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Pyrolysis of centimetre-scale wood particles: New experimental developments and results

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A B S T R A C T

This work is devoted to the pyrolysis of centimetre-scale wood particles, for temperature ranging between 450 and 1050 °C. A specific device has been designed to perform pyrolysis tests on a single particle and to collect both thermal and chemical data which are necessary to describe pyrolysis at centimetre-scale. Temperature profiles inside the sample are monitored during pyrolysis. Char, gas, tars and water yields, as well as the elemental composition of each class of products are measured. The yields of the main gaseous species (CO, CO_2, CH_4, C_2H_4 and H_2) are monitored during the reaction. Tars are collected, and six compounds are quantified.

1. Introduction

Facing the worldwide growing demand of energy while reducing the anthropogenic greenhouse gas emissions, leads to the increasing exploitation of renewable energy sources [1]. In this context, biomass, which is currently the fourth largest source of energy in the world, appears to be the main renewable solid energy resource available which can provide liquid, gaseous and solid fuels [2,3]. Biomass includes a wide range of biological materials from microalgae to municipal waste. Lignocellulosic biomass, which refers to plants composed of cellulose, hemicelluloses and lignin, represents an important resource of renewable energy equal to twice the world consumption of primary energy in 2004 [4]. The recoverable production comes mainly from wood production and agricultural waste [4,5]. Wood as chips is a common feedstock to process for biomass upgrading into energy [6]. Typical granulometry for woodchips involved in industrial installations lies between 8 mm and 100 mm [7]. Among the industrial reactors designed to perform wood conversion, particular technologies are characterized by a particle residence time of several minutes, for example fluidized bed reactors. Centimetre-scale particles like wood chips are injected in such reactors [8].

It is of interest to better understand the pyrolysis of centimetre-scale particles, as it is a key step in the processes of biomass thermo-chemical conversion. Pyrolysis is either a pre-treatment step or it is the first step of combustion or gasification. It consists in a thermal degradation of biomass polymers under inert atmosphere. It results in the production of char, tars, water and gas. Char is the carbonaceous solid residue and in this paper, tars refer to condensable products excluding water.

Literature contains relevant approaches to simulate a centimetre-scale wood particle pyrolysis [9–11]. Models have different degrees of complexity looking at kinetic schemes, numerical approaches and considered phenomena. From the simplest to the most complex one, all models require an experimental data set to be validated. Both thermal and chemical data are necessary to describe centimetre-scale particle pyrolysis. Thermal data mainly consist of external heat flux or internal temperature profiles; chemical data should include yields of char, gas, tars and water, species characterization and quantification.

On the one hand most of experimental studies describe pyrolysis of thermally thin particles at micrometric or millimetric scales. Heating can be assumed to be uniform inside the particle body for small samples, but the encountered conditions in industrial processes with centimetre-scale particles are often different. It is therefore of interest to investigate experimentally the pyrolysis of thermally thick particles. On the other hand experimental studies carried out on large particles are mainly focused on structural change and particle mass loss measurements [9]. There is a lack of experimental data, both thermal and chemical, which can be used to validate a pyrolysis model of a single centimetre-scale particle. This study aims to contribute to fill in this gap by presenting experimental developments and measurements of products yields and temperature during pyrolysis of a single beech wood particle. For

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Table 1
Overview of the characteristics of different experimental setups used to study the pyrolysis of large particles.

	Ref.	A	B	C	D	E	F
Macro-TG	[12]	350–500 °C	✗	furnace power: 1 kW convective heat transfer coefficient evaluated at 8.4 W m^{-2} K^{-1}	√	Not evaluated	✗ Gas yields are not measured online
Macro-TG	[13]	700–900 °C	√	✗	√	Not evaluated	√ GASBOARD3100 flue analyzer
Macro-TG	[14]	up to 900 °C	√	✗	✗	Not evaluated	√ Gas chromatographer Varian CP-4900 microGC
Macro-TG	[15]	up to 900 °C	√	✗	√	Not evaluated	√ FTIR microGC
Xenon arc lamp reactor	[16]	up to 900 °C	√	Heat flux 80 kW/m^2 and 130 kW/m^2	√	√	✗ Mass loss is not measured online URAS 10E CO/CO2 analyzer SIGNAL Hydrocarbon analyzer model 3000
Lamp reactor	[17]	up to 700 °C	√	Heat flux 28–80 kW/m^2	√	✗	√ microGC
Tubular reactor	[18]	up to 950 °C	✗	Furnace power 576 kW	✗	✗	✗
Other facilities	[19]	300–860 °C	√	✗	√	✗	✗ Mass loss is not measured online
Other facilities	[20]	up to 1327 °C	√	✗	√	Not evaluated	√ Ceramic capillary connected to a mass spectrometer

A: What is the available temperature range?
B: Is the heating rate controlled?
C: Is the external heat flux characterized?
D: Are internal temperature profiles measured?
E: Is the residence time of pyrolytic vapours lower than a few seconds?
F: Are sample mass loss and gas yields measured online? What is the equipment for gas analysis?

this purpose a specific device called PYRATES has been designed and built. Performances of this new experimental setup are compared with those of existing devices in literature. The pyrolysis of cylindrical centimetre-scale particles of beech wood is then studied in the temperature range 450–1050 °C.

2. Literature review about experimental investigations

This literature review is focused on experimental setups where a single centimetre-scale particle is involved. Four categories of experimental setups are distinguished [9]:

Macro-Thermo-Gravimetric setups (macro-TG) [12–15]
Lamp reactors [16,17]
Horizontal tubular reactors [18]
Other facilities [19,20]

Table 1 proposes an overview of setups characteristics regarding some selected criteria.

Macro-TG is the most frequently used device for studying the pyrolysis of centimetre-scale wood samples. It provides information on both mass loss and temperature variations of the involved biomass particle. Macro-TG experiments have a main drawback: the heating rate is much lower than that in real industrial reactors.

