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Fast pyrolysis of biomass: A review of relevant aspects. Part I: Parametric study

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Abstract
Recent years have witnessed a growing interest in developing biofuels from biomass by thermochemical processes like fast pyrolysis as a promising alternative to supply ever-growing energy consumption. However, the fast pyrolysis process is complex, involving changes in phase, mass, energy, and momentum transport phenomena which are all strongly coupled with the reaction rate. Despite many studies in the area, there is no agreement in the literature regarding the reaction mechanisms. Furthermore, no detailed universally applicable phenomenological models have been proposed to describe the main physical and chemical processes occurring within a particle of biomass. This has led to difficulties in reactor design and pilot industrial scale operation, stunting the popularization of the technology. This paper reviews relevant topics to help researchers gain a better understanding of how to address the modeling of biomass pyrolysis.

Keywords: Fast pyrolysis, biomass, heating rate, particle size, temperature, mineral matter, kinetics, modeling.

Pirólisis rápida de biomasas: Una revisión de los aspectos relevantes. Parte I: Estudio paramétrico

Resumen
Existe gran interés en el desarrollo de biocombustibles a partir de biomasa mediante procesos termoquímicos, que ha ido creciendo en los últimos años como alternativa promisoria para satisfacer parcialmente el consumo creciente de energía. Sin embargo, el proceso de pirolisis rápida es complejo, e involucra cambios de fase y fenómenos de transferencia de masa, energía, cantidad de movimiento, fuertemente acoplados con las tasas de reacción. A pesar de numerosos estudios realizados en el área, no hay consenso respecto a mecanismos de reacción, ni se han propuesto modelos fenomenológicos detallados para describir los procesos físicos y químicos que ocurren dentro de una partícula de biomasa, esto ha traído dificultades en el diseño y operación de reactores a escala piloto e industrial, dando lugar a la popularización de la tecnología. Este trabajo presenta un estudio de diferentes líneas de investigación, para ayudar a los investigadores a obtener una mejor comprensión del tema.

Palabras clave: Pirólisis rápida, biomasa, tasa de calentamiento, tamaño de partícula, temperatura, material mineral, cinética, modelado.

1. Introduction

The worldwide estimated energy consumption in recent years is of the order 515 EJ yr^{-1} (10^{18} J/year), 80% of which is supplied from petroleum fuels. This consumption tends to increase over time due to phenomena associated with population growth and increasing demands from emerging countries such as Brazil, Russia, India and China (BRIC) [1,2]. Biomass, solar radiation, wind, water, and geothermal are potential alternative energy sources that can be used in the near future. However, biomass is the only renewable source of carbon for biofuels production and the only alternative available which can be quickly inserted into the biofuels markets matrix [3].

Another important developing country, Colombia, has an availability of about 72 million tons/year of biomass mainly consisting of sugarcane bagasse, banana, corn, coffee, rice, and oil palm waste. The energy potential from these is close to 332 million GJ yr^{-1}, equivalent to 7.4% of the total energy consumption in the country [4]. The latter statistic shows that there is a realistic opportunity to use waste biomass for biofuels production in Colombia.

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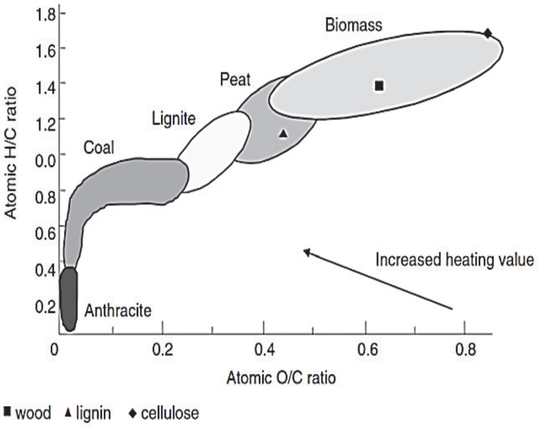

Figure1. Van Krevelen diagram.
Source: [3]

Fast pyrolysis of agro-industrial residues for bio-oil production is a promising technology. The development of this technology is relevant and appropriate due to the fact that it does not compete with food security (unlike the transesterification and fermentation processes) commonly used to produce ethanol and biodiesel. Additionally, it can be easily incorporated into existing petroleum refining infrastructure, achieving a reduction in operating costs [5- 8].

Pyrolysis processes involve heating biomass feedstocks to temperatures between 400-600°C in an inert or oxygen-less atmosphere to produce bio-oil, bio-char, and non-condensable gases with high calorific value (rich in CO, CH_4, H_2) [9]. Bio-oil can be integrated into refineries as a raw material; bio-char can be integrated into the pyrolysis process for reaction heat or sold for other purposes; the gas can be recirculated into the reactor to provide heat, or can be used in subsequent processes like catalytic methane reforming or Fisher Tropsch procedures [10].

The pyrolysis char product is a solid residue similar to high rank coal, as seen in the Van Krevelen diagram in Fig. 1; as pyrolysis takes place, the volatiles are released and the bio-char is obtained with a high carbon content, and a low oxygen/carbon ratio similar to high rank coals.

