#### Accepted Manuscript

Title: Biomass energy behavior study during pyrolysis process by intraparticle gas sampling

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PII:	S0165-2370(14)00097-7	
DOI:	http://dx.doi.org/doi:10.1016/j.jaap.2014.04.0	
Reference:	JAAP 3188	
To appear in:	J. Anal. Appl. Pyrolysis	
Received date:	22-11-2013	
Revised date:	17-4-2014	
Accepted date:	18-4-2014	

Please cite this article as: S. Ciuta, F. Patuzzi, M. Baratieri, M.J. Castaldi, Biomass energy behavior study during pyrolysis process by intraparticle gas sampling, *Journal of Analytical and Applied Pyrolysis* (2014), http://dx.doi.org/10.1016/j.jaap.2014.04.012

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1	Biomass energy behavior study during pyrolysis
2	process by intraparticle gas sampling
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15	Keywords: biomass, pyrolysis, intraparticle, gas sampling, energy change, thermodynamics
16	
17	Highlights (max 85 characters)
18	• Gas component detection in concert with thermal analysis was used during pyrolysis
19	• First biomass intraparticle gas sampling technique presented
20	• Possible connection of reactions occurring within the solid sample
21	• Surface and center temperature variation observed with attempted explanation
22	• Potential for Gas analysis to give an insight on reaction sequences occurring

23

24

25 Abstract: Understanding pyrolysis kinetics is imperative for industrial biomass conversion applications. One of the lesser known aspects of wood pyrolysis concerns the actual energy 26 27 change happening during the process within the biomass sample. The use of gas component 28 detection methods in concert with thermal analysis can help in better understanding the reaction 29 sequence and mechanisms during pyrolysis. The aim of this paper is to present an innovative 30 intra-particle gas sampling technique that can provide insight on the reaction sequence and 31 energy changes inside biomass particle. To our knowledge, this is the first intraparticle gas 32 sampling measurement performed during non-oxidant thermal treatment of biomass. The 33 pyrolysis experimental tests have been performed on birch wooden spheres, on two different 34 diameters 19.0 mm and 31.8 mm. The thermogravimetric (TG) analysis revealed a rapid mass 35 loss in the temperature range 290°C to 410°C and a total mass loss of 75% - 76%. The DSC 36 analysis showed exothermic behavior above 305°C and two maximum peaks at 350°C and 37 413°C. Evolved gases such as H<sub>2</sub>, CH<sub>4</sub>, CO CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> were extracted 38 through a probe using a micro sample system. The measurements showed a simultaneous release 39 of CO<sub>2</sub> and CO with a maximum occurring around 325°C, for larger samples. The CO release, 40 while lower in absolute concentration, is much more stable during the entire heating of the 41 particle. The measurements showed a pronounced transition between hydrogen release and 42 subsequent hydrocarbons release. The saturated hydrocarbons such as methane and ethane were 43 observed in high quantities, 19% and 0.9% respectively. The chemical species concentration 44 profiles of the evolved gases from the particle center could enable a corresponding temperature 45 calculation.

#### 46 **1.** Introduction

For the optimal design of thermal treatment reactors, the knowledge of mechanisms and transformations occurring during the thermochemical conversion processes is fundamental. Understanding of pyrolysis becomes important because it can convert biomass into intermediate fuels with improved combustible properties and represents a previous stage to other biomass thermochemical processes such as gasification and combustion [1]. Therefore understanding pyrolysis kinetics is imperative for the assessment of items including the feasibility, design, and scaling of industrial biomass conversion applications [2].

54 Wood pyrolysis is a complex process influenced by several parameters which directly affect 55 the yields and characteristics of the products obtained. Although many experimental and 56 modeling studies [2–4] focused on explaining the pyrolysis mechanisms to transform feedstock 57 into valuable products, there still remains a number of aspects not fully understood. In particular, 58 many of these studies are based on thermogravimetric analysis and reveal different temperature 59 profiles developing during the process [5,6] mainly without correlation with gas species detection or quantification of volatiles released. The present research proposes to understand the 60 61 chemical species temporal (or thermal) evolution setting the stage for clarifying the energy 62 changes throughout the sample decomposition, by identifying component gases evolved and 63 comprehending the reactions occurring.

