

THE BIOMASS PYROLYSIS FOR STEAM GASIFICATION: EXPERIMENTAL STUDY FOR NUMERICAL DEM SIMULATION

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Abstract - In this paper, an experimental procedure was developed to establish global kinetics at particle scale of pyrolysis reactions for steam gasification in the temperature range 400°C-900°C. Our work consists to group all the needed data for DEM (Discrete Element Method) simulation by experimental manipulation of wood steam gasification. The DEM approach was developed by Cundall and Strack (1979) [1] but is used only recently which explains that there is a lack of available data in the literature for this approach. We have chosen the experiments as a function of numerical parameters necessity, which needs to be at the particle scale and separated reactions. For that, we use four different experiments that we produce in the same conditions in inert atmosphere of nitrogen: a quartz and steel tubular reactor in a cylindrical oven, and a TGA apparatus. The main result is the density evolution which seems to be only dependent of temperature during pyrolysis.

1. Introduction

The recent discussions on climate change, CO₂ emissions, and the limited availability of fossil fuels have renewed the interest in gas from biomass and wood. Advantages of fluidized bed reactors are, e.g., the good heat and mass transfer between the gas phase and the individual particles and a good performance for a wide range of fuel qualities. In order to improve and optimize the thermal efficiency and to predict product gas composition and emission rates, numerous mathematical models for biomass have been developed [2]. The difficulty lies in the implementation of experimental data required for numerical models in order to be able to reproduce and to deduce a sizing tool for larger scale of reactors [2] [3] [4]. Looking at the literature, the data and parameters sets to describe the reactions are usually according to the oven temperature and / or the gas temperature [5] [6]. The wood particle is considered as small enough to become thermally thin and heats up quickly compared to the reaction time, so, it was considered "isotherms" at the oven temperature [7] [8]. These data can be used for generalized global (engineering process) or averaged (Eulerian) numerical models on a set of wood particles gasification [3]. To understand the impact of the coupling exchange between the gas-particle phases, we are interested in a more local approach called "Discrete Element Method (DEM)" [1]. This is an intermediate between the Eulerian and Lagrangian approach, as it allows to follow a "package" of particles by Lagrangian method. For this approach, the experimental data described in the literature are therefore not suitable. So, we have set up an experimental protocol at the scale of one wood particle only. We will present here a complete experimental protocol with all necessary data for DEM approach. The original appearance of these manipulations resides on estimating the density function of the temperature during the pyrolysis of wood particle, with the monitoring of the volume, temperature, and the mass over time [2] [9]. Our manipulations are decomposed on three different experiments for the pyrolysis: two different

reactors (steel and quartz) in the same oven for wood pyrolysis, in order to view the particle (quartz reactor: to follow particle volume), and coupled to a microGC-TCD (Gas Chromatography and Thermal Conductivity Detector) to monitor the outlet gases composition over time (steel reactor: for sealing reasons). The third experiment in TGA (ThermoGravimetric Analysis) allows to reproduce the thermal evolution of the particle, measured in previous experiments (quartz reactor) and estimate the mass loss over time. These experiments were conducted under conditions representative of a bubbling fluidized bed, i.e with a flash pyrolysis (pyrolysis time of wood particle is around 1min). The consistency of the DEM approach has ever been checked for hydrodynamic point of view with the comparison results between experiments and simulations for a shallow dense fluidized bed, and even for heat transfer in a quasi-static particle bed [10], and a feasibility study on the reaction model was made to test whether the change in diameter and density were possible following reactions implemented [11].

2. Experimental description

2.1. Pyrolysis: quartz and steel tubular reactors

2.1.1. Quartz tubular reactor

The pyrolysis reactor is a cylindrical quartz tube (with an 35mm inner diameter), heated by a cylindrical oven. The use of quartz allows to perform tests until 1000°C and to visualize the particle during pyrolysis. A PID regulation system remain the oven temperature constant. The particle is spouted into the hot zone instantaneously (fast pyrolysis). The reactor is fed with inert gas (nitrogen) in order to obtain only pyrolysis reactions) (Fig. 1). The cylindrical sample

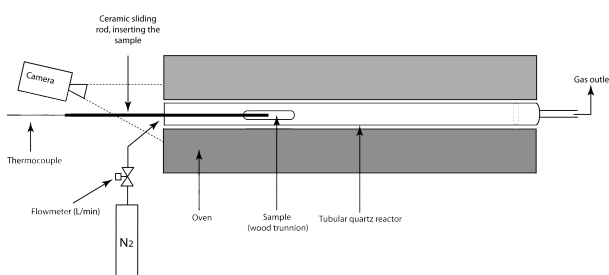


Figure 1: Sketch of pyrolysis reaction in quartz tubular reactor.

