Yield, Composition and Active Surface Area of Char from Biomass Pyrolysis

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Biomass materials represent promising carriers for both heat, energy and chemicals production. Nevertheless, several aspects must be intensively investigated and understood, leading to a better design and optimization of industrial combustors, gasifiers and pyrolyzers. The first objective of this work is to update the POLIMI multistep kinetic mechanism of biomass pyrolysis, focusing on the prediction of both yield and composition of the solid residue (biochar). To this end, a large set of literature experimental data was collected and organized into a database, which was further used to finely tune and validate the proposed kinetic mechanism. Then a method to estimate the biochar active surface area is introduced, deriving from the biochar composition predictions. Keeping the previous agreements with the rate of biomass pyrolysis, formation and distribution of gas and tar products, the novelty of this work is the additional potential to predict the evolution of biochar yield and composition in a wide range of operative conditions, predicting also some important surface features. The model describes the solid residue as a mixture of pure carbon together with lumped metaplastic compounds, which represent the whole range of oxygenated and hydrogenated groups bonded to the carbonaceous matrix. These metaplastic species are released to the gas phase with their own kinetics and describe both mass loss and elemental composition change of the biochar. These are relevant topics because a comprehensive evaluation of biochar composition and its structural characteristics is crucial for an accurate description of the successive oxidation and gasification processes.

1. Introduction

The increasing world energy demand, scarcity of new fossil fuels reserves and global warming alerts are pushing the efforts to the development of renewable and sustainable sources for energy and chemicals. Interest in biomass is increasing for several reasons: worldwide availability, neutrality of greenhouse gases emissions, high renewability rate. Biomass conversion into energy and chemicals also offers a solution for several agro industrial wastes, such as residues from harvests and wood processing, black liquor from pulp industry, manure from animal raising and even solid municipal waste (Ullah et al., 2014).

Thermochemical conversion of biomass offers promising technologies, as it can be used for most kinds of feedstock, differently from trans-esterification and fermentation processes, which are feed-specific. However, high moisture content can reduce the process affordability. For all the technologies available, pyrolysis is the first conversion step, in which the material is heated under inert atmosphere, releasing a very complex mixture of condensable tar, gas, and biochar residue (Bridgwater, 2012). By changing the operating conditions, the process can be addressed in order to enhance the yield of the expected products.

Torrefaction, pyrolysis, gasification and combustion are the main thermochemical conversion technologies available. Slow pyrolysis is a suitable alternative when high yields of biochar are desired. (Ranzi et al., 2017a and 2017b). If the reactor temperature is kept under 650 K, providing heating at low rates and long residence times (hours), this process gives yields up to 50 wt.% of biochar. Biomass isolated compounds produce biochar in different amounts. The lowest yield is for cellulose, followed by hemicellulose and lignin, which reaches up to 50% (Demirbas, 2004). Moreover, the presence of inorganic matter affects the yield and composition of biochar. It enhances biochar and gas yields by catalysing the decomposition of sugars,

consequently reducing bio-oil yields. After their volatile fraction is released, inorganics produce ashes, which remain partially bonded and trapped in the solid matrix.

The biochar is an amorphous carbon structure containing significant amounts of oxygen and hydrogen, minor amounts of nitrogen and sulphur, together with metal oxides (i.e. ashes), which are formed during pyrolysis from the inorganic matter present in the raw material. The carbon content usually ranges from 65 to 95% depending on the initial biomass composition and pyrolysis operating conditions. Hydrogen and oxygen contents progressively drop when pyrolysis temperature rises. Their content directly influences biochar conversion during oxidation/gasification. In particular, it affects the total active area and thus the overall reactivity.

Although coal from char at high temperatures (T>1000-1200°C) can undergo a progressive graphitization (annealing) (Senneca and Salatino, 2011), this process should be less relevant for biochar, because of its higher reactivity and less severe operating conditions.