One of the lesser known aspects of wood pyrolysis concerns the actual energy change happening during the process within the biomass sample. This has real scale applicability with respect to the overall energy balance [7] and specifically the energy consumption through the process. The heat of reaction has a significant influence on thermal conversion routes[8], and understanding the effect of the reaction heat is important in modeling thermochemical processes ultimately leading to predictive capability. However, reports of the thermal effects of pyrolysis

70 reactions have been found to vary widely, ranging from exothermic to endothermic under similar 71 conditions. Furthermore, this exothermic/endothermic variation is observed over a range of 72 reported test conditions [8–11]. Results reported in literature show that mainly the thermal 73 degradation of cellulose is endothermic, while the char formation reaction is exothermic [12]. 74 However these processes overlap during thermal decomposition and lead to a composite result. 75 Importantly subsequent reactions involving released gases are difficult to quantify and may 76 provide additional endothermic enthalpy due to cracking type reactions or exothermic enthalpy 77 related to condensation reactions.

78 Thermal analysis is an extensively used technique which provides insight regarding the 79 apparent kinetics of heterogeneous reactions. However, the data obtained by thermo analytical 80 techniques alone does not provide complete information to draw mechanistic conclusions about a 81 solid state decomposition process [13]. To fully understand the reaction sequences occurring, 82 thermal analysis methods must be coupled with evolved gas analysis. This enables a better 83 quantitative assessment of the gases released corresponding to thermal decomposition. The use 84 of gas component detection methods in concert with thermal analysis can help in this effort. 85 Importantly the identification of the origin of the gaseous components must be done to accurately 86 recognize the relevant reactions associated with solid decomposition.

Recent studies show interest in mass transfer and energy change happening in the core of the biomass samples and along its radius [9,14,15]. These experiments are performed by placing thermocouples inside the wood samples and measuring the temperature profiles [9,10,16]. The temperatures measured inside the biomass are compared with those measured on the surface of the sample or inside the reactor. The sequence of temperature variation, translated as exothermic or endothermic reactions, could explain some of the transformations occurring during pyrolysis, yet only as an overall aggregate or net reaction process. Some research groups have observed a

94 temperature peak, which has been interpreted as exothermic reactions typically present at 95 operating temperatures of 500°C [9]. These energy changes were attributed to the experimental 96 conditions (the sample size, the nature of the atmosphere, and the presence of impurities) [10] or 97 as exothermic decomposition of the remaining solid [9]. In other studies, under slow pyrolysis 98 conditions, small particles of cellulose and wood show a global endothermic behavior, whereas 99 samples with larger particle sizes exhibit exothermic behaviors [17]. This difference was 100 explained in terms of the enhanced interaction of hot pyrolysis vapors with the decomposing 101 solid, which involves an exothermic reaction that leads to the formation of char [8].

102 Though several studies on this topic are available in the literature, none of them present 103 intraparticle gas analysis of the evolved chemical species which is important to the 104 understanding of the reaction relevant to the decomposition process.

The aim of this paper is to present an innovative intra-particle gas sampling technique that can provide insight on the reaction sequence and energy changes inside biomass particle. To our knowledge, this is the first intraparticle gas sampling measurement performed during nonoxidant thermal treatment.

109 **2.** Material and methods

#### 110 2.1 Feedstock characterization

111 The pyrolysis experimental tests in this work have been performed on birch wooden spheres 112 [16]. The conclusions attained could be applied to other geometries taking into account the 113 corresponding coordinates and boundary conditions [1], although this work focuses more on the 114 newly obtained experimental results.