Biomass is made up of a mixture of polymers with different physicochemical structures, so thermal decomposition proceeds by stages. Initially, hemicellulose which is a weak structure and with lower molecular weight, breaks down in a temperature range 200-300 °C, followed by the cellulose which decomposes between 300-450 °C, and finally, the lignin breaks down between 250-500 °C which is the major contributor of char production at the end of pyrolysis [11–14].

Depending on operating conditions, the pyrolysis can be classified as slow pyrolysis or fast pyrolysis. The former is used for obtaining char as the main product (50-75% yield), bio-oil (15-20% yield) and non-condensable gases (20-30% yield). On the other hand, fast pyrolysis processes mainly produce bio-oil (50-70% yield), whose performance is limited to the type of biomass, operating temperature, gas residence time in the reactor, heating rate, particle size, and mineral content.

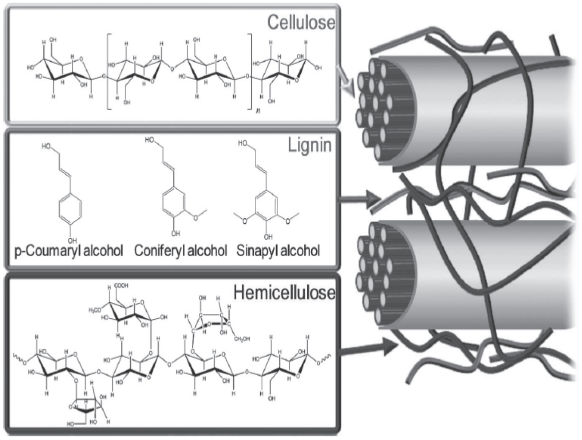

Figure 2. General structure of lignocellulosic materials.
Source: [16]

High heating rates are required, more than 1000 °C s^{-1}, for achieving high selectivity towards the production of bio-oil. A particle size of between 1-5 mm is required to get high heating rates, reactor temperatures between 400-600 °C and gas residence time less than 1s. There is extensive and varied information about what type of biomass to use, operating conditions, and reactor type (fixed bed, fluidized rotating cone, ablative reactor, and others). These have not been agreed upon among the different authors; therefore, the main parameters (operational parameters such as temperature, heating rate, particle size, gas and solid residence time, initial biomass moisture, and structural parameters such as biomass-type, crystallinity, and mineral material content) affecting the bio-oil production by fast pyrolysis process of biomass are described in this first review.

2. Biomass Structure

As shown in Fig 2, biomass can be defined as a heterogeneous mixture of polymers mixed with a small fraction of inert material. The organic fraction consists of polymers containing three major macromolecules: cellulose, hemicellulose, and lignin. Some biomasses also have a lower amount of lipids, pectin, and extractives which do not exceed 10% $w\ w^{-1}$ [15].

Cellulose corresponds to about 40-60% of the total biomass weight, hemicellulose 15-25%, and lignin (15-25%) [16–18]. Cellulose is a linear, mostly crystalline polymer whose structural unit is glucose, which is linked through β-D glycosidic bonds. They stick together to form chains with more than 10,000 structural units (a.k.a. degree of polymerization). Cellulose polymers form fibers inside biomass, which provide structure to the cell walls. Hemicellulose is an amorphous polymeric structure shorter than cellulose (polymerization degree 100), and branched; it is made up mainly of sugars with 5 and 6 carbons per unit (e.g. xylose, glucose). On the other hand, lignin is a complex non-crystalline macromolecule, composed of a variety of aromatic constituents as sinapyl, coniferyl, and coumaryl alcohols (see Fig 2) linked by β-ether linkages [18]. Lignin and hemicellulose are responsible for keeping cellulose fibers attached.

Mineral matter depends on the kind of biomass, it comprises between 2-25% of the total solid weight and commonly consist of minerals such as Na, K, Ca, Mg, Mn, Co, Zn, and Cu like oxides or like salts such as chlorides, carbonates, phosphates and sulphates [19-20]. These minerals play an important role in thermal decomposition of biomasses, acting as catalysts of some reactions such as biomass dehydration and catalytic cracking of the volatiles.

2.1. Physicochemical nature of biomass

It has been observed under slow heating rates (1-100 °C min^{-1}) [21-22] that the maximum weight loss for the hemicellulose is 80% (w w^{-1}) at 258 °C; for cellulose, it is close to 94% (w w^{-1}) at 400 °C; and for lignin only 54% (w w^{-1}) is decomposed at 900 °C. There are few studies to determine how volatile production changes due to other compounds in the biomass (protein, fatty acids, sugars).

Xiu-John et al. [22] confirmed through thermogravimetric studies that the presence of extractives catalyzes reactions that increase aldehydes and acid compounds (acetic acid, formic acid), while the absence of them improves the water and carbon dioxide production. The presence of extracts in biomass favors the bio-oil production (can be easily volatilized and condensed), but also modifies its quality; for example, the fatty acids present in biomass favor the formation of bio-oil with high viscosity, less oxygen content, and high calorific value.

There are other structural parameters which have been scarcely studied, have great importance, including the degree of crystallinity, bond orientation and degree of polymerization of the cellulose. These parameters affect the chemical composition of volatiles released during pyrolysis.

