid material (greater than 70 wt%), while solid yield is low (FUNKE et al., 2017). Thus, intermediate pyrolysis aims to obtain a balanced relation between solid and liquid product yield.

The operation conditions of intermediate pyrolysis are temperatures in the range of 400 to 650 °C, heating rate ranging from 100 to 300 °C·min⁻¹, and residence time of the biomass in the reactor between 1 and 15 minutes (OUADI et al., 2013). Table 4 shows some parameters of intermediate pyrolysis.

Intermediate pyrolysis of biomass results in about 40-60 wt% liquid yield, 20-30 wt% non-condensable gases and 15-25 wt% charcoal (KEBELMANN et al., 2013). The advantage of intermediate pyrolysis when compared to fast pyrolysis is that the liquid fraction resulting from the thermal degradation process of the biomass does not include large amounts of reactive tar, which allows its direct use in boilers

Table 4. Some parameters of the intermediate pyrolysis process.

| Reactor type | T (°C) | Heating rate | Main product | Reference |
|----------------------|---------|-----------------------------|--------------|-------------------------|
| Single screw reactor | 500 | 100 °K·min ⁻¹ | Bio-oil | (FUNKE et al., 2017) |
| - | 500-650 | 0.1-10 °C·min ⁻¹ | Bio-oil | (TRIPATHI et al., 2016) |
| Fixed bed reactors | 550 | 3 °C·min ⁻¹ | Bio-oil | (TORRI et al., 2016) |

or motors (TRIPATHI et al., 2016). The lower amount of reactive tar in the pyrolygneous liquid is due to the lower heating rate than in fast pyrolysis, where the heating rate can be higher than 1000 °C·s⁻¹. A lower heating rate leads to the formation of smaller amounts of tar due to the slower and controlled reactions during degradation of the biopolymers

(HORNUNG, 2013). The solid fraction (biochar) is suitable both for energy use and for agricultural use as biofertilizer (MOHAMMED et al., 2016a).

The adaption of intermediate pyrolysis had the objective of overcoming problems encountered when using fast pyrolysis (TORRI et al., 2016). The need to use low moisture

raw material is the main drawback to fast pyrolysis, as well as the aforementioned production of high levels of tar and the contamination of pyroligneous liquor by high quantities of ash from the thermal degradation process (FUNKE et al., 2017). Slow pyrolysis in turn produces significantly lower pyroligneous liquor yield, and thus the objective of slow pyrolysis is generally to obtain the solid fraction (charcoal) (MOHAMMED et al., 2016b).

Intermediate pyrolysis can be applied to larger raw materials (up to about 20 mm) such as pellets and wood chips (ATREYA et al., 2017), but for optimization of the process, dimensions ranging from 1 to 5 mm are more recommended (KEBELMANN et al., 2013). This is another advantage of this method compared to fast pyrolysis, which requires raw material with reduced dimensions (less than 1 mm) and dry biomass (HOSSAIN; DAVIES, 2013; YANG et al., 2014). Intermediate pyrolysis is interesting, especially for use in small and medium-sized industries, since it is a relatively simple and reliable process (TORRI et al., 2016).

In the last two decades, significant advances have been made in intermediate pyrolysis technologies. Use of the Haliclean reactor, a gas tight rotary kiln, and the Pyroformer reactor, an auger screw reactor, has established new milestones in terms of gravimetric yield and the quality of the liquid resulting from the thermal degradation of biomass (HORNUNG, 2013).

The intermediate pyrolysis process shows potential for generating clean and renewable energy by producing fuels from renewable sources, which have a lower polluting

potential than fossil fuels. The pyrolysis process can be applied to a wide range of raw materials from various industrial processes that are currently considered as waste, including sewage sludge, algae, agro-industry and forestry sector waste. Furthermore, the approach can be used with materials having high moisture content (MONTTOYA et al., 2017).