Lignin-cellulosic materials are characterized by a remarkable variability in the physical and chemical properties. Therefore, a fundamental characterization is required for better emphasizing the influence of feedstock characteristics on thermal process behavior. One of the morphological

properties of the feedstock which influences its thermal decomposition is the size of the sample.
Thus, two different diameters have been chosen for the birch wooden spheres: 19.0 mm and 31.8
mm, (tolerance: ±0.8 mm).

121 The feedstock has been characterized in terms of proximate and ultimate analysis using 122 representative samples consisting in three small diameter particles and three large diameter 123 particles (wood spheres). The moisture content has been determined by drying the selected 124 particles for 24 hours in an oven at 105°C (UNI CEN/TS 14774-2). The dried particles have been 125 ground with a mixer mill (MM400, Retsch) and the chemical composition has been determined 126 with an elemental analyzer (FlashEA 1112, Thermo Fisher Scientific). The ash content has been 127 determined according to UNI CEN/TS 14775. Volatile matter (VM) and fixed carbon (FC) have 128 been calculated on the basis of the average residual mass data obtained from thermogravimetric 129 analyses of the samples, performed on a STA449F3 (Netzsch) at a constant heating rate of 20 °C 130 min<sup>-1</sup> under inert nitrogen atmosphere in a temperature range from 40 to 800°C (data not shown).

131 The proximate and ultimate analysis of the feedstock is presented in Table 1.

132 2.2 Thermal analysis: Thermogravimetric analysis. Differential scanning calorimetry.

The behavior of biomass samples during devolatilization was determined with thermogravimetric (TG) analysis. The results show the spherical sample mass variation in time, providing information on phase transformation during the treatment process. The time variable data enables a detailed analysis of each transformation phase of the product and the possibility to correlate the evolved gas composition with decomposition stage [18].

Thermogravimetric data are obtained using a Netzsch Luxx 409 thermo analyzer, which combines both differential thermal analysis (DTA) and thermogravimetry (TG). Due to the size of the TGA crucible, the birch wood spheres used for these experiments are smaller in diameter than the ones subjected to pyrolysis in the tubular furnace, but maintaining appropriate aspect

ratios. Therefore two different diameters (9.5 mm and 5.7 mm) were chosen for the TGA experiments. For better reproducibility of the pyrolysis experiments, an inert environment was ensured by a introducing a purge gas flow (80 mL/min) of argon and a constant heating rate of 50°C/min in a temperature range from 25°C to 500°C. Typical sample mass of 0.25 g and 0.15 g respectively, were studied.

147 The physical and chemical changes occurring during birch wood non-oxidant thermal 148 treatment were also quantified through differential scanning calorimetry (DSC). The data was 149 obtained using a TA Instruments Q200 calorimeter, in similar operating conditions as the TG, for 150 better comparison of the results. Samples of 0.06 - 0.065 g were subjected to heating at 151 temperatures between 25°C and 500°C. The furnace was heated to a constant heating rate of 152 50°C/min and a gas flow of 80 mL/min of nitrogen purged through the system. The tests have 153 been repeated, placing the samples in aluminum pans covered by a lid. The results show heat 154 flow changes during process and give important insight respect to exothermic/endothermic 155 behavior of the birch wood.

#### 156 2.3 Intra-particle sampling. Experimental set-up

The pyrolysis tests have been performed in a tubular stainless steel reactor (internal diameter: 38 mm; length: 305 mm) inserted in an electrically heated furnace (Fig. 1a). The temperature inside the furnace is kept constant at 500°C through a temperature controller (CN7800, Omega), connected to a K-type thermocouple placed on the external wall of the reactor. For ensuring a non-oxidant environment inside the reactor a helium flow of 340 ml/min was injected, and kept constant through a calibrated mass flow controller (GFC17, Aalborg). Helium has been chosen as inert gas to enable detection of nitrogen in the event of air leakage into the system.

