



Short communication

Biomass energy behavior study during pyrolysis process by intraparticle gas sampling



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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 H₂, CH₄, CO, CO₂, C₂H₄, C₂H₆ and C₃H₆/C₃H₈ were extracted through a probe using a micro sample system. The measurements showed a simultaneous release of CO₂ 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.

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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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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

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.

knowledge, this is the first intraparticle gas sampling measurement performed during non-oxidant thermal treatment.

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

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