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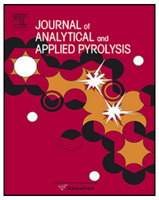

Short communication

Biomass energy behavior study during pyrolysis process by intraparticle gas sampling

Simona Ciuta[a,*], Francesco Patuzzi[b], Marco Baratieri[b], Marco J. Castaldi[a,**]

[a] *Chemical Engineering Department, City College, City University of New York, 160 Convent Avenue, New York, NY 10031, USA*
[b] *Free University of Bozen-Bolzano, piazza Università 5, 39100 Bolzano, Italy*

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ABSTRACT

Understanding pyrolysis kinetics is imperative for industrial biomass conversion applications. One of the lesser known aspects of wood pyrolysis concerns the actual energy change happening during the process within the biomass sample. The use of gas component detection methods in concert with thermal analysis can help in better understanding the reaction sequence and mechanisms during pyrolysis. 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 non-oxidant thermal treatment of biomass. The pyrolysis experimental tests have been performed on birch wooden spheres, on two different diameters 19.0 mm and 31.8 mm. The thermogravimetric (TG) analysis revealed a rapid mass loss in the temperature range 290–410 °C and a total mass loss of 75–76%. The DSC analysis showed exothermic behavior above 305 °C and two maximum peaks at 350 °C and 413 °C. Evolved gases such as H_2, CH_4, CO CO_2, C_2H_4, C_2H_6 and C_3H_6/C_3H_8 were extracted through a probe using a micro sample system. The measurements showed a simultaneous release of CO_2 and CO with a maximum occurring around 325 °C, for larger samples. The CO release, while lower in absolute concentration, is much more stable during the entire heating of the particle. The measurements showed a pronounced transition between hydrogen release and subsequent hydrocarbons release. The saturated hydrocarbons such as methane and ethane were observed in high quantities, 19% and 0.9% respectively. The chemical species concentration profiles of the evolved gases from the particle center could enable a corresponding temperature calculation.

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].

Wood pyrolysis is a complex process influenced by several parameters which directly affect the yields and characteristics of the products obtained. Although many experimental and modeling studies [2–4] focused on explaining the pyrolysis mechanisms to transform feedstock into valuable products, there still remains a number of aspects not fully understood. In particular, many of these studies are based on thermogravimetric analysis and reveal different temperature 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 chemical species temporal (or thermal) evolution

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[*] Corresponding author. Present address: Chemical Engineering Department, Grove School of Engineering, City College of New York, 140th Street and Convent Avenue, Steinman Hall, Room 314, New York, NY 10031, USA. Tel.: +1 718 715 9079.
[**] Corresponding author. Present address: Chemical Engineering Department, Grove School of Engineering, City College of New York, 140th Street and Convent Avenue, Steinman Hall, Room 307, New York, NY 10031, USA. Tel.: +1 212 650 6679.
E-mail addresses: sciuta@che.ccny.cuny.edu, ciuta_simona@yahoo.com (S. Ciuta), mcastaldi@che.ccny.cuny.edu (M.J. Castaldi).

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setting the stage for clarifying the energy changes throughout the sample decomposition, by identifying component gases evolved and 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 reactions have been found to vary widely, ranging from exothermic to endothermic under similar conditions. Furthermore, this exothermic/endothermic variation is observed over a range of reported test conditions [8–11]. Results reported in literature show that mainly the thermal degradation of cellulose is endothermic, while the char formation reaction is exothermic [12]. However these processes overlap during thermal decomposition and lead to a composite result. Importantly subsequent reactions involving released gases are difficult to quantify and may provide additional endothermic enthalpy due to cracking type reactions or exothermic enthalpy related to condensation reactions.

Thermal analysis is an extensively used technique which provides insight regarding the apparent kinetics of heterogeneous reactions. However, the data obtained by thermo analytical techniques alone does not provide complete information to draw mechanistic conclusions about a solid state decomposition process [13]. To fully understand the reaction sequences occurring, thermal analysis methods must be coupled with evolved gas analysis. This enables a better quantitative assessment of the gases released corresponding to thermal decomposition. The use of gas component detection methods in concert with thermal analysis can help in this effort. Importantly the identification of the origin of the gaseous components must be done to accurately 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 temperature peak, which has been interpreted as exothermic reactions typically present at operating temperatures of 500 °C [9]. These energy changes were attributed to the experimental conditions (the sample size, the nature of the atmosphere, and the presence of impurities) [10] or as exothermic decomposition of the remaining solid [9]. In other studies, under slow pyrolysis conditions, small particles of cellulose and wood show a global endothermic behavior, whereas samples with larger particle sizes exhibit exothermic behaviors [17]. This difference was explained in terms of the enhanced interaction of hot pyrolysis vapors with the decomposing solid, which involves an exothermic reaction that leads to the formation of char [8].