164 The sampling of the evolved gas has been performed by means of a sampling probe inserted in 165 the center of the particle through an opening bored into the particle enabling an interference fit of

166 the probe with the biomass sample (Fig. 1b). The inert, passivized sampling probe (internal 167 diameter: 0.76 mm, length: 914 mm) was directly connected to a gas chromatograph (3000 168 microGC, Inficon) used for the online analysis of the evolved gas. Gases were extracted through 169 the probe using the internal microGC pump. The microGC is equipped with two columns, a 170 Molsieve column for the detection of He, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO and a Plot-U column for the 171 detection of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>. In addition, the temperatures at the center and at the 172 surface of the particle have been measured by means of closed bead K-type thermocouples. The insertion point for the thermocouple at the center of the particle has been drilled to three quarter 173 174 of the radius (i.e. 7.1 mm and 11.9 mm for the small, respectively large particle) to avoid 175 impacting the sampling probe (Fig. 1b).

In each test, the particle at ambient laboratory conditions has been inserted into a pre-heated reactor at 500°C. The time required for each microGC analysis is about three minutes which roughly corresponds to the time scale of the particles' thermal degradation time (4-6 minutes for the smaller particle and 8-10 minutes for the bigger one). Therefore multiple tests have been done at the same conditions at least three times with an offset of GC sampling to obtain a gas evolution profile.

Based on the gas composition detected and on the quantification of the gas release in time (thermogravimetric analysis), a temperature assessment of the gas mixture evolved inside the particle could be carried out. This calculation could provide a comparison with the temperature profiles given by the thermocouple measurements. The temperature could be determined iteratively considering that the gas release reactions take place adiabatically and at constant pressure.

188 **3. Results** 

189 3.1 Thermal analysis

The mass loss profiles with temperature and time for the two birch spheres (9.5 mm and 5.7 mm) subjected to pyrolysis treatment are shown in Fig. 2. The devolatilization behavior is very similar to other lignin-cellulosic materials [19,20].

The initial stage of mass loss (1.52 mass% for the 9.5 mm sample and 1.70 mass% for the 5.7 mm sphere), below 100°C, is associated with the release of weakly bonded water [21,22]. Biomass decomposition is essentially associated with the decomposition of its three main components (hemicellulose, cellulose and lignin) [21,23].

Both particles began slowly decomposing at approximately 126°C with the rates increasing near 220°C. The thermogravimetric curve for the 9.5 mm sample shifted to higher temperatures by up to 20°C, compared to the 5.7 mm particle.

The TG curves showed a sharp drop in biomass weight, 68% overall for the 9.5 mm particle and 65% overall for the 5.7 mm particle in the temperature range of 278°C and 430°C. This major weight loss is normally attributed to the release of volatile matter (devolatilization phase) [21].

Above 430°C, the mass loss decrease is becoming less significant (6.4% and 4.5% of the initial biomass weight for the 9.5 mm and for the 5.7 mm particle, respectively). This section of the TG profile can be attributed to the decomposition of remaining lignin in the solid residue or char, which usually progresses until 800°C [24].

The thermal decomposition of birch wood showed a single DTG peak (as shown in Fig. 2). The highest mass loss is found in the temperature range of 350–400°C which corresponds to the degradation of cellulose, while the slight shoulder peak generally denotes decomposition of lignin at higher temperatures. However, in this case, the decomposition of both hemicellulose and cellulose can be observed in a single DTG peak, denoting overlapping reaction sequences between lignocellulose materials that increase the complexity of the overall biomass pyrolysis

reaction chemistry [24]. The difference in decomposition of the two particles is observed in Fig. 2, where for the same temperature value slightly more mass (from the total mass) is being lost from the smaller particle. For example the DTG curve shows 15%/min for the small particle at 290°C compared to 10%/min for the large particle. This behavior is noticed between 290°C and 430°C, while the overall mass loss is greater in the big particle case, but no more than 3%.

