Review of Synthetic Fuels and New Materials Production Based on Pyrolysis Technologies

Petar Gvero, Indir Mujanić, Saša Papuga, Srđan Vasković and Ranko Anatunović

Abstract The production of synthetic fuels and new materials from biomass is a wide subject, and because of that, the author has decided to focus on thermochemical conversion processes, particularly pyrolysis, which is a widely used technology and one of the most promising for synthetic fuel production. The technology of pyrolysis is explained, as well as the differences between slow and fast pyrolysis. Fast pyrolysis technology is particularly promising for liquid fuel production and is specially processed, as are the types of pyrolysis reactors commonly used in practice, such as fluidized beds and ablative, vacuum and microwave reactors. According to the demand of certain technologies for the use of pyrolysis products for energy, some requirements in regard to the quality of the products are very strict, and technologies related to the use of catalysts and catalytic processes in pyrolysis have been analyzed. Liquid products of the pyrolysis process were analyzed from the perspective of content and use in the energy sector, as well as in the chemical industry. Analysis related to the gaseous products of pyrolysis and their use for energy purposes is also presented.

P. Gvero (✉) · I. Mujanić
Faculty of Mechanical Engineering, University of Banja Luka, Bulevar vojvode Stepe Stepanovica 71, 78000 Banja Luka, Bosnia and Herzegovina
e-mail: gvero.petar@gmail.com

I. Mujanić
e-mail: indir.mujanic@gmail.com

S. Papuga
Faculty of Technology, University of Banja Luka, Bulevar vojvode Stepe Stepanovica 73, 78000 Banja Luka, Bosnia and Herzegovina
e-mail: sasapapuga@gmail.com

S. Vasković · R. Anatunović
Faculty of Mechanical Engineering, Vuka Karadzica 30, 71123 East Sarajevo, Bosnia and Herzegovina
e-mail: srdjan_vaskovic@yahoo.com

R. Anatunović
e-mail: rankoantunovicmf@gmail.com

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1 Introduction to the Biomass Pyrolysis Process

Pyrolysis is a thermochemical process that involves the heating of material in the absence of oxygen, which leads to thermal degradation into gaseous, liquid and solid products. This process thermally decomposes biomass into gas, liquid and solid by rapidly heating it to above 300–400 °C, usually going up to 700 °C. The result of the thermal decomposition process of biomass is the production of char and non-condensable gas (the primary slow pyrolysis products), as well as condensable vapours (the liquid product obtained from fast pyrolysis) (Goyal et al. 2008; Venderbosch and Prins 2011).

Pyrolysis processing of biomass is developed through primary and secondary mechanisms. The primary mechanism involves the breaking of chemical bonds within the polymers, resulting in a release of volatile compounds and a solid residue that are still able to react. After that, the volatile compounds react through secondary mechanisms, such as the cracking and recombination of the molecules (Collard and Blin 2014). During pyrolysis, the heavier hydrocarbon molecules of the biomass are broken down into smaller hydrocarbon molecules, non-condensable gases like CO, CO_2, and solid carbons such as char:

$$C_nH_mO_p + heat \rightarrow \sum_{liquid} C_aH_bO_c + \sum_{gas} C_xH_yO_z + \sum_{solid} C.$$

Unlike combustion, the pyrolysis process is not exothermic; however, this statement should be taken conditionally, because questions relating to the heat of the pyrolysis reactions are complex. In this context, some authors have identified that biomass pyrolysis proceeds in two reactive steps, the first being the primary pyrolysis process and the second being related to the further reactions of the primary char. The heat of reaction in the second step is exothermic and almost independent of experimental conditions and char yield. On the other hand, the literature shows a wide variation in the reaction heat of the primary pyrolysis process dependent on the initial biomass particle weight and on the type of retort used in the measurements (Rath et al. 2003).

Pyrolysis is one of the potential routes to harnessing energy and useful chemicals from biomass. It is a process that has been used for centuries, representing, as it does, the basis for wooden charcoal production. In the last decade, pyrolysis processes have become more attractive, because they present the basis for production of the second generation of synthetic fuels, as well as new materials and chemicals. The structural constituents of biomass, cellulose, hemicelluloses, lignin and extractives, pass through the pyrolysis process at different rates and by different pathways and reaction mechanisms (Vamvuka 2011). The process of thermal decomposition of biomass is very complex, because it depends on the type of material, temperature, pressure, heating rate, reaction time, etc. The process parameters are responsible for the determination of the relationship between the pyrolysis product components and their characteristics. From a chemical kinetics perspective, the kinetics of the thermal decomposition of biomass materials is complicated, as it involves a large number of reactions in parallel and in series. Several studies indicate the existence of slight interactions between cellulose, hemicelluloses and lignin components in biomass particles during the thermal decomposition process (Vamvuka 2011).

The focus of this text is to present the status of the technologies and the solid, liquid and gaseous products yielded from different types of technology developed on the basis of the biomass pyrolysis process, mainly related to their use in the energy and environmental sectors.

Table 1 indicates the product distribution obtained from different modes of the pyrolysis process (Bridgwater 2004).

Pyrolysis processes can be "slow" or "fast," depending on the operation conditions in the reactor. The terms "slow" and "fast" in regard to pyrolysis are not precise from the perspective of heating rates and time. Some of the main characteristics of slow and fast pyrolysis are as follows:

- Slow pyrolysis is an irreversible process of thermal decomposition of the organic components of a biomass material, in which biomass particles are heated up to 500 °C. Residence time varies from 5 min to 30 min (Mohan et al. 2006). During conventional pyrolysis, the process of biomass devolatilization is slow, and as a result of this, tar and char are the main products of the process. In a case of biomass carbonization (charcoal production), the process characteristics are slower heating rates and longer residence times for the particles, which can vary from hours to days, depending on the particle size and type, as well as reactor type and outside conditions. Under these circumstances, gaseous products do not escape from the particle as rapidly as they do in fast pyrolysis. Heating rates in conventional pyrolysis are typically much slower than those in fast pyrolysis (5–7 K/s) (Goyal et al. 2008). But depending on the reactor system and fuel particle characteristics, heating rates can be higher, from 0.1 to 2 K/s per second, and characteristic process temperatures are around 500 °C. Gas residence time may be greater than 5 s. Torrefaction is a process of thermochemical treatment of a biomass in a temperature range of about

