PYROLYSIS AS A KEY PROCESS IN BIOMASS COMBUSTION AND THERMOCHEMICAL CONVERSION

by

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Original scientific paper
DOI: 10.2298/TSCI151129154G

Biomass is a fuel with a highly volatile content and due to that, pyrolysis as a part of the combustion process, has a dominant role in the overall process development, as well as on final products and the process efficiency. It is of key importance to investigate the influence of the process parameters; as temperature, furnace/reactor environment, fuel properties, type, particle size, geometry, and the structure of the pyrolysis process has an influence regards the design of the combustion/pyrolysis equipment and the final products of the processes. This paper gives some results of the investigation's related to this problem, mainly focussing on wooden biomass as the most important biomass type, as well as a comparison with relevant documented literature. Besides that, pyrolysis based technologies are one of the key directions in synthetic fuels production based on biomass. Biomass pyrolysis process parameters are crucial in reactor design as well as the quantity and quality of the final products. This paper provides discussion dedicated to this aspect with a focus on slow pyrolysis, targeting charcoal as the key product, and fast pyrolysis, targeting synthetic gas as the key product.

Key words: *biomass, wood, pyrolysis, combustion, volatiles, fuel, synthetic*

Introduction

Pyrolysis is the key process and the first stage of combustion or thermochemical conversion of high volatile fuels, for biomass. Pyrolysis is a thermochemical process which uses the heating of material with an absence of oxygen, which leads to its thermal degradation to become gaseous, liquid and solid products. Pyrolysis can also be considered as a crucial part of biomass gasification and the combustion process which determines the overall devolatilization time, as well as the quantity and quality of the resulting products [1]. Exposition of the biomass particle to the conditions of the furnace or reactor will start a lot of processes, which then combines complex chemical reactions with their own kinetics, as well as the complex transportation phenomena related to the transport of the species, heat, momentum, *etc*.

Although pyrolysis is not the central phenomenon of some thermochemical processes, it is usually an essential input for the definition of the other processes; for example the additional combustion of the volatiles in multi-step furnaces. Biomass is a very complex ma-

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terial from the aspect of chemical composition, as well as its physical characteristics; as is the size, geometry, porosity, anisotropy of the structure. Thermal decomposition of biomass results from the decomposition of the consisting polymeric chains (cellulose, lignin, hemicelluloses). The result of this is the production of char and non-condensable gas (the main slow pyrolysis products) and condensable vapours (the liquid product aimed at in fast pyrolysis) [2, 3]. During practical applications (*e. g.* fluidised bed reactors, fixed bed reactors, *etc.*) large biomass particles were usually used (from several millimetres up to centimetres), as were pellets or fragments of certain size. This implies that gradients of temperature exist in the biomass particle, and that the temperature variation is generally slower inside. Even in particles larger than one millimetre, considerable temperature and concentration gradients are present [3, 4]. Furthermore, the products generated by the decomposition of biomass polymers must diffuse into the mass of matter. Some documented results have in fact shown the influence of sample size on the amount of tar and gas yields; these variations are dependent on the overall conversion rate, which is controlled by the rate of heat and mass transfer inside the particles [4, 5]. This implies that process dynamics, as well as particle size, depends on the internal particle structure.

Unlike combustion, the pyrolysis process is not exothermic, but this statement should be taken with reservation, because questions relating to the heat of pyrolysis reactions are complex.

Each of the structural constituents of biomass (hemicelluloses, cellulose, lignin, extractives) pyrolyze at different rates and by different mechanisms and pathways [6]. At least four parallel reactions leading to char, liquids and gases have to be mastered to optimize the process. Gaseous products are mainly constituted of CO, H_2, CO_2, CH_4 and other light hydrocarbons, while tar is made by hydrocarbons of a higher C content and other organic compounds which are volatile at the temperature of pyrolysis and condense at low temperature; generally tar is considered as being constituted of compounds with a condensing temperature that is higher than benzene. Char is the solid residual after pyrolysis; it consists of carbonaceous solid compounds with a high C/H ratio [3]. Pyrolysis of biomass proceeds through a series of complex, concurrent and consecutive reactions and provides a variety of products [7]. Pyrolysis processes, can generally be divided into "slow" and "fast" depending on the operational conditions in the reactor, but it is important to say that there is not a strict distinction between these two types of process.