Flash Pyrolysis

Flash pyrolysis occurs with heating rates above $1000\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$, at moderate temperatures (about $500\text{ }^{\circ}\text{C}$), with small residence times, which can be less than 1 second, and with very small particles of biomass (generally less than $200\text{ }\mu\text{m}$) (KAN; STREZOV; EVANS, 2016), in order to maximize heat transfer. The process favors the formation of liquid products and minimizes the formation of charcoal and non-condensable gases (AARUM et al., 2017). The flash process can be performed in a range of different configurations of reactors, with fluidized bed reactors being the most commonly used reactor type (ARTETXE et al., 2015). Table 5 shows some parameters of flash pyrolysis.

Flash pyrolysis yields about 60-80 wt% liquid (bio-oil), 15-25 wt% solids, and 10-20 wt% non-condensable gases (AMUTIO et al., 2012). Process by-products such as energy gases and charcoal can be used to power the system. The charcoal may also be used for the production of activated charcoal for use in purification processes for metal or acid catalysts (BEDIA et al., 2011). In addition, its potential for soil amelioration can also be explored (JHA et al., 2010).

Table 5. Parameters of the flash pyrolysis process.

| Reactor type | T ($^{\circ}\text{C}$) | Heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$) | Main product | Reference |
|------------------------|--------------------------|---|--------------|------------------------|
| - | 765 | 10800 | Bio-oil | (SAFDARI et al., 2019) |
| Fluidized bed reactors | 650 | > 1000 | Bio-oil | (VAMVUKA et al., 2011) |
| Fluidized bed reactors | 800 | > 1000 | Bio-oil | (BAHNG et al., 2009) |

In flash pyrolysis, the bio-oil yield is optimized when anhydrous or low moisture biomass is used. The low viscosity bio-oil produced has an extremely complex chemical composition and contains hundreds of different components (CONRAD et al., 2015; MORTENSEN et al., 2011), for example, compounds such as aldehydes, ketones, aromatic hydrocarbons, carboxylic acids, phenolics and sugars (EIBNER et al., 2017). The compounds present in the bio-oil, such as phenols, can be used in the production of resins. In addition, syringol and guaiacol are also found in significant concentrations in flash pyrolysis oils and are used in the production of biodegradable polyesters and polyethers (HORNE; WILLIAMS, 1996). The bio-oil from flash pyrolysis can be used directly as fuel for burning in boilers, engines and other energy generation systems (XIU; SHAHBAZI, 2012).

The technique of flash pyrolysis is interesting since wood, sewage sludge (ARTETXE et al., 2015), agro-industry and polymer waste such as plastic can be used as feedstock (ALVAREZ et al., 2015). The production of bio-oil produced by flash pyrolysis of lignocellulosic biomass can be carried out in mobile units in small and medium rural properties, which results in income generation in the field (AMUTIO et al., 2012). The bio-oil obtained has the potential to replace gasoline, diesel and natural gas for power generation or as a substitute for conventional fuels in ovens, boilers and gas turbines (CZERNIK; BRIDGWATER, 2004; KANAUIA et al., 2014).

In addition to bio-oil, flash pyrolysis can be used to produce activated carbon, as studied by (GRIMA-OLMEDO et al., 2016), who evaluated the recovery of forest residues of *Eucalyptus sp.* It was observed that the activation of the charcoal surface depends on the temperature at which the thermochemical conversion process is conducted. It was found that the highest activation was reached at a

temperature of 800 °C, where the specific surface of the charcoal increased, due to the increase of the pore diameters, but as a disadvantage of the use of high temperature, yield losses were observed in the pyrolysis process. At 600 °C, although there was a significant increase in the specific surface and volume of micropores, it was observed that the activation time was not an influential parameter. At 400 °C it was observed that the activation process was not very significant.

Both the yield and the chemical composition of the products obtained by means of flash pyrolysis are significantly influenced by the pyrolysis parameters (temperature and heating rate), production system (reactor) and the characteristics of the biomass used as a feedstock (AARUM et al., 2017; GRIMA-OLMEDO et al., 2016).