For example, Ponder et al. [23] studied the effects of the orientation and position of glucans links (cellulose constituent units) in the production of volatiles. They observed that position and bond orientation do not have a significant effect on levoglucosan yields (main compound obtained from the devolatilization of cellulose). It is important to note that this study is only an approximation since they used low and medium molecular weight glycosides (150 Dalton) whose behavior is different from cellulose molecules (polymerization degree>1000).

Mettler et al. [24] demonstrated that a high degree of polymerization in cellulose increases the production of levoglucosan and decreases the formation of char. Researchers believe that small molecules or species with low degrees of polymerization are closed chemical structures like glucose rings that break off and form new linear structures, which then undergo decomposition reactions producing light compounds, whereas it is easier to break glycosidic bonds joining the glucose units present in larger molecules.

The maximum stress points and therefore the most feasible to fracture during pyrolysis are precisely those which are located at the interface of the amorphous and crystalline structures [25]. Therefore the maximum temperature required for cellulose decomposition is greater for more crystalline structures [26]. The latter is mainly due to the extra energy for destroying the structure formed in the crystal lattices due to hydrogen bonds. In addition, the ring structure of glucose is easily maintained in crystal structures due to the network formed by hydrogen bonds.

The crystalline lattice acts as a thermal energy sink; therefore, the fragmentation of amorphous cellulose produces more oligomers (e.g. cellobiosan, cellotriosan) than monomers (glucose, levoglucosan, celobiosan).

2.2. Particle Size

All types of biomass are poor heat conductors, so it is easy to find a temperature profile inside a particle when it is submitted to fast heating. This profile is more remarkable in bigger particles, so, biomass size and shape affect the residence time of volatiles inside the particle, favoring cracking reactions that reduce the yield of condensable gases [15,17-28]. Therefore, secondary reactions between char and volatiles take place more easily in bigger particles, which increase the yield of char instead of bio-oil production [28].

In general, particle size is directly related to the rate of heating, and for fast pyrolysis processes, the formation of bio-oils is favored with high heating rates which are obtained with small particle sizes (<1 mm) [15,20,28-32]. It should be clarified that in industrial processes or pilot scale, the costs associated with grinding processes to reduce the biomass size, are high, and this may limit the profitability of the process.

Bridgwater et al. [32] have reviewed the specifications of particle sizes for different pyrolysis technologies. For example: particle sizes of less than 200 mm are recommendable for jet rotary cone technology, less than 6 mm are for fluidized bed reactor and circulating bed, and less than 10 cm for rotary disc ablative processes. In the literature there is no unanimous agreement on the ideal particle size to increase the production of bio-oil.

Shena. J et al. [33] found that bio-oil yields obtained from mallee (Australian Eucalyptus) in a fluidized bed reactor decreases as the particle diameter increases from 0.3 to 1.5 mm. Beige et al. [35] reported that the maximum bio-oil yield obtained from fixed-bed pyrolysis of safflower is reached with a 0.42 mm particle size. Onay et al. [36], Nurul et al. [37] have reported ideal particle sizes of between 0.85 to 200 mm for fixed-bed pyrolysis of rapeseed, whereby bio-oil yields of up to 60% (w w^{-1}) are obtained.

2.3. Initial moisture content of biomass.

The initial moisture content of some biomasses can be high, close to 90% w w^{-1}, which requires an increase of energy supplies, affecting the energy efficiency of the process [33] and the costs associated with biomass drying. The most economical and widely used energy source for drying biomass is solar radiation, which can reduce the moisture content to values between 12 and 3% w w^{-1}, depending on atmospheric conditions.

The quality and yield of bio-oil recovered in fast pyrolysis processes is directly related to the initial moisture content of biomass. High moisture content produces a bio-oil with low viscosity, high stability to the decomposition of anhydrous sugars and dissolution of polar fragments, and physically looks like a homogeneous phase [34]. However, the direct use is restricted due to ignition and combustion problems in burners and boilers caused by the high water content.

2.4. Mineral material content

Biomasses contain traces of mineral material (K, Na, Ca, Zn, Cu, P, Mg, Mn..), usually oxides or salts such as chlorides, sulphates, carbonates and phosphates [35]. The proportions of these minerals depends on the kind of biomass, storage, collection methods, drying, and grinding conditions. The content of inorganic material is an important parameter for the study of side reactions; generally, as the mineral material content in biomass increases, the bio-oil performance decreases and gas and char production increases [11,15,16,20,31-32,36-37]. The latter is due to the catalytic effect of the mineral matter in the dehydration and decarboxylation reactions. In recent years, numerous works have been published aimed at understanding the effect of mineral matter on final product distribution [19,35,38-41].

A theoretical study to determine the effect of inorganic material on the fast pyrolysis process is not feasible yet. Raveendran, R, et al. [38] evaluated the effect of mineral content on the yield of volatiles and char, for 20 different biomasses, which were studied with and without the demineralization step (acid wash). Comparing the experimental results, it was found that higher char yields are obtained for the biomass without washing, in comparison with demineralized biomasses. In corn cob pyrolysis, washing produced a 57% decrease in the char yield and 21% increase in the oil yield. Despite the good results obtained, testing was performed in a fixed bed reactor with temperature set at 500 °C and particle sizes between 100 and 250 mm (10 and 25 cm). Under these conditions intra-transfer phenomena of particles are likely [15,20,28], and it is unclear whether variations in the results are due to the minerals catalytic effects or associated with resistance to heat and mass transfer.