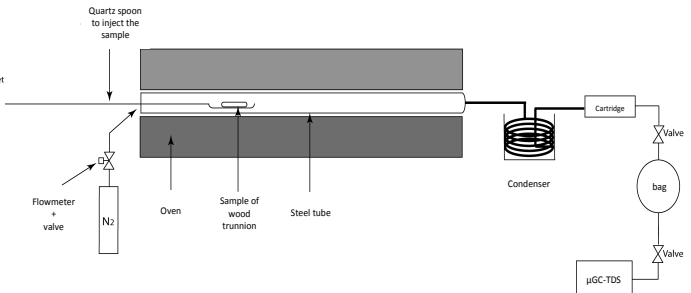


Figure 2: Schematic representation of pyrolysis in steel tubular reactor.

of wood (beech) typically used for these experiments has an average initial weight of 1.35 g for an average diameter of 8 mm and a length of 40 mm. It has been previously perforated on two centimeters deep to introduce the thermocouple (diameter of 1mm). The thermocouple was thermally isolated by a perforated ceramic tube (diameter of 4mm). We place the trunnion at the extremity of ceramic tire, which constitutes a rigid particle transportation from the outside to the inside of the furnace. Moreover, the particle volume evolution is measured using a

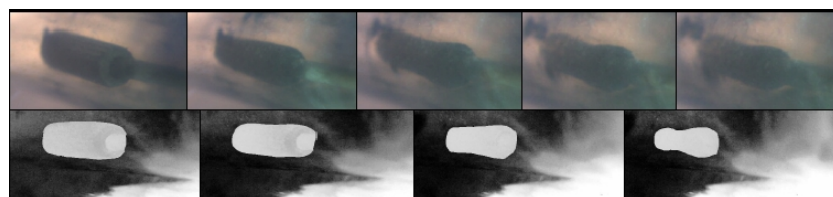


Figure 3: Pictures of trunnion during pyrolysis.

30 frames per second camera (Fig. 3). The obtained images are manually post-processed to extract the contours of the particle. Then, using the ImageJ software, we measure the apparent particle dimensions (diameter, length). After an initial calibration of diameter and length based on the initial known volume, the particle volume is deduced from image analysis by making the assumption that particle globally conserves a cylindrical form. We only control the oven temperature. The introduction of trunnion inside the oven is constrained by the camera vision field angle, which imposes to place trunnion at the extremity of oven. So, we have an important heat loss due to trunnion position. we retain only two experimental results :

- Oven preheated to 900 °C, the final particle temperature to 646 °C.
- Oven preheated to 1000 °C, the final particle at 490 °C.

So, in our experiments, the particle heating depends on location in the reactor and not on the oven temperature. In this part, we will differentiate experiments by the name of the imposed oven temperature for convenience.

Steel tubular reactor

Here is globally the same experiment than quartz reactor, where the wet trunnions are injected in the medium of reactor, in inert atmosphere of nitrogen (at 0.552 L/min), with a steel reactor in order to ensure a good seal to analyze the composition of outlet gases (Fig. 2). The test apparatus consists of a stainless steel reactor and a quartz spoon to insert for wood sample. The reactor output is connected to a filled cartridge of silica gel and a serpent condenser, in order to capture the water and tar from the pyrolysis gases, for the protection of microGC-TCD (Gas Chromatography-Thermal Conductivity Detector). For this experiment, we can not reproduce the thermal evolution of the previous experimentation because we can not introduce thermocouple inside the reactor. By this way, we choose to produce pyrolysis at typical temperature of flash pyrolysis such as 600 °C, 700 °C, 800 °C and 900 °C. The aim of this experiment is to identify the stoichiometric factors for global pyrolysis reaction. In the literature, there is not a big difference between global and detailed chemical mechanisms for pyrolysis reactions (with primary and secondary reactions) because of the complexity to quantify experimentally the produced components for each reaction[2] [12] [4]. So, in our case, we choose to develop a global reaction for pyrolysis modeling from experimental results.

