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# High temperature pyrolysis of lignocellulosic biomass for biogas production

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*In this paper, the (first) results of a systematic comparison of the influence of the heating regimes on the pyrolysis of biomasses are presented. Flash and fast pyrolysis regimes as those encountered in the industry are reproduced. The more severe the heating regime the larger the amount of syngas produced and the smaller the amount of solid residues and tar. Cellulose pyrolyses much better than lignin. At high temperature and in flash pyrolysis, there is no evidence of tar production. The specific volume of syngas produced can be above 1 Nm<sup>3</sup>/kg.*

**Keywords:** biomass for energy, pyrolysis.

## I. INTRODUCTION

To meet the objective of reducing the greenhouse gas emissions by 55% in 2030 as stated by Europe and by around 90% in 2050, it is clear that a significant shift away from the fossil resources is required. This is particularly challenging for the energy sector. Biomass transformation into fuels has already been investigated in the last two decades [1]. Biological transformation of biomass (into methane) is a mature route but the resources of adequate biomass will not be large enough and other transformations techniques are needed like “thermochemical conversion” [2]. Some industrial successes are known like coal and biomass co-combustion [3] but more versatile possibilities are offered by the pyrolysis of the biomass (thermal decomposition of the biomass under anaerobic conditions) leading either to a production of gas (syngas), oil or char depending on operating parameters. Only limited industrial demonstration is available today about the various pyrolysis regimes [4, 5] but difficulties were reported [6]. It was suggested that the technological readiness is below 5 [7] and only bio-oil production has gone over pilot scale (TRL>5-6) and is commercially available. The present work focused on high temperature pyrolysis regimes for which mostly syngas and some char are expected. Syngas is a mixture of CO, H<sub>2</sub>, CO<sub>2</sub>,

H<sub>2</sub>O and trace pollutants and char is mostly fixed carbon and ash. Transforming the syngas and the char into hydrogen or methane is considered rather straightforward by the chemical industry BUT the yield and the purity of the syngas should be high enough [8]. Tar, soot, acid gases are poisoning the catalysts needed to ensure the downstream water gas shift reactions.

To our knowledge, little has been done to assess the syngas production potential by pyrolysis [9, 10] and especially the following questions need be addressed further:

- What is the influence of the heating regime (max temperature, heating rate) to promote syngas production?
- What is the influence of the heating regime on the emission of pollutants (acid gases, tar, soot)?
- What is the influence of the composition of the biomass?

It is the ambition of the present work to provide some answers. A specific device (a pilot) was devised to do experiments in conditions that mimics what industrial ovens could reach in terms of heating regime.

The experimental system is presented in section 2 and the results are shown in section 3 and discussed in section 4.

## II. EXPERIMENTAL DEVICE

### A. Selection of the experimental conditions

High temperature (around 1000°C) and high heating rates are expected to favor gas production [11]. In practice 1000°C is a practical upper boundary for large ovens and there is a need to investigate further the influence of the temperature.

Regarding industrial reactors, rotary kilns and fluidized beds reactor are mature technologies compatible with large production rates [12]. The cold biomass is introduced as

particles or pellets of cm size to ease the manipulation. The maximum corresponding heating rate is achieved in a fluidized bed and is limited by the heat transfer inside the pellet so typically a temperature rise of 10 °C/s (for a 1 cm wood pellet immersed in a 1000°C atmosphere with a specific mass of 600 kg/m<sup>3</sup>, a specific heat capacity of 2000 J/kgK and a heat conductivity of about 0.2 W/mK). In the forthcoming this regime will be called “fast pyrolysis”. A smaller rate is expected inside a rotary kiln, the latter being limited by the heat transfer rate from the wall through the porous bed giving a typical heating rate of 0.1 °C/s (assuming a heat conductivity of 0.3 W/m.K and a thickness of the bed of 0.1 m). This is the “slow pyrolysis”. Note that an extremely rapid heating rate can theoretically be reached for small enough particles but very small particles will be in thermal equilibrium with the surrounding gas so that the limiting heating rate will be that of the atmosphere. For a meter sized reactor under a flow velocity on the order of a m/s at 1000°C temperature of the walls, the convective heat transfer coefficient is typically 10-20 kW/m<sup>2</sup> so that the typical heat rate can be above 100°C/s. This is a “flash” pyrolysis”. The experimental conditions were selected to reproduce such conditions.

Regarding biomasses, it is known that they are a mixture of cellulose, hemicellulose, lignin, ash in various proportions and that this has an influence on the pyrolysis [5]. This also need be considered.

### B. Experimental setup

The experiments were carried out using a Nabertherm 30-3000 R100/750/12 tubular oven driven by a B170 controller (Fig. 1). The reaction takes place inside a 310S stainless steel sleeve 1,3 m long and 90 mm inner diameter. As explained later, it is continuously fed with nitrogen from the left end side whereas the gases are emerging from the right end side.

Figure 1. Nabertherm 30-3000 R100/750/12 tubular oven

This tube is longer than the oven since the heating zone is about 70 cm. The non heated extremities were carefully insulated by packing rock wool inside (and maintained by a steel disk) to ensure a homogeneous temperature in the hot zone and to prevent dust and gases to circulate in the colder extremities (Fig. 2). A satisfactory temperature profile was obtained. With this arrangement the temperature can be varied from ambient to 1200°C.