Though several studies on this topic are available in the literature, none of them present intraparticle gas analysis of the evolved chemical species which is important to the 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 non-oxidant thermal treatment.

Table 1
Proximate and ultimate analysis of birch wood.

Proximate analysis (dry basis; moisture: as received basis)				
Moisture	Ash	FC	VM	
8.2 ± 0.5	0.8 ± 0.1	13.2 ± 1.1	85.9 ± 1.3	
Ultimate analysis (dry ash free basis)				
C	H	N	O	S
47.6 ± 0.4	6.9 ± 0.2	0.1 ± 0.0	45.3 ± 0.7	0.1 ± 0.0

Mean ± standard deviation ($n \geq 3$); oxygen by difference.

2. Material and methods

2.1. Feedstock characterization

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

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

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

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

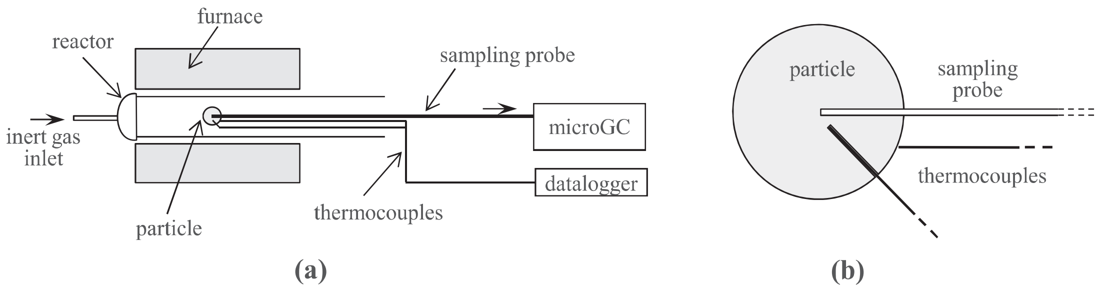

Fig. 1. (a) Schematic representation of the bench scale system used for the intraparticle gas measurements under pyrolysis conditions; (b) detail of the sampling probe and thermocouple locations within the particle.

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.

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

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.

The sampling of the evolved gas has been performed by means of a sampling probe inserted in the center of the particle through an opening bored into the particle enabling an interference fit of the probe with the biomass sample (Fig. 1b). The inert, passivized sampling probe (internal diameter: 0.76 mm, length: 914 mm) was directly connected to a gas chromatograph (3000 microGC, Inficon) used for the online analysis of the evolved gas. Gases were extracted through the probe using the internal microGC pump. The microGC is equipped with two columns, a Molsieve column for the detection of He, H_2, O_2, N_2, CH_4 and CO and a Plot-U column for the detection of CO_2, C_2H_4, C_2H_6 and C_3H_6/C_3H_8. In addition, the temperatures at the center and at the 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 of the radius (i.e. 7.1 mm and 11.9 mm for the small, respectively large particle) to avoid 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 3 min which roughly corresponds to the time scale of the particles' thermal degradation time (4–6 min for the smaller particle and 8–10 min 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.

3. Results

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

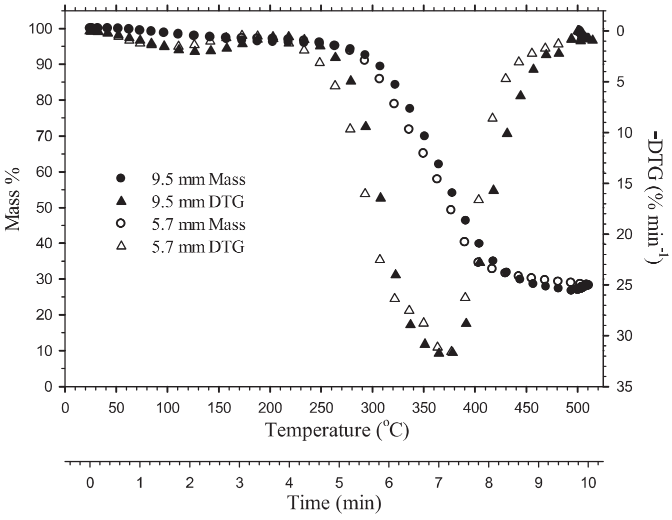

Fig. 2. Birch wooden spheres TG analysis.