2. Multistep Kinetic Mechanism of Biomass Pyrolysis

Before discussing biochar composition it is useful to briefly explain the kinetic mechanism used to describe the biomass pyrolysis process. The detailed pyrolysis model applied in this work is based on the recently updated POLIMI model (Ranzi et al., 2008; Ranzi et al., 2017a). When the biochemical composition is not available, it is possible to characterize the sample based on its elemental analysis. Biomass pyrolysis is obtained as a simple combination of cellulose, hemicellulose, lignin and extractive decomposition (Debiagi et al., 2015). Because of its variability, lignin is characterized in terms of three reference components (Faravelli et al., 2010). Three reference components allow to distinguish hemicellulose in hardwood, softwood and grass/cereal feedstocks. A multistep kinetic mechanism, based on global and apparent first order reactions, describes the decomposition of each reference component. Volatiles are represented by 28 real and lumped species, including permanent gases and condensable species (tars). Several pyrolysis products are pseudo-species trapped in the metaplastic phase and released as volatiles at high temperatures. The solid residue is then represented by pure carbon and the sum of species still trapped in the metaplast. The progressive release of these species causes a decrease of biochar and a rising of its carbon content. The simple combination of the pyrolysis reference components is capable of predicting the overall lignocellulosic biomass decomposition. Along with the release of main gaseous and condensable components, the model describes the biochar elemental composition (C/H/O). The model can also be applied for more complex systems involving heat and mass transfer, for example CFD simulations (Gentile et al. 2016). Major details on model features are already discussed in the previous referred papers.

In the present work, we further refine the model, improving the description of biochar formation with more reliable predictions of yields and composition, for different biomass feeds and pyrolysis conditions. Therefore, a large set of literature experimental data was collected and organized in database format. The data show large variability of the residual biochar yield and its H/C/O elemental composition for the whole set of biomass samples at different temperatures. Despite the variabilities, clear trends are observed for yield of residual biochar and its carbon content, which increase with the rising of pyrolysis temperature, whereas oxygen and hydrogen content progressively decreases. Biochar yields and composition cannot simply be related to pyrolysis temperature. This variability also depends on initial biomass composition, heating rate, hold time, and other process conditions. Moreover, ash catalytic effects and secondary charification reactions (Anca-Couce et al., 2014a and 2014b) further influence this complex scenario.

3. H/C/O Composition of Biochar and Model Validation

Together with pyrolysis operating conditions, biochemical or elemental composition of the biomass and biochar composition are the required data for reproducing the experiments. However, not all the biomass samples in the database contain the data required for simulation, therefore comparison with literature are limited to about one third of the ~250 experimental data collected. These biomass samples were first characterized in terms of reference species and then simulated obtaining yield and composition of residual biochar. The predicted solid residue is composed by the fixed carbon and the sum of residual metaplastic species. H/C/O composition of the residue biochar is calculated simply accounting for mass fractions of residual species. To better show the model performance, feedstock composition and characterization of a couple of examples are reported in Figure 1. As temperature rises, the oxygen and hydrogen content drops, caused by weaker bonds breakage releasing light gases, resulting in reduction of biochar yield and increase of carbon content.

The parity diagrams in Figure 2 show biochar yield and composition of the whole set of comparisons (80 samples). In order to better analyze these data, experiments are first divided into:

- Low heating rate (LHR): experiments in TGA and reactors with programmed heating rate.

- High heating rate (HHR): experiments in fluidized bed, drop tube, pyroprobe and similar devices.

Both these categories are further subdivided depending on low and high final temperature (550°C is defined as the threshold temperature). Finally, TGA category refers to TGA experiments in which C/H/O data of biochar is not provided. These comparisons show that the model is reasonably capable of predicting both biochar yield and its composition at several different temperatures and heating conditions. Thus, biochar yields reduce as increasing the temperature (both HHR and LHR), first because of biomass devolatilization and then with metaplastic release. In parallel, carbon increases, and oxygen and hydrogen reduce. A correct prediction not only of biochar yield, but also its elemental composition is of utmost importance, because it strongly affects successive biochar reactivity in combustion and gasification processes (Morin et al., 2016).

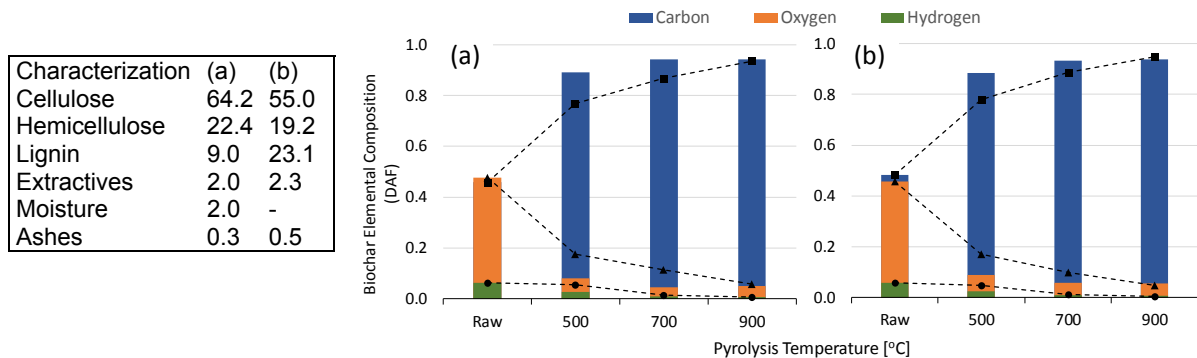| Characterization	(a)	(b)
Cellulose	64.2	55.0
Hemicellulose	22.4	19.2
Lignin	9.0	23.1
Extractives	2.0	2.3
Moisture	2.0	-
Ashes	0.3	0.5