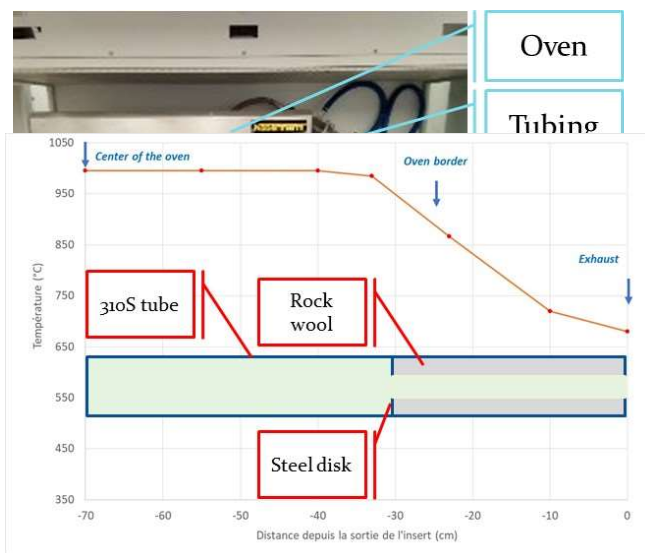
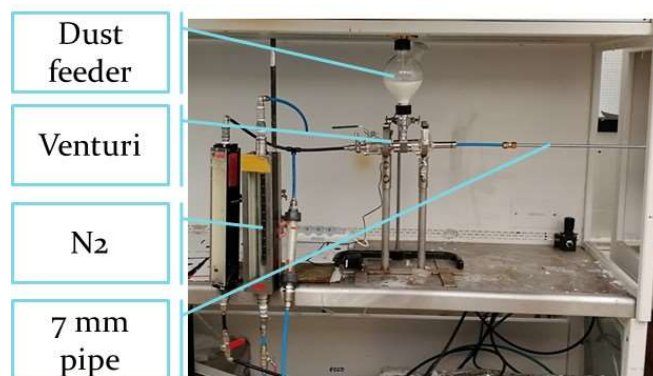


Figure 2. internal arrangement and temperature profile (under a nitrogen flowrate of 3 Nm<sup>3</sup>/h)

Nitrogen is continuously fed via a 7 mm steel pipe not far from at 20 cm from the center of the oven. The first objective is to ensure the thermal homogeneity. The second objective is to mix thoroughly the syngas and dilute it so that a reliable measure of the concentrations is possible and so that the flowrate of syngas could be deduced (nitrogen is a tracer in this case). The third objective is to inject the powdered biomass to reproduce a flash pyrolysis. The flowrate of nitrogen is carefully controlled using rotameters. The flowrate varies depending on the experimental conditions (up to 3 Nm<sup>3</sup>/h to convey and disperse the particles for “flash pyrolysis” experiments). The 7 mm pipe is also insulated to prevent the thermal degradation of the powder before emerging in the oven.

For “flash pyrolysis” experiments the powder is fed into the nitrogen line inside a venturi using a dust feeder (HI Lambda



doser) at a rate between 1 and 20 g/mn (Fig. 3). In a confined environment a jet (that issuing the 7 mm pipe) recirculates close to the injection point and the heat transfer rate is rather large. A few cms are enough to reach the maximum temperature. A lower bound for the heating rate is given by the ratio between the maximum temperature and the residence time. The mass flowrate of gas is 1 g/s and that contained in the heating zone of the oven is about 1.2 g. the residence time is then about 1s so that the heating rate is on the order 1000 °C/s (the particle size is small enough to ensure thermal equilibrium even at such high heating rate).

Figure 3. Nitrogen supply, venturi, dust feeder and 7 mm pipe

For “fast and slow pyrolysis”, a fixed quantity of biomass (1-10g) is deposited in a thick (3 mm thickness) steel rectangular tray (20 mm high, 20 mm large and 80 mm long). The tray (Fig. 4) is inserted from the exhaust orifice of the oven and guided towards the center of the oven in an open top duct.



Figure 4. the tray containing the biomass and its guiding open pipe.

To obtain a “fast pyrolysis” regime, the tray is rapidly inserted inside the oven when the latter has reached its targeted temperature. To control the heating regime, the tray was filled with dry sand (90 g) and K thermocouples (shielded, 1 mm) weighted were inserted inside, at the bottom, in the middle and at the top of the sand deposit. A typical temperature reading is shown on Figure 5. At the center, the heating rate is about 4°C/s. To extrapolate to the biomass, the correlation proposed by Dupont et al. [13] can be used bearing in mind the specific heat capacities of sand and tested biomasses (see after) are typically about 830 and 2000 J/kgK and that the respective masses when the tray is full are 90 g and 15 g. The heating rate for the “fast pyrolysis” regime is then about 10°C/s.

To obtain a “slow pyrolysis” regime, the tray was prepared and inserted before starting the heating of the oven. Again, the nitrogen flowrate ensures a homogeneous temperature inside. The ramp is set to 600°C in our hour and the corresponding heating rate is about 0.2°C/s.