The DTG curves show a common peak at 380°C, which represents the maximum volatilization rate. The results are similar to other thermogravimetric studies encountered in the literature on non-oxidant thermal treatment of wooden biomass [19,25,26]. Very often, it is possible to observe distinct events of degradation from the DTG curve, when dealing with very small amounts of material. The results obtained may be influenced by the size of the particle, and a convolution of several pyrolysis unit processes are observed, starting from the outside and moving towards inside of the particle.

The heat flow variation during sample decomposition is shown in Fig. 3. To mitigate the difference of heat and mass transfer between different runs of same DSC experiment, the sample mass was kept at 6 mg.

The thermal changes occurring are clearly distinguished in the graph through the heat flow peaks. At low temperatures (below 200°C) one endothermic peak between 50°C and 190°C was observed.

The endothermic reactions taking place during the pyrolysis process are associated with moisture loss and heating of the wood sample. The presence of a third peak between 305°C and 390°C, with a maximum at 350°C confirms there is an overall exothermic behavior during wood decomposition [27,28]. The DSC curve suggests the occurrence of several overlapped exothermic processes during the thermal degradation of biomass and, essentially, of its main components [29]. Many studies on biomass component degradation revealed decomposition

temperatures of 200 - 260°C for hemicellulose and 260 - 360°C for cellulose [21,30], depending 238 239 however on experimental conditions such as heating rate or environment. In this case it seems 240 that hemicellulose and cellulose decomposition are overlapping causing an exothermic peak with 241 a maximum at 350°C. The DSC analysis reveals a second exothermic peak above 400°C which 242 might be attributed to the last stage of degradation of lignin [29] and some other secondary 243 reactions causing char or tar formation [21,30]. It is exactly this convolution of thermal 244 information that we are trying to address with the newly developed technique. The DSC data 245 shows exothermic reactions in the bulk material happening at temperatures greater than 300°C 246 albeit for the aggregate reaction set occurring (i.e. the net or overall reaction). Due to significant mass loss at temperatures above 300°C, confirmed by the TG/DTG analysis, the exothermic 247 248 behavior could not be completely understood by differential scanning calorimetry and because of 249 double peaks observed in the data. Therefore further investigations of temperature profiles 250 obtained by thermocouple measurements (Fig. 4a and 4b) and gas sampling will help elucidate 251 the actual transformations occurring during pyrolysis process.

252 *3.2 Temperature measurement* 

253 The temperature profiles for both the particles show temperatures in the center which are 254 exceeding the temperatures measured on the surface of the biomass samples. This trends were 255 encountered in other available studies in literature [9]. For the 31.8 mm particle the average 256 temperature difference between the center peak and the surface is almost 50°C, while for the 257 smaller 19.0 mm particle this difference represents approximately 25°C. The influence of 258 particle size on thermal decomposition and energy change inside the biomass sample is 259 emphasized through the time difference between the two particles when the center peak appears. 260 If for the small 19.0 mm particle the temperature in the center exceeds the surface temperature 261 after 2.5 to 3 minutes, for the larger 31.8 mm particle the temperature peak is significantly

262 delayed to 6.5 to 8 minutes. Although the same trend was obtained compared to some studies 263 reported in literature, when the experiments were repeated at the same conditions (triple 264 repetitions) the profiles revealed significant differences for the same size particle. It can be 265 noticed from Fig. 4 (a and b) that the center peak of temperature does not happen in the same 266 moment of time for the three repetitions. Furthermore, the temperature where the center 267 thermocouple reading exceeds the surface thermocouple reading is offset. Due to the 268 heterogeneity of biomass, this offset and variable maximum temperature may be a result of 269 different reactions occurring inside the particle. For example, if one condition has more 270 hydrolysis reactions compared to cracking or condensation reactions, the aggregate enthalpy 271 change will be different. It is anticipated as the intraparticle sample technique is further refined, 272 elucidation of the reaction sequences will be possible.