Figure 1 - Pyrolysis of Wood mixture (a) and Coconut shell (b) (Fagbemi et al., 2001). Characterization of biomasses in terms of reference components. Comparison of experiments (bars) and model predictions (lines).
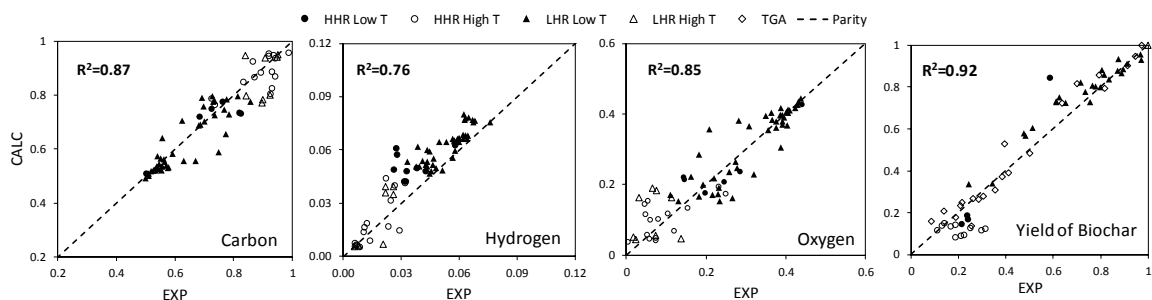

Figure 2 - Parity diagram of experimental and predicted values of biochar yield and elemental composition

These results were obtained after modifications of the pyrolysis model, mainly on solid residue components. We describe the solid residue as a mixture of metaplastic and fixed species. Metaplastic species represent all the weaker-bonded functional groups and species trapped into the carbonaceous matrix. The kinetics of hydrogen and hydrocarbon species in the metaplast was changed by increasing their release rates, reducing H content at intermediate temperatures. Moreover, dehydration reactions of solid residue at high temperatures was also revised. The final and completely devolatilized carbonaceous matrix, which in the previous models was considered as pure carbon, now contains small amounts of hydrogen and oxygen, to better agree with high temperature biochar composition. The updated and upgraded pyrolysis model is available on the CRECK Modeling website (http://creckmodeling.chem.polimi.it/).

Despite this tuning activity, which improved correlation indexes, these results still maintain a large scatter, as indicated in Figure 2. At intermediate temperatures, systematic deviations of H content can still require further kinetic modifications on volatile release. Anyway, these deviations are also caused by large simplifications of pyrolysis model and biomass characterization, as well as by experimental uncertainties, including poor knowledge of biomass origin and composition, and incomplete description of operating conditions. The scatter of the HHR experiments in Figure 2 highlights systematic biochar underpredictions, whereas an opposite deviation is observed for the LHR data. At high temperatures and high heating rates, the release of metaplastic species should be partially reduced. Jia et al. (2017) also reached similar conclusions, when

investigating model performance on a fluidized and a fixed bed reactor. Although model predictions better agree with experiments at intermediate temperature conditions, the pyrolysis model still needs further refinements at high heating rates.

4. Biochar Surface Area

The biochar reactivity in oxidation/gasification is affected by surface area (chemical structure), surface accessibility (porosity), active area (adsorption spots), catalytic active sites (native or added inorganics), as well as by gasification agents (Di Blasi, 2009). Surface accessibility and area depend mostly on the initial cellulose, hemicellulose and lignin content in lignocellulosic samples, together with pyrolysis conditions. Generally, the specific surface (m^2/g) of a solid is measured through Brunauer–Emmett–Teller (BET) analysis, based on the adsorption of N_2 or CO_2, giving different results depending on their pore penetration capacity. CO_2 is able to diffuse also through micropores, providing results much higher compared to N_2, when the biochar micropore volume is significant. Typical values of specific surface are 1-200 m^2/g with N_2 and 100-800 m^2/g with CO_2 measurements, depending mostly on initial biomass composition and pyrolysis conditions. In general, low temperature pyrolysis biochar has a higher amount of micropores than high temperature biochar. At lower temperatures, devolatilization forms micropores and increases total pore volume and surface area. Under high temperatures, the union of neighboring pores can predominate leading to a decrease in the surface area. While BET analysis is a well-known technic to measure total surface area of a solid, the actual available area for adsorption of gasification agents is not easily measured. This is an important aspect for defining biochar reactivity and in the next Section we derive this parameter through the predictions of the pyrolysis model.