Another study was undertaken by Patwardhan et al. [39], who evaluated the effect of mineral matter on the yield of char and volatiles obtained during pyrolysis of Avicel microcrystalline cellulose. In contrast to the experiments carried out by Raveendran [38], the authors use particle sizes of 50 microns to minimize the effects of heat and mass transfer, and the experiment was conducted in a Frontier free-fall pyrolysis micro reactor coupled to a gas chromatograph, ensuring high heating rates (5000°C/s). In this study, the authors impregnated cellulose with solutions of 0.5 to 5% w/w of salts such as NaCl, KCl, $MgCl_2.6H_2O$, $CaCl_2$, $Ca(OH)_2$, $Ca(NO_3)$, $CaCO_3$, and $CaHPO_4$ to evaluate which of these minerals exerts a greater influence on the global production of volatile levoglucosan, acetol, furaldehyde, 5HMF (Hydroxy-methyl-furfural), glycol aldehyde, and formic acid. They determined that low concentrations, 0.5% w/w, increases char yield up to 10% and also increases the yield of low molecular weight species such as acetol, glycol aldehyde, and formic acid while levoglucosan levels decrease. They found that the most impacting minerals on volatile yields were, in order: K^+, Na^+, Ca^{+2}, Mg^{+2}, Cl^-, NO^-, OH^-, CO^{2-}, $PO^{3-.}$ Despite the fact that the experiments were carefully prepared, these behaviors cannot be applied to biomass, because the interaction with cellulose can be changed by the presence of lignin and hemicellulose, and cellulose in biomass has different degrees of crystallinity that may interact differently with minerals.

Yang, H. et al. [35] studied the effect of KCl, K_2CO_3, Na_2CO_3, $CaMg\ (CO_3)_2$, Fe_2O_3 and Al_2O_3 on the performance of the char produced by slow pyrolysis of cellulose, hemicellulose, and pure lignin. They used 0.1 weight ratios between the inorganic and the organic component (cellulose, hemicellulose, and lignin). According to the authors, none of the minerals studied except K_2CO_3, had any appreciable effect on the yield of char, in contrast with work reported by Shimomura et al. [42], Patwardhan et al. [19], Richards et al. [43], Nik-Azar et al. [44], Zsuzsa et al. [45].

It has also been found that the presence of alkali and alkaline metals promotes dehydration reactions of cellulose and lignin. These reactions decrease the levoglucosan yield and increase the char production. In contrast, adding anions (chloride, nitrates, sulfates) increases levoglucosan performance and decreases char yields [45]. For example, sodium restricts both the cellulose and hemicellulose transglycosylation reactions, and facilitates demethoxylation, demethylation, and dehydration of lignin [46]. The presence of (what?) improves the interaction with functional groups-COOH,-OH, forming alkali-oxygen clusters that promote cracking reactions [47], and the presence of silicon also decreases the production of volatiles [43].

To study the effects of mineral matter on the volatile and char yields, samples of biomass (natural or synthetic) are subjected to washing with deionized water and acidic solutions (HCl, H_2SO_4, HNO_3, H_3PO_4), or the addition of minerals in solution ($Na_2\ (NO_3)$, $K_2(NO_3)$, $Ca(NO_3)$, etc.) [48-49]. These methods of pre-treatment of raw materials have limitations, which makes it difficult to explain the results. Acid washing with strong acids for example, dissolves hemicellulose and cellulose (hydrolysis) almost entirely [45,49]; therefore, the results obtained are due to the combined effects, so it would not be clear which of the two effects exerted greater influence on yields.

Techniques for mineral addition by impregnation are simple physical adsorptions on the particle surface; therefore, the mineral dispersion is different at found in virgin biomass (mineral distribution throughout the entire volume). Another difficulty with impregnation techniques is that cations and anions are added simultaneously to the biomass (impregnated saline solutions are used), and in these cases the cations and anions may have different interactions with volatile and char [53].

In some biomasses, not all minerals can be removed by washing (acid, alkaline, or neutral). These metals can be bonded chemically to the organic matrix, forming associations with oxygen-rich functional groups (-COOH,-COH,-OH) or lignin phenolic groups [49,54]. In these cases, the ion exchange techniques have been effective to demineralize biomasses or to study the effect of an isolated cation (with anions removed). In this technique, the sample is initially washed with an acid solution to remove unbound minerals present in virgin biomass. Then, to remove chemically bonded minerals, the sample is immersed in a concentrated saline solution (nitrates, sulphates) in which the anions exert strong attraction to the electrophilic cations bound to the biomass. This facilitates the exchange of cations between salt and biomass. Finally, washing with distilled water removes all anions and cations on the surface of the biomass. Few studies have been reported with this methodology [49, 52]. Although it may isolate the effects of the specific anions and assess the impact of a single metal, the processes of pre and post treatments alter the original biomass structure; therefore, results can be limited and must be explained carefully.