Table 1 Typical yields (dry wood basis) produced by different modes of wood pyrolysis (Bridgwater 2004, adapted with the permission of Thermal Science)

Process	Conditions	Liquid (%)	Char (%)	Gas (%)
Fast pyrolysis	Moderate temperature, short residence time particularly vapour	75	12	13
Carbonization	Low temperature, very long residence time	30	35	35
Gasification	High temperature, long residence time	5	10	85

200–320 °C, with the aim of improving the properties of solid biomass fuels; it can be treated as a slow pyrolysis process.
- Fast pyrolysis can also be called short residence timed pyrolysis, because residence time is a few seconds to a fraction of a second and heating rates reach 300 K/s (Goyal et al. 2008). Fast pyrolysis is usually a high-temperature process (400–650 °C, although it can go up to 1250 °C, depending on the purpose of the process), in which biomass is rapidly heated in the absence of oxygen (Mohan et al. 2006; Vamvuka 2011; Tripathi et al. 2016). The intermediate pyrolysis of a biomass is a process that results in bio-oil with low tar yields and viscosity, which stands as the true distinction between the intermediate pyrolysis and fast pyrolysis processes. Depending on the heating rate, fast pyrolysis can be a "flash" pyrolysis, in which temperature can range between 777 and 1027 °C or up to 1200 °C, depending on the purpose of the process (Panwar et al. 2012; Tripathi et al. 2016). Generally, flash pyrolysis refers to heating rates greater than around 1000 °C/s (Radlein and Quignard 2013; Tripathi et al. 2016). The yield of fast pyrolysis processes is 60–75% wt. of liquid bio-oil, 15–25% wt. of solid char, and 10–20% wt. of non-condensable gases, depending on the feedstock material (Panwar et al. 2012). The most important characteristics of the fast pyrolysis process can be divided into four groups (Panwar et al. 2012): (1) very high heating and heat transfer rates in the process, which requires adequate preparation of the raw material, principally a fine grinding of the biomass feed, (2) a carefully controlled pyrolysis reaction temperature, usually within the range of 450–600 °C, (3) typical residence times for the vapours of <2 s, and (4) rapidly cooled pyrolysis products (vapours and aerosols) so as to have bio oils as the final products.

Pyrolysis plays a key role in the reaction kinetics of all thermo chemical conversion processes (such as combustion, gasification and pyrolysis), and due to that fact, the reactor design is crucial, as is determination of the distribution, composition and properties of the process's products. (Panwar et al. 2012). At least four parallel reactions leading to char, liquids and gases have to be mastered to optimize the process. The biomass pyrolysis pathways are shown in Fig. 1 (Bridgwater 2012).

The products spectrum related to the different pyrolysis pathways is given in Fig. 2.

As presented in the text above, it can be summarized that a lower process temperature, longer vapour residence time, and slow pyrolysis with large wood particles favours the production of charcoal. This is especially true for a slow thermal treatment under pressure. Higher process temperatures and longer residence times lead to biomass conversion into gaseous products, while moderate temperatures and shorter vapour residence times make for optimal conditions for liquids as process products, particularly the fast pyrolysis of small biomass particles (Meier and Faix 1999; Bridgwater 2004). The technical and economic limitations of the pyrolysis process are obvious, and due to that, it is possible to find different concepts for pyrolysis reactors, targeting certain specific products. The most widely used concepts will be briefly explained in the following text.

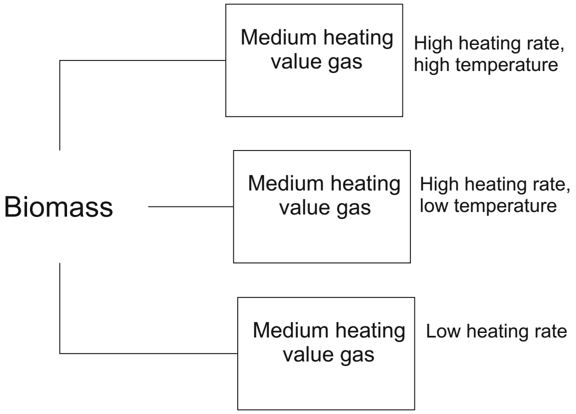

Fig. 1 Biomass pyrolysis pathway (adapted from Bridgwater 2004, with reprint permission from Thermal Science)

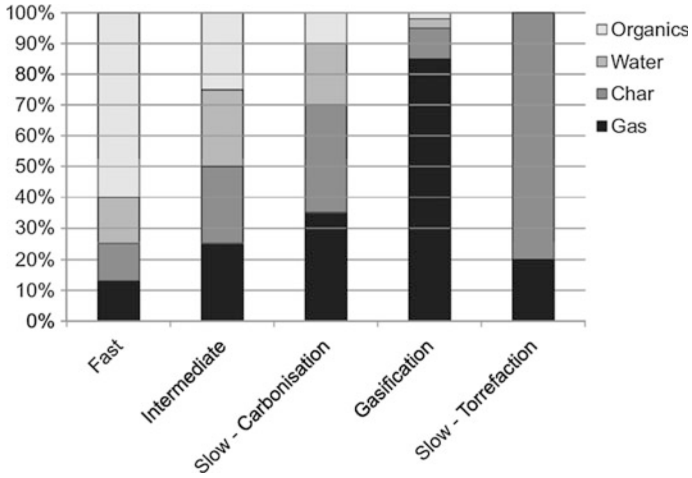

Fig. 2 Products spectrum from pyrolysis (Bridgwater 2012, with reprint permission from Elsevier)

2 Fast Biomass Pyrolysis Reactor Types

There are different kinds of reactor, depending on the purpose of the process.

In commercial biomass pyrolysis reactors, the following can be used as heat carriers: the wall of the reactor (vacuum reactors), gas (fixed bed reactors), solid particles (fluidized bed reactors) or a combination of the above-mentioned carriers.