4.1 Active Surface Area

Laine et al. (1963) produced char from coal at 2800°C and calculated experimentally the total surface area of these samples from 0 to 35% burn-off levels. BET analysis of the solids were performed with N_2 at 78K and values from 76 to 128 m^2/g were found for total surface area. They distinguished graphitized and edge carbon atoms. Only edge carbons are available for oxygen adsorption. Then, adsorption experiments were performed at 573 K, condition in which oxygen interacts with carbon surface forming carbon-oxygen complexes in the active areas, and the release of CO and CO_2 is negligible. Assuming that each oxygen was adsorbed onto one edge carbon atom, and that it occupies an area of 8.3 $Å^2$, the active area was observed to vary from 0.25 to 3.5% of total surface area, depending on burn-off level.

Combining these assumptions and model predictions for biochar elemental composition, Figure 3 reports possible molecular structure (clusters) for biochar under different pyrolysis temperatures, heated at 20 K/min. The evolution of biochar molecular structure is based on essential data from Raman spectroscopy, SEM and FT-IR experiments (Apaydın-Varol and Pütün, 2012; Liu et al., 2010). Moreover, Le Brech et al. (2016) observed that biochars produced at temperatures below 350°C are rich in aliphatic groups, while above 350°C the entire structure is dominated by aromatic clusters. Low pyrolysis temperature biochars keep similarities with the original biomass with the presence of carboxy, methoxy, methyl, acetyl and hydroxy groups, as reported for the 200, 400 and 600°C molecules. As pyrolysis temperature goes up, these weaker-bonded groups are progressively released, forming larger polyaromatic structures, with lower hydrogen and oxygen contents, leading to graphene-like structures (Guizani et al., 2017). The progressive size of clusters shows the evolution of biochar amorphous structure to graphene/graphite-like ordering. Graphite is made of hundreds of thousands of graphene layers, which is ordered in honeycomb configuration and has very reduced, or even no hydrogen and oxygen content. In this configuration, each carbon has three stable sp2 bonds to neighboring carbon atoms. The resonance effect of the free moving electrons in this structure both stabilize the structure and distribute the electrical charge (Asbury Graphite Mills Inc., 2006), without the need of hydrogen atoms bonded to each edge carbon atom.

From these structures, total and active surface area were estimated assuming that the covalent radius of C/H/O atoms are 70, 25 and 60 picometers, and that they are perfect spheres (Slater, 1964). Total area was simply estimated through the sum of all the atomic areas, whilst the active area was estimated summing the area of edge atoms in each structure, excluding the non-edge atoms. Table 1 reports, for each structure obtained, the elemental composition, the number of atoms and the percentage of active/total surface area. The graphene-like structures were considered 3 cluster-layers. From these results, a simple correlation was derived, allowing to estimate this ratio with the percentage of carbon (mass) in the biochar. As expected, these results show a progressive drop of this ratio with the increase of temperature and carbon contend. It is worth to notice that oxygen content in the 700°C biochar is slightly higher than the 600°C biochar, which is caused by the release metaplastic species G{CH_4} and G{C_2H_4} at this range of temperature from the biochar, slightly increasing the oxygen content, which is further reduced by the release of the remaining metaplastic species.