2.2. Pyrolysis: TGA (ThermoGravimetric Analysis)

The thermobalance consists of a sealed chamber to control the atmosphere of sample, a oven with a thermocouple inside to manage and register the temperature of a weighing module (microgram). Microbalance is under inert atmosphere (argon here, 0.2 NL/min). To avoid fouling of TGA enclosure, it is necessary to work with little mass quantity about 50 mg. Thus, the sample can be considered thermally thin. To keep a representative form from the pyrolysis quartz experiment, we cut disc from initial wood trunnion of about 1.8 mm of thickness. To obtain the same operating conditions (than quartz pyrolysis reactor), we match the heating rate from direct temperature measurement in the heart of the particle. By the dynamic of mass evolution, corresponding to the wood degradation during pyrolysis, we can estimate the global kinetic of pyrolysis reaction and, combining to the volume measurements, we can deduce the particle density over the trunnion temperature in time.

3. Experimental pyrolysis results

3.1. Images post processing: volume particle evolution during pyrolysis

The images from the camera was manually post-processed by the drawn particle outline for each picture. Using the ImageJ software, it is able to estimate the diameter and length equivalent of the closest ellipse to the original surface, measured in pixels. These dimensions are initially known and permit to quantify the scale change between pixel dimension and centimeters. Thus, it is possible to deduct the evolution of the particle volume depending on the temperature. To obtain an estimate of uncertainties made from measurements of particle size via the camera, we compare with the final results of volume particle measurement by camera and caliper. With the caliper, we have an uncertainty which can vary from 1.5 % and 20 %. The uncertainty with camera is more difficult to estimate, for this reason, we compare directly our manual to the camera measurements ; By this way, we obtain between 10 % and 27 %. Globally, because of the imprecision of manual measurements by a caliper, we can conclude that diameter and length camera estimation are acceptable.

3.2. Composition of pyrolysis gases

We use a microGC-TCD device, directly joined to the steel reactor outlet, to measure the concentration in a known aspirated volume for analysis. From these indications, we can deduce the volume fraction of each component, and knowing the molar mass for each gas element, the equivalent mass of it. Then, we compare the total mass of products (char + gases + condensates) with the initial wood particle mass in order to evaluate the reliability of our experimental data. A balance of 100 % corresponds to the totally initial mass of wood, which means that we detect all the products from the wood pyrolysis. And as we can see in the Table 1, we generally overestimate the amount of gases measured by the microGC-TCD with results obtained in a range of [102 ; 118]. Nevertheless, the order of magnitude is correct. Finally, we can infer that the sealing system is effective and we can be confident in the measurement of the majority of gases from pyrolysis.

Oven temp.	Initial wood mass	Final char mass	Water mass	Tar mass	H ₂ (%)	CH ₄ (%)	CO (%)	CO ₂ (%)	C ₂ H ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	Mass balance (%)
600	1.25	0.21	0.19	0.44	0.0020	0.034	0.227	0.157	0.009	0.003	0	102
700	1.46	0.22	0.23	0.4	0.0055	0.06	0.43	0.192	0.026	0.008	0.001	108
800	1.48	0.21	0.23	0.3	0.0096	0.107	0.54	0.29	0.046	0.007	0.002	118
900	1.35	0.2	0.21	0.24	0.01	0.096	0.433	0.275	0.04	0.002	0.003	112

Table 1: Pyrolysis gases composition. All the temperature are in celsius degrees and the mass are in grams.

For comparison, we relied on the work of Dufour et al. [13], who studied the characterization of gases pyrolysis as a function of the oven temperature. Their results were presented as a global composition of pyrolysis products, and, with more details, the concentration of produced gases components. Their work was done in similar experimental conditions than ours, but it was more focused on the influence of temperature on final composition of pyrolysis products. To compare their experimental results to ours, we express the data from dry wood mass (i.e the percentage of biomass d.a.f (dry, ash free)): $Mass_{element} (g/kg_{d.a.f}) = \frac{Mass_{measured}}{Mass_{initial\ dry\ wood}}$ & $\%dry\ wood\ mass = \frac{Mass_{element}}{Mass_{total}}$

Looking at the overall results of the products of pyrolysis way (Fig. 4), we obtain a peak of gases production at 800 °C, the char production is relatively constant around 15%, contrary to the tar production which decreases with the temperature. In comparison with Dufour, we