Slow pyrolysis is an irreversible process in which thermal decomposition of the biomass material occurs at temperatures up to 500 °C and residence time varies from 5 to 30 min [8, 9]. During conventional pyrolysis, the biomass is slowly devolatilized and volatiles do not escape as rapidly as they do in fast pyrolysis. Due to that, tar and char are the main products, particularly in pyrolysis below 300 °C, which favors the production of char, water, CO_2 and CO, whereas heating at higher temperatures (300-500 °C) favors the production of tar, containing anhydrosugars, oligosaccharides and some pyran and furan dehydration products [9]. Depending on the system, heating rates are between 0.1 to 2 °C/s and gas residence time may be greater than 5 s [9].

Fast pyrolysis is characterised with a short residence time, which can be from a few seconds to a fraction of a second. Fast pyrolysis is usually a high-temperature process (400 to 650 °C) in which biomass is rapidly heated in the absence of oxygen [6, 8]. Depending on the heating rate, fast pyrolysis can be a "flash" pyrolysis where the temperature can be in the range of 777-1,027 °C [10]. Generally, flash pyrolysis refers to heating rates that are greater than about 1,000 °C/s [11]. The yield of fast pyrolysis processes is dominantly liquid bio-oil, rather than char and non-condensable gases, depending on the feedstock used [11].

In all thermo-chemical conversion processes, pyrolysis plays a key role in reaction kinetics and therefore also the in reactor design and determining product distribution, composition, and properties [10].

Biomass combustion is a complex process that consists of consecutive heterogeneous and homogeneous reactions, and a single particle of the biomass combustion process; shown in a simplified way it consists of:

- heating and drying,
- pyrolysis (devolatilization),
- flame combustion, and
- char combustion.

The time used for each part of the process depends on the biomass fuel type, geometry, temperature and the combustion environment. In a more detailed description, the devolatilizaiton process can be described as four phases:

- the evolution of volatiles,
- ignition of volatiles,
- flaming, and
- flame extinguishing.

All types of biomass are fuels with a high content of volatiles (in the most of the cases it is around of 80-85%), and due to that, devolatilization (pyrolysis) is the most important process for efficient combustion of such a fuels. Modern technologies developed for biomass combustion already took this process in to consideration, because in the opposite case, incomplete combustion can occur in the furnace, which can lead to an increase of the emissions of unburnt pollutants such as:

- CO,
- soot,
- volatile organic compounds (VOC),
- tar, and
- polycyclic aromatic hydrocarbons (PAH).

Besides that, incomplete combustion leads to a decreasing of combustion efficiency, furnace efficiency, as well as the overall boiler efficiency.

The intention of this paper is to review crucial aspects of the biomass particle behaviour under three pyrolysis conditions in order to give the clearest picture regards the influence of biomass type, geometry, and environment (reactor/furnace) conditions on the process. Wooden biomass is the most representative biomass type and due to that most of the examples and results will be based on that.

The influence of biomass type, particle size and geometry on the pyrolysis process

The influence of biomass type (variety and chemical composition) on the characteristics of pyrolysis

There are a lot of biomass types and this means that there is a wide range of variety in physical properties, which can significantly change the pyrolysis process evolution and can affect the final products and results. Even modifications of the same biomass type can behave in a different way during pyrolysis or the combustion process; for example, wood chips, wood pellets and torrefied wood, produced from the same type of the wood show different behaviours when exposed to combustion of the pyrolysis process. The pyrolytic properties of biomass are controlled by the chemical composition of its major components, namely cellulose, hemicelluloses, and lignin and their minor components including extractives and inorganic materials. The fuel properties and process conditions affect the pyrolysis and combustion characteristics, altering the heat generation, heat transfer and reaction rates in a complicated manner [12]. Unfortunately, most of the measurements produced from different laboratories are not directly comparable because of the differences in the experimental configurations. This is particularly in relation to the heat transfer mechanisms from the reactor heating system to the particles, as well as the specific characteristics of the biomass (wood variety, size, shape, moisture content) and nature and content of the main constituents (cellulose, hemicellulose, lignin and extractives) [13]. Generally, in comparing the chemical compositions of hardwoods and softwoods, hardwoods have a higher content of cellulose and hemicelluloses then softwoods. However, softwoods have a higher content of lignin than hardwoods. This could be important; if it is known that thermal degradation process of cellulose begins at temperatures >240 °C, and about 450 °C it is completely finished [14]. Hemicelluloses are thermally degrading from between 200 °C to 260 °C. Thermal degradation of lignin begins at 200 °C and between 225 °C and 450 °C the reaction process becomes exothermic [15]. Some additional findings showed that lignin reaction began at low temperatures, but pyrolysis can be extended to higher temperatures [15, 16]. Thermal degradation of lignin produce 1.5 times more of coke than cellulose [14]. Analysis of the pyrolytic behaviour of the hardwoods and softwoods exposed to certain heat fluxes at final sample temperatures of 600-950 K, show that higher heat flux is required to achieve 50% of conversion for the softwoods which is as a result of the higher degradation temperatures required for softwood lignin [13]. In the wooden biomass the cellulose content oscillates between 40 and 60%, and the content of lignin varies between 21 and 30%. Other important components of wood are pentosanes and hexosanes, soft woods contain up to 20% pentosanes and hexosanes and hard woods contain between 20 and 30% [17].