In comparison with macro-TG, lamp reactors provide a controlled and constant external heat flux, which is representative of those encountered in industrial gasifiers [17]. These reactors are particularly adapted to the study of primary pyrolysis, because the design minimizes tars cracking reactions by using a high flow rate of carrier gas to sweep produced volatiles at particle surface [16].

Tubular reactors are also used to study pyrolysis of centimetre-scale particles. The heating rate is not well controlled and the residence time of pyrolytic vapours in the heating area is quite large: it can reach a few seconds. The reactor volume is also quite large relative to the involved quantity of biomass, which results in the dilution of the species produced during a test. The mass loss of the solid is not monitored continuously [18].

Other devices, which do not belong to the previously described categories, have also been identified [19,20]. In these experimental set-ups the particle is dropped into the pre-heated reactor through a retractable vertical tube and the surface temperature of the sample is measured by Laser-induced phosphorescence technique [20].

The review about experimental setups used to investigate the pyrolysis of centimetre-scale particles shows that there is no available device where temperature or heat flux is imposed, heating conditions are controlled and homogeneous secondary reactions are limited.

Moreover very few studies determine the yields of the different classes of pyrolysis products (gas, tars, water and char). When yields are determined, the mass balance is not often presented. The variations of solid mass, density, shape or size of the particle and qualitative observations on the particle appearance are the main focus of most experimental works [18,20–23]. For example, studies on single particle reactors provide mainly time-resolved data about particle structural changes. Gaseous components yields (CO, CO_2, H_2O, CH_4, H_2) and sample mass are measured. However tars are not analyzed [19,20]. In studies involving a tubular furnace the produced gases are collected in a sampling bag and eight of them are quantified (CO, CO_2, H_2O, CH_4, H_2, C_2H_2, C_2H_4, C_2H_6 and C_6H_6) [18]. Generally, it is difficult to find accurate thermal characterization of the furnace coupled with results of pyrolysis products chemical analysis. However, study of large particles pyrolysis must take into account the coupling of thermal and chemical phenomena [24]. In other words, there is a lack of full coherent experimental data set which can be used to validate pyrolysis models of a single centimetre-scale particle.

This article presents a new experimental setup called PYRATES developed with the aim to fill in this gap.

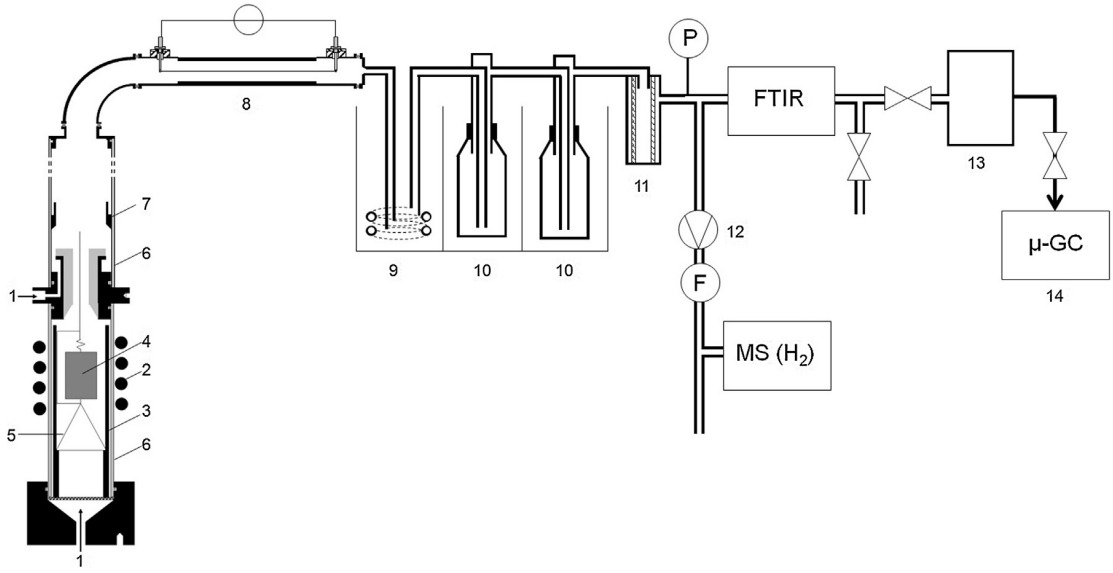

Fig. 1. Experimental device PYRATES.
(1) Nitrogen inlets; (2) Inductor; (3) Inconel pipe heated by induction; (4) Wood sample; (5) Metallic sample holder; (6) Quartz pipes; (7) Tar collector; (8) Electrostatic precipitator; (9) Ice trap; (10) Isopropanol and dry ice traps; (11) Cartridge filter; (12) Pump; (13) Tedlar bag; (14) micro-Gas Chromatography; P: Pressure indicator; F: Flow metre.

3. Materials and methods

3.1. PYRATES experimental device

The experimental device called PYRATES is depicted in Fig. 1.

This equipment has been developed to study the pyrolysis of a single centimetre-scale sample. A 12 kW induction furnace heats an Inconel pipe with a four-coil inductor (see Fig. 2). The temperature of the Inconel pipe can not exceed 1300 °C. The temperature at the surface of the Inconel pipe is measured and regulated with a two-colour pyrometer (IMPAC infratherm) between the two central coils. A quartz pipe provides the sealing of the furnace. The power of the inductor is controlled, with a GEFRAN 2500 regulator, to fix the temperature of the Inconel pipe. With this equipment, the heating rate of the Inconel pipe can reach 500 °C s^{-1}. Pyrolysis tests were carried out with temperature set points ranging between 500 °C and 1100 °C.

A metallic holder maintains the wood sample on the axis of the Inconel pipe. At the bottom of the Inconel pipe, a metallic grid retains char pieces when the sample cracks during pyrolysis.

The Inconel pipe is swept by nitrogen at ambient temperature (2Nl min^{-1}) to carry away the vapours produced during pyrolysis. Above the Inconel pipe, this flow is mixed with nitrogen at ambient temperature (1–3Nl min^{-1}) to cool down the volatile matter and quench the secondary homogeneous reactions. PYRATES setup presents the advantage to have a small heating area so that secondary homogeneous reactions should be limited. The propensity of occurrence of such reactions is discussed further.