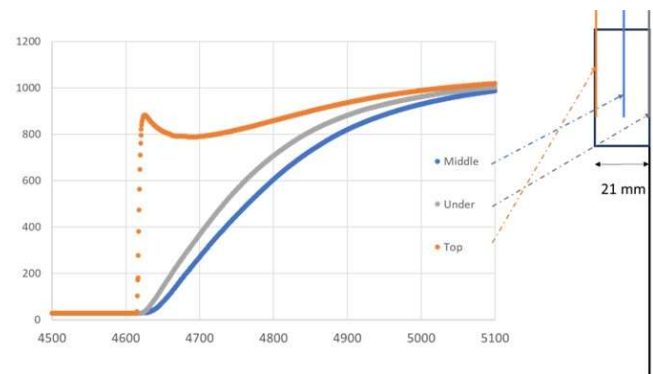


Figure 5: Fast heating regime of 90g dry sand in the tray / oven regulated at 1050°C

As said, the temperatures of the oven and in the tray were recorded using a SEFRAM device. The masses were measured using a Sartorius ED6202S scale (accuracy  $\pm 0.01$  g). the flowrate of nitrogen is very stable but may vary by  $\pm 0.1$  Nm<sup>3</sup>/h. To measure the composition of the syngas, a fraction of it (60 l/h) was pumped toward a XSTREAM XEGP (CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> and O<sub>2</sub>) towards a Horiba 2000 analyzer (SO<sub>2</sub> and NO<sub>x</sub>). Before entering the analysers, the sample was bubbled in isopropanol to remove tar, water and solids and then went through a dessicator containing silicagel (Fig. 6). The sample was pumped downstream the bubbler and dessicator (less than 1% error of linearity so a precision of  $\pm 0.1\%$  for all gases at 10% volume fraction). Note the response time of the sampling system is on the order of a minute.

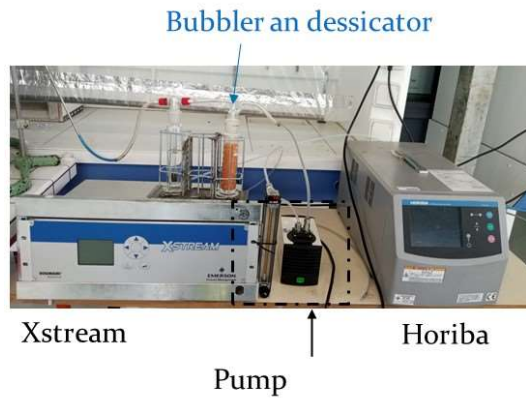


Figure 6. gas analysers

The Karl Fisher method was implemented (C30 Coulometric KF Titrator) on isopropanol samples to assess the H<sub>2</sub>O fraction in the syngas. Tars are not quantified in the present experiments but the color of the isopropanol sample can be an indication since tar tends to color isopropanol in a deep yellow or brown.

### C. Test conditions

Preliminary experiments revealed that pyrolysis becomes efficient above 900°C (below, a lot of unreacted biomass remains). Temperatures ranging from 900°C to 1100°C were selected.

To investigate the influence of the biomass, tests were done with cellulose, lignin and a third product, starch with an atomic composition comparable to that of cellulose but with a different molecular configuration (Table I: mass proportions). Lignin was provided from CIMV (Compagnie Industrielle de la Matière Végétale), cellulose from Thermo Scientific (90 μm, CAS 9004 34-6) and starch from Thermo Scientific.

TABLE I. MASS PROPORTIONS

Biomass	C	H	N	S	O	ash
lignin	59.65	5.72	1.81	0.02	31.22	1.58
cellulose	43.4	6.23	0	0	49.86	0.51
starch	42.2	6.2	0	0	43.33	8.27

The test matrix is shown on Table II.

TABLE II. TESTS PERFORMED

Heat rate and ref	Biomass	Temperature (°C)
Slow1	Cellulose	900

Slow2	Lignin	900
Fast1	Cellulose	900
Fast2	Cellulose	900
Fast3	Cellulose	1000
Fast4	Cellulose	1100
Fast5	Lignin	900
Fast6	Lignin	1000
Fast7	Lignin	1100
Flash1	Cellulose	900
Flash2	Cellulose	1000
Flash3	Cellulose	1100
Flash4	Lignin	900
Flash5	Lignin	1000
Flash6	Lignin	1100
Flash7	Starch	1100

## III. RESULTS

### A. Data reduction

The results for test “flash 2” are given as an illustration. On Figure 7 is shown the evolution of the gas composition measured by the XSTREAM analyzer. The introduction of the dust starts at  $t=70$  s approximately and ceases 5 mns later at time  $t= 370$  s which corresponds to the drop in the concentration measurements. The gradual increase of the concentrations is due to the time required to sweep the sampling line/volumes (and similarly for the decrease).