For a biomass with higher cellulose content, the pyrolysis rate became faster, while, the biomass with higher lignin content gave a slower pyrolysis rate, which means that pyrolysis of cellulose and hemicellulose will proceed to completion before the pyrolysis of lignin reaches a very advanced stage [18, 19]. The cellulose and lignin content in the biomasses were one of the important parameters required to evaluate pyrolysis characteristics. The combustion characteristics for the actual biomass depends on the char morphology produced [18].

Wood structure and physical characteristics influence on the process

Wood is of particular interest as a most important biomass type and it is important to know that there are a lot of differences in the structures of hardwood and softwood, which has a large influence on the heat and mass transfer processes occurring during pyrolysis. Due to the nature of woody biomass materials, their pore structure and physical properties are anisotropic; hardwoods have a more complicated morphology then softwood, the structure of the softwood is a simple, primitive type distinctly different from that of hardwoods. Softwood (such as spruce) has long fibres (1.9-5.6 cm) and a more homogeneous structure, while hardwood (such as beech) has a heterogeneous structure and small fibres (0.4-1.9 cm) [14, 20]. These specifics have a strong influence on the diffusion mechanisms related to heat and species transfer trough biomass particle. For example, gas permeability along wood fibres is 10^3

higher than it is across wood fibres; therefore, the anisotropic structure is likely to play an important role in the intra-particle gas transport during both the pyrolysis and gasification process [20]. The physical structure of wood imposes a considerable restraint on the movement of products of pyrolysis at low temperatures, but this restraint largely disappears in the temperature ranges of 300-320 °C. Below this temperature range, due to a longer residence time of the products in the particle as well as exposure to the heated surfaces and increased pressure in the fuel particle, autocatalysis effects were increased, while above this temperature range, products flow in the direction of least resistance, away from the unreacted wood, and autocatalysis is less important [19]. Some authors presented data indicating that pressure in the wooden particle during volatiles generation process can be around 0.3 bar, depending on material porosity [21, 22].

Regarding to mass transfer in the biomass particle during pyrolysis, two types of diffusion processes occur: diffusion of the bonded moisture through cell walls, and diffusion of the gases mixture. Diffusion is the dominant transport mechanism during pyrolysis that occurs on the lower heat fluxes and temperatures, whilst at higher temperatures, convection is dominant. It is important to emphasize that during the development of mass transfer models in a biomass, particles exposed to the pyrolysis process particle anisotropy have been taken by most of the authors dealing with complex models [22]. The most important and most illustrative example of the wood structure and physical properties influence is heat transfer through the wood particle during the pyrolysis process; a particularly effective conductivity model which will be presented in the text below.

Effective thermal conductivity of the biomass particle

As mentioned above, diffusion mechanisms have a significant influence on overall process. Effective thermal conductivity includes all heat transfer mechanisms and illustrates the behaviour of thermal characteristics during pyrolysis process. Effective thermal conductivity can be expressed as:

$$\lambda_{eff} = \lambda_{cond} + \lambda_{rad} \tag{1}$$

where λ_{cond} is total thermal conductivity and λ_{rad} is radiative thermal conductivity.

Total thermal conductivity is made up of two terms, the conductivity of solid phase λ_s and the conductivity of gaseous phase λ_g:

$$\lambda_{con} = \lambda_S + \lambda_g \tag{2}$$

The conductive component is made of the thermal conductivity of the initial sample (virgin wood) and thermal conductivity of char and also thermal conductivity of the gaseous phase:

$$\lambda_{con} = \eta\lambda_{wood} + (1-\eta)\lambda_{char} + \varepsilon_p\lambda_g \tag{3}$$

where is η an interpolation factor:

$$\eta = \frac{m}{m_0} \tag{4}$$

represents the ratio of the instantaneous mass of the particle and the initial mass of the dry particle, ε_p is the porosity of the wood particle.