2.5. *Volatiles and solids residence time*

It is important to take into account the residence time of volatiles and solids inside reactor to ensure high yields of bio-oil. It is generally accepted that the residence time of volatiles must be low (a few seconds) to minimize cracking reactions [19,29,33]. The residence times of volatiles and solids are usually different. High biomass residence times are needed to ensure complete devolatilization, while volatile time should be short to minimize secondary reactions [14,41,55]. These times are directly related to the operating conditions (carrier gas flow) and the technology used in the pyrolysis process; for instance, the residence time of solids in fixed bed reactors is higher ($t \rightarrow \infty$), while in fluid bed reactors the residence time for both solids and volatiles tends to be very short (a few seconds) depending on the height of the reactor and the gas flow.

From the operational viewpoint, the residence time of volatiles and solids can be manipulated with the carrier gas flow or vacuum (Pyrovac technology). Short residence times of volatiles inside the reactor, however, may be counterproductive for several reasons. Firstly, they can promote solids entrainment (high carrier gas flow) and therefore reduce biomass conversion and further promote the obstruction of cyclones and even contaminate the bio-oil recovered in the condensation steps. Besides this, particles could not achieve high heating rates because the reactor is cooled by forced convection. The residence time of volatiles is associated with heat exchangers dimensions; very low residence time (inside reactor) imply designs with large volumes of condensers or cooling systems in multiple stages which brings higher investment costs.

2.6. *Reaction temperature*

The devolatilization process is sequential and depends on the temperature reached by the particle (see Fig 3). The first stage is comprised between 20-120 °C and corresponds to water evaporation from the biomass, and subsequently between 120-300 °C is a region with no appreciable biomass weight loss, where in small quantities of some light gases are released such as CO, CO2 and steam, coming mainly from dehydration reactions, decarboxylation from R-OH groups belonging to hemicellulose and lignin. [18,28,56,57]. Insofar as cellulose, it has been demonstrated [26,31,58–60] that between 200-350°C, the depolymerization reactions gives rise to oligomers and anhydrous sugars (levoglucosan, cellobiosan, cellotriosan, glucose, etc.), known by many researchers as “active cellulose” and “molten cellulose” or simply "intermediary liquid compound” [61].

The greatest weight loss occurs at between 300 and 400 °C (about 80%), corresponding to the maximum rate of volatiles released. In this stage, random fragmentation of cellulose, hemicellulose, and glycosidic bonds generates volatile compounds with a high oxygen content, leaving a carbonaceous residue known as char [27,50]. At temperatures above 400 °C, CO and CO_2 are released by depolymerization reactions from the lignin-rich aromatic carbonaceous matrix. The effect of temperature on the bio-oil production is well understood and widely explored in the literature. It was found that the maximum bio-oil yield is obtained between 400-500 °C, depending on the type of biomass [8,19]. At higher temperatures, volatile cracking reactions are promoted, which reduce the yield of bio-oil and increase the production of non-condensable gases. [28,33,62,63].

The effect of temperature on the production of bio-oil by cellulose (Avicel) and maple fast pyrolysis in fluidized bed and entrainment flow reactor was studied by Scott et al. [64]. They hold constant particle size at 100 microns, volatile residence time at 500 ms and the process temperature between 400-700 °C. The authors found that maximum production of bio-oil was achieved in the fluidized bed reactor at 450 °C, with yields of 80% and 90% for maple and cellulose respectively, while for entrainment flow reactors yields were 70 and 60%, respectively, at 600 °C. Heo et al. [65] pyrolyzed sawdust with particle diameter of 0.7 mm in a fluid bed reactor to estimate the temperature effect on bio-oil yields. They found that the best performance is achieved at 450 °C (60 % w/w). Similar results are reported in [51-53]. There is a parabolic behavior for bio-oil production with temperatures of between 400-450 °C whereby the yield of bio-oil increases because the rate of biomass devolatilization increases (this is reflected in char reduction) and the bio-oil yield decreases at temperatures > 450 °C because of volatile cracking (reflected by the higher yields of non-condensable gases).

Other studies have reported the effect of temperature on the yield of pyrolysis bio-oils [61,32,53]. In addition to altering the production of bio-oil, changes in temperature affect the composition released during devolatilization. [54]. At low temperatures (<300°C), most volatiles derive from decomposition of hemicellulose and cellulose links, resulting in levoglucosan, levoglucosenone, hydroxymethyl furfural, acetic acid, acetone, guiacyl, acetone, glyoxal,

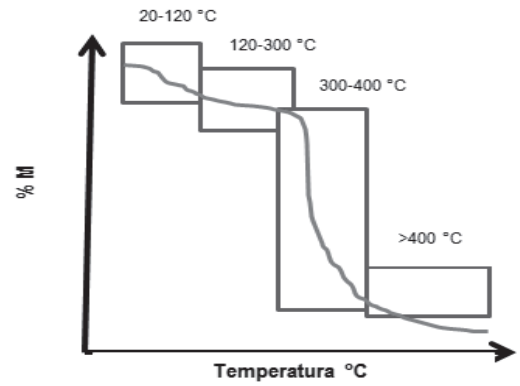

Figure 3. Stages of thermal decomposition biomass.
Source: The authors

methanol, and formic acid. Fu et al. [55] demonstrated the presence of formic acid, methanol, ethane, ethylene, formaldehyde, acetone, hydrogen cyanide, carbon monoxide, and carbon dioxide during pyrolysis of cotton stalk, corn, and rice in a temperature range of 300-400 °C. At temperatures above 400 °C, they found benzene, carboxylic acids, phenols, p-cresol, furans, furfural, in noteworthy amounts (>1% w w^{-1}) [19].