Fast Pyrolysis

In fast pyrolysis, the system operates continuously. The biomass is heated to moderate temperatures, which are generally in the 450-650 °C range, if bio-oil is the product of interest (DHYANI; BHASKAR, 2018), although the peak temperature in fast pyrolysis can reach maximum operating temperatures of 700 °C-1400 °C if gas production is the primary interest (KAN et al., 2016). Fast pyrolysis is noteworthy because it is performed under conditions with high biomass heating rates that benefit high heat transfer coefficient. The biomass is heated so rapidly that it reaches the maximum operating temperature peak before it decomposes. The heating rate can reach 1000 °C·s⁻¹ – 10000 °C·s⁻¹ (YU et al., 2017) in a short residence time of 0.5-2 s (XIU; SHAHBAZI, 2012). However, recent literature presents that some fast pyrolysis systems can achieve residence times of 10 s (TRIPATHI et al., 2016) (Table 6).

The changes in operating conditions and parameters affect the pyrolysis reactions for the formation of the products

and by-products. The primary reactions occur through the absorption of thermal energy during the pyrolytic process, leading to the breakdown of the weak bonds, followed by depolymerization of the chemical structures that make up the lignocellulosic materials. These reactions are responsible for the formation of volatiles, which condense, and liquid, gas and solid products are generated –the latter resulting from the non-volatilized feedstock. The residence time of these products and the increase in absorption of thermal energy in the pyrolysis process cause secondary reactions forming light gases and compounds of low molecular weight.

Fast pyrolysis technologies are considered as an advanced process whose basic principle is to maximize the gravimetric yield of low energy density liquid (bio-oil) from the biomass used as fuel. The short residence time of the primary pyrolysis products in the reactor contributes to (i) non-formation of the non-condensable gaseous products, preventing the subsequent thermal and catalytic fragmentation of the vapors, and (ii) minimization of the formation of coal, preventing the recombination of primary products (TRIPATHI et al., 2016).

The main product in fast pyrolysis, (bio-oil) is a dark liquid composed mainly of water, carboxylic acids and carbohydrates (QUISPE et al., 2017), and yields of up to 75 wt% can be achieved (BRIDGWATER, 2012; DHYANI; BHASKAR, 2018). The bio-oil represents the total liquid collected in the condensers and filters, and it includes the organic liquid, the reaction water and the water of the biomass. The byproducts of rapid pyrolysis are (i) carbonaceous solids (biochar), having a yield of approximately 12 wt% with an upper limit of 25 wt%, and (ii) non-condensable gases (syngas) with a yield of approximately 13 wt% with upper limit of 30 wt% (ROY; DIAS, 2017). Biochar decreases with increasing pyrolysis temperature due to combustion of organic materials and degradation of cellulose and hemicelluloses (TRIPATHI et al., 2016). A part of the gases can be used within the process to realize and maintain the intrinsic reactions in the system, thus avoiding the formation of waste streams that are not flue gases and ashes, Figure. 1.

Table 6. Parameters of the fast pyrolysis process.

| Reactor type | T (°C) | Heating rate (°C·min ⁻¹) | Main product | Reference |
|-----------------------|---------|--------------------------------------|--------------|------------------------|
| Tilted-slide reactor | 650 | 1560 | Bio-oil | (CHOI et al., 2019) |
| Fluidized bed reactor | 550 | 2400 | Bio-oil | (DUAN et al., 2019) |
| Microwave-enhanced | 600 | 850 | Bio-oil | (KLINGER et al., 2018) |
| Fluidized bed reactor | 500•900 | 60-6000 | Bio-oil | (SAFDARI et al., 2019) |

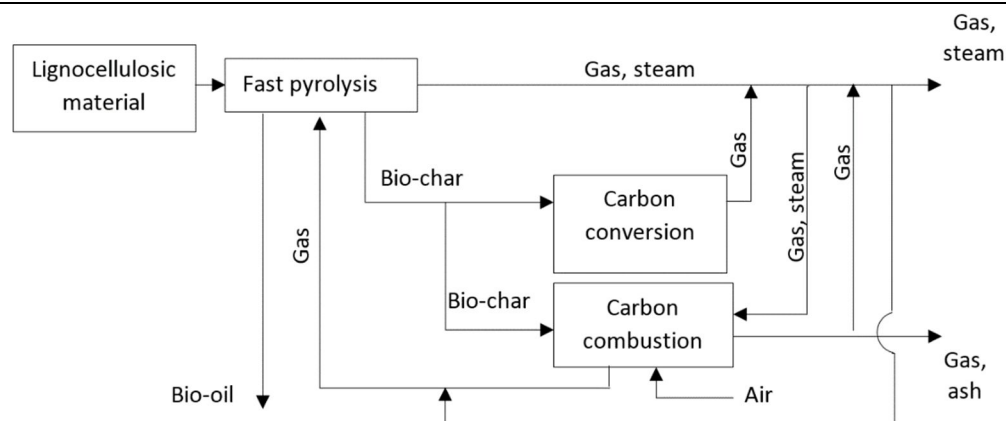


Figure 1. Basic concept of an advanced rapid pyrolysis process.