The thermal conductivity of wood is based on a model of a single wood cell which assumes that the cell has a unit overall dimension [22]. On that basis and using serial and parallel electric circuit's analogy, mathematical terms for thermal conductivity in transverse (radial) and longitudinal directions are obtained:

$$\lambda_{gP} = \frac{(1-a)Z\lambda_P'^2 + aZ\lambda_a\lambda_P'}{(1-a)^2\lambda_P' + a(1-a)\lambda_a + aZ\lambda_P'} \tag{5}$$

$$\lambda_{gU} = \lambda_U'(1-a^2) + \lambda_a a^2 \tag{6}$$

where $a = (\varepsilon_p)^{1/2}$, λ_a is thermal conductivity of the air, λ'_p is transverse thermal conductivity of the cell wall substance, Z is a fraction of the overall cell wall width, which could be considered as effective for conduction. Table 1 gives the results obtained for beech and spruce wood [23] (Longitudinal and transversal terms mean orientation of the fibres along or transversally, relative to the sample cylinder axis).

Table 1. Thermal conductivities of beech and spruce wood

Wood type	Longitudinal [Wm^{-1}K^{-1}]	Transfersal [Wm^{-1}K^{-1}]	Ratio [LT^{-1}]
Beech (ε_p = 0.55)	0.4082	0.1447	2.82
Spruce (ε_p = 0.752)	0.2356	0.0836	2.81

Thermal conductivity of char is the function of temperature according to [23]:

$$\lambda_{koksa} = 0.091 + 8.2\cdot 10^{-5}T \tag{7}$$

Thermal conductivity of the gaseous phase is also modelled as a function of temperature according to [24]:

$$\begin{aligned}\lambda_{gas} &= -7,494\cdot 10^{-3} + 1,709\cdot 10^{-4}T - 2,377\cdot 10^{-7}T^2 + \\ &+ 2,202\cdot 10^{-10}T^3 - 9,463\cdot 10^{-14}T^4 + 1,581\cdot 10^{-17}T^5\end{aligned} \tag{8}$$

The radiative transfer component is modelled according to Bikerbak Ozil terms because it includes porosity:

$$\lambda_{rad} = \frac{4\varepsilon_p}{(1-\varepsilon_p)}\sigma\, f d_p T^3 \tag{9}$$

To include particle anisotropy Panton-Rittman terms were used for radiation exchange factor:

$$f = \frac{\omega}{2-0,55\omega} \tag{10}$$

$$f = \frac{1}{1+2(d_p/L_p)(1/\omega-1)}\ \text{-longitudinal} \tag{11}$$

where ω is emissivity, d_p and L_p are characteristic dimensions of wood pore and fibre.

In order to take into account fuel particle's pore diameter change during the pyrolysis process, the following term was used:

$$d_p = \eta d_{p,wood} + (1-\eta) d_{p,char} \tag{12}$$

Based on the presented model and on wood sample characteristics, we achieved results presented in fig. 1 [25]. Figure 1 shows that pyrolysis process dependency on thermal characteristics of wood is not uniform for all cases; effective thermal conductivity varies from 0.11 to 0.28 W/mK [25]. This is in the range of the other studies (0.03 to 0.4 W/mK) where it was observed that final tar yield increases at the expense of gas, while the char yield is almost constant, as λ_{con} increases, reduction in conversion time is predicted [26]. When the heat was transferred at a much faster rate, the time for complete conversion was much shorter. A comparison with product yields from primary pyrolysis indicates that variations in λ_{con} mainly affect the extent of secondary reactions.

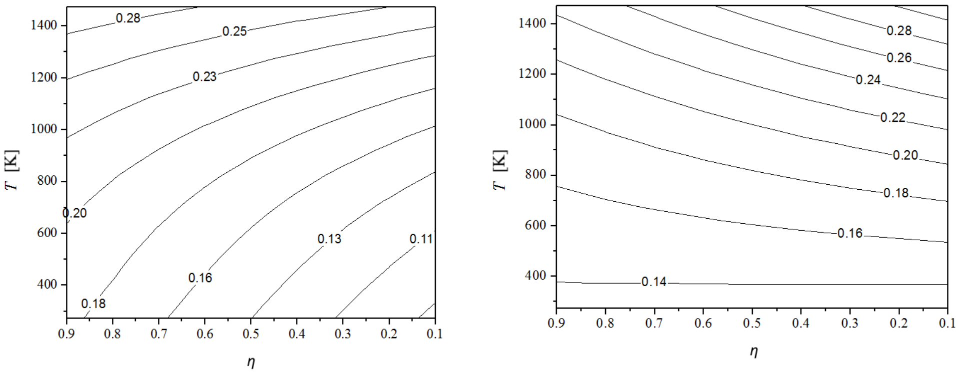

Figure 1. Thermal conductivity of the pyrolysing large beech wood particle with longitudinal (left) and radial (right) oriented fibres [25]