As the temperature rises, the composition of volatile compounds decreases and higher thermally stable polyhydroxy aromatic compounds (PHA) begin to be produced. For instance, the percentage of aldehydes, alcohols, paraffin, and acetone gradually decreases for temperatures between 580-800°C, and new compounds such as benzene, naphthalene, cresol, toluene, PHA (polyhydroxy aromatics) such as pyrene, phenanthrene, and anthracene, and others [20,56-57] are generated. However, these temperatures are higher than the conditions normally used in the fast pyrolysis processes (500-550°C) found high concentrations of. Despite all the studies conducted to evaluate the effect of temperature on the yield of char, bio-oil and non-condensable gases, there is ambiguity in the definition of the temperature of pyrolysis. Unfortunately, in both laboratory scale and industrial scale pyrolysis equipment, it is not possible to directly measure the temperature of the biomass particles, and it is generally assumed to be equal to the reactor temperature [28,58], or in some cases is estimated by mathematical modeling [59-60]. However, these assumptions, in most cases, are far removed from reality, with mismatches (thermal lag) of temperatures as high as 100 °C. For slow pyrolysis conditions with small particle sizes (less than 1mm), this assumption is valid due to the higher heating times, where it is easy to achieve thermal equilibrium between the biomass particles and the surrounding. [61-63]. In general, the temperature lags are greater when the heating is undertaken at high temperatures or high heating rates. This thermal lag causes errors in estimating actual particle temperature, which can over-estimate the kinetic parameters such as the activation energy and the coefficient of the reaction rate [62-63].

2.7. Heating Rate

The heating rate of biomass particles is perhaps the main parameter that allows us to obtain a difference between slow pyrolysis processes from fast pyrolysis. This parameter, in other words, the time it takes to reach biomass reaction temperature. It has been reported that heating rates of the order 1 C/min-100°C/min are required for slow pyrolysis processes [15,20] and it is required to achieve heating rates higher than 1000°C/min for fast pyrolysis processes [64-65].

High heating rates promote cellulose and hemicellulose depolymerization reactions, minimizing the volatiles residence time inside the particle and secondary reactions. It also favors the volatiles cracking. So, the condensable gas release goes on quickly [66] thus achieving high yields of bio-oil and the lowest production of char. Chaiwat et al. [67] proposes a set of competitive reactions between cellulose depolymerization and dehydration, as shown in Fig 4. These results are supported by Agarwal et al. [68] who, through computer simulation, studied the changes affecting the cellulose during the fast pyrolysis process.

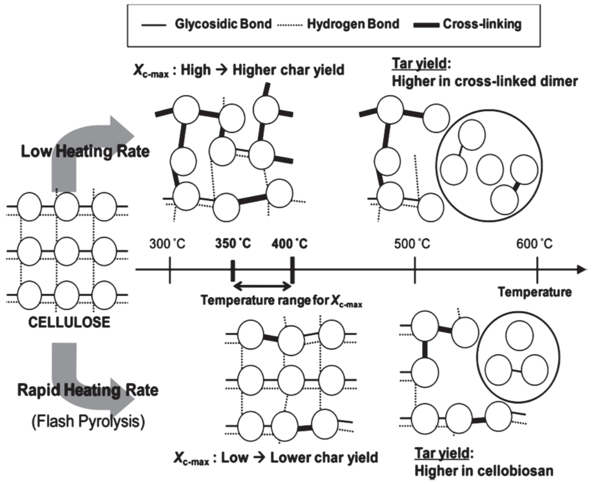

Figure 4. Effect of the heating rate on the mechanism of thermal decomposition of the cellulose.
Source: [67]

The authors found that there is a change in the hydrogen-type bond in cellulose structures. Low temperatures and low heating rates promote intra-chain hydrogen bonds of cellulose functional groups, increasing the probability of collision to produce a dehydration reaction. For high heating rates, inter-chain hydrogen bonds are stronger achieving greater separation between the cellulose molecules and thus decreasing the possibility of collisions that facilitate the dehydration reaction. There are many reports in literature pointing out the importance of the effects of the heating rate on the yields of bio-oil and char. The study by Ozlem et al. [69] of the fast pyrolysis of safflower seeds in a fixed-bed reactor showed that the effect of the heating rate on the yield of bio-oil and biochar was evaluated for 3 grams of this sample (particle size 1.25 mm) and heating ramps of 100, 300, 800 °C/min. The results show that for heating rates above 300 °C/min, maximum yields are 55% for bio-oil and at least 17% for char.

Thangalazhy et al. [70] conducted a study at micro-scale level, using a pyroprobe (Pyroprobe model 5200, CDS Analytical Inc., Oxford, PA) to evaluate the effect of temperature and heating rate on yield and the distribution of some compounds in the bio-oil.