A first fraction of organic vapours is condensed on the wall of the quartz pipe and collected in the tar collector (see Fig. 1). The rest of the droplets, entrained by the gas flow are trapped in a 0.5 mA and 7 kV electrostatic precipitator. The gas then passes into three cold traps in series to collect the rest of the condensable pyrolytic vapours, mainly water and acetic acid. The first cold trap is at 0 °C and the others are at −70 °C using a mix of carbonic ice and isopropanol. Then the gas goes towards the online analyzers. A cartridge filter is used to protect the analyzers. The gas is finally collected into a tedlar bag; part of the flow is analyzed with the Mass Spectrometer.

3.2. Wood samples

Each experiment is carried out with a single beech wood particle, which is a cylinder, 20 mm in diameter and 30 mm in height. Sample dimensions are representative of typical centimetre-scale woodchip [7]. The grain direction is parallel to the cylinder axis.

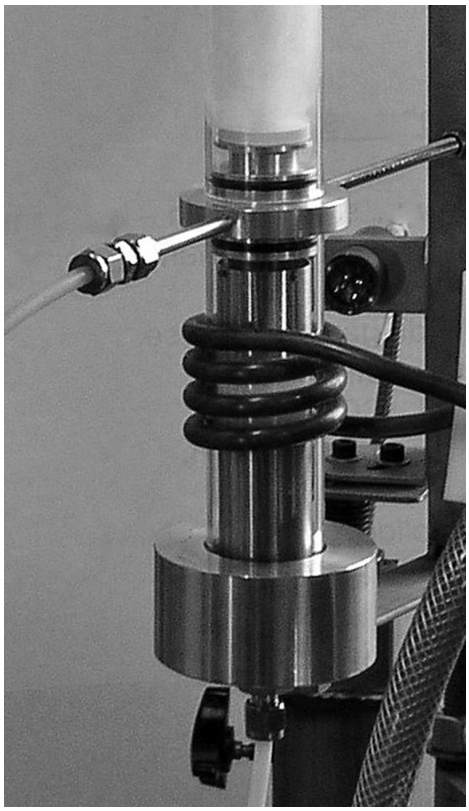

Fig. 2. Picture of a part of the heating area of PYRATES.

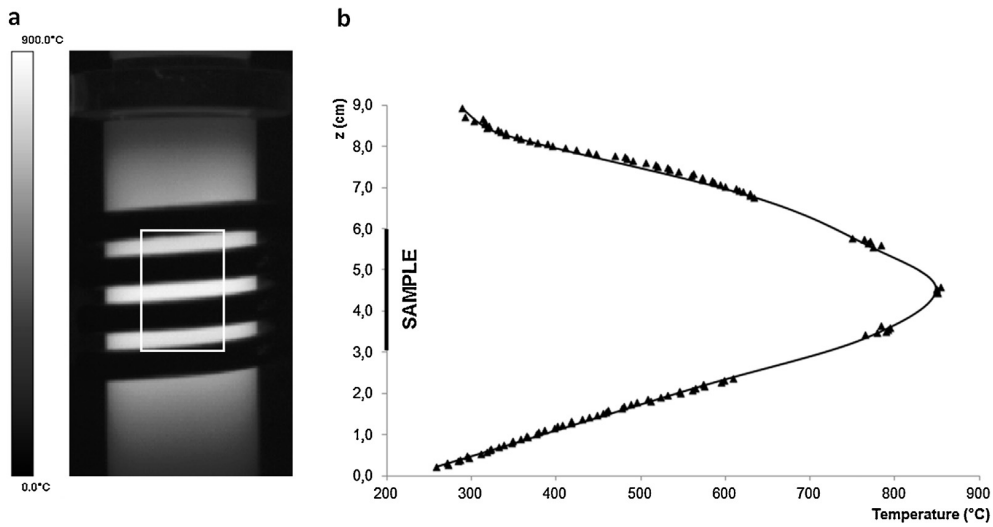

Fig. 3. (**a**) Thermal camera picture of the Inconel pipe with furnace temperature set to 800 °C. The white rectangle represents the position of the sample inside the Inconel pipe. (**b**) Typical temperature profile along the Inconel pipe deduced from the thermal camera picture.

All samples originate from the same trunk in order to limit the dispersion of the results due to feedstock variability. Samples are first dried in an oven at 105 °C during 12 h following the procedure NF EN 14774, and subsequently stored in a desiccator.

The wood elemental composition is found to be 48.70% in carbon, 6.04% in hydrogen and 44.46% in oxygen. Oxygen content is obtained by subtraction knowing that ash content is 0.80% at 550 °C. The proximate analysis results from FCBA Grenoble Laboratory are: cellulose 41% ± 1%, hemicelluloses 30% ± 2% and lignin 25 ± 2%.

3.3. Ceramic samples

Some calibration tests were carried out with monalite M1 ceramic samples having the same dimensions as the wood samples. Ceramic has been chosen as it is an inert porous material. It is not affected by induction furnace and it has known physical properties, close to the ones of wood. The thermal properties are: density: $\rho = 850\,\mathrm{kg\,m^{-3}}$; thermal conductivity: $\lambda(T) = 2.03 \times 10^{-8}.T^2 + 3.91 \times 10^{-5}.T + 1.97 \times 10^{-1}$ in $\mathrm{W\,K^{-1}\,m^{-1}}$ (with T in K, between 293 and 1373 K); heat capacity: $Cp = 960\,\mathrm{J\,kg^{-1}\,K^{-1}}$; emissivity: $\varepsilon = 0.85$–0.95.

3.4. Determination of the char/tars/water/gas yields and products analysis

The mass of char is measured after each experiment. Methods used to determine tars, water and gas yields are here described. Furthermore, CHN are measured and O is deduced giving the CHON composition of these three products.