The technical requirements for pyrolysis reactors with the aim of obtaining a high yield of good quality oils are (Meier and Faix 1999):

1. The achievement of rapid heat transfer from the heating medium to the fuel particle, (the heating medium can be a gas and/or a solid material), and high heating rates (low temperature gradient) inside the particle in which pyrolysis takes place;
2. Rapid mass transfer from the inside of the particles to the surface, and further rapid mass transfer from the hot reactor to the cold trap (rapid quenching) are both necessary.
3. The residence time of the pyrolysis vapours in the hot zone of the reactor should be no longer than a few hundred milliseconds (in the case of the production of chemicals) or 2–3 s (in the case of low viscosity fuel production). Consequently, secondary reaction cannot be completely avoided under technical conditions.

2.1 *Fluidized Bed Reactors*

The bubbling (BFB) and circulating fluidized bed (CFB) reactors are well known, representing a proven technology that has been in practical use in the chemical industry and energy sector for a long time. Both reactor types (BFB and CFB) have a long operating history, providing good temperature control in the reactor and very efficient heat transfer from the bed to the biomass particles. As reactor designs, they are characterized as providing high heat transfer rates in conjunction with uniform bed temperatures, both being necessary attributes for fast pyrolysis. The heat transfer limitation lies within the particle, thus requiring very small particles of typically no more than 3 mm to obtain good liquid yields (Bridgwater et al. 1999). A substantial carrier gas is needed for fluidization or transport. By selecting the appropriate size for the bed fluidizing media, as well as the flow rate of the carrier gas, it is possible to adjust the pyrolysis gas/vapour residence time in the freeboard area of the reactor (the area above the fluidized bed), which means that the residence time can be set to a desired value, generally between 0.5 and 2.0 s (Wan Isahak et al. 2012). In some optimistic scenarios, at least 10–20 m^2 of the bed surface area is required per ton/hour of biomass fed material in this kind of reactor (Venderbosch and Prins 2011). Generally, in the bubbling fluidized bed reactors, an operating temperature of 500–550 °C in the bed usually results in the highest liquid yields, at about 0.5 s residence time, however, the larger reactors can operate at a somewhat lower temperature, with longer residence times (Wan Isahak et al. 2012). It is important to know that for this type of reactor, the sand-to-biomass (fluidized bed to fuel particle) heat transfer is efficient, over 500 W/m^2K, while the heat transfer from the heating coils to the fluidized bed is relatively low, the gas-to-coil wall heat transfer being estimated as 100–200 W/m^2K, due to the thermal resistance inside the coils (Venderbosch and Prins 2011).

In a circulating fluidized bed reactor (CFB), the feed biomass particles, due to the nature of the process, have to be smaller than those used in bubbling bed reactors (BFB); the typical size of the particles is in the range of 1–2 mm

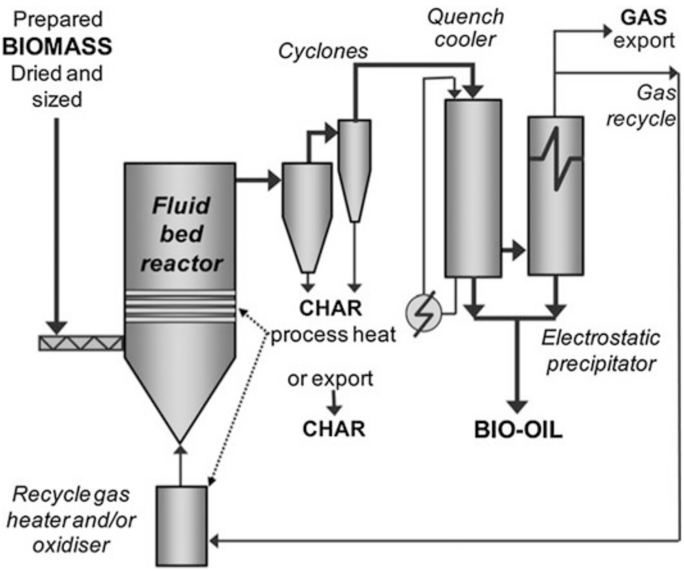

Fig. 3 Bubbling fluidized bed reactor with an electrostatic precipitator (Bridgwater 2012, with reprint permission from Elsevier)

(Wan Isahak et al. 2012). In CFB reactors, the residence times for the particles is in the range of 0.5–1.0 s in the high heat transfer pyrolysis zone, before it is entrained over to the char combustion section or the main reaction zone (Wan Isahak et al. 2012) (Fig. 3).

2.2 *Ablative Pyrolysis Reactors*

Ablative pyrolysis or surface pyrolysis takes place at 550–600 °C and higher rates, essentially independent of the feedstock particle size. It seems to be very promising for an industrial application, because it fulfils the requirements of flash pyrolysis with regard to high heating and mass transfer rates regardless of the use of large wood chips (Meier and Faix 1999; Vamvuka 2011). The key advantage is the ability to process much larger particles, as the mechanism of heat transfer in the reactor is different, and the absence of a fluidizing or transport gas, both of which contribute to a more compact and intensive reaction system (Vamvuka 2011). The process in this type of reactor depends on the way in which the wood particles are pressed against a heated surface and rapidly moved. During this process, wood particles melt at the heated surface and leave an oil film behind, after which the oil evaporates. This process uses larger particles of wood and is typically limited by the rate of heat supply to the reactor. This concept allows for the design of compact and intensive reactors that do not require a carrier gas, although the weak points of this concept are the ablative surface area and its control, as well as the moving parts at a high temperature (Bridgwater et al. 1999).

The most famous ablative pyrolysis reactor is the rotating cone reactor. In this high intensity reactor, biomass of an ambient temperature is mixed with hot sand. Upon being mixed with hot sand of 550 °C, the biomass decomposes into 70% wt condensable vapours, 15% wt non-condensable gases and 15% wt char. An important characteristic of this reactor type is the absence of a carrier gas, as it is the rotating action of the cone that propels the solids from the reactor's entrance to its exit. Because of the absence of a carrier gas, the vapour products are not diluted and their flow is minimal. An undiluted and concentrated product flow from the reactor leads to small downstream equipment with related minimal investment costs (Vamvuka 2011).