When compared to the results of Laine et al. (1963), we are predicting much higher percentage of active area, as expected. The materials here investigated are much more amorphous, porous and reactive when compared to high carbon content chars from coal. The proposed correlation is able to predict a drastically drop of active area when solid structure becomes richer in carbon, reaching about 6% of active area at pure carbon content. It is still above the average values of Laine's work, as they were experimenting with very high temperature biochar, and therefore high-graphitized samples. As biochars rarely undergo graphitization reactions, considering more layers is outside of the scope of this work.
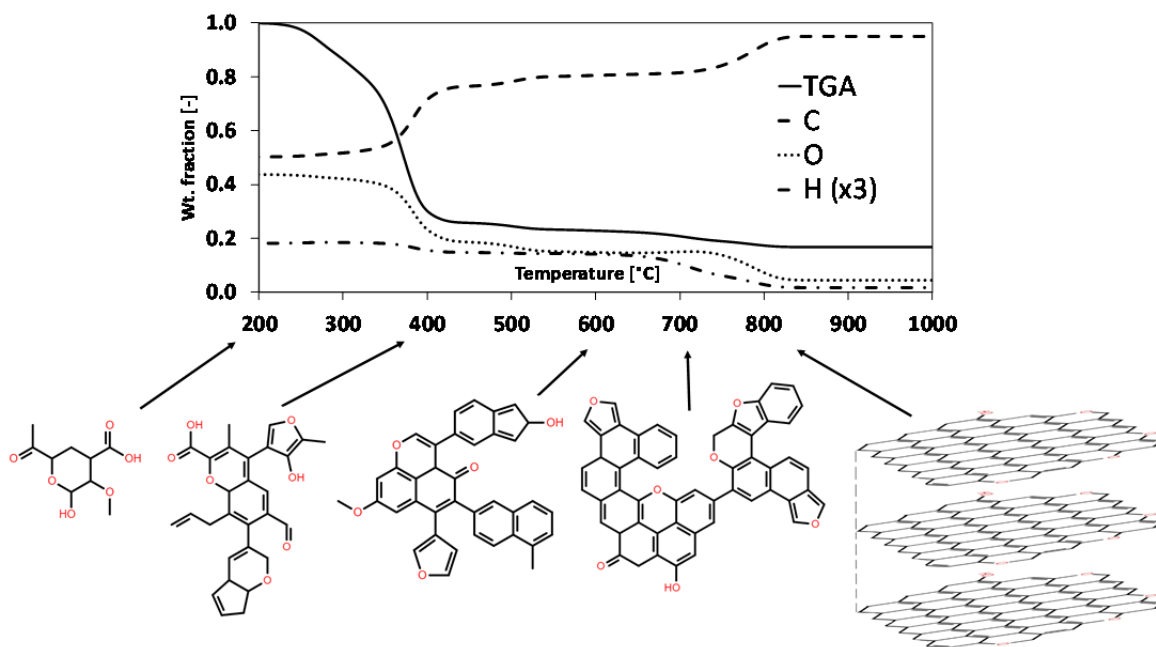

Figure 3 – Evolution of composition and possible molecular structures of biochar at different pyrolysis temperature (20 K/min).

Table 1 - Elemental composition, number of atoms and percentage of active/total surface area estimated with pyrolysis model predictions.

T [°C]	Wt.% - Molar Ratio			Active Area / Total Area (%)
	C	H	O	
200	50.3 – 1	6.05 – 1.44	43.7 – 0.65	73.5
400	71.5 – 1	5.18 – 0.87	23.3 – 0.24	60.0
600	80.5 – 1	4.71 – 0.70	14.8 – 0.14	56.8
700	81.5 – 1	3.52 – 0.52	15.0 – 0.14	52.1
800	91.8 – 1	0.95 – 0.12	7.3 – 0.06	25.0
900	95.0 - 1	0.56 – 0.07	4.4 – 0.04	20.4

$$\%Active\ Area = -0.028 \times C^2 + 2.8 \times C + 8.7$$
$$R^2 = 0.982$$
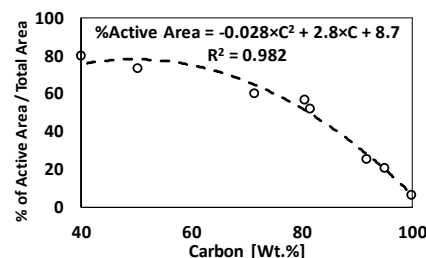
5. Conclusions

The present work investigated the capability of the POLIMI biomass pyrolysis model to predict the yield and composition of the residual biochar. The results showed that besides the model simplicity, it reliably predicts these aspects, for several different feedstocks and operating conditions. Biochar yield is an important factor for the optimal design of thermochemical conversion processes, whereas biochar elemental composition strongly influences its reactivity in gasification and oxidation environments. The experimental data agreement with both characterization procedure and pyrolysis predictions allows an estimation of the evolution of biochar active area. Not all of the biochar surface area measured experimentally is available for gasification reactions, as it depends on adsorption sites. Therefore, we proposed some molecular structures to match the elemental composition of biochars obtained at different temperatures, and estimated the corresponding active areas. These properties are essential information to model the heterogeneous reactions of biochar in combustion/gasification and will be applied for modelling biomass thermochemical conversion.

The next step of this investigation is defining a kinetic mechanism of heterogeneous biochar reactions with oxidizing gases (O_2, CO_2, H_2O), fully compatible with previous biomass characterization procedures and pyrolysis kinetic mechanism, providing a complete tool for simulating biomass thermochemical conversion.

Acknowledgments

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