3.5. Tars characterization and quantification

After an experiment, the liquid fractions collected in the different traps are weighed. Tar traps are washed with isopropanol. All the fractions are gathered. Samples are stored at 4 °C protected from light exposure and filtrated before analysis with 0.45 μm microfilters (Millex-Gx). Analyses are performed either by GC–MS (Perkin Elmer Clarus 500/Clarus 600S) or by GC–FID (Agilent 7890 Å), both equipped with DB-1701 capillary column 60 m × 0.25 mm, 0.25 μm film thickness and injector (split-splitless). Helium is used as carrier gas with a constant flow of 1.0 mL min^{-1}. The oven temperature is programmed from 318 (held for 4 min) to 508 K at a heating rate of 6 K/min and held at 508 K for 13 min. A sample volume of 1 μL (around 2% of pyrolysis liquid in isopropanol) is injected.

GC–MS is used to identify the compounds in the samples: the peak identification is based on computer matching of the mass spectra with the NIST library and on the retention times of known species injected in the chromatographic column.

GC–FID is used to quantify six compounds among the main species formed during a test: acid acetic, levoglucosan, hydroxyacetone, phenol, 2,6-dimethoxyphenol and 2-methoxyphenol. These six compounds have been chosen either because they are major species formed during pyrolysis or because they are characteristic products of the degradation of lignin, hemicelluloses or cellulose. Pure standards from Interchim are used for the calibration. Different samples of know concentrations covering the experimental range are analyzed to build up a calibration curve for each quantified compound. Yields are calculated from comparison with calibration results. This method is semi-quantitative and gives access to tendencies.

3.6. Gas characterization and quantification

The gases are collected in the tedlar sampling bag. After an experiment the content is analyzed by micro-gas chromatography with an Agilent 3000A spectrometer equipped with four columns (two mol-sieve 5 Å × 10 m, PPU 8 m and CP wax 52 × 10 m), with respective inlet temperatures set at 90 °C, 90 °C, 80 °C and 40 °C. The carrier gas is helium except for the column used to analyze hydrogen (one of the mol-sieve 5 Å column) whose carrier gas is argon. Ten species are quantified: CO, CO_2, CH_4, C_2H_4, H_2, C_2H_6, C_3H_8, C_2H_2, C_6H_6 and C_7H_8. We consider that these species represent all the gaseous compounds produced. Error on total gas yields is evaluated on the range 0.6–8% depending on the operating temperature.

A Nicolet IR 550 Fourier transformed infrared FTIR spectrometer measures continuously the concentrations of CO, CO_2, CH_4 and C_2H_4. The concentrations of the gases are further determined by Classical Least Squares (CLS) algorithm using Omnic and Quant setup software. FTIR cell (3 m long pass) is maintained at 150 °C (acquisition time: 4s; resolution: 1 cm^{-1}). A mass spectrometer Adixen ASM102S measures continuously the concentration of H_2. The time delay between gaseous emission by the particle and its quantification was estimated to 10s.

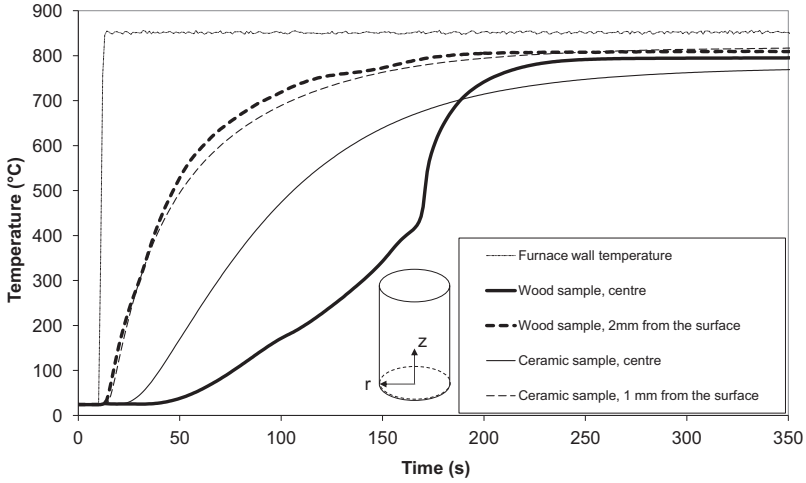

Fig. 4. Temperature as function of time, measured at the centre and next to the surface of wood and ceramic samples, for a temperature furnace set to 800 °C. The temperature evolution of the Inconel pipe wall is also plotted.

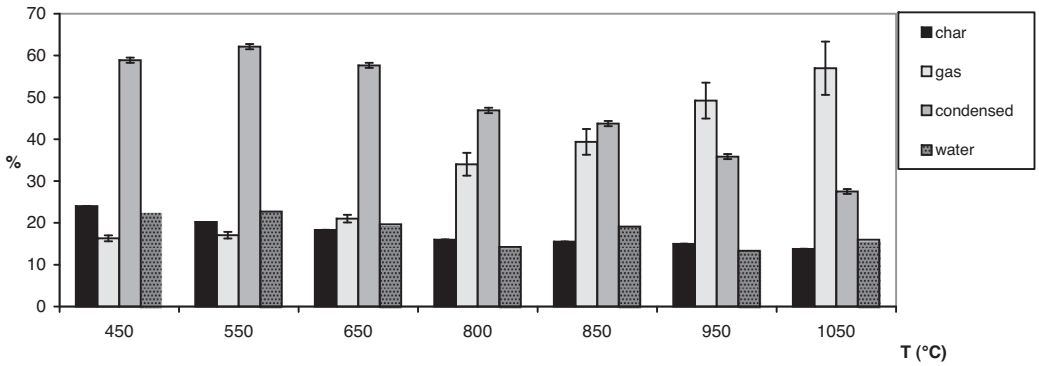

Fig. 5. Global mass yields of beech wood pyrolysis at different temperatures between 450 and 1050 °C.

Curves obtained by continuous analysis are integrated to calculate the total amount of CO, CO_2, CH_4, C_2H_4 and H_2 produced during pyrolysis. Total amounts are calculated with the hypothesis that these 5 species represent all the gaseous species produced during pyrolysis. The calculated values are compared to the ones obtained by micro-GC analysis of the tedlar bag content. The difference on 21 experiments reaches 13% in average, this can be explained by the hypothesis made to do the calculus.