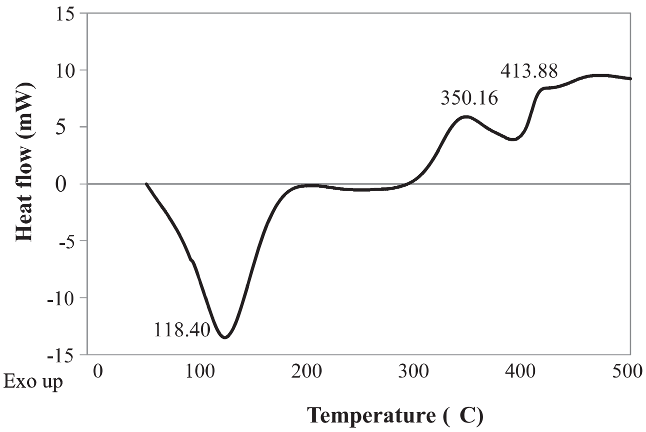

Fig. 3. Birch wooden spheres DSC analysis.

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 however on experimental conditions such as heating rate or environment. In this case it seems that hemicellulose and cellulose decomposition are overlapping causing an exothermic peak with a maximum at 350 °C. The DSC analysis reveals a second exothermic peak above 400 °C which might be attributed to the last stage of degradation of lignin [29] and some other secondary reactions causing char or tar formation [21,30]. It is exactly this convolution of thermal information that we are trying to address with the newly developed technique. The DSC data show exothermic reactions in the bulk material happening at temperatures greater than 300 °C 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 behavior could not be completely understood by differential scanning calorimetry and because of double peaks observed in the data. Therefore further investigations of temperature profiles obtained by thermocouple measurements (Fig. 4a and b) and gas sampling will help elucidate the actual transformations occurring during pyrolysis process.

3.2. Temperature measurement

The temperature profiles for both the particles show temperatures in the center which are exceeding the temperatures measured on the surface of the biomass samples. These trends were encountered in other available studies in literature [9]. For the 31.8 mm particle the average temperature difference between the center peak and the surface is almost 50 °C, while for the smaller 19.0 mm particle this difference represents approximately 25 °C. The influence of particle size on thermal decomposition and energy change inside the biomass sample is emphasized through the time difference between the two particles when the center peak appears. If for the small 19.0 mm particle the temperature in the center exceeds the surface temperature after 2.5–3 min, for the larger 31.8 mm particle the temperature peak is significantly delayed to 6.5–8 min. Although the same trend was obtained compared to some studies reported in literature, when the experiments were repeated at the same conditions (triple repetitions) the profiles revealed significant differences for the same size particle. It can be noticed from Fig. 4a and b that the center peak of temperature does not happen in the same moment of time for the three repetitions. Furthermore, the temperature where the center thermocouple reading exceeds the surface thermocouple reading is offset. Due to the heterogeneity of biomass, this offset and variable maximum temperature may be a result of different reactions occurring inside the particle. For example, if one condition has more hydrolysis reactions compared to cracking or condensation reactions, the aggregate enthalpy change will be different. It is anticipated as the intraparticle sample technique is further refined, elucidation of the reaction sequences will be possible.