The fast pyrolysis process requires careful preparation of the feedstock, which comprises (i) reduction in size, (ii) drying, (iii) milling of the biomass to obtain a particle size of <5 mm, preferably between 2 mm and 3 mm, that is sufficiently small to ensure a fast reaction, (iv) mechanical and pneumatic classification, and (v) transport to the reactor. The particle size of the feedstock influences the yields of bio-oil, bio-char and syngas significantly (ROY; DIAS, 2017). As the particle size increases, the heat transfer rate decreases, increasing the bio-char yield and decreasing the amount of bio-oil and syngas produced. Lower particle size limits the internal heat transfer, benefiting the yield of bio-oil (PHAM et al., 2017).

A number of different reactor types are used, of which bubble fluidized bed (BFB) reactors are the most researched, and this reactor type has a long history of usage in industrial operations, since it is used in the processing of petroleum and chemical products. BFBs operate at uniform temperatures and provide the high heat transfer rates necessary for fast pyrolysis (HWANG et al., 2016). BFB reactors have the following characteristics: (i) a system constructed with standard and simple components; (ii) suitability for batch or continuous operations; (iii) a large gas-solid contact area; (iv) limited tolerance for particle size differences; (v) integrated filter systems that prevent emissions; (vi) continuous removal of gaseous by-products from the reactor, which benefits equilibrium reactions; (vii) homogeneous gas flow resulting from use of a gas distribution plate; (viii) short residence times; (ix) precise temperature control; (x) high mass and heat transfer due to the direct contact of the particulates with the gas; (xi) uniform temperature stability at high product consistency; (xii) low operating cost when compared to circulating fluidized bed reactors; (xiii) compact size; and (xiv) fast heating and cooling.

Vacuum Pyrolysis

The vacuum pyrolysis process operates in the absence of oxygen with moderate heating rates compared to the slow pyrolysis process and low pressures, ensuring a rapid removal of the reactor vapors (ALTUN et al., 2003). Thus, the lower residence time of the steam reduces the secondary reactions and the lower heating rates compared to the rapid pyrolysis process result in a lower yield of bio-oil. The pressures and temperatures used during the vacuum pyrolysis are generally 0.05 MPa-0.20 MPa and 450-600 °C (TRIPATHI et al., 2016). The lower pressure enables the organic materials to decompose and their components to volatilize at the low operating temperature (CHENG, J., 2017).

Studies show that during vacuum pyrolysis the porosity of the solid by-product significantly improves; the biochar develops microporous/macroporous structures. This property depends, in addition to the process itself, on the lignin and cellulose composition of the feed lignocellulosic material. For the same operating conditions, biomass with high lignin content will produce bio-char with a macroporous structure, whereas biomass with high cellulose content will produce biochar with a microporous structure (MA et al., 2017).

The most significant difficulty facing the pyrolysis processes is its economic viability, which depends on factors such as: (i) plant feed capacity and feed thread efficiency, (ii) separation and recovery efficiency of bio-oil and thinning of bio-char in cyclones, and (iii) control of leakage of gases produced in the process.

Conclusions

From this review, it becomes clear that the pyrolysis process is influenced by several parameters, depending on the main type of product desired. The main parameters are the

temperature, the heating rate, the type of reactor and the raw material. Temperature and heating rate are the parameters that have received most attention in the literature on pyrolysis of biomass. High rates and intermediate temperatures (450-650 °C) maximize the yield of bio-oil, while slow heating rates and intermediate temperatures (400-450 °C) favor solid yield product. Currently, most work in the literature has mainly addressed pyrolysis as the main conversion process for the energetic use of agricultural and forest residues.

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