3.7. Water analysis

The water content of the pyrolysis liquid is determined by Karl Fisher titration, according to the standard ASTM E203-96, with a Titroline Karl Fisher apparatus. The relative uncertainty on the determined mass of water is evaluated to 1%.

4. Results and discussion

4.1. Heating of the sample

During the pyrolysis of quite large wood samples, chemical phenomena are strongly coupled with thermal phenomena. As a preliminary step, it is thus necessary to describe accurately the process of heating in the PYRATES setup. Both external and internal heat transfer limitations are here identified and characterized.

4.2. External heat transfers

In this equipment, the sample exchanges heat with both the wall of the Inconel pipe by radiation and the surrounding gas by convection. The temperature profile at the surface of the Inconel cylinder is recorded with a thermal camera FLIR SC5500. This work is performed for each studied temperature, between 450 and 1050 °C. The data obtained at 800 °C are presented in Fig. 3. The four coils cooled by water hide part of the Inconel pipe, defining three inter-coil spaces. The temperature of the Inconel pipe in the central inter-coil space is close to the temperature set point of the furnace. In the inter-coil spaces above and below, the temperature is around 75 °C below the temperature set point.

These results are used to calculate the heat transfer coefficients for radiation, over the temperature range investigated in this work (450–1050 °C). The coefficients for radiation have been calculated after linearizing the radiation equation with the emissivity $\varepsilon = 0.90$, the Stefan-Boltzmann constant σ and the sample surface temperature $Tp = 20$ °C, and results are summarized in Table 2.

$$h_{rad} = 4.\varepsilon.\sigma.[(Tf + Tp)/2]^3$$

On the other hand, heat transfer coefficients for convection are calculated and results are also given in Table 2. It is concluded that the sample is predominantly heated by radiation. Indeed the heat transfer coefficient for radiation is at least two times higher than the coefficient for convection.

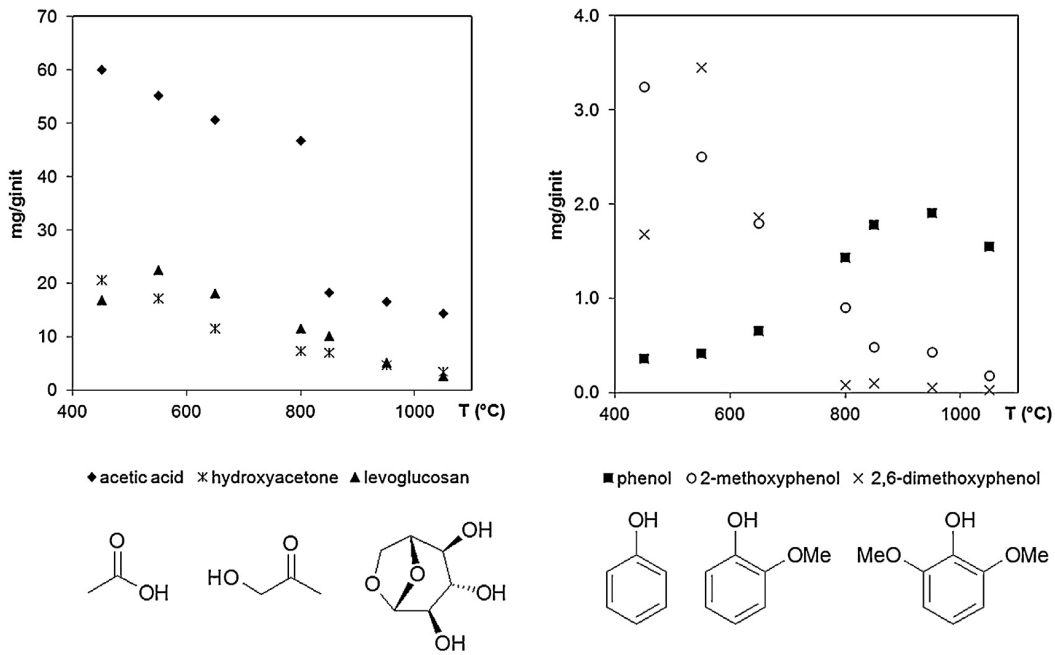

Fig. 6. Yields of six tar species: acetic acid, hydroxyacetone, levoglucosan, phenol, 2-methoxyphenol and 2.6-dimethoxyphenol, determined with a semi-quantitative method. Values are given in mass divided by the initial mass of the sample.

These results enable to calculate the total external heat flux received by the sample during the process Q_{ext}, as function of its surface temperature Tp.

$$Q_{ext} = h_{rad}(Tf - Tp) + h_{conv}(Tg - Tp)$$

In first approximation supposing that furnace temperature Tf is equal to gas temperature Tg and using the calculated values of heat coefficients presented in Table 2, the total external heat flux at the beginning of the pyrolysis at 800 °C can be estimated to 65 kW/m^2.

4.2.1. Internal heat transfer

Thermocouples (K type) are imbedded in wood and ceramic samples to record the internal temperature at different depths and radii. The accurate positions of the thermocouples are determined by X-ray tomography. Ceramic samples are chemically inert and are employed to characterize the particle heating without influence of its reactivity.

Fig. 4 compares internal temperature evolutions inside ceramic and wood samples near the surface and at the centre at 800 °C. Temperature are measured next to the sample surface: $r = 8$ mm and $z = 5$ mm for wood sample; $r = 9$ mm and $z = 5$ mm for ceramic sample, and on sample centre: $r = 0$ mm and $z = 5$ mm for wood sample; $r = 2$ mm and $z = 5$ mm for ceramic sample. The evolution of temperature on the centre of the wood sample differs clearly from that on the ceramic sample. As it is well known, the comparison between temperature measurements in wood and ceramic samples highlights that both chemical and thermal phenomena are involved during pyrolysis.

Table 2
Heat transfer coefficients for radiation h_{rad} and convection h_{conv} at the sample surface.