273 *3.3 Gas component distribution* 

The gas sampling experiments were performed as previously mentioned on two sizes of birch wood spheres. The distribution of the evolved gases inside the particle is presented in Fig. 5 (a and b) and Fig. 6 (a and b).

The size of the particle clearly influences the concentrations of the evolved gases; the amounts of the main components were present in higher amounts in the larger particle compared to the smaller one. Shown in Fig. 5a are the major components measured as a function of center temperature as measured by thermocouple insertion for the 31.8 mm particle size.

The measurements show a simultaneous release of  $CO_2$  and CO with a maximum occurring around 325°C. The evolution behavior agrees with the maximum mass loss rate in the DTG curve.  $CO_2$  reaches a maximum concentration of 49.5% which is significantly higher than CO at 23.7%. The highly oxygenated structure of the biomass is expected to give rise to high emission

of CO and CO<sub>2</sub> [24]. However, CO<sub>2</sub> rapidly decreases to a concentration nearly equal to CO concentration by  $350^{\circ}$ C.

Literature [24,30,31] refers to the  $CO_2$  release during biomass pyrolysis as mostly caused by decomposition of hemicellulose at low temperatures (<500°C) and by lignin at high temperatures (>500°C), whilst cellulose only contributes to a small portion of it at low temperatures. The formation of  $CO_2$  is possibly attributed to the cracking of C–C and C–O bonds connected with the main branch of hemicellulose. A possible explanation is that the  $CO_2$  is formed from the decomposition of bound water combining with a CO release from the biomass matrix or from the thermal decarboxylation of acetic acid [32].

The CO release, while lower in absolute concentrations is much more stable during the entire heating of the particle and may be considered reaching a constant concentration of 21%.

296 CO was mainly released out with the cracking of carbonyl (C–O–C) and carboxyl (C=O). The 297 contribution of cellulose pyrolysis to CO release was minor, and it was found that CO release 298 was mostly caused by the pyrolysis of hemicellulose in this temperature range [30]. Some other 299 authors [33] indicate that decarbonylation reactions of carboxide-containing compounds cause 300 the release of CO, the decarboxylation reactions of carboxide- containing compounds cause the 301 release of CO<sub>2</sub>, which is also related to the internal dehydration of cellulose and the formation of 302 char. CO presence at higher temperatures might be due to the decarboxylation process in the 303 aromatic condensation of lignin [33]. The evolved gas profiles confirm the literature, but reveal 304 more insight provided by our new sampling technique. The hydrogen profile (shown in Fig. 5b) 305 matches that of CO<sub>2</sub> and it reaches a pronounced maximum near 325°C followed by a significant 306 reduction. For example, the total CO<sub>2</sub> concentration decrease is 59% from the maximum reached 307 near 325°C to approximately 20% at higher temperatures. The concentration of hydrogen 308 decreased from its maximum of 0.72% to concentrations near 0.40% at higher temperatures,

which represents a decrease by nearly 41%. On the contrary, the CO concentration profile
reaches a slight maximum of 23.7% at 325°C and is practically maintained.

311 Fig. 5b presents the species concentration profiles for the 31.8 mm particle as a function of 312 measured center temperature and is complementary to Fig. 5a. Here the measurements show a 313 pronounced transition between hydrogen release and subsequent hydrocarbons release. As 314 discussed above the hydrogen reaches its maximum concentration near 300-325°C followed by a 315 significant reduction. Nearly coincident with the decline in hydrogen and CO<sub>2</sub>, a sharp increase 316 in hydrocarbon release is observed. The hydrocarbon concentrations remain below 0.1% until 317 temperatures greater than 325°C. Methane evolution follows a similar trend with temperature, as 318 shown in Fig. 5a, with values of concentration nearly one order of magnitude higher than the 319 values reached by the other hydrocarbons. This is expected since methane is more stable than 320 higher order hydrocarbons. Shown in Fig. 5b is an aggregate concentration of three carbon 321 hydrocarbons (propene and propane) labeled C3's. This was done as it was difficult to 322 distinguish between the different three carbon compounds due to the separation method used 323 which enabled higher sampling rates but lost some speciation resolution. Future experiments 324 will focus on development of a method that allows both rapid sample acquisition without loss of 325 speciation. It is interesting to note that saturated hydrocarbons such as methane and ethane are 326 observed in high quantities. This could indicate that any free hydrogen is immediately bound as 327 the biomass structure starts to decompose, again suggesting that the molecular hydrogen, i.e. H<sub>2</sub>, 328 measured comes from bound water and not from the biomass matrix itself.