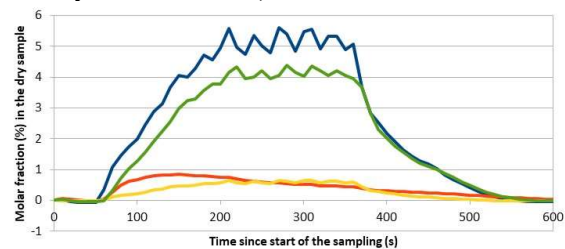


Figure 7. XSTREAM readings for Flash2 test with nitrogen flowrate  $F_{N_2}=1.6$  Nm<sup>3</sup>/h and a biomass rate  $m=3$  g/mn

Unfortunately, the concentrations traces are sometimes more difficult to interpret typically for “fast” pyrolysis exhibiting highly transient signals (1 to 3 mn). In such situations, the sampling response time was somewhat too large and the results are only indicative. We also had difficulties with the condensation of water vapor in the bubbler which induced variations in the sampling flowrate. This had a significant influence on the estimate of the water content in the exhaust.

On Fig.8, the proportions of acid gases are shown. The plateau occurs when the analyzer is disconnected to fill a bag for a GC analysis for verifications.



Figure 8. HORIBA readings for Flash2 test with nitrogen flowrate  $F_{N_2}=1.6$   $Nm^3/h$  and a biomass rate  $m=3$   $g/min$

In such test, when spraying the dust, it is hard to distinguish residues in the oven and the exhaust seems transparent and the isopropanol sample also (see later).

The molar fractions  $x_{i,0}$  on Fig. 7 and Fig. 8 are measured on a dried sample. The water molar fraction,  $x_{H_2O}$  is deduced from the analysis of the isopropanol:

$$x_{H_2O} = \frac{y_w \cdot M_{isopropanol}}{Q_{sample}} \cdot \frac{V_{molar}}{MM_{H_2O}} \quad (1)$$

Where  $y_w$  is the mass proportion of water in the isopropanol (mass  $M_{isopropanol}$  in the bubbler),  $Q_{sample}$  is the volume of gases pumped towards the analyzers.  $MM_{H_2O}$  is the molar mass of water and  $V_{molar}$  the volume of a mole of gas. In this test, we found  $x_{H_2O}=0.02$ . Note  $x_{H_2O}$  is an averaged value over the sampling time and should strictly be compared to similar averages. Then, the (averaged) molar fraction of gas  $i$  in the exhaust stream, including humidity is:

$$x_i = x_{i,0} \cdot (1 - x_{H_2}) \quad (2)$$

Raw data are presented in the appendix providing the operational details,  $x_{H_2O}$ , the quantity of solid residue, the maximum (or plateau value) and the averaged values for  $x_{i,0}$  over the reaction period.

The balances and yields can be derived from the averaged  $x_i$ . For instance, if we admit that most of the gases, in volume, are  $H_2O$ ,  $CO$ ,  $CO_2$ ,  $CH_4$  and  $H_2$  (verified later on the mass balance) in addition to  $N_2$ , then the volume emerging from the oven reads,  $Q_{outlet}$ :

$$Q_{outlet} = \frac{Q_{N_2}}{1 - (x_{CH_4} + x_{H_2} + x_{CO_2} + x_{CO} + x_{H_2O})} \quad (3)$$

Where  $Q_{N_2}$  is the amount of nitrogen having flown through the oven during the measurement (sampling time). In practice, we are interested into the fraction containing  $CO$ ,  $CH_4$  and  $H_2$  which we will call "syngas" as the valuable part of the exhaust. The ratio between the volume of this syngas,  $V_{syngas}$ , and the mass of biomass is seen an important parameter and is obtained as:

$$V_{syngas} = \frac{x_{CH_4} + x_{H_2} + x_{CO}}{(1 - (x_{CH_4} + x_{H_2} + x_{CO} + x_{CO_2} + x_{H_2O}))} \cdot \frac{Q_{N_2}}{M} \quad (4)$$

Where  $M$  is the quantity of biomass submitted to the test. For Flash2 test,  $V_{syngas} = 1.1$   $Nm^3/kg$  and the syngas contains similar proportions of hydrogen and  $CO$ .

The mass balance for carbon and hydrogen is performed based on the element analysis of the biomasses (Table I : the mass fraction of carbon is named  $w_C$  and that for hydrogen  $w_H$ ) and quantities of pyrolyzed products. For gas  $i$ :

$$Q_i = x_i \cdot Q_{outlet} \quad (5)$$

Solid residues,  $M_{res}$ , (very black) are assumed to be pure carbon for cellulose and lignin since the ash content is so small. Then:

$$\eta_H = \frac{(2 \cdot Q_{H_2} + 2 \cdot Q_{H_2O} + 4 \cdot Q_{CH_4}) \cdot MM_H}{V_{molar} \cdot M \cdot w_H} \quad (6)$$

And

$$\eta_C = \frac{(Q_{CO} + Q_{CO_2} + Q_{CH_4}) \cdot MM_C}{V_{molar} \cdot M \cdot w_C} + \frac{M_{res}}{M \cdot w_C} \quad (7)$$

Where  $MM_H$  and  $MM_C$  are respectively the molar masses on monoatomic hydrogen and carbon. For "Flash2" test,  $\eta_H=0.99$  and  $\eta_C=0.8$  suggesting a very good pyrolysis.