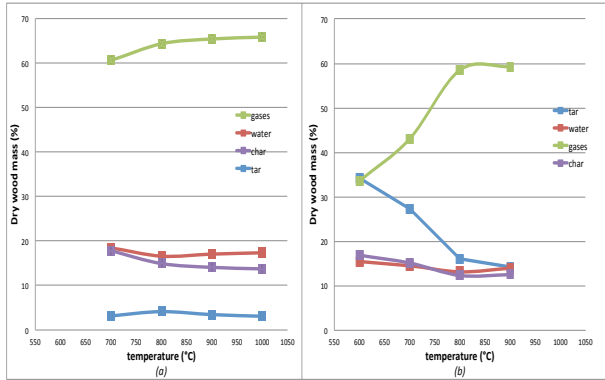


Figure 4: Global composition of pyrolysis products: the graph on (b) is our results, the graph on (a) is Dufour et al. [13] results.

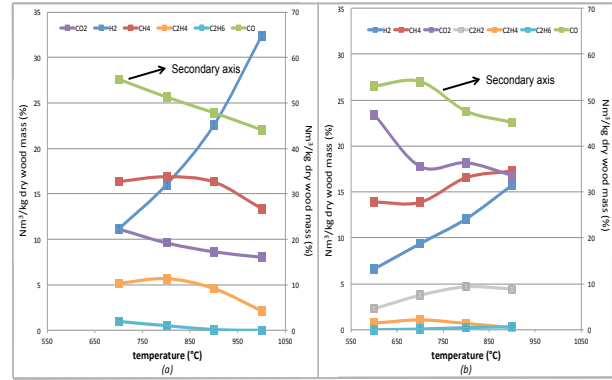


Figure 5: Pyrolysis gases composition: the graph on (b) is our results, the graph on (a) is Dufour et al. [13] results.

produce more tar and less gases. Globally, the difference is relatively important between the two graphs but, the trends evolutions are respected. This can be due to the initial nature of used wood which was different that our case, in fact, Dufour used dry wood chips in his experiments. The order of global dynamics for each components are well conserved. For more details, we can extract the evolution of the different components of produced gases (Fig. 5) during pyrolysis. Among analyzed gases components, we detect the C_2H_2 in more than Dufour experiment, which is not negligible and directly impacts the composition in H_2 : for example, we obtain 9% again 12% for Dufour et al. [13] at 700°C, or 16% again 22% for Dufour et al. [13] at 900°C. But, globally, the trends are respected with the decreasing of concentration for each gases except the H_2 (and CH_4 in our case only), which increases with the temperature. Finally, our results reasonably consistent with those from literature.

3.3. Dynamic of particle mass loss during pyrolysis

To deduce the kinetics parameters, we use the mass loss dynamic TGA apparatus. The aim is to share the mass with volume and gases composition of each pyrolysis experiment. For this, we impose the same wood particle temperature way in time for TGA as you can see in Fig.6. We also try to estimate the temperature at the surface of particle considering conductive and radiative transfer from temperature inside the wood trunnion. For each experiment of pyrolysis, we did two experiments in TGA, with measured particle inside and particle surface temperature, that train a little difference between mass loss due to the heating rate difference (which is more important for particle surface estimation). But, the TGA induces some instabilities for all trend changes (appearance of oscillating signal, see Fig.6) which can not permit to conclude on the heating rate influence on the mass loss between the experiments. So, we should limit the change of trend to reproduce particle temperature of quartz pyrolysis reactor. About this graph (Fig. 6), we can see that the mass loss is separated into two distinguished zones: ones begins at 100 °C which corresponds to the water evaporation temperature inside the wood particle, marked by a flat level, corresponding to the latent heat of water, until 300°C, the next zone, which marks the pyrolysis step. We can also notice that more heating rate is important higher is the particle mass loss. These results are physically corrects.