Figure 2 shows the results of the experiments with the wood particle immersed in a fluidized bed. These results shows that the orientation of radial fibre led to an increase of the reaction time in comparison with longitudinal samples, and this influence is more significant with particles of larger dimensions as with smaller particles the differences between the times of pyrolysis reactions were small [27]. It is possible to explain the differing times of the pyrolysis reaction of radial and longitudinal samples as the permeability and thickness of the wood samples. Radial samples have lower permeability, *i. e.* a higher mass resistance to volatile out flow. The internal pressure generation was found to be quite important because it controls the mass transfer of volatiles and thus affects both the heat transfer and the residence time of the pyrolysis gases for secondary decomposition [21, 22, 28]. Chan's investigation showed that the mass transfer by hydrodynamic flow is far greater than the rate of diffusion during pyrolysis of large wood particles [29]. Some other authors show the influence of particle geometry and microstructure during pyrolysis in a fluidized bed at 500 °C. The experiments were with large cylinders (2-14 mm) with different lengths (10-50 mm), smaller milled wood particles, and the smallest particles (<0.140 mm). They found that the microstructure does have a profound effect on product yields, but only in the case of the smallest particles, which consist only of out of cell wall material and have lost their typical wood channel structure; show a clearly higher oil yield and lower char yield [30]. It is also important to say that biomass particles shrink significantly and become less dense during pyrolysis (devolatilization) process, these effects became intensive with the increase of the fuel particle size, with increase of primary pyrolysis production at the centre of the particle [31]. As the shrinkage reduces the insulating effect of the char, the pyrolysis time reduces significantly for large fuel particles (0.02 m) which implies that the higher pyrolysis rates are due to a higher heat transfer rate from a shrunken surface to the core of the particle, which results in an increased overall production rate of pyrolysis products in the particle [32]. According to some research, a cylindrical wood particle on an average shrinks by 20% in the radial direction and by 10% in the longitudinal direction at the end of pyrolysis (devolatilization) [33].

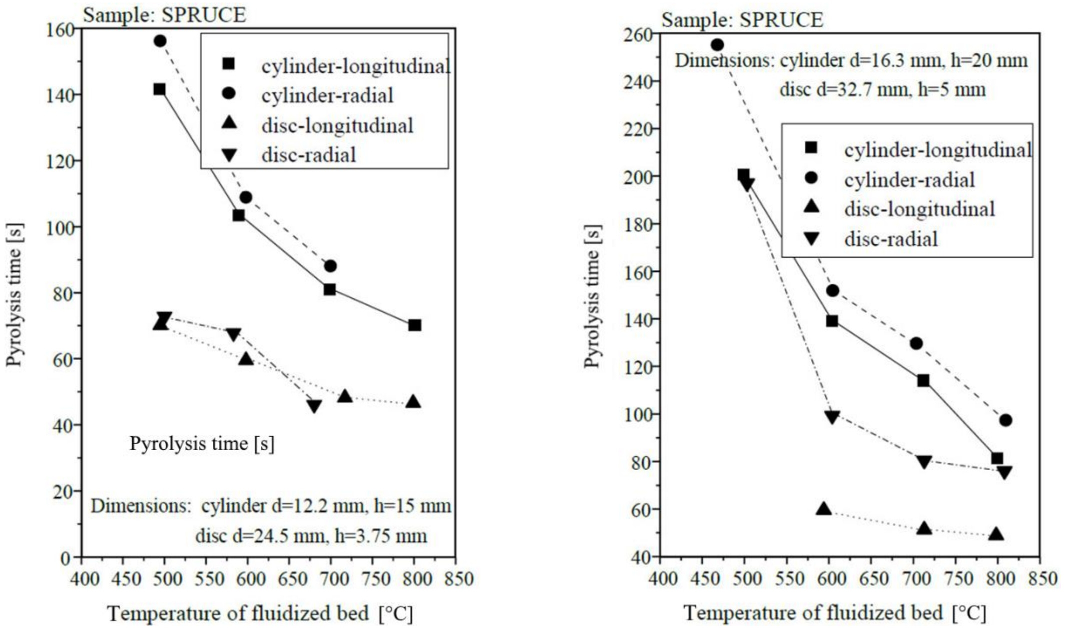

Figure 2. The influence of the wood fibres structure, fibres orientation and wood sample geometry on pyrolysis time

Moisture in fuel can have a large influence on the pyrolysis process, some authors found that even for relatively small particles of radius 1.5 mm, 50% moisture delays the pyrolysis by almost 1 s compared to a particle with 5% moisture [34]. Some other authors also investigated the influence of moisture, which increases as particle size increases, influencing delays on the overall process [33]. The conversion times increase almost linearly with the initial moisture content, but differences in the primary product (char, gas, and liquids) yields and gas composition are negligible [35].