About the acid gases,  $NO_x$  is nearly absent which is logical given the temperatures.  $SO_2$  should better be expressed as a mass of sulfur (S) emitted in the atmosphere by kg of biomass:

$$m_S = \frac{Q_{SO_2}}{V_{molar} \cdot M} \cdot MM_S \quad (8)$$

For "Flash 2" test,  $m_S$  is 0.94  $g/kg$ .

## B. Results

Some indication about the reproducibility is given in Table III with the results of the same experimental configuration

reproduced twice (the gas percentages are the portions of CO, H<sub>2</sub> and CH<sub>4</sub> in the syngas).

TABLE III. REPEATABILITY (FAST 1 AND 2)

Test	V <sub>syngas</sub>	%CO	%CH <sub>4</sub>	%H <sub>2</sub>	ηC	ηH	m <sub>s</sub>
Fast1	0.51	67	12	22	0.46	0.31	1.39
Fast2	0.53	68	11	21	0.48	0.31	1.70
%gap	4	1	9	5	4	0	12

The gap is typically a few percent which in reasonable agreement with the cumulated uncertainties about the gas flowrate and concentration measurements. On that aspect, the results of Table III are similar and this indicates some repeatability.

The graphical evolution of the specific volume of syngas (again only the part of the exhaust gases containing H<sub>2</sub>, CO and CH<sub>4</sub>) is shown on Fig. 9.

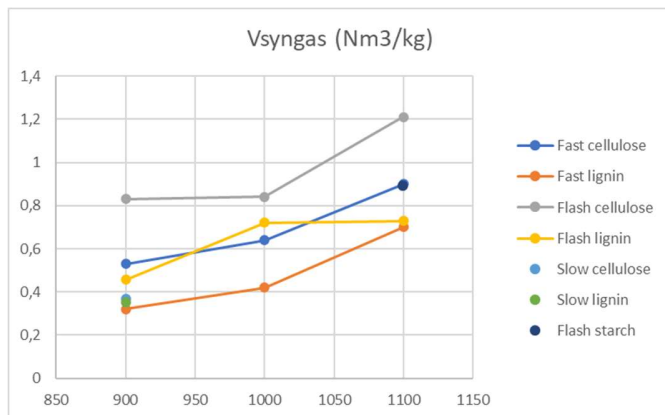


Figure 9. V<sub>syngas</sub> as function of the temperature of the reaction for the various dusts and the various heating rates

At a given temperature and for a given biomass, V<sub>syngas</sub> increases significantly with heating rates. For cellulose heated at 900°C : “flash” (0.8 Nm<sup>3</sup>/kg) > “fast” (0.5 Nm<sup>3</sup>/kg) > “slow” (0.35 Nm<sup>3</sup>/kg). There is a general trend towards increasing with the reaction temperature. The incidence of the nature of the biomass is rather clear. V<sub>syngas</sub> is greater for cellulose than for lignin for most pyrolyzing conditions. Starch seems to produce less syngas that cellulose despite a rather close atomic composition.

The composition of the syngas is shown on Fig. 10. First temperature does not seem to play a great role. Surprisingly, the composition of the syngas is nearly identical for all biomasses under the flash pyrolysis regime with approximately the same proportions of hydrogen and CO. Differences as function of the

biomass are more apparent for the other heating regimes. In the fast heating regime, lignin produces much more methane and releases less CO.

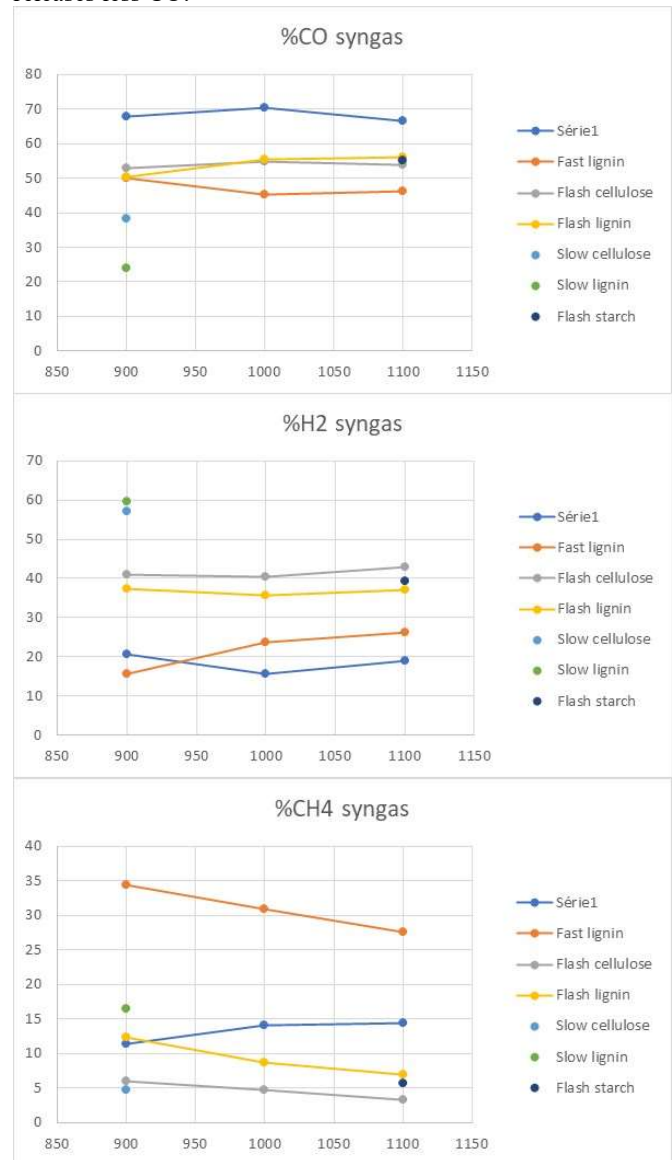


Figure 10. Syngas composition as function of the temperature of the reaction for the various dusts and the various heating rates