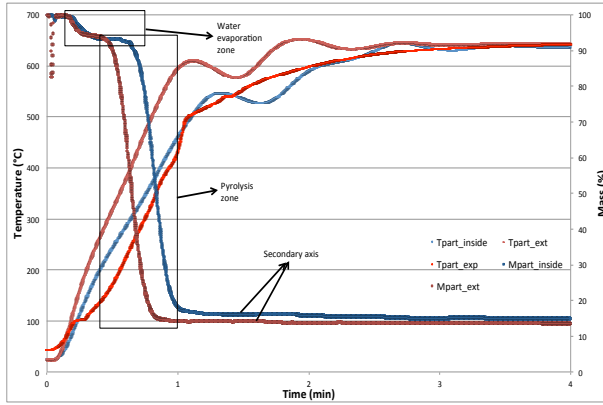


Figure 6: Mass evolution and comparison in temperature between quartz reactor & TGA.

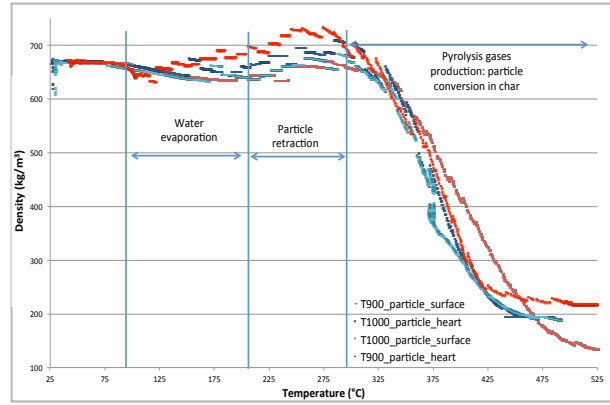


Figure 7: Density of wood during pyrolysis as a function of temperature.

3.4. Density evolution of wood during pyrolysis: TGA and Quartz Reactor

According to this conclusion, we share results from TGA and quartz reactor to deduce the density evolution with temperature. To do the mass conversion from a disk to an entire trunnion, we apply mass correspondence from the initial average of a trunnion: $Mass_{trunnion}(g) = Mass_{average\ of\ trunnion}(g) * \frac{Mass_{measured}(\%)}{100}$. Then, to estimate the density, we divide this mass by the volume as you can see in the Fig.7. We represent the density as a function of the temperature for different particle final temperatures and heating rate (from measurements of particle temperature and the estimation (by thermal balance) of particle surface temperature). Globally, for each case, the density decreases with the temperature. In this graph, the evolution of density can be separated into three characteristics zones: water evaporation, particle retraction and pyrolysis gases production. In the first part, the bound water is evaporated when particle reaches 100°C, so the volume of trunnion reduces a little. In the second zone, the volume of particle continues to diminish without any change of mass, according to the increasing of particle density, due to the augmentation of temperature which acts on the pores reduction of wood. In the third zone, the density dramatically decreases in a very short time and a gradient of temperature around 300°C to 450°C, which corresponds to a flash pyrolysis. Moreover, all the curves have the same reaction description, and, seems to show that the density is only a function of temperature. This point is very important in term of numerical modeling because it can extremely simplify the models normally used for the density during pyrolysis, with many assumptions on the volume and mass evolutions [2]. We can directly take the experimental data as evolution of density if it is only dependent of temperature, and, in the other part, we are able to describe the behavior of particle volume evolution during pyrolysis (as we have described by the three characteristics zones of particle density); I.e we are able to say if the wood particle becomes more porous, or little, or the two phenomena in the same time. Others experiments were done and need to be exploited for comparison to our results in order to estimate the reproducibility and the range of heat rate and temperature.

3.5. Determination of pyrolysis reaction kinetics

To determine the chemical kinetics, the idea is to develop a mathematical model to predict the mass loss of the samples over time depending on the reaction temperature: $\frac{dm(t)}{dt} = k * (m - m_0)$ For that, it is currently used a formulation by exponential expression deduced as the following method of resolution. The evolution of mass loss can be described by a kinetic term k (s^{-1}) as a