Tf (°C)	450	550	650	800	850	950	1050
h_{rad} (W m^{-2} K^{-1})	27	35	46	65	72	89	108
h_{conv} (W m^{-2} K^{-1})	15	16	17	19	20	21	22

4.3. Pyrolysis products

Global yields of char, tars, water and gas are first presented. With the aim of describing tars, around twenty compounds are characterized and six are separately quantified. Then the main gaseous species yields are determined to finally present the results of elemental analysis of pyrolytic products.

4.3.1. Global mass yields of pyrolytic products

Global mass yields are the yields of char, tars, water and gas obtained after pyrolysis of a dry beech particle. Balances for global mass yields (sum of pyrolytic product masses compared to initial particle mass) reach 98% ± 3%.

As the temperature increases (see Fig. 5) the char yield decreases from 23% at 450 °C to 13% at 1050 °C and the condensed product yield decreases from 60% to 26%. The condensed product yield is the sum of all liquid fractions collected, that is to say tars and water. Condensed water yield is unchanged and is 18% in average. The gas yield increases from 14% at 450 °C to 59% at 1050 °C.

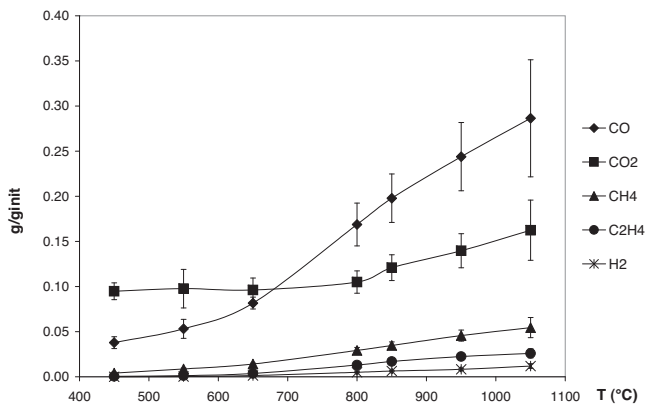

Fig. 7. Yields of the main gaseous products measured by micro-GC, as function of the temperature. Values are given in mass divided by the initial mass of the sample.

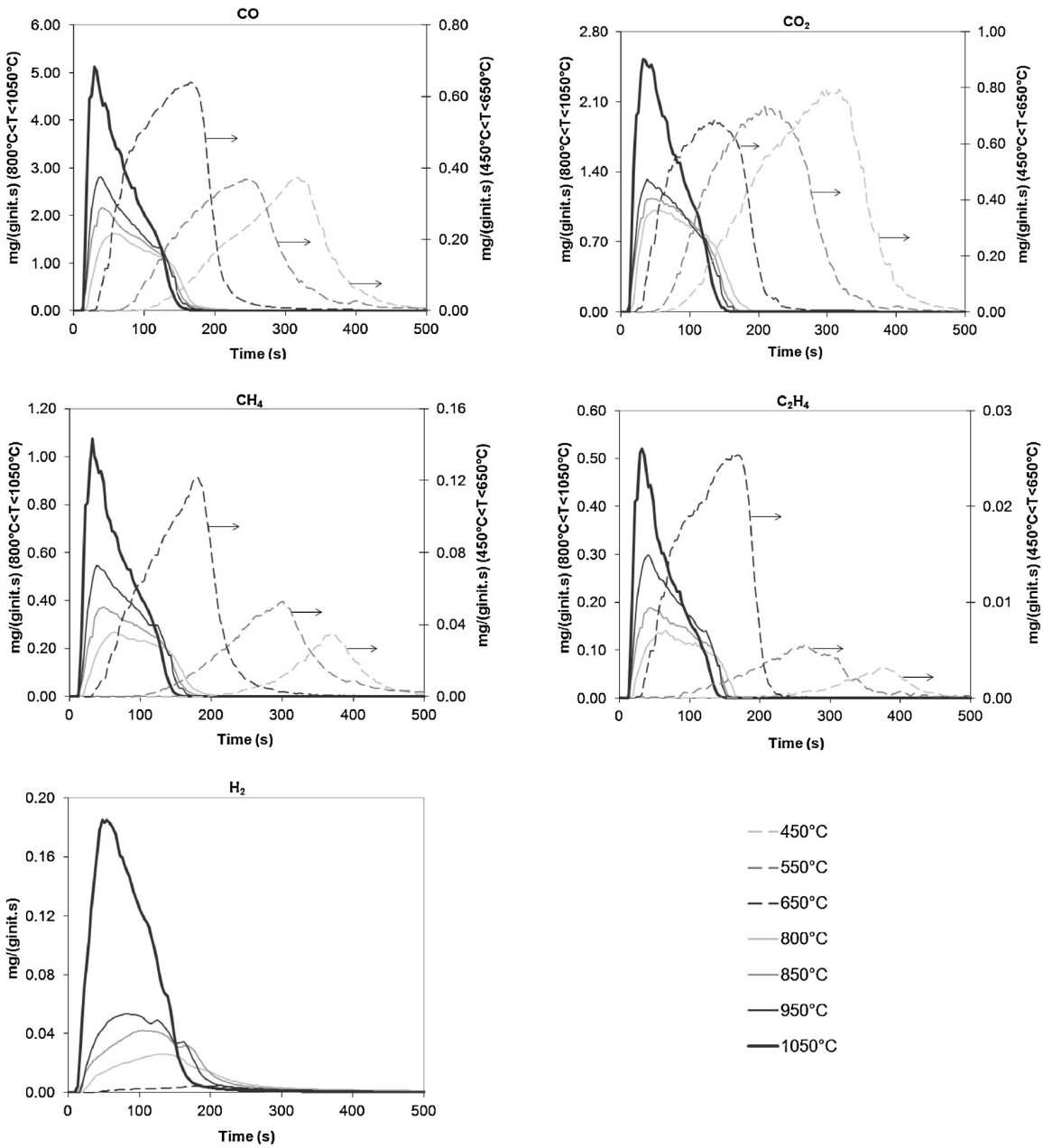

Fig. 8. Evolutions of the instantaneous yields of main gaseous species as function of time, for the different temperatures investigated in this work. For all species, values correspond to the mass flow normalized by the initial mass of the sample.