The experiments were carried out with pine and grass, warming up the filament of pyrolyzer to reach 50,100, 500, 1000, 2000 °C/s. An interesting result was that at constant temperature (550°C), regardless of the filament heating rate, the final product distribution was the same (30% yield for pine wood bio-oil and 17% for forage grass), that is why biomass is resistant to heat transfer (poor thermal conductivity) its heating rate is different from the filament, and under these conditions the particle is always heated at 50°C/s. These experiments were carefully prepared; however, yields are far lower than usually reported by other researchers, [19,69,71-72]. It was not possible to recover the entire sample of bio-oil due to condensation in the tubing that connected the probe to the GC-MS, or cracking reactions in the injection port and the GC oven. Van Waaij et al. [73], developed laboratory scale equipment "wire mesh reactor," which reached controlled heating rates of up 7000 °C/s. This achieved bio-oil yields of about 84% (w w^{-1}) and 5% char. The authors attribute these results to the precise temperature control, low residence time and instantaneous volatile cooling, which minimize secondary reactions effects when compared to traditional systems such as fluidized, packed, and circulating beds, in which nothing can be measured or the heating rate and temperature controlled.

The heating rate also plays an important role on the quality of bio-oil and char structure obtained. Bio-oils can be obtained with lower moisture content at higher heating rates, primarily due to inhibition of secondary reactions such as volatile dehydration and cracking [74] and due to water-soluble fractions (formic acid, methanol, acetic acid) and heavy fractions (rich in phenol and its derivatives). The CO and CO_2 also increase at high heating rates [32]. Ketones content, levoglucosan, phenol, and toluene levels also go up with the heating rate for the fast pyrolysis of pine wood and grass when the heating rate exceeds 50 -1000°C/s. Higher heating rates do not show a marked effect on the performance of each sub product [70].

With high heating rates, a biochar is obtained with smaller volume pores and a specific surface area. This heating rate can generate significant pressure gradients between the inside and outside of the particle because the volatiles are produced quickly and do not have the ability to instantly be evacuated. This causes some internal structures to crack, increasing the end proportion of macropores in connection with the micropores. Besides this, the biomass passes through a melting phase (metaplastic) which warps the internal structures and blocks the pores. [54-55].

Although this parameter is very important to define the conditions of fast pyrolysis, we highlight that it cannot be measured experimentally; its estimation is limited to theoretical models. Often these parameters are subjective, this may depend on the devices used (reactor), models' assumptions, experimental conditions (kind of biomass, carrier gas flow, and particle size) making it difficult to compare experimental results obtained for global yields and kinetic parameters published in scientific papers [76]. Regarding this last point, there is ambiguity as to the value of the heating rate. In most cases, the heating rate is reported the controller setpoint in the heating elements (electrical resistance, radiation lamp, hot plate), rather than a particle heating rate, assuming a linear heating, mathematically represented as: $T=\beta t+To$ with β, t and To as the heating rate, time and initial temperature of the particle respectively [13,26,57].

This simplification can be valid under certain experimental conditions, such as those used in thermogravimetric analysis, or pyrolysis subjected to kinetic control conditions (small particle sizes <100um). Fig 5 shows that for large particles (>1mm), temperature gradients exist and heating rates at each point are different, modifying reactivity patterns at each point within the biomass (the reaction rate depends on the heating rate and reaction

Table 1.
Main devices used in the study of fast pyrolysis processes.

Reactor	Temp. Max °C	Heating Rate °C/s	Time S	Pressure atm	Particle Size	Remarks
Drop Tube	1500	10^4 - 10^5	0.1-4	Vac-69	Powder	High heating rates. It is not possible to measure particle temperatures. Moderate gas residence time. Errors of 5% in closing mass balances.
Wire Mesh	1500	1000	1-3600	Vac-69	Powder	Uncertainty in particle temperature measurement. Short residence times of volatiles. Low uncertainty in the mass balances.
TGA	1200	1	Hours	Vac-2	< 2mm	Low heating rates and temperatures. High volatile residence time. Good estimation of sample temperature. Online monitoring sample weight.
Radiation	2000	10^4 – 10^6	Msec	1	Powder	High heating rates. Inaccurate temperature measurement.
Shock Tubes	2400	10^6	µs	Vac	Fine	Complete destruction of volatile (side reactions). Temperature measurement uncertainty.
Pyroprobe (electrical resistance)	700	20000	10-3600	Vac-1	Fine	Direct measurement of volatile and light gases. Indirect measurement of the sample temperature. In this moment the heating rate on the sample is not reported with the quartz tube sample holder.
Fluidized Bed	1200	1000-10000	1-3600 S	1-100	mm	High uncertainties in the closure of mass balances. Volatile quantifying uncertain. It is not possible to accurately determine particle temperature and residence time.
Drive Bed	700-800	1000-10000		1-100	1-5	
Thin Film	1000	10^4 – 10^6	Msec	Vac-2	µm	Accurate temperature measurement of the particle. High volatile residence times.
Ablative	600	-----	S	1	cm-m	Volatile cracking reactions. Solids temperature measurement is not possible. Difficult volatile monitoring.
AUGER.	600	------	Min	1	Chips	Bio-oil contamination of sand. Difficult estimation of solids temperature. Higher volatile residence times.
Vortex	600	-----	Min		1-5	The estimation of solid temperature is difficult.
Microwave	Power: 500-2000W	------	Min	1	Pulv.	It favors the formation of hot spots in the sample (uneven heating). It is not possible to make precise sample temperature control. .Selective heating of polar groups.