factor of mass in time and by integration, knowing the boundary conditions : $m(t = 0 \text{ s}) = m_0$; $m(t = \infty) = m_\infty$, the solution becomes: $\frac{m(t)}{m_0} = (1 - \frac{m_\infty}{m_0}) * \exp(-kt) + \frac{m_\infty}{m_0}$ To fit the curve of mass loss obtained by TGA, we need to adjust the parameter k . This parameter can directly be deducted from the solution equation of mass loss with time. By this way, we obtain the k term as a function of time. To have the relation between the mass dynamic and the temperature, it is usually used the description by the Arrhenius law: $k = k_0 \cdot \exp(\frac{-E_a}{RT})$. In our case, we choose to describe our experimental pyrolysis reaction by a global reaction which needs only one reaction for pyrolysis description as following: Wood \implies Char + Pyrolysis gases + Tar. In fact, if you see the literature, because of the difficulty to separate the different reactions for wood pyrolysis, with in more the primary and secondary steps of reaction, finally, the very detailed model are not more accurate than a global model. The experimental conditions (presented by Deglise et al.(1987) [14]) are also very influent in the final products of pyrolysis, which is also at the origin of the divergence between the models that we can find in the literature. For that, the method consists to read the parameters at the origin intercept obtained by the linear regression with a good correlation coefficient of 0.99, corresponding to $\ln(k_0)$, and the slope factor corresponds to the term $\frac{-E_a}{R}$. Finally, reading the equation of linear interpolation, we deduce the parameters for Arrhenius law: $E_a = 80740.6 \text{ J/mol}$ and $k_0 = 33894.2 \text{ s}^{-1}$. In the literature, we can find a lot of data of pyrolysis reaction for different experimental conditions like it is referred in the Table 2. Finally, in this table, it appears that the majority of values for activation energy, E_a ,

Table 2: Experimental kinetic constants of pyrolysis reaction.

Author (Ref.)	Experimental system	T_f (K)	Reaction mechanism	Number of reactions	E (kJ/mol)	A (s^{-1})
Gerber and al. [15]	Bubb. fluidized bed reactor	670	semi-global	3	88.6	$1.43 \cdot 10^4$
					112.7	$4.13 \cdot 10^6$
					106.5	$7.38 \cdot 10^5$
Grieco and Baldi [16]	Isother. tube furnace	[520, 640]	global	1	87.5	103500
Branca and Di Blasi [16]	Isother. quartz furnace reactor	[528, 708]	semi-global react. mechanism	3	76.2	26903
					142.8	$5.91 \cdot 10^9$
					43.8	9.97
Thurner and Mann[17]	Isother. tube furnace	[573, 673]	global	1	106.5	$2.47 \cdot 10^6$
Gordon and Knight[16]	Entrained react. flow	[677, 822]	global	1	89.52	$1.483 \cdot 10^6$
Reina et al.[18]	TGA	[498, 598]	global	1	124.87	$7.68 \cdot 10^7$
		[973, 1173]	global	1	91.53	$6.33 \cdot 10^2$
Di Blasi.[19]	Isothermal tube furnace	≤ 1400	global	1	69-91	
		[700, 800]	global	1	56-106	

are included between 60 and 120 kJ/mol, and for exponential pre-factor term, A , the values are more divergent from 10^3 and 10^9 , but it's too approximative. We can conclude that our results are coherent with the literature.

4. Conclusion

In this paper an experimental procedure was developed to establish global kinetics at particle scale of pyrolysis and steam gasification reactions in the temperature range 400°C-900°C. These global kinetic parameters are useful to simulate practical systems (characterized by high heating rate) for a specific approach, which is the DEM method. The pyrolysis reaction of wood was well known and studied since fifty years but was not adapted for DEM approach. It was characterized as a function of the final temperature of reaction, the heating rate and the residence time of particles. Many assumptions were formulated to traduce the evolution of density and volume which varies proportionally with the mass of particle or adapted variations with specific porous exchange surface. Hence, our experiments were set up to evaluate the volume and mass evolution as a function of temperature and time dependence. For that, we need three different experiments that we produce in the same conditions in inert atmosphere of nitrogen: a

quartz and steel tubular reactor in a cylindrical oven, and a TGA apparatus. In the quartz reactor, we measure the temperature and volume of particle in time, in the steel reactor, we obtain the final gas composition of pyrolysis by the outlet connection with microGC-TCD, and, in the TGA, we obtain the mass evolution with time and temperature. Grouping all of these results, we obtain the density evolution of wood particle during pyrolysis and seems to be only dependent of temperature. Finally, we deduce the global reaction of pyrolysis due to mass degradation and gases composition analysis. To summarize, our work consists to group all the necessary data for DEM simulation of wood steam gasification knowing all experimental conditions. We are currently working on the reproduction of these experiments for others temperature of particle and heating rate to confirm our results. The next step is to do a simulation with the experimental parameters and compare it to our experiments results. And, at the end, to produce simulation at industrial scale, and compare it to literature data to evaluate our model.

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