Fig. 6a displays the profiles of the major components for the small particle as a function of measured center temperature. Because of more rapid consumption of the particle in the process, the data points obtained by gas sampling from the smaller particle are less frequent than the larger particle. The general trend of CO<sub>2</sub> and CO evolving earlier and at the highest

333 concentrations agrees well with the trends observed for the 31.8 mm particle measurements. 334 However, here CO<sub>2</sub> and CO concentrations are much closer and follow similar trends. For the 335 31.8 mm particle there was a steady production of CO and a more prominent profile for  $CO_{2}$ . 336 Yet when the measured center temperature reaches about 450°C similar concentrations for CO, 337 CO<sub>2</sub> and CH<sub>4</sub> were observed. Importantly the total amounts measured in the 19.0 mm particle are 338 nearly a factor of three less than the 31.8 mm particle. While this is still under investigation, it is 339 could be due to more tars being generated compared to the larger particle. The gases evolved in 340 the 19.0 mm particle have a much shorter path to diffuse and reach the surface compared to the 341 31.8 mm particle. This may explain the reason for the similarity in concentration between CO 342 and CO<sub>2</sub> for the 19.0 mm particle and the major difference for the 31.8 mm particle above 400°C. 343 Specifically as the smaller particle is being heated any bound water has a greater potential to 344 diffuse out of the particle before decomposing compared to the larger particle where the water 345 would have a longer time in contact with the biomass surface.

346 Fig. 6b shows the minor components measured for the 19.0 mm particle as a function of measured center temperature. The measurements show nearly a factor of three lower overall 347 348 concentrations compared to the 31.8 mm particle even if the gas evolution trends are similar. 349 The onset of hydrocarbon evolution occurs nearly coincident with an observed decrease in CO and CO<sub>2</sub> and begins at higher temperatures. In the incipient phases of the devolatilisation 350 351 process, the main gas component is the CO<sub>2</sub>. Its concentration started to decrease after 3 to 4 352 minutes when it reaches its minimum of 25%. The secondary reactions of volatiles produce 353 mostly CO, H<sub>2</sub> and CH<sub>4</sub> rather than CO<sub>2</sub> [34] this being noticed by the increase of these 354 components percentage, achieving their maximum before 5 minutes of applied thermal 355 treatment. As expected, the pyrolysis process lasted longer for the bigger particle treatment, 17.5 356 minutes compared to 10 minutes for the small particles.

357 The chemical species concentration profiles of the evolved gases from the particle center can 358 enable a corresponding temperature calculation [35]. This is one of the major values of this type 359 of measurement. The calculation could be performed as an enthalpy balance between reacting 360 biomass, the gas evolved and the solid residual product. Since the reactants (biomass) and 361 products (measured gases and residual) are known, the temperature can be determined assuming 362 an adiabatic condition. The gas composition and temperature calculation could give an insight on 363 the mechanisms and energy change happening. Currently additional biomass and residue 364 characterization is being performed, improving the system speciation and leading to accurate 365 calculations in future work.

#### 366 4. Conclusions

This innovative research technique can support an extensive kinetic study of biomass decomposition during non-oxidant thermal treatment and presents a new method to help clarify the energy changes occurring during biomass pyrolysis, by analyzing the evolved gases and identifying the temporal (or thermal) profiles. To our knowledge, this is the first intraparticle gas sampling measurement performed during biomass pyrolysis, setting the stage for a more detailed development.