It is also the case that the same biomass type changes its behaviour after palletisation which changes low bulk density of the initial biomass material (usually less than 150 kg/m^3), to high bulk density over 600 kg/m^3, which is essential for biomass to compete with other sources of energy, but also affects the behaviour of due to changes in the nature of transport mechanisms in the fuel particle. A detailed particle simulation that included mass and heat transfer and devolatilization showed that wood pellets and wood logs need different strategies for the models development, due to the difference in directions of the volatile flow. In the case of the wood logs model, it should exclude convective heat transfer by volatiles if the fibres align to longitude direction while this is an important part in the models for pellets [36].

Influence of the particle size and geometry

According to the above presented information it is obvious that due to the influence of particle size and geometry is not possible to analyse separately the influence of biomass particle morphology and anisotropy. It is also important to emphasize that some earlier work on the pyrolysis of wood in a fluidised bed showed that the influence of the particle size, geometry and grain orientation becomes less significant when the heating rate is low [37]. Figure 3 shows that theoretical investigations indicate the impact particle shape, anisotropy and size have on overall particle reactivity, also indicating different reaction pathways [38]. This was investigated and proved by other authors who developed and validated theoretical models which indicated that the impact of shape increases with increasing size and is much greater at sizes relevant to biomass utilization in practical conditions [39, 40]. The same authors indicate that the pyrolysis process is a heat transfer dominant process instead of a kinetics dominant process, as both shape and size influence the conversion time dramatically, especially for large particles [39].