Hydrogen and carbon mass balances are shown on Fig. 11, separating the carbon and hydrogen contained in what we named “syngas” from the carbon the hydrogen contained in the other gases, water vapor and CO<sub>2</sub>. As said below, the “fast” pyrolysis results are less accurate than the others due to the (too) short duration of the reaction as compared to the response time of the

sampling line. The estimate of the water content is also to be considered cautiously due to the variations of the sampling flowrate especially again during the short “fast” pyrolysis tests.

Globally, the carbon mass balance is not closed. CO<sub>2</sub> is less than 15% of the carbon budget. Slow and fast pyrolysis of lignin produces a lot of solid carbon deposits (in the tray) unlike cellulose. The amount of carbon recovered under the form of the syngas increases with the temperature (fast pyrolysis of lignin from 900 to 1100°C : yield from 0.23 to 0.45) and the heating rate (pyrolysis of cellulose at 900°C from “slow” to “fast” : yield from 0.18 to 0.48). This amount is larger for cellulose than for lignin (flash pyrolysis at 900°C : yield 0.23 for lignin and 0.56 for cellulose).

The hydrogen mass yield seems much closer to 1 on average. Sometimes it is even above 1 which is not logical but is due to the experimental difficulties expressed before. About the titration method the authors also consider, it may not be reliable enough especially when very small and very large quantities of water are produced. It can only be said that water vapor is a large contributor.

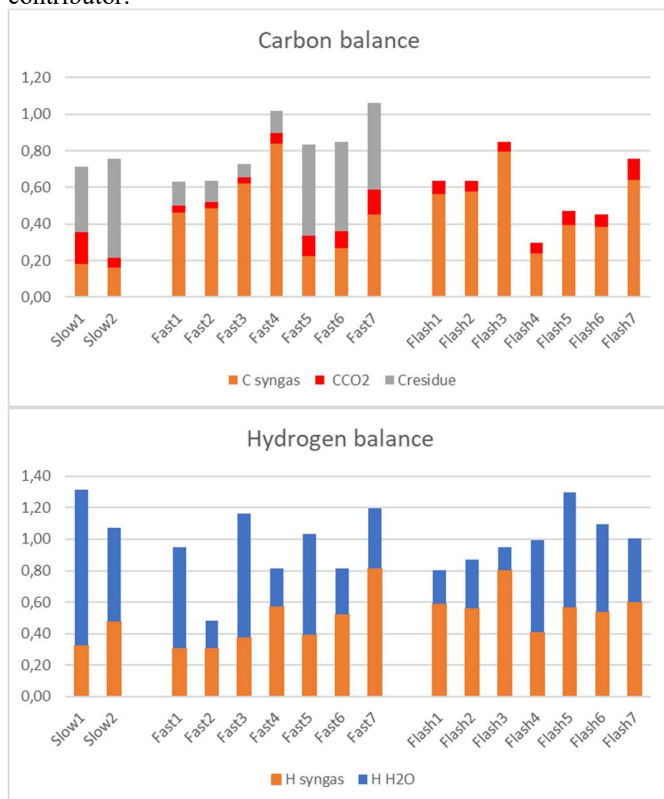


Figure 11. Carbon and Hydrogen mass balances for all tests

Where is the missing carbon ? Preliminary GC measurements (not shown) suggest that the dry gases do not content more than N<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>. Water is trapped into the isopropanol and possibly other condensable vapors. It can be wondered whether tar is trapped also. Some photographs of the amounts of isopropanol used for the different tests are shown on Fig. 12.

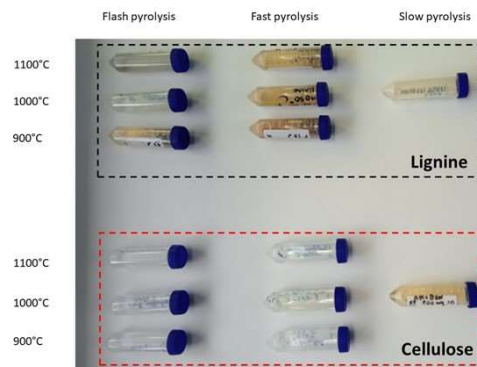


Figure 12. contents of the isopropanol bubbler after each test.

Tar is clearly present for lignin tests. Much less for cellulose. The amount of tar apparently diminishes while increasing the severity of the pyrolysis (temperature and heating rate). Since the carbon balance is not close even with cellulose under harsh conditions where tar seems absent, it is postulated that soot under the form of tiny particles is formed and could be trapped somewhere.