In general, ablative pyrolysis has two major limitations. First is the difficulty of getting sufficient heat transfer from hot gases to the ablative surface. The temperature difference between the hot flue gas (around 800 °C) and the pyrolysis reactor (500 °C), and the value of the heat transfer coefficient, are relatively small. Second are the difficulties in the contact between feedstock of diverse morphologies (particle shape, structure, and density) and the ablative surface. In practice, relatively few feedstocks would be suitable for ablative pyrolysis (Venderbosch and Prins 2011).

A technique related to ablative pyrolysis is screw and "auger pyrolysis," in which the biomass is transported along a hot tube by mechanical displacement using twin augers. These are particularly suitable for feed materials that are difficult to handle or feed, or are heterogeneous. This is essentially a type of transported bed reactor, as the twin auger is effectively a series of sealed pockets that advance the feed to the discharge port. Heat may be supplied by heating the walls of the auger tube barrel or by circulating pre-heated sand that is mixed with the biomass (Radlein and Quignard 2013). The nature of mechanically driven reactors is that very short residence times are difficult to achieve compared to BFB and CFB reactors, and hot vapour residence times usually vary within the range of 5–30 s, depending on the design and size of the reactor (Bridgwater 2012) (Fig. 4).

2.3 *Vacuum Pyrolysis*

Vacuum pyrolysis is a process characterized by heating rates comparable to those of slow pyrolysis, but it removes pyrolysis products as rapidly as in the previous methods, thereby simulating fast pyrolysis. Vacuum pyrolysis of biomass is generally conducted at a temperature of 450–600 °C and at a total pressure of 0.05–0.20 MPa (Tripathi et al. 2016; Vamvuka 2011). The advantages of the vacuum pyrolysis process are: (1) the technology allows for the processing of larger biomass particles than most fast pyrolysis reactors, (2) heating rates in vacuum pyrolysis are very low, compared with the other systems described above, (3) the use of vacuum pyrolysis leads to larger equipment and higher costs. Liquid product yield and

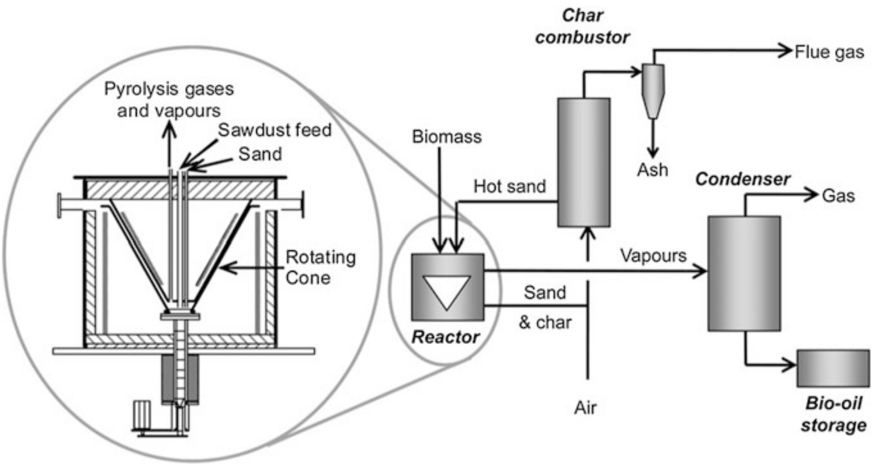

Fig. 4 Rotating cone pyrolysis reactor and integrated process (Bridgwater 2012, with reprint permission from Elsevier)

quality of vacuum pyrolysis are achieved through the removal of the vapours as soon as they are formed, by operating under a low pressure (Tripathi et al. 2016). Total liquid yields are typically lower by up to 60–65% compared to 75–80% wt from the previous two methods, but the liquid products of vacuum pyrolysis are significantly different compared to the other fast pyrolysis processes, and include water content, a higher heating value and other physical properties (Vamvuka 2011; Bridgwater et al. 1999; Bridgwater 2012). This is due to the fact that a vacuum allows for decomposition of the organic components under the lower temperatures (Tripathi et al. 2016).

2.4 *Microwave Pyrolysis*

By comparing microwave pyrolysis with the other conventional pyrolysis technologies, it can be seen that microwave heating is fundamentally different from all other pyrolysis techniques. Microwave pyrolysis includes the transfer of energy to the biomass particle through the interaction of the molecules within the particle. The advantage of microwave heating is non-contact, volumetric and selective heating, and that the heat is generated within the material rather than from an external source (which means heating goes from the interior of the fuel particle), resulting in rapid heating of the biomass particle and high heating efficiency (Wu et al. 2014; Huang et al. 2016). It is also important to emphasize that microwave pyrolysis is a technology that offers a way to recover the energetic and chemical value of the waste materials, through the production of potentially useful pyrolysis products, appropriate for future reuse (Lam and Chase 2012).

From the other side, this approach, compared to the other pyrolysis technologies, generates an enlargement of the production rates. Microwave heating requires a material with a high dielectric constant or loss factor, such as water, and due to that, water is rapidly driven off, after which the particle heats up and begins forming char. Another problem related to microwave pyrolysis is the phenomenon of hot spot formation, which has an influence on the inhomogeneity of the microwave field, and therefore can have significant influence on the yield and characteristics of the pyrolysis products (Huang et al. 2016).

In general, the technology of microwave pyrolysis can produce more solid and gas products (primary component content is H_2 = 39%, CH_4 = 9%, CO = 33% and CO_2 = 23%) but less liquid product than conventional pyrolysis (Huang et al. 2016).

Besides the above-mentioned pyrolysis technologies, many variations and modifications exist with the aim of obtaining products with the most appropriate content and characteristics adequate for the end use. Some of the technologies and approaches will be described briefly in the following text.

2.5 *Catalytic Pyrolysis*

Catalytic biomass pyrolysis is a promising thermochemical conversion route for biomass treatment, introduced with the aim of improving the quality of the products, chemicals and bio-oils with existing achievement levels in petrochemical products and the industry. The introduction of the catalysts into the pyrolysis process enhances chemical reactions, including cracking, decarbonylation, decarboxylation, hydrocracking, hydrodeoxygenation, and hydrogenation, and it could be applied at different phases and positions of the process (Dickerson and Soria 2013).