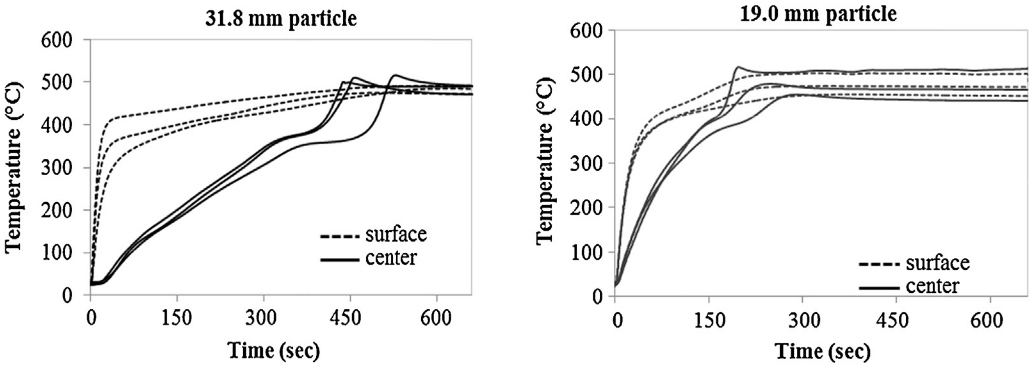

Fig. 4. Triple test temperature profiles in the center and on the surface of (a) 31.8 mm particle, (b) 19.0 mm particle.

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 Figs. 5a and b and 6a 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_2 [24]. However, CO_2 rapidly decreases to a concentration nearly equal to CO concentration by 350 °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

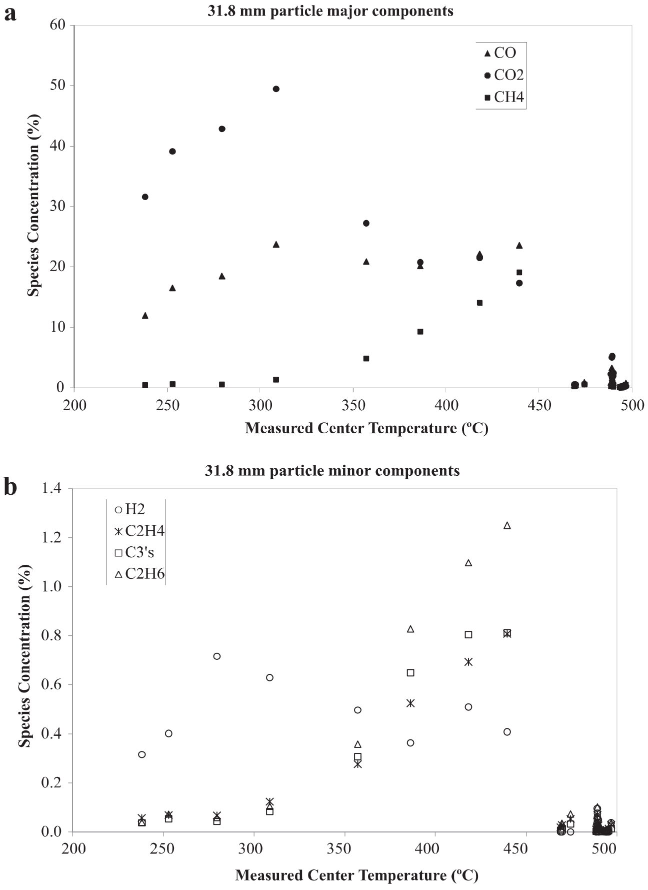

Fig. 5. (a) 31.8 mm particle gas distribution for major components evolved. (b) 31.8 mm particle gas distribution for minor components evolved.