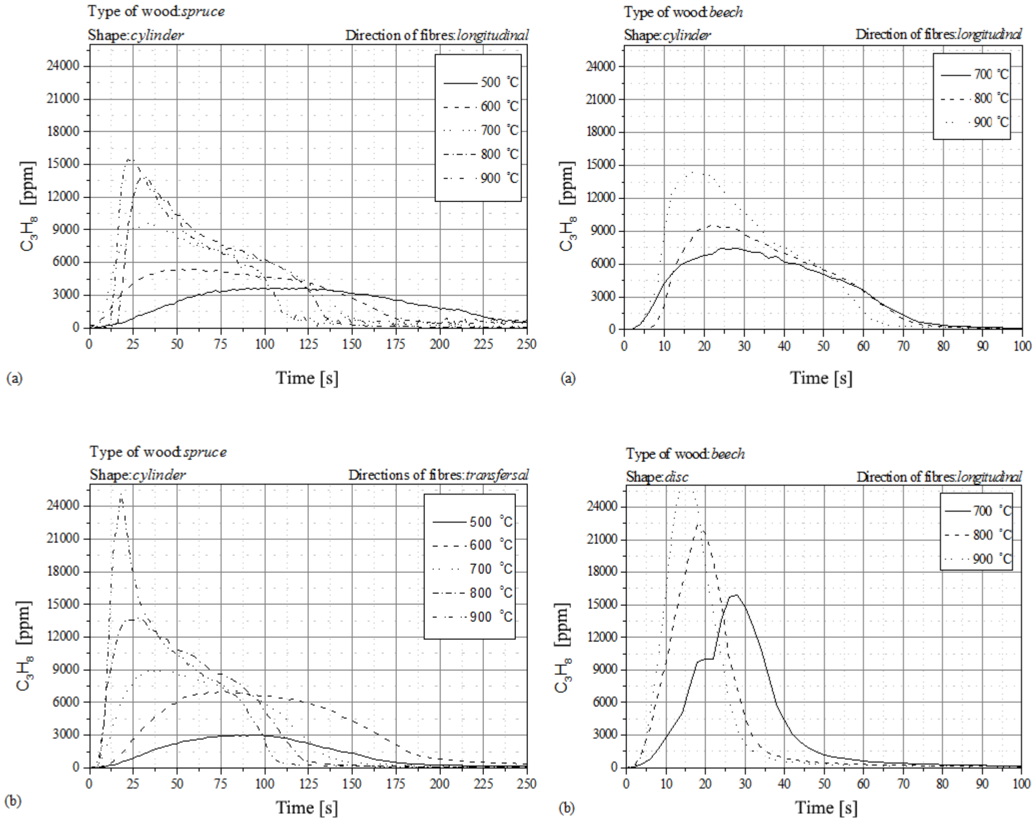

Figure 3. Influence particle anisotropy (left diagrams – hydrocarbons content of pyrolysis gas, for spruce wood cylinders (∅ = 17 mm, *h* = 23 mm), (a) longitudinal fibres orientation, (b) transversal (radial) fibres orientation) and geometry; (right diagrams – hydrocarbons content of pyrolysis gas measured by FID for beech wood samples with the same volume but different shape, longitudinal grain orientation; (a) cylinder with ∅ = 12.2 mm and *h* = 15 mm, (b) disc with ∅ = 24.4 mm and *h* = 3.75 mm) on the pyrolysis process measured by FID and expressed as C_3H_8-equivalent at different temperatures

Some authors used aspect ratio (D/L) as a parameter in the analysis of wood cylinders pyrolysis, and they found that by decreasing the aspect ratio, more heat entered from the side of the particle surface, and lower thermal conductivity in the radial direction caused a temperature gradient in the cylinder [40]. When the intra-particle temperature gradient was large, primary tar which had been formed in the biomass with a relatively low temperature, passed through the side surface layer at high temperatures; enough to advance intra-particle tar decomposition before the tar was released. This resulted in the enhancement of intra-particle tar decomposition [40]. According to this, specific shapes of the gas curves presented on fig. 3 show that due to thermal gradients, conditions for tar formations and cracking reactions obviously exist. High temperatures and large particles in the reactors make ideal conditions for the appearance of secondary reactions in the particle.

Experiments with wood spheres were provided by several authors from small (5 mm) to large (20 mm) in fluidized bed reactors, and it was confirmed that high bed temperatures and low wood sphere diameters favour an increase in the product yield of gas, minimizing char and tar production [38, 39, 41]. The authors investigated particle burnout times and also found that in particles with similar volume (mass), the cylindrical particles are found to lose mass faster than spherical particles and the burnout time is shortened by increasing the particle aspect ratio [42].

Investigations into the correlation of increase of temperature of the process and yield are also showed that the temperature increase led to a considerable increase of the volatile yield and that the molar ratio between CO and CO_2 in the “light” fraction of volatiles increased drastically with the temperature increasing [27, 28]. Experiments of the pyrolysis process in a fluidized bed and freeboard showed a strong influence of the reaction temperature on the yield of the volatile products, with the temperature rise from 400 to 800 °C increased the total yield of volatile products, from 79% at lower temperatures (500 °C) to 86% at high temperatures (800 °C) [27].

Pyrolysis products

The above presented results, can be analysed from two aspects: pyrolysis as a part of the combustion process (with the purpose to generate heat), and pyrolysis as a process with the purpose of generating some products (solid, liquid or gaseous products). In the first case it is obvious that biomass material characteristics and fuel particle geometry have a strong influence on the combustion process. The selection of different types of combustion technologies, for example fluidized bed and grate combustion for the same fuel, will show different behaviours of the particle and overall process dynamics, mainly caused by the intensification of the heat transfer processes in the fluidized bed.

If the second aspect of the pyrolysis process is analysed, it is also visible that a strong influence exists between the characteristics of biomass material and the pyrolysis process results. By interchanging the reactor type which defines heating rate characteristics, the residence time and the temperature levels, it is possible to achieve different goals targeting specific products type. On the basis mentioned in previous chapters, as well as on the conclusions of some other authors, it can be summarized that lower process temperature, longer vapour residence times and slow pyrolysis with large biomass particles favours the production of charcoal. High temperatures and longer residence times increase the biomass conversion to gas and moderate temperatures and short vapour residence times are optimal for producing liquids, particularly in the fast pyrolysis of small biomass particles [43, 44].

Solid products

Biochar is primarily carbon (~85%), but it can also be oxygen and hydrogen. Unlike fossil fuels, biomass contains very little inorganic ash. The lower heating value (LHV) of biomass char is about 32 MJ/kg [45].

During biomass pyrolysis, depending on the type of biomass and process parameters, between 10 to 35% of biochar is produced [46]. Lower process temperatures (up to 500 °C) and longer vapour residence times (5 to 30 min) favour the production of charcoal [8, 9, 47, 48].