Depending on the position of the catalyst in the reactor, catalytic pyrolysis is usually divided into two different processes: (1) in situ and (2) in-bed processes (Shun et al. 2013). In the in situ process, catalysts are applied during pyrolysis, and the biomass is cracked to produce pyrolytic vapours that pass through catalyst beds, where they are converted into bio-oil, as well as gaseous and solid by-products. During the in-bed process, catalytic pyrolysis occurs in a reactor where biomass feedstock and catalysts are mixed together, which allows for direct contact between them, but in processes with a separate char combustor, the catalyst can be regenerated continuously (Venderbosch and Prins 2010; Shun et al. 2013). It is important to emphasize some negative effects related to catalytic upgrading: during this process, concentration of the aromatic and polycyclic aromatic species, particularly PAH (Polycyclic Aromatic Hydrocarbons), increases, the effect being more intensive with an increase in the catalysis temperature (Yaman 2004).

Using condensation of pyrolysis vapour to obtain bio-oil and the evaporation of bio-oil for upgrading purposes is not thermally efficient. Therefore, the introduction of catalysts into the pyrolysis process before the condensation of vapour in order to induce vapour-phase catalytic reactions is a worthwhile and promising route. There are a lot of materials used as catalysts among zeolites, HZSM-5, HY, ZSM-5, etc., and they can be divided into primary and secondary catalysts (Wan Isahak et al. 2012; Tripathi et al. 2016). Primary catalysts are the ones that are mixed into the biomass material before pyrolysis, and secondary catalysts are not mixed with biomass, but rather are kept in a separate reactor located in back of the main pyrolysis reactor (Tripathi et al. 2016). Regarding the availability of catalysts, for example, zeolites with different porous structures, such as ZSM-5, are already a commercial product and widely used as a catalyst for biomass pyrolysis in fluidized beds (decreasing the concentration of liquid products and increasing the yield of gaseous products), while HZSM-5 and HY are very efficient in the conversion of highly oxygenated crude bio-oils or pyrolysis vapours to hydrocarbons, in which light aromatic hydrocarbons (benzene, toluene, xylene and naphthalene) are dominant (Bulushev and Ross 2011; Wan Isahak et al. 2012). According to some reports, the Al-MCM-41 catalyst effectively removed acids from the bio-oil, but in comparison with ZSM-5, it had low hydrothermal stability (leading to delamination) (Bulushev and Ross 2011). For the hydrodeoxygenation process or hydro treating processes, hydrogen rich solvents are usually used and their activation takes place through the use of a catalyst. In this case, catalysts usually take the form of metal oxides, which lead in the direction of the removal of oxygen, water and carbon dioxide. Catalytic cracking of pyrolysis vapours is another method by which bio-oils containing oxygen are catalytically decomposed into hydrocarbons (Titiloye 2014). There are some natural catalysts in biomass that have influence on pyrolysis products, such as metallic minerals that can change the final product's yield (Sharma et al. 2015).

2.6 *Hydropyrolysis*

Hydropyrolysis represents an attempt in the development of pyrolysis technology to reduce certain problems that are related to the products of fast pyrolysis, such as acidity, high water content, and viscosity (Balagurumurthy et al. 2013). The main goal of the hydrolysis process is to reduce oxygen content in bio-oil products by using a single step process, and attempts have been made to integrate fast pyrolysis with the hydrocracking process by adding hydrogen under high pressure into the reactor (Bridgwater 2012; Balagurumurthy et al. 2013). The presence of hydrogen in the reactor prevents the formation of free radicals and olefins, which are responsible for the instability of bio-oils produced through the fast pyrolysis process (Balagurumurthy et al. 2013).

3 Liquid Products from the Pyrolysis Process

Liquid products of the biomass pyrolysis process, so-called “bio-oils,” are a complex mixture of water and organic chemicals, and may consist of more than 300 organic compounds (Bulushev and Ross 2011). They were formed through the fast and simultaneous chemical reactions of depolymerization and fragmentation of the main biomass constituents: cellulose, hemicellulose, and lignin, with a rapid increase in the process temperature (Krutof and Hawboldt 2016). After this phase, rapid quenching then “freezes in” the intermediate products of the fast degradation of biomass constituents. Rapid quenching captures a lot of pyrolysis products that would otherwise continue to react (molecule degradation, cleaving or condensation) if the residence time at a high temperature was extended (Mohan et al. 2006). As already mentioned above, the yield and composition of biomass pyrolysis products depend on the characteristics of the biomass feedstock (type, geometry, etc.) and operating parameters of the reactor. Water content is typically in the range of 15–35% wt, although values outside this range have been reported. As already mentioned, chemically, pyrolysis bio-oil is a complex mixture of water and organic chemicals, which includes alcohols, aldehydes, ketones, esters, phenols, guaiacols, catecols, syringols, sugars, furans, alkenes, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, hydroxyaldehydes, hydroxyketones, other carboxylic acids, aromatics, nitrogen compounds and miscellaneous oxygenates (Mohan et al. 2006; Vamvuka 2011; Radlein and Quignard 2013). Their average molecular weight varies within the range of 300–1000 g mol^{-1}. The compound with the highest concentration is hydroxyacetaldehyde (up to 10% wt), followed by acetic and formic acids (5 and 3% wt, respectively) (Vamvuka 2011; Radlein and Quignard 2013). Bio-oils also have a low pH value (2-3,7) due to the presence of carboxylic acids, as well as having more nitrogen and chlorine than petroleum, which are unsuitable characteristics, but generally contain less sulphur than petroleum (Bulusheva and Rossa 2011; Kan et al. 2016).