The last point is about SO<sub>2</sub> (Fig. 13). SO<sub>2</sub> emissions (g/kg) increase with the temperature from 1.5 to 2.5 for fast pyrolysis of cellulose. Still for cellulose, flash pyrolysis produces less SO<sub>2</sub> (-44%) but the situation is more complicated with lignin. Starch has the lowest SO<sub>2</sub> emission at 1100°C.

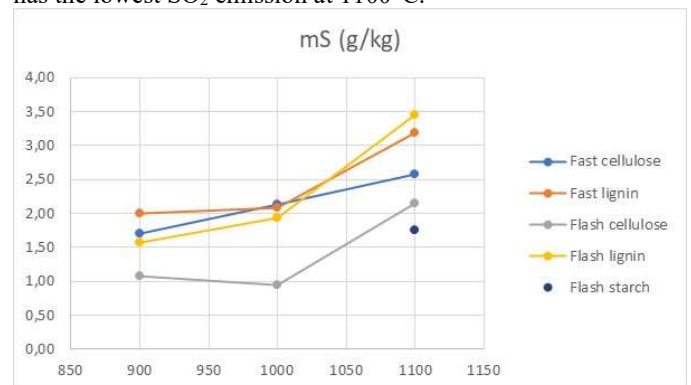


Figure 13: emissions of SO<sub>2</sub> for the various biomasses, temperatures and heating regimes.

#### IV. DISCUSSION





### A. Heating rate

Slow to flash heating rates of cellulose and lignin at 900°C greatly favors the production of gas. Similar conclusions were drawn earlier (for instance in [14]) on rice husk heated at 850°C with a gas yield growing from 0.25 to 0.75. The composition of the syngas also changes but without a clear correlation with the composition of the biomass. The specific behavior of CH<sub>4</sub> was noticed which might reveal a thermal degradation of tar [15]. In this cited study, the authors found a direct correlation between the amount of CH<sub>4</sub> produced and the degree of degradation of benzene, a molecule representing tar. A chemical path was proposed. Slow heating rate leads to char formation and fast heating rates favors tar chemistry. Competing chemical mechanisms exist between char/gas on one side and tar on the other side which seems to account for the slow and fast pyrolysis [16]. But it fails to explain the flash pyrolysis regime where both methane and char tend to disappear. Note for this specific regime, the kinetic limit could be kicked [17].

As noted above, the carbon balance of the “measured” products (solid residue+ sampled gases) as compared to what available in the biomass is not closed. In slow and fast pyrolysis, the isopropanol of the bubbler is colored suggesting tar has been dissolved. This is coherent with the significant amount of CH<sub>4</sub> as said in the preceding paragraph and confirms other observations [18].

### B. Temperature of the pyrolysis

It has been often shown, in line with the present measurement, that increasing the temperature strongly favors the production of gases [9, 11, 19]. There is not much data above 1000°C but increasing further the temperature may increase the yield [20] as found in the present work.

The carbon yield increases with the reaction temperature probably partly at least because of tar decomposition into gases. Yan Zhang et al. [20], observed a decrease in the tar yield from 10% at 900°C to 2% at 1100°C in flash type of pyrolysis.

To our knowledge, there is limited information available on SO<sub>2</sub> and NO<sub>x</sub> emissions during the pyrolysis of biomasses. The presence of NO<sub>x</sub> is not detectable. The sulfur content emitted in the gases by kg of biomass is roughly multiplied by two from 900°C to 1100°C. For coal [21], SO<sub>2</sub> emissions do not increase with the temperature ( 600-1200°C range).

### C. Nature of the biomass

Cellulose produced more gases than lignin under the same conditions which was also observed earlier. In [22], at 900°C and 6°C/s heating rate, cellulose produces 510g/kg of gases and lignin 235g/kg. This seems reasonably in line with the present testing (see tests Fast 1 and Fast 5 knowing the specific mass of the syngas is about 0.85 kg/m<sup>3</sup>).

The nature of the biomass has an influence on the composition of the gases only in slow and fast regime and this difference is manifested by a much larger content of methane for lignin. Similar trends were found before [22].

Starch and cellulose are close in terms of atomic composition. Only the flash pyrolysis regimes at 1100°C were compared. The syngas compositions are exactly the same, but the specific volume of syngas produced is smaller (0.9 Nm<sup>3</sup>/kg for starch and 1.2 Nm<sup>3</sup>/kg for cellulose). Note however the starch sample contains more ash (8.3 % as compared to 0.5%) and, in practice, is more humid (5% as compared to less than 1%). Correcting for those inerts will provide a specific volume of syngas of 1.05 Nm<sup>3</sup>/kg with is now closer to that of cellulose but still smaller. Furthermore, the carbon yield is still below that for cellulose and more CO<sub>2</sub> is produced. This might illustrate the influence of the bounding of the various atoms in the molecule. Note that starch could also represent biomasses perhaps more realistically than cellulose.