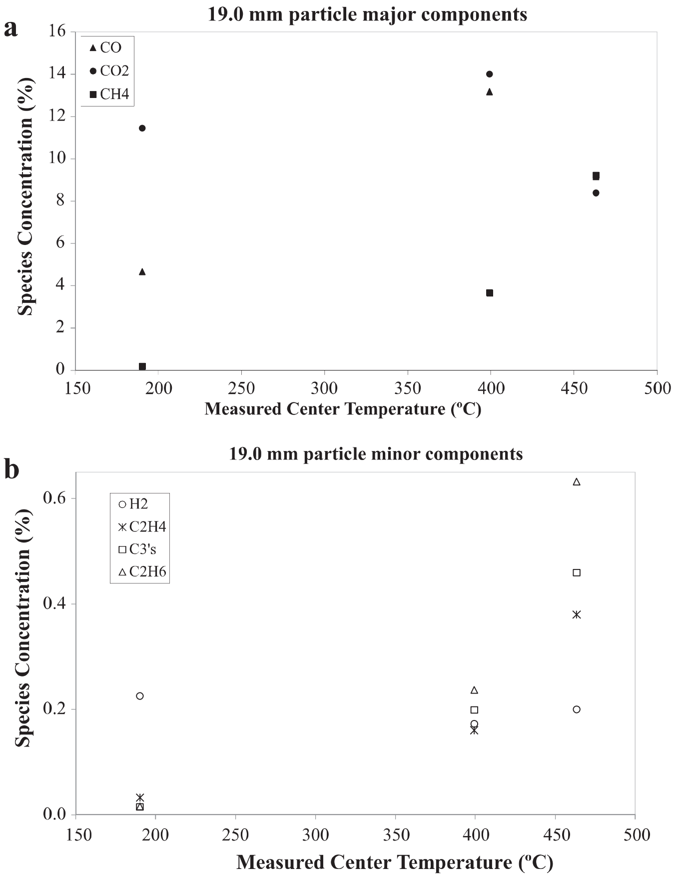

Fig. 6. (a) 19.0 mm particle gas distribution for major components evolved. (b) 19.0 mm particle gas distribution for minor components evolved.

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%.

CO was mainly released out with the cracking of carbonyl (C—O—C) and carboxyl (C═O). The contribution of cellulose pyrolysis to CO release was minor, and it was found that CO release was mostly caused by the pyrolysis of hemicellulose in this temperature range [30]. Some other authors [33] indicate that decarbonylation reactions of carboxide-containing compounds cause the release of CO, the decarboxylation reactions of carboxide-containing compounds cause the release of CO_2, which is also related to the internal dehydration of cellulose and the formation of char. CO presence at higher temperatures might be due to the decarboxylation process in the aromatic condensation of lignin [33]. The evolved gas profiles confirm the literature, but reveal more insight provided by our new sampling technique. The hydrogen profile (shown in Fig. 5b) matches that of CO_2 and it reaches a pronounced maximum near 325 °C followed by a significant reduction. For example, the total CO_2 concentration decrease is 59% from the maximum reached near 325 °C to approximately 20% at higher temperatures. The concentration of hydrogen 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.

Fig. 5b presents the species concentration profiles for the 31.8 mm particle as a function of measured center temperature and is complementary to Fig. 5a. Here the measurements show a pronounced transition between hydrogen release and subsequent hydrocarbons release. As discussed above the hydrogen reaches its maximum concentration near 300–325 °C followed by a significant reduction. Nearly coincident with the decline in hydrogen and CO_2, a sharp increase in hydrocarbon release is observed. The hydrocarbon concentrations remain below 0.1% until temperatures greater than 325 °C. Methane evolution follows a similar trend with temperature, as shown in Fig. 5a, with values of concentration nearly one order of magnitude higher than the values reached by the other hydrocarbons. This is expected since methane is more stable than higher order hydrocarbons. Shown in Fig. 5b is an aggregate concentration of three carbon hydrocarbons (propene and propane) labeled C3's. This was done as it was difficult to distinguish between the different three carbon compounds due to the separation method used which enabled higher sampling rates but lost some speciation resolution. Future experiments will focus on development of a method that allows both rapid sample acquisition without loss of speciation. It is interesting to note that saturated hydrocarbons such as methane and ethane are observed in high quantities. This could indicate that any free hydrogen is immediately bound as the biomass structure starts to decompose, again suggesting that the molecular hydrogen, i.e. H_2, 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_2 and CO evolving earlier and at the highest concentrations agrees well with the trends observed for the 31.8 mm particle measurements. However, here CO_2 and CO concentrations are much closer and follow similar trends. For the 31.8 mm particle there was a steady production of CO and a more prominent profile for CO_2. Yet when the measured center temperature reaches about 450 °C similar concentrations for CO, CO_2 and CH_4 were observed. Importantly the total amounts measured in the 19.0 mm particle are nearly a factor of three less than the 31.8 mm particle. While this is still under investigation, it is could be due to more tars being generated compared to the larger particle. The gases evolved in the 19.0 mm particle have a much shorter path to diffuse and reach the surface compared to the 31.8 mm particle. This may explain the reason for the similarity in concentration between CO and CO_2 for the 19.0 mm particle and the major difference for the 31.8 mm particle above 400 °C. Specifically as the smaller particle is being heated any bound water has a greater potential to diffuse out of the particle before decomposing compared to the larger particle where the water would have a longer time in contact with the biomass surface.