Liquid fuel production from the pyrolysis process is interesting because liquid fuels are easier to transport, store and can be an alternative energy source. The disadvantages of biomass as a raw material in pyrolysis processes for the purpose of producing liquid fuels are the variations in the characteristics (which can strongly depend on the location), the low energy density and the necessity of careful organization of the supply logistics in order to avoid or reduce unnecessary production costs. Water content in bio-oil pyrolysis products is another important issue, as high water content is one of the major barriers to bio-oil’s utilization as a fuel, which is also the case with the oxygen content, especially in regard to its use in IC engines or certain other sophisticated devices. In medium and low speed engines, bio oils can be used directly, while high speed engines require blends of bio oil with methanol and cetane-improving additives (Krutof and Hawboldt 2016; Wan Isahak et al. 2012). Biomass pyrolysis oils can be used directly as a liquid fuel for boilers, or as a fuel for diesel engines and gas turbines, for the purpose of heat and electricity generation, or it can be catalytically upgraded in order to achieve standards of transport grade fuels (Panwar et al. 2012). The lower heating value (LHV) of bio-oils is only 40–45% of that exhibited by hydrocarbon fuels. On a volume basis, it is 60% of the heating value of hydrocarbon oils, because of the high oxygen content, the presence of water and the higher density. A typical higher heating value of bio-oil is 15–20 MJ/kg, due to its considerable oxygen content, which is in the area of 30–40% wt (Kan et al. 2016; Vamvuka 2011).

Some recent research has shown that fast pyrolysis products can be used to generate electricity. Bio-oil combustion tests have shown that pyrolysis bio-oils can replace heavy and light fuel oils in industrial boiler applications. It was shown that pyrolysis bio-oils are more similar to light fuel oil, although there are significant differences in ignition, viscosity, energy content, stability, pH, and emission levels (Venderbosch and Prins 2011). For their use in furnaces and boilers, some modifications to the systems are necessary, said systems usually requiring some supplementary fuel for the start and sometimes for the regulation of the combustion process due to variation in the quality of the bio oils (Krutof and Hawboldt 2016). The recent analyses have shown that the high feasibility and cost efficiency of electricity generation through the use of pyrolysis bio-products as a fuel are more beneficial than those of any other biomass conversion method in the long term (Malik and Sangwan 2012).

Bio-oil can also provide fuel for transportation. Initially, it was thought that bio-oil could be directly fired in diesel engines, but the acidity, viscosity, and presence of particulate matter make it unsuitable even for stationary diesel engines. Thus, bio-oil must be upgraded to a fuel suitable for transportation. In general, bio-oils are upgraded in FCC reactors at atmospheric pressure or in high-pressure hydrotreating reactors in order to reduce their oxygen content, as well as through the use of a supercritical water method in order to produce fuel with a higher heating value (Venderbosch and Prins 2011; Wan Isahak et al. 2012).

Pyrolysis is expected to play an important role in future biorefineries, either as a central unit or as a peripheral unit for valorizing biorefinery side-streams for enhanced economic viability (De Wild and Reith 2011).

The different thermal characteristics, particularly the thermal stability of hemicellulose, cellulose and lignin, provide an opportunity to use pyrolysis as a technology for the thermal fractionation of biomass into products, which can then serve as substitutes for conventional petrochemical products (De Wild and Reith 2011). The main phase of cellulose conversion occurs from 300 to 390 °C, with the highest decomposition rate generally appearing at reaction temperatures of 330 to 370 °C (Collard and Blin 2014). Products that can be yielded from cellulose pyrolysis at reaction temperatures in the range of 200–400 °C, are: levoglucosan, hydroxyacetaldehyde, 1,6-anhydro-β-D-glucofuranose, furfural, hydroxymethylfurfural, furan, and other C1-C4 oxygenates (e.g., methanol, formaldehyde, formic acid, acetone, acetol, lactones, etc.). It can also be used as glucose, polymers, antibiotics and a food browning agent in ‘liquid smoke’ (De Wild and Reith 2011). For reaction temperatures higher than 400 °C, the process’s residue becomes more aromatic (Collard and Blin 2014). The main phase of hemicelluloses conversion occurs from 150 to 350 °C, and can yield: acetic acid, furfural, furan, furanone, methanol, other C1-C4 oxygenates (e.g., formaldehyde, hydroxyacetaldehyde, acetone, acetol, lactones, etc.), C5 and C6-anhydrosugars, and humic substances. It can also be used on the market as a bulk-chemical, a vinegar (food), a cleansing agent, vinyl acetate, acetic anhydride, esters, a solvent, a road de-icer (as calcium acetate), an intermediate commodity chemical, a resin, an adhesive, a food flavouring agent and a precursor to speciality chemicals (Collard and Blin 2014; De Wild and Reith 2011).

Perhaps the most promising biomass component is lignin, the main conversion step of which occurs in the temperature range of 200–450 °C, with the highest decomposition rate generally occurring in the range between 360 and 400 °C. Hundreds of compounds have been identified in GC analysis as fragments from lignin (amongst others, phenols, eugenols, and guaiacols) and holocellulose (sugars, acetaldehyde, and formic acids). Large fractions of acetic acid, acetol, and hydroxyacetaldehyde have been identified; (poly) phenols are also present, sometimes in rather high concentrations (Collard and Blin 2014; Venderbosch and Prins 2011). The market applications for chemicals produced through the lignin pyrolysis process can be in fine chemicals, pharmaceuticals, food flavouring agents such as ‘liquid smoke,’ the fragrance industry, bulk-chemicals, wood-adhesives, resins, plastics, fuel additives, solvents, fuel, antifreeze, ethanol denaturant, 2nd energy carrier for H_2 and bio-diesel (De Wild and Reith 2011).

4 Gaseous Products

Similarly to char, about 10–35% of gaseous components (syngas) are produced through slow pyrolysis processes; a higher syngas yield is possible in flash pyrolysis at high reaction temperatures (Jarihul et al. 2012). The gaseous pyrolysis products contain: carbon dioxide, carbon monoxide, methane, hydrogen, ethane, ethylene, minor amounts of higher gaseous organics and water vapour on a mass basis, but generally, pyrolysis gas consists mainly of CO and CO_2, with smaller percentages of C_xH_y, (mainly CH_4) and H_2 (Vamvuka 2011; Neves et al. 2011). The primary gases of the fast pyrolysis process (less than 5% wt of the dry feed) contain about 53% wt CO_2, 39% CO, 6.7% hydrocarbons (including methane) and 0.8% H_2. In practice, a portion of the organic vapours and tars undergo secondary reactions, and are cracked to secondary gases, containing 9% wt CO_2, 63% CO, 27% HC and 1.4% H_2. The LHV of these primary gases is 11 MJm^{-3}, and that of pyrolysis gases formed after a severe secondary cracking of the organic vapours is 20 MJm^{-3} (Vamvuka 2011; Kan et al. 2016). Based on the collected data, the heating rate seems to have little effect in determining the composition of the pyrolysis gas (Neves et al. 2011). Reactor temperature has a significant influence on pyrolysis processes and the resulting product distribution. Studies have also shown that an increase in reactor temperature correspondingly increased the syngas flow rate, which lasted for a shorter period of time and then reduced dramatically. High moisture content in raw biomass particles creates unfavourable effects on syngas production, by contributing to the extraction of water-soluble components from the gaseous phase, consequently causing a significant decrease in yields of gaseous products (Jarihul et al. 2012). The yields of CO, CH_4 and H_2 show a similar pattern of change as a function of the pyrolysis reaction temperature, but the observed trend of CO_2 is different; the yield of CH_4 (where, C_xH_y mainly accounts for C2 hydrocarbons) appears to have linear dependency on the yield of CH_4 (Neves et al. 2011).