Source: The authors

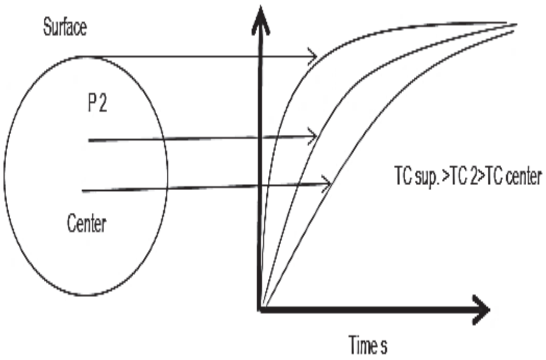

Figure 5. Temperature profile within a biomass particle.
Source: The authors

temperature). This consideration has been ignored in many studies [26,37,58-61], where normally the same reaction rate expression is used to describe the reactivity of the whole particle. Obviously, this can cause problems when predicting the final product distribution, because each point inside the particle has different kinetic parameters due to changes in the heating rates and temperatures. For fast pyrolysis studies, there are many techniques and devices, which can ensure conditions of high heating rates such as: PY-MBMS (Pyrolysis-Molecular Beam Mass Spectrometry), TGA (Thermogravimetric analyzer), flash radiation lamps, wire mesh reactors, discharge tubes, free fall reactors (Drop tube reactor), among others. Table 1 summarizes the main characteristics of these devices. Of these devices, the most commonly used in kinetic studies are the free fall reactors, Py-MS, reactors, and wire mesh (hot wire) [62], [63]. Within the academic community, wire mesh reactors have gained acceptance over other technologies for their versatility (can be used to study almost any kind of biomass and coal without many modifications to the reactor), directness of the temperature measurement (this data is important for kinetic parameters estimation), shortness of the volatiles' residence time (<1s), minimization of side reactions, and allowance of kinetic control.

3. Final remarks

Several investigations have been carried out to produce clean energy based on biomass fast pyrolysis. In its first part, this paper presented a general review of the effect of the main operational parameters on the global products distribution (Bio-oil, bio-char and syngas). However, a good understanding of the process enables the maximization of pyrolysis products. The following conclusions and recommendations can be drawn:

- Bio-oil production by pyrolysis is still an immature technology and it is not commercially viable yet. Bio-oil production technologies have to overcome many technical and economic challenges to compete with traditional fossil fuels.
- Along with the technology, a proper selection of biomass is also a critical issue for achieving high yields of bio-oil. Biomasses with a high cellulose content may be suitable, because of the greater amount of bio-oil derived from them. Similarly, biomass with low water content is desirable to reduce drying costs and improve oil quality.
- In general, the cellulose and hemicellulose tend to produce the largest amount of volatiles; lignin is difficult to break up even at high temperatures; it normally retains its structure and is associated with char production.
- Temperature and heating rates are the most important parameters in biomass pyrolysis. Average temperatures between 500-550°C usually maximize the bio-oil yield. Temperatures above or below this range bring on the production of char and gas respectively.
- A combination of parameters such as: moderate reaction temperatures (500°C), high heating rates (>1000°C/min) and short residence time of volatiles (less than 2s) maximize the bio-oil yield.
- The initial moisture, mineral matter content, flow, and kind of carrier gas are parameters directly related to the promotion of secondary reactions that adversely affect the production of condensable volatiles and maximize the char yield.
- Carrier gas reduces the residence time of condensable volatiles, which helps to minimize the cracking and re-polymerization reactions of vapors. Furthermore, it is important to ensure a rapid quenching of these vapors to recover as much of the bio-oil as possible.
- Small particles (<1mm) are preferred for achieving high heating rates, uniform distribution of temperatures and higher yields in the bio-oil production. Larger particles tend to decrease the biomass conversion, bringing on char formation, mainly because there are mass and energy transfer restrictions that encourage the participation of secondary reactions.
- For fast pyrolysis studies, there are many techniques and devices which can ensure conditions of high heating rates. Wire mesh and thin film reactors have gained acceptance within the academic community for kinetics studies (laboratory scale only). To achieve high bio-oil production, fluidized bed reactors are preferred. Most devices used in parametric studies for pyrolysis processes have limitations in terms of temperature measurements and online compounds quantifications due to the short reaction times and products interference with the recorded signals (changes in emissivity of the sample, tar deposition on lenses, and wide molecular weight distribution). Further research is needed in this line to better understand the primary and secondary reactions and the coupling with energy, mass, and momentum transfer processes in and out of the particles.

A second review article will be presented to deepen the understanding of the phenomena involved in the process of biomass fast pyrolysis. The second paper will focus on the reaction models proposed in scientific papers and modeling at particle level of the formation of an intermediate liquid phase within the particle during the degradation of biomass.

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