## V. CONCLUSION AND PERSPECTIVES

In this paper, the (first) results of a systematic comparison of the influence of the heating regimes on the pyrolysis of biomasses are presented. The techniques used are described which favors online measurements. Flash and fast pyrolysis regimes as those encountered in the industry are reproduced. The more severe the heating regime the larger the amount of syngas produced and the smaller the amount of solid residues and tar. Cellulose pyrolyses much better than lignin. At high temperature and in flash pyrolysis, there is no evidence of tar production. Very preliminary results of GC analysis of the gas phase and of the trapped liquid phase suggest only very small molecules are produced in the gases and no tar is detected. Yet, the experiments need to be reproduced using more refined metrology especially for the water content.

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Test #	Biomass	Temp (°C)	FN2 (Nm3/h)	Gas sampling (l/h)	Biomass mass (g)	Solid residue (g)	Xstream reaction time (min)	H2 specific vol (Nm3/kg)	CO2 specific vol (Nm3/kg)	H2O specific vol (Nm3/kg)	Max H2 on dry sample (% v/v)	Max CO on dry sample (% v/v)	Max CH4 on dry sample (% v/v)	Horba sampling time (min)	S specific mass (g S/kg)
Slow1	Cellulose	900	1,97	50	15,3	2,38	83,3	0,21	0,017	0,14	0,74	0,3	1,1	0,2 X	X
Slow2	Lignin	900	1,172	55	19,94	6,46	88,3	0,21	0,058	0,084	0,41	0,21	0,15	0,17 X	X
Fast1	Cellulose	900	1,688	50	10,26	0,58	2,5	0,11	0,06	0,34	0,48	1,86	6,87	1,29	4,9
Fast2	Cellulose	900	1,876	50	19,5	0,98	3	0,11	0,06	0,36	0,13	1,96	7,46	1,26	9,9
Fast3	Cellulose	1000	1,688	50	15,1	0,87	1,67	0,11	0,09	0,45	0,39	2,9	11,83	2,35	2,13
Fast4	Cellulose	900	1,782	50	15,1	0,77	2,05	0,13	0,16	0,46	0,46	1,22	3,39	3,39	2,08
Fast5	Lignin	900	1,976	50	15,13	0,75	3,33	0,05	0,13	0,46	0,46	0,56	2,45	1,22	6,4
Fast6	Lignin	1000	1,782	50	15,12	4,39	3,83	0,1	0,13	0,11	0,2	1,25	2,33	1,6	8,7
Fast7	Lignin	1100	1,629	50	15,05	4,28	4,17	0,16	0,2	0,34	0,28	2,44	5,51	3,13	3,19
Flash1	Cellulose	900	1,6415	50	14,02	0	5	0,34	0,05	0,44	0,16	4,1	5,2	0,6	9,9
Flash2	Cellulose	1000	1,5	50	14,5	0	5	0,34	0,04	0,46	0,23	5,55	6,85	0,41	9,6
Flash3	Cellulose	1100	1,875	50	23,6	0	7,8	0,52	0,04	0,65	0,48	4,1	5,16	0,58	6,7
Flash4	Lignin	900	1,629	50	11,9	0	3,83	0,17	0,056	0,23	0,07	0,4	2,34	3	6
Flash5	Lignin	1000	3,283	50	16,5	0	5,83	0,25	0,07	0,4	0,09	0,5	1,72	2,48	10
Flash6	Lignin	1100	3,283	50	14,5	0	4,83	0,27	0,05	0,41	0,08	0,33	1,87	2,62	6,25
Flash7	Starch	1100	3,293	50	26,35	0	6,07	0,50	0,85	0,49	0,1	2,09	2,70	0,34	1,45

Test #	Biomass	Temp (°C)	Vsyngas (Nm3/kg)	% CO syngas (v/v)	% CH4 syngas (v/v)	% H2 syngas (v/v)	C yield in syngas	H yield in syngas	C yield in products	H yield in products
Slow1	Cellulose	900	0,367	38	5	57	0,18	0,33	0,71	1,32
Slow2	Lignin	900	0,382	24	16	60	0,16	0,47	0,71	1,07
Fast1	Cellulose	900	0,51	67	12	22	0,46	0,31	0,63	0,95
Fast2	Cellulose	900	0,53	68	11	21	0,48	0,31	0,63	0,48
Fast3	Cellulose	1000	0,64	70	14	16	0,62	0,37	0,73	1,16
Fast4	Cellulose	900	0,53	68	11	21	0,48	0,31	0,63	0,48
Fast5	Lignin	900	0,42	50	34	16	0,23	0,39	0,82	0,83
Fast6	Lignin	1000	0,42	45	31	24	0,27	0,52	0,85	0,82
Fast7	Lignin	1100	0,7	49	29	23	0,45	0,82	1,06	1,19
Flash1	Cellulose	900	0,83	53	6	41	0,56	0,59	0,63	0,80
Flash2	Cellulose	1000	0,84	55	5	40	0,58	0,56	0,63	0,87
Flash3	Cellulose	1100	1,21	54	3	43	0,79	0,80	0,85	0,95
Flash4	Lignin	900	0,495	50	12	37	0,24	0,41	0,30	0,99
Flash5	Lignin	1000	0,495	50	12	37	0,24	0,41	0,30	0,99
Flash6	Lignin	1100	0,73	56	7	37	0,39	0,54	0,45	1,09
Flash7	Starch	1100	0,89	55	6	39	0,64	0,60	0,76	1,00