Syngas from the biomass pyrolysis process can be used as a renewable alternative fuel for internal combustion (IC) engines and industrial combustion processes. Some studies have shown that internal combustion engines using syngas as fuel produced about 30% less engine power output compared to petrol, due to the difference in quality (Jarihul et al. 2012). One of the pathways for the upgrading of the gaseous components produced and its use in IC engines is so-called bio-methane production through the synthesis process of the pyrolysis vapours (Gorling et al. 2013).

5 Solid Products

The thermal decomposition of biomass that occurs in the absence of oxygen, along with slow heating rates, creates solid products with the generic name of charcoal or biochar. These products can be, depending on the process parameters, further divided into fuel charcoal, activated charcoal and bio-coke, which also have some fine differences regarding their application.

Biochar is primarily carbon (~85%), but it can also contain mineral fractions, oxygen and hydrogen. The advantage of biomass, unlike fossil fuels, is low ash content; in the case of wood, it is 0.5 to 1%, and biochar ash has a low inorganic ash content. Due to the high carbon content and low water content, the lower heating value (LHV) of biochar is about 32 MJ/kg, which is substantially higher than the raw biomass material, and its liquid product (Basu 2013).

The yield and characteristics of biochar produced through pyrolysis processes depends on the design of the reactor, the physical and chemical characteristics of the biomass particles, and the operating parameters, such as heating rate, temperature and residence time in the reaction zone. During biomass pyrolysis, depending on the reactor type, type of biomass and process parameters, between 10–35% of biochar is produced, while slow pyrolysis at temperatures from 300 to 800 °C favours biochar yield (35%) (Jahirul et al. 2012). Lower process temperatures and longer vapour residence time favor the production of charcoal (Bridgwater 2012; Demirbas 2004). Due to that, charcoal production from biomass requires slow heating and a long duration pyrolysis process, at relatively low temperatures, around 400 °C, but as has already mentioned, the process parameters depend on the particular kind of pyrolysis technology. For example, comparing the microwave and conventional pyrolysis technologies in biochar production, it can be recognized that some of the conventional technologies require reaction temperatures higher than 600 °C and that their products can be low grade, with PAH and CO_2 formation, while microwave pyrolysis requires less energy consumption in the process and, as a result, produces a high quality biochar (Li et al. 2016).

Torrefaction has been developed as a possible option for improving the fuel characteristics of biomass, so that it can be used more efficiently as a clean and adequate fuel for the processes of combustion and gasification, with higher energy density (HHV = 20–25 MJ/kg) (Collard and Blin 2014). In this process, which actually represents slow (<50 °C/min) low-temperature pyrolysis, biomass is treated at temperatures in the range of 200–300 °C. Treatment at these temperatures results in the loosing of the fiber structure of the biomass particles and improves the grindability characteristics of the fuel. The most unstable oxygenated fractions, originated from hemicelluloses, are converted, with the result being a change (reduction) in the O/C (to around 0.5) and H/C ratios and improvement of the uniformity in properties among different biomass feedstocks, due to which they can be used as substitutes for coal (Bridgeman et al. 2010; Collard and Blin 2014; Basu et al. 2014).

During the pyrolysis (carbonization) process, volatiles (gaseous components) react with the char layer when flowing out of the particle to form char. A longer residence time of volatiles leads to greater char formation, due to these secondary reactions; at the same time, this has the consequence of decreasing the char reactivity by covering the active sites and the inorganic matter, which could play the role of a catalyst in the process. The time during which the char particle remains at final temperature, e.g., soaking time, also influences the char's reactivity. In this case, the decrease in reactivity is a result of the rearrangement of the char structure to a better alignment of the plane layers of carbon. The mineral matter and ash content, and its presence in the biomass pyrolysis (and carbonization) process, favors an increase in char and gas yield and its reactivity (Venderbosch and Prins 2011).

Hence, agricultural residues, with their high sodium and potassium content, and generally higher ash content than wood, provide more char with higher reactivity than wood. Ammonium salts containing phosphorus can also promote char formation during pyrolysis, reducing oil yields (Venderbosch and Prins 2011). It was found that hot biochar acts as a catalyst and favours the cracking of vapours during the fast pyrolysis process (Sharma et al. 2015). When it comes to the dependence of char yield on the type of biomass, lignin is often considered to be the component of wood that produces the most char, but hemicellulose has also been reported as giving relatively high char yields (Jahirul et al. 2012). Cellulose forms char through secondary reactions with the char layer that are very dependent on the size and geometry of the biomass particle, the char yield increasing with increasing particle size (Demirbas 2004; Bellais 2007). At the same time, the differences in char yields become less important between small and large particles in the case of pyrolysis at high reaction temperatures; this is explained by the heating rate, and the residential time of the volatiles (Bellais 2007).

Biochar is generally characterized by its physical properties, such as particle size, particle size distribution, internal surface area, moisture content, porosity, volatile matter content and pH, and its chemical composition, represented through elemental analysis and the carbon yield in char, the cation exchange capacity and the heating value. Taking into consideration the variety of feedstock biomass materials and pyrolysis operating conditions in different reactor types, it is expected that it would be difficult to predict biochar behaviour (Marshall 2013).

The implementation of pyrolysis systems in the context of biochar production has numerous benefits and applications, such as agriculture, active carbon production, waste management, renewable energy and climate change mitigation.