At 450 °C the following distribution is obtained, char: 23%, condensed species: 60%, gas: 14% (see Fig. 5). By comparison with literature values in Table 3, this distribution is representative of an intermediate pyrolysis heating. The heating of the sample surface is high but the heating rate at the particle centre is much slower.

Table 3
Classical distributions of wood pyrolysis products (wt.% dry basis) at 300–550 °C for different pyrolysis regimes [9].

	Char	Condensed species	Gas
Slow pyrolysis	35	35	30
Intermediate pyrolysis	25	50	25
Fast pyrolysis	12	75	13

4.3.2. Tar characterization and quantification

From GC–MS analysis, the number of tar species can be estimated to almost 300 in agreement with literature [25]. Acetic acid is always the major tar compound produced. Our objective is here to present a non-exhaustive description of the collected species. Around twenty tars can be characterized using the method presented in Materials and Method section. The choice was made to quantified six species among the main tars produced and that can be considered as classical degradation products. Fig. 6 represents the yields of the six considered species over the temperature range studied. Results are obtained from GC–FID analysis and semi-quantitative method presented in Section 3. These six species represent in average 23%w of the tars collected. Indeed around 40 compounds among the main produced tars should be quantified to characterize only 40% of the collected tars [25].

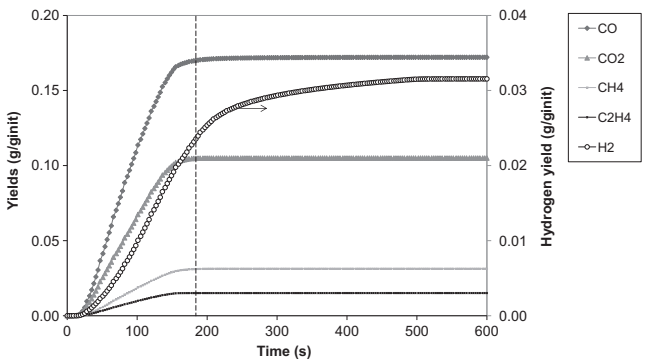

Fig. 9. Cumulated yields of the five major gaseous species at 800 °C. Values are given in mass divided by the initial mass of the sample.

Acetic acid, hydroxyacetone and levoglucosan are typical products of cellulose and hemicelluloses degradation. 2-methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol) come from lignin degradation. Phenol can be produced either from cellulose, hemicelluloses or lignin thermal transformation [25]. The yields of all compounds decrease as temperature increases with the exception of phenol. Indeed, both guaiacol and syringol compounds can react to form phenol [26].

4.3.3. *Gas yields and composition*

Fig. 7 presents the yields of the main gaseous species produced during pyrolysis. As expected, gas composition shows a clear dependence on temperature. The yields of all gaseous species are enhanced by increasing the temperature.

Two pyrolysis situations can be identified looking at the gaseous species produced during pyrolysis. At temperatures ranging between 450 °C and 650 °C, wood pyrolysis produces mainly

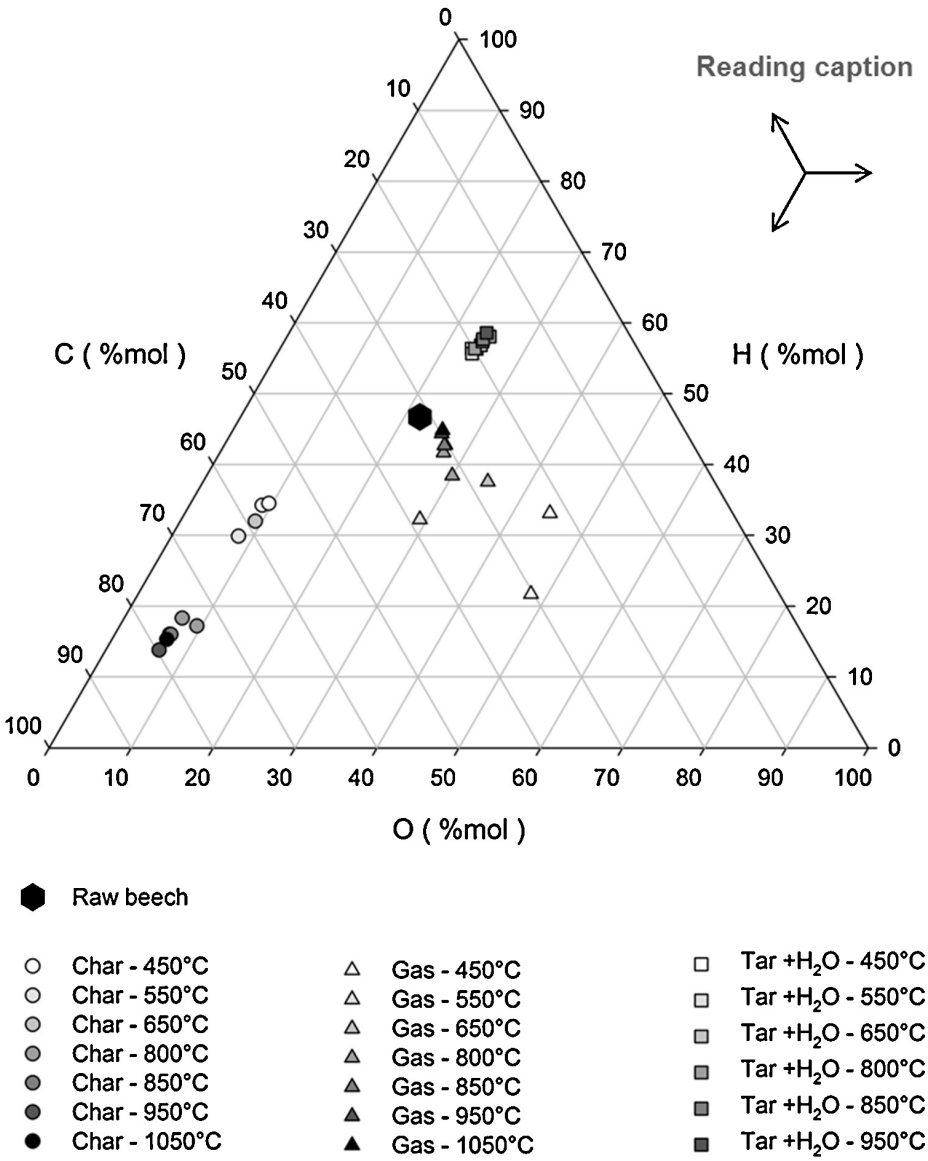

Fig. 10. Elemental composition of the products of beech sample pyrolysis, at different temperatures between 450 and 1050 °C.

carbon dioxide, whereas pyrolysis ranging between 800 °C and 1050 °C produces mainly carbon monoxide.