373 The behavior of wood samples during devolatilization was determined with thermogravimetric 374 (TG) analysis and differential scanning calorimetry (DSC). The DSC data revealed the presence 375 of two exothermic peaks between 305°C and 390°C and above 400°C. The temperature profiles 376 for both the particles show temperatures in the center which are exceeding the temperatures 377 measured on the surface of the biomass samples. The gas measurements showed a simultaneous 378 release of CO<sub>2</sub> and CO with a maximum occurring around 325°C. The CO release, while lower 379 in absolute concentrations is much more stable during the entire heating of the particle. The measurements show a pronounced transition between hydrogen release and subsequent 380

hydrocarbons release. The total amounts measured in the 19.0 mm particle are nearly a factor of three less than the 31.8 mm particle. The chemical species concentration profiles of the evolved gases from the particle center can enable numerous investigations such as mechanistic development, intermediate reactive species identification and accurate corresponding temperature calculations. The calculation could be applied as an enthalpy balance between the biomass material and the gaseous and solid residual product finally answering the question regarding the endothermic or exothermic nature of the decomposition as a function of time or

388 sample temperature.

#### 389 Funding Sources

- 390 This research was partially supported by Earth Engineering Center/City College of New York
- and the Grove School of Engineering at City College, City University of New York and by Free
- 392 University of Bozen-Bolzano Foundation.

#### 393 Acknowledgment

The authors greatly acknowledge the insightful discussions with Prof. Naomi Klinghoffer of CCNY Chemical Engineering and member of the Combustion and Catalysis lab group as well as Prof. Ryan Anderson of Montana State University, Bozeman and the supportive environment of the Chemical Engineering Department at CCNY.

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490	Table	S
491	Table	e 1

492 Proximate and ultimate analysis of birch wood

Proximate analysis (dry basis; moisture: as received basis)				
Moisture	Ash	FC	VM	
$8.2 \pm 0.5$	$0.8 \pm 0.1$	$13.2 \pm 1.1$	85.9 ± 1.3	
<u>Ultimate analysis</u> (dry ash free basis)				
С	Н	Ν	0	S
$47.6 \pm 0.4$	$6.9 \pm 0.2$	$0.1 \pm 0.0$	$45.3 \pm 0.7$	$0.1 \pm 0.0$

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Mean  $\pm$  standard deviation ( $n \cdot 3$ ); oxygen by difference

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507	Figure captions
508	Fig. 1. (a) Schematic representation of the bench scale system used for the intraparticle gas
509	measurements under pyrolysis conditions; (b) detail of the sampling probe and thermocouple
510	locations within the particle.
511	Fig. 2. Birch wooden spheres TG analysis
512	Fig. 3. Birch wooden spheres DSC analysis
513	Fig. 4. Triple test temperature profiles in the center and on the surface of a) 31.8 mm particle, b)
514	19.0 mm particle
515	Fig. 5a. 31.8 mm particle gas distribution for major components evolved
516	Fig. 5b. 31.8 mm particle gas distribution for minor components evolved
517	Fig. 6a: 19.0 mm particle gas distribution for major components evolved
518	Fig. 6b: 19.0 mm particle gas distribution for minor components evolved



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particle

(a)

Fig. 1. (a) Schematic representation of the bench scale system used for the intraparticle gas
measurements under pyrolysis conditions; (b) detail of the sampling probe and thermocouple
locations within the particle.

**(b)** 

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**Fig. 4.** Triple test temperature profiles in the center and on the surface of a) 31.8 mm particle, b)







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**Fig. 5b.** 31.8 mm particle gas distribution for minor components evolved

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#### 19.0 mm particle major components

# $0.6 = \begin{bmatrix} 0.12 \\$

Measured Center Temperature (°C)

#### 19.0 mm particle minor components