Potential agricultural applications include soil improvement, fertilization in organic food production, which can be used in the production of greenhouse growth media, nutrient-enriched soil supplementation and carbon sequestration. The use of biochar as a component for fertilization in agriculture may enhance crop yield through increased nutrient and moisture retention, improvement of soil structure, absorption of pollutants, reduction of use of artificial fertilizers, etc. Biochar in combination with water, ammonia and carbon dioxide in soil makes ammonium bicarbonate (NH_4HCO_3), which stays in the soil and doesn't cause damage to adjacent water and ecosystems. The application of biochar in the fertilization process may also reduce the release of nitrous oxides from agricultural land, with the additional benefit of reducing both GHG and N_2O emissions. It is also used in the sequestration of carbon in soil, which results in a reduction of carbon dioxide levels in the atmosphere through the uptake by plants (Dutta 2010; Brownsort 2009).

The volatile components of biochar (in this context, biochar is a material used in agriculture) have been identified as key properties for its suitability in soil amendment applications. As a result, volatile matter content has been specifically measured and is being correlated to the existence of toxic polycyclic aromatics (PAHs), whose level is strictly regulated, biochar with lower levels of PAH being considered to be quality (Brownsort 2009; Dutta 2010; Marshall 2013). Biochar pyrolysis systems (for agricultural purposes) use low cost technology and low grade biomass raw materials, which allow for the sustainable use of existing local resources, such as agricultural residues and fresh biomass (waste from the cultivation of fruit, viticulture, etc.), to deliver benefits as soil fertilisers while still providing energy products.

Biochar can potentially play an important role in sequestration processes, for the long term storage of carbon. After production and incorporation into soils, under certain conditions, biochar can remain stable over a long period of time (Brownsort 2009). Carbon from agricultural and forest residues, when left on the ground, is released over time into the atmosphere as CO_2 or CH_4, however, if biomass is converted into biochar, as much as 50% of the carbon contained in the biomass stays in the soil as a stable biochar residue (Basu 2013).

Charcoal produced through pyrolysis (carbonization) was one of the earliest fuels used in human civilization. It has high fixed carbon content and a modest amount of volatile matter, and can be used as a renewable fuel. Charcoal can also be used directly for clean heat and power generation or co-fired with other solid fuels in conventional generating plants. At the same time, the use of biochar can mitigate problems with direct biomass combustion, such as non-homogenous combustion, low bulk density, high water affinity, low energy content, and rotting characteristics. In its traditional form as charcoal, it is used extensively for cooking. The use of pyrolysis technology in appropriate scales in developing countries may be a way to improve otherwise inefficient traditional charcoal-making processes, reducing the biomass requirement for the same charcoal output and allowing for the use of agricultural wastes as an alternative feedstock to wood, with the potential for co-products to provide electrical power as well (Brownsort 2009).

The potential for the alleviation of climate change through the use of pyrolysis biochar systems lies in the combination of the two above-mentioned benefits of their application—the reduction of greenhouse gas emissions by avoiding their release from agriculture, waste disposal and the combustion of fossil fuel, and the sequestration of atmospheric carbon dioxide in a stable form of carbon.

Another important feature of biochar is that it can be used as a bio-adsorbent, either by treating the biochar itself as an adsorbing agent or by using the biochar as a precursor for activated carbon. Bio-adsorbents can be used for land reclamation, water remediation or air emission control. This is accomplished through adsorption of heavy metals, pollutants and other contaminants.

Biochar can be used as a raw material in active carbon production if its pores' structure and surface area are appropriate for this purpose. The biochar obtained from the biomass pyrolysis process has a direct influence on the subsequent char oxidation step, since the amount and type of pores in the char particle determines accessibility of gas to the active surface sites, and biochar produced through slower pyrolysis processes has higher surface area properties (Chhiti and Kemiha 2013; Marshall 2013).

Activated carbon has a very high adsorption capacity, due to its large pore surface area, and its use is mainly related to water purification systems, as well as air and gas cleaning. The principle of production of active carbon is the removal of the tarry products from conventional fuel charcoal, by thermal (usually by using steam), chemical (treatment by acids) and mechanical means. This so-called activation process makes the pores in charcoal particles more accessible for absorption (by increasing its absorption characteristics) and increases the pore surface area by orders of magnitude (Demirbas 2004; Basu 2013).

Biochar produced in pyrolysis processes can have surface area values ranging from 0.5 to 450 m^2/g, which are significantly lower than those of commercially activated carbons produced from coal and petroleum sources (500–1200 m^2/g).

Other potential applications of solid pyrolysis products include the manufacturing of metallurgical (redefined as bio-coke) and advanced materials (nanotubes, fibres, composites, etc.) (Marshall 2013). Bio-coke is produced specifically for metal extraction as a substitute for conventional coke, which is produced from coking coal. It needs certain specific properties for its use in blast furnaces in regard to adequate compressive strength and good fracture resistance. Using bio-coke in blast furnaces has a great potential to reduce net CO_2 emissions from the iron and steel industries by replacing fossil coal (Basu 2013).

6 Conclusion

This paper has shown the importance of understanding the biomass pyrolysis process and its mechanisms as a key for the technologies that produce various types of products from biomass raw material. Pyrolysis is primarily interesting as a method for production of solid, liquid and/or gaseous fuels, but also products of interest to other industries and branches of the economy. For that reason, slow and fast pyrolysis were both explained, as well as the different types of reactor that are already in use at different stages, from the experimental to the fully commercial, from the very simple to the high-tech processes supported by catalysts. A short review of the catalysts and catalytic processes was presented. The authors have tried to give some details about solid, liquid and gaseous pyrolysis products, their characteristics and use, primarily as fuels, but also as materials that can be used in agriculture and other industries. Pyrolysis products can be used directly or must be upgraded, depending on the technology requirements, but it is important to emphasize that pyrolysis products can be competitive with fossil fuels and oil-derived products, particularly from the aspect of sustainability and the environment. All of this was mentioned in this paper in an attempt to shed more light on pyrolysis-based technologies, giving added value to biomass as a valuable and renewable resource that can obviously play a more important role in the economy of the countries and areas which are rich in this resource.

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