Five minor gaseous species are also identified: two alkanes (ethane and propane), one alkyne (acetylene) and two aromatics (benzene and toluene). The minor species represent from 1.9 to 4.4%w of the quantified gaseous species for respective pyrolysis temperatures of 450 and 1050 °C.

The five main gaseous species produced are continuously measured by FTIR, for CO, CO_2, CH_4 and C_2H_4, and by mass spectrometry for H_2. Fig. 8 reports the evolutions of their instantaneous yields during the sample pyrolysis over the temperature range 450–1050 °C. Note that a double scale is used for *Y*-axes.

Chemical reactions can be considered as completed when the CO concentration goes down again to the baseline. From experimental results presented in Fig. 8, pyrolysis duration lies between 160s and 440s for the experiments at 1050 and 450 °C respectively.

The shapes of the gaseous products yields highlight two pyrolysis situations. For temperature greater than or equal to 800 °C, the instantaneous yields of CO, CO_2, CH_4, C_2H_4 and H_2 reach their maximum value in the first half of pyrolysis. For temperatures lower or equal to 650 °C, the maximum value of the instantaneous yields is reached in the second half of pyrolysis. These results are scarce in literature and constitute a very useful data set to work with, in particular for simulation purposes with a multistep kinetic model of biomass pyrolysis [27]. Similar observations have been made in [17] on time derivative curves of the mass fraction evolution for beech wood.

Fig. 9 represents the cumulated mass yields at 800 °C of CO, CO_2, CH_4, C_2H_4 and H_2. Around 180s after the beginning of the test, hydrogen is still produced, whereas the gaseous emission of the other major species is finished. 36% of total hydrogen yield is produced by the char after the end of the emission of CO, CO_2, CH_4 and C_2H_4.

4.3.4. Elemental analysis of pyrolytic products

The elemental composition of pyrolysis products for different temperatures of the furnace is presented on the ternary diagram in Fig. 10. The parent beech composition is indicated in order to support interpretation. Oxygen percentage is not measured directly; it is obtained by subtraction. The elemental composition of tars is determined for the entire amount collected in the PYRATES device. Gas elemental composition is calculated from gas yields presented in the previous paragraph.

Char contains amounts of *O* varying between 5 and 10%mol and amounts of *H* varying between 14 and 35%mol. When increasing the pyrolysis temperature, char loses progressively *H* and *O* to tend to pure carbon as expected. Note that there is no significant variation in the elemental composition of condensed products. Two pyrolysis situations can be distinguished when looking at the char elemental composition variations: wood pyrolysis at temperatures ranging between 450 °C and 650 °C produces a char with a large hydrogen content (around 35%mol) while wood pyrolysis at a temperature between 800 °C and 1050 °C leads to *H* content around 15%mol only. This distinction corresponds to the one previously observed when looking at the main gaseous compound produced.

Balances for *C*, *H* and *O* analysis defined as the sum of char, tars, water and gas elemental compositions compared to initial biomass composition lie between 82% and 113% which is satisfactory.

4.3.5. Some insights on secondary reactions

Secondary reactions can occur both outside and inside the particle and could be here either homogeneous or heterogeneous reactions. Phenol is typically a product from secondary tar reactions. This compound was identified among the condensable species from our experiments showing that tar cracking reactions can occur. Let discuss their occurring propensity outside or inside the particle.

Extra-particle reactions are homogenous secondary reactions of tar cracking. Such reactions – which are highly dependent on temperature [28] – may be limited in PYRATES setup. This is confirmed by three experimental evidences: (i) from 450 °C to 1050 °C the nature of the organic molecules characterized in the tars is unchanged; (ii) as it was said before, there is no significant variation in the elemental composition of condensed products; (iii) at 800 °C and 1100 °C, the residence time of species in the hot area was modified by doubling nitrogen flow from 2 to 4Nl min^{-1}, and the tar yields slightly increased respectively of 2 and 16%. In contrast with extra-particle reactions, intra-particle ones may have an important effect on product yields and compositions. The two pyrolysis situations which were identified looking at (i) the instantaneous yields of the main gaseous species; (ii) the main gaseous compound produced and (iii) char elemental compositions can be explained by the secondary reactions which take place inside the sample.

5. Conclusions

The objective of this work was to acquire a consistent set of the thermal and chemical data necessary to describe pyrolysis of a large wood sample. This includes the thermal history inside the sample and the devolatilisation, kinetics and yielded products.

This was achieved performing experiments of pyrolysis of moisture-free wood cylinders at different temperatures, from 450 °C to 1050 °C. Experiments were carried out in a newly designed experimental device with high heating rate capabilities. Based on temperature measurements of the furnace wall and into the particle the sample heating has been accurately characterized. Global mass yields and elemental analysis of char, tars, water and gas are also presented with very good balances (98% in average). The yields of the main gas (CO, CO_2, CH_4, H_2 and C_2H_4) and tars (acetic acid, hydroxyacetone, levoglucosan, phenol, guaiacol and syringol) have been determined. The main gaseous species have been continuously analyzed during the reaction, showing that hydrogen is still produced even after the end of the main gaseous emissions. Two pyrolysis regimes are distinguished looking at the char elemental composition and the major gaseous species produced during pyrolysis.

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