Liquid products

The different thermal stabilities of hemicellulose, cellulose and lignin provide an opportunity to use pyrolysis for a thermal fractionation of the biomass in products that can substitute petrochemical products [49]. Pyrolysis liquids are formed by rapidly and simultaneously depolymerizing and fragmenting cellulose, hemicellulose, and lignin with a rapid increase in temperature. Rapid quenching then “freezes in” the intermediate products of the fast degradation of hemicellulose, cellulose, and lignin.

As already mentioned, fast pyrolysis is usually a high-temperature process (400 to 650 °C) in which biomass is rapidly heated in the absence of oxygen [6, 8]. Depending on the heating rate, fast pyrolysis can be a “flash” pyrolysis, with a heating rate about 1,000 °C/s, where the temperature can be in the range of 777-1,027 °C [9-11]. 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 used [11]. Pyrolytic oil may be used directly as a liquid fuel for boiler, diesel engine, gas turbine for heat and electricity generation, or catalytically upgraded to transport grade fuels [9]. 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 heating value of bio-oil is 17 MJ/kg [6].

Gaseous products

Similar to biochar, about 10% to 35% of bio-gas is produced in slow pyrolysis processes; a higher syngas yield is possible in flash pyrolysis with high temperatures [46]. The pyrolysis gas contains carbon dioxide, carbon monoxide, methane, hydrogen, ethane, ethylene, minor amounts of higher gaseous organics and water vapour, on a mass basis, the pyrolysis gas consists mainly of CO_2 and CO, with lower amounts of C_xH_y, CH_4 and H_2 [6, 50]. In practice, a part of the organic vapours and tars undergoes in secondary reaction and it is cracked to secondary gases. The LHV of these primary gases is 11 MJ/m^3 and that of pyrolysis gases formed, after severe secondary cracking of the organic vapours, is 20 MJ/m^3 [6]. Based on the collected data, the heating rate seems to have little effect on determining the composition of the pyrolysis gas [50]. As it was already shown on fig. 2 and fig. 3, reactor temperature (beside of the raw biomass material characteristics) has a significant influence on pyrolysis processes and the resulting product distribution.

Conclusions

Pyrolysis is one of the most important processes which has to be understood in order to achieve adequate results, in combustion or other thermochemical processes. The analysis of the aspects related to the fuel specifics used wood as biomass representative, and were focused on the influence of physical structure, as well as chemical composition on the pyrolysis process. It was shown that the chemical composition of biomass and its main constituents (lignin, cellulose, and hemicelluloses) plays an important role in the pyrolysis process. It was also shown that wood particle pyrolysis process is dependent on its size, geometry and specific, anisotropic structure. These parameters have a strong influence on the final products of the process, as well as on overall dynamics of pyrolysis or combustion process. It is also shown that pyrolysis temperature and the environment also have a strong influence on the final products and overall process dynamics. The reactor or furnace environment, which can intensify heat transfer between particles, as fluidized bed in combination with the above mentioned fuel specifics increase influence of fuel characteristics. In this case the effects of fuel particle geometry and anisotropy have stronger influence on transport mechanisms in the fuel particle and products dynamics and yield.

The analysis of our own results and review of related research, show the importance of fuel and environment characteristics on the pyrolysis and combustion process of biomass, and which should be taken into consideration during the design of any reactor or combustion system planned to use biomass as fuel.

Nomenclature

Z – fraction of overall cell wall width which could be considered as effective for conduction, [–]
T – temperature, [K]
d_p – pore diameter, [m]
L_p – fibre length, [m]

Greek symbols

λ_{cond} – total thermal conductivity, $[\mathrm{Wm^{-1}K^{-1}}]$
λ_{rad} – radiative thermal conductivity, $[\mathrm{Wm^{-1}K^{-1}}]$
λ_s – conductivity of solid phase, $[\mathrm{Wm^{-1}K^{-1}}]$
λ_g – conductivity of gaseous phase, $[\mathrm{Wm^{-1}K^{-1}}]$
ε_p – porosity of the wood particle, [–]
λ_a – thermal conductivity of the air, $[\mathrm{Wm^{-1}K^{-1}}]$
λ'_p – transverse thermal conductivity of the cell wall substance, $[\mathrm{Wm^{-1}K^{-1}}]$

Acronym

LHV – Lower heating value, $[\mathrm{MJkg^{-1}}, \mathrm{MJm^{-3}}]$

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Paper submitted: November 29, 2015
Paper revised: May 4, 2016
Paper accepted: May 5, 2016