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 concentrations compared to the 31.8 mm particle even if the gas evolution trends are similar. The onset of hydrocarbon evolution occurs nearly coincident with an observed decrease in CO and CO_2 and begins at higher temperatures. In the incipient phases of the devolatilization process, the main gas component is the CO_2. Its concentration started to decrease after 3–4 min when it reaches its minimum of 25%. The secondary reactions of volatiles produce mostly CO, H_2 and CH_4 rather than CO_2 [34] this being noticed by the increase of these components percentage, achieving their maximum before 5 min of applied thermal treatment. As expected, the pyrolysis process lasted longer for the bigger particle treatment, 17.5 min compared to 10 min for the small particles.

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

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.

The behavior of wood samples during devolatilization was determined with thermogravimetric (TG) analysis and differential scanning calorimetry (DSC). The DSC data revealed the presence of two exothermic peaks between 305 °C and 390 °C and above 400 °C. The temperature profiles for both the particles show temperatures in the center which are exceeding the temperatures measured on the surface of the biomass samples. The gas measurements showed a simultaneous release of CO_2 and CO with a maximum occurring around 325 °C. The CO release, while lower 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 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 sample temperature.

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References

[1] R. Bilbao, A. Millera, M.B. Murillo, Temperature profiles and weight loss in the thermal decomposition of large spherical wood particles, Ind. Eng. Chem. Res. (1993) 1811–1817.
[2] J.E. White, W.J. Catallo, B.L. Legendre, Biomass pyrolysis kinetics: a comparative critical review with relevant agricultural residue case studies, J. Anal. Appl. Pyrolysis 91 (2011) 1–33.
[3] D. Neves, H. Thunman, A. Matos, L. Tarelho, A. Gómez-Barea, Characterization and prediction of biomass pyrolysis products, Prog. Energy Combust. Sci. 37 (2011) 611–630.
[4] J. Ratte, F. Marias, J. Vaxelaire, P. Bernada, Mathematical modelling of slow pyrolysis of a particle of treated wood waste, J. Hazard. Mater. 170 (2009) 1023–1040.
[5] S. Singh, C. Wu, P.T. Williams, Pyrolysis of waste materials using TGA-MS and TGA-FTIR as complementary characterisation techniques, J. Anal. Appl. Pyrolysis 94 (2012) 99–107.
[6] C. Casajus, J. Abrego, F. Marias, J. Vaxelaire, J.L. Sánchez, A. Gonzalo, Product distribution and kinetic scheme for the fixed bed thermal decomposition of sewage sludge, Chem. Eng. J. 145 (2009) 412–419.
[7] G. Ionescu, E.C. Rada, M. Ragazzi, C. Mărculescu, A. Badea, T. Apostol, Integrated municipal solid waste scenario model using advanced pretreatment and waste to energy processes, Energy Convers. Manage. 76 (2013) 1083–1092.
[8] C. Gomez, E. Velo, F. Barontini, V. Cozzani, Influence of secondary reactions on the heat of pyrolysis of biomass, Ind. Eng. Chem. Res. 48 (2009) 10222–10233.
[9] W.C. Park, A. Atreya, H.R. Baum, Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis, Combust. Flame 157 (2010) 481–494.
[10] I. Turner, P. Rousset, R. Rémond, P. Perré, An experimental and theoretical investigation of the thermal treatment of wood (*Fagus sylvatica* L.) in the range 200–260 °C, Int. J. Heat Mass Transfer 53 (2010) 715–725.
[11] I. Milosavljevic, V. Oja, E.M. Suuberg, Thermal effects in cellulose pyrolysis: relationship to char formation processes, Ind. Eng. Chem. Res. 35 (1996) 653–662.
[12] A. Dufour, B. Ouartassi, R. Bounaceur, A. Zoulalian, Modelling intra-particle phenomena of biomass pyrolysis, Chem. Eng. Res. Des. 89 (2011) 2136–2146.
[13] B.a. Howell, Utility of kinetic analysis in the determination of reaction mechanism, J. Therm. Anal. Calorim. 85 (2006) 165–167.
[14] G.-Q. Chen, Z.-H. Luo, X.-Y. Lan, C.-M. Xu, J.-S. Gao, Evaluating the role of intraparticle mass and heat transfers in a commercial FCC riser: a meso-scale study, Chem. Eng. J. 228 (2013) 352–365.
[15] T. Pattanotai, H. Watanabe, K. Okazaki, Experimental investigation of intraparticle secondary reactions of tar during wood pyrolysis, Fuel 104 (2013) 468–475.
[16] R. Bilbao, J. Arauzo, M.B. Murillo, M.L. Salvador, Gas formation in the thermal decomposition of large spherical wood particles, J. Anal. Appl. Pyrolysis 43 (1997) 27–39.
[17] M.J.J. Antal, G. Varhegyi, Cellulose pyrolysis kinetics: the current state of knowledge, Ind. Eng. Chem. Res. 34 (1995) 703–717.
[18] C. Marculescu, S. Ciuta, Wine industry waste thermal processing for derived fuel properties improvement, Renew. Energy 57 (2013) 645–652.
[19] A. Carmona, E. Martı, J.A.C. Ferrer, Use of thermogravimetry/mass spectrometry analysis to explain the origin of volatiles produced during biomass pyrolysis, Ind. Eng. Chem. Res. (2009) 7430–7436.
[20] T. Qu, W. Guo, L. Shen, J. Xiao, K. Zhao, Experimental study of biomass pyrolysis based on three major components: hemicellulose, cellulose, and lignin, Ind. Eng. Chem. Res. 50 (2011) 10424–10433.
[21] B. Zapata, J. Balmaseda, E. Fregoso-Israel, E. Torres-García, Thermo-kinetics study of orange peel in air, J. Therm. Anal. Calorim. 98 (2009) 309–315.
[22] Q. Liu, S. Wang, Y. Zheng, Z. Luo, K. Cen, Mechanism study of wood lignin pyrolysis by using TG–FTIR analysis, J. Anal. Appl. Pyrolysis 82 (2008) 170–177.
[23] H. Zhou, Y. Long, A. Meng, Q. Li, Y. Zhang, The pyrolysis simulation of five biomass species by hemi-cellulose, cellulose and lignin based on thermogravimetric curves, Thermochim. Acta 566 (2013) 36–43.
[24] A.A. Salema, M.T. Afzal, F. Motasemi, Is there synergy between carbonaceous material and biomass during conventional pyrolysis? A TG-FTIR approach, J. Anal. Appl. Pyrolysis 105 (2014) 217–226.
[25] Q. Liu, Z. Zhong, S. Wang, Z. Luo, Interactions of biomass components during pyrolysis: a TG-FTIR study, J. Anal. Appl. Pyrolysis 90 (2011) 213–218.
[26] A. Barneto, J. Carmona, Use of thermogravimetry/mass spectrometry analysis to explain the origin of volatiles produced during biomass pyrolysis, Ind. Eng. Chem. Res. (2009) 7430–77436.
[27] J. Collazo, J.A. Pazó, E. Granada, Á. Saavedra, P. Eguía, Determination of the specific heat of biomass materials and the combustion energy of coke by DSC analysis, Energy 45 (2012) 746–752.
[28] F. He, W. Yi, X. Bai, Investigation on caloric requirement of biomass pyrolysis using TG–DSC analyzer, Energy Convers. Manage. 47 (2006) 2461–2469.
[29] M.a. Lopez-Velazquez, V. Santes, J. Balmaseda, E. Torres-Garcia, Pyrolysis of orange waste: a thermo-kinetic study, J. Anal. Appl. Pyrolysis 99 (2013) 170–177.
[30] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, Fuel 86 (2007) 1781–1788.
[31] Y. Su, Y. Luo, W. Wu, Y. Zhang, S. Zhao, Characteristics of pine wood oxidative pyrolysis: degradation behavior, carbon oxide production and heat properties, J. Anal. Appl. Pyrolysis 98 (2012) 137–143.
[32] I.D.P.R. Moreira, Performance of simplified G2 model chemistry approaches in the study of unimolecular mechanisms: thermal decomposition of acetic acid in gas phase, J. Mol. Struct. Theochem. 466 (1999) 119–126.
[33] S. Xin, H. Yang, Y. Chen, X. Wang, H. Chen, Assessment of pyrolysis polygeneration of biomass based on major components: product characterization and elucidation of degradation pathways, Fuel 113 (2013) 266–273.
[34] Z. Luo, S. Wang, Y. Liao, J. Zhou, Y. Gu, K. Cen, Research on biomass fast pyrolysis for liquid fuel, Biomass Bioenerg. 26 (2004) 455–462.
[35] J.M. Smith, H.C. Van Ness, M.M. Abbott, Introduction to chemical engineering, Thermodynamics (2005).