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Study of light, middle and severe torrefaction and effects of extractives and chemical compositions on torrefaction process by thermogravimetric analysis in five fast-growing plantations of Costa Rica

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ABSTRACT

Light (T_{light}), middle (T_{middle}) and severe (T_{severe}) torrefaction processes by TGA in woody biomass were evaluated in relation to devolatilization rate (D_{rate}), maximum devolatilization rate (DR_{max}), temperature at the level of 50% weight loss (T_{50}), rate of weight loss at T_{50} (R_{50}) and weight loss during torrefaction ($W_{loss\text{-}DT}$). The relationship between these parameters with cellulose, lignin and extractives content was established. The TGA and devolatilization curves showed that DR_{max} was of 4.16, 1.80 and 0.70%/min for T_{light}, T_{middle} and T_{severe} respectively. $W_{loss\text{-}DT}$ in T_{light} ranges between 3 and 6%, between 9 and 14% in T_{middle} and from 11 to 16% in T_{severe}. *G. arborea* showed the highest $W_{loss\text{-}DT}$, with 29.10% for T_{severe} and *C. Lusitania and T. grandis* the lowest $W_{loss\text{-}DT}$, with 15% for T_{severe}. The duration of D_{max} was of 5 min in T_{light} and T_{middle} and 6 min in T_{severe}. Cellulose, lignin and carbon presented statistically significant correlations with R_{50}, T_{50}, $W_{loss\text{-}DT}$ and DR_{max}. Ash content was correlated with $W_{loss\text{-}DT}$ and DR_{max} in all torrefaction condition. Extractives in dichloromethane was significantly in many parameters. We conclude that the torrefaction of different woody species can be optimized as biomass feedstocks with a specific temperature and time of torrefaction.

1. Introduction

Biomass is gaining relevance as an additional source of energy, as it could counteract global warming caused by fossil fuel consumption [1]. Batidzirai et al. [2], mention that biomass will account for 71.5% of the global energy generation in 2035. However, biomass shows a number of characteristics that hinder its direct utilization as a source of energy, such as moisture content, hygroscopic character, low energy density, storage difficulties, among others [3,4].

Some technologies using thermal treatment of the biomass contribute in further exploitation of that kind of materials for energetic purposes, as they can solve some of the difficulties discussed above [4]. Among those thermal treatments, torrefaction seems to offer an effective response [5]. Biomass torrefaction occurs between 200 and 300 °C, taking from minutes to hours, usually at atmospheric pressure in the presence of inert atmosphere (i.e. without oxygen). This type of treatments includes benefits over the materials, such as higher heating value, lower atomic O/C and H/C ratios and moisture content, higher hydrophobicity, improved grindability, among others [6–8]. Due to its advantages, torrefaction is a technique used in different types of biomass [5], including agricultural crops [9] and different kinds of woody species [10]. In the case of woody species, these present heterogeneity as to their chemical nature as well as the quantity and characteristics of the products and by-products during the torrefaction process [8].

The modification of the properties of biomass produced by the torrefaction process is related to temperature conditions [11]. For example, under low torrefaction temperatures, water and substances with low molecular weight are freed and hemicellulose starts to decompose, while cellulose and lignin are scarcely affected

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Abbreviations

T_{BT}	temperature at the beginning of torrefaction
C	carbon content
C/N	carbon-to-nitrogen ratio
N	nitrogen content
E_{HW}	extractives in hot water
E_{CW}	extractives in cold water
CH_2Cl_2	dichloromethane
Et-To	ethanol-toluene solution
1% NaOH	1% aqueous solution of sodium hydroxide
TGA	thermogravimetric analysis
DTG	derivative thermogravimetry
t_{bmd}	time of beginning of maximum devolatilization rate
t_{bt}	time of beginning of torrefaction
t_{peak}	time of maximum devolatilization rate during torrefaction
t_{fmd}	final time of maximum devolatilization rate
t_{ft}	time of final of torrefaction
DR	devolatilization rate
DR_{max}	maximum devolatilization rate
T_T	torrefaction temperatures
t_T	torrefaction times
T_{50}	temperature at the level of 50% weight loss
R_{50}	rate of weight loss at T_{50}
$W_{loss-BT}$	weight loss before torrefaction
$W_{loss-DT}$	weight loss during torrefaction
$W_{maintained}$	weight maintained at the end of torrefaction

[5,12]. By contrast, the structure of cellulose and lignin becomes affected at more severe conditions [13,14].

Although different types of biomass have their own torrefaction temperature ranges, some authors have categorized the temperatures in three ranges: light torrefaction with temperatures ranging from 200 to 235 °C, middle torrefaction with temperatures between 235 and 275 °C and severe torrefaction with temperatures from 275 to 300 °C [5]. In light torrefaction, there are mainly presented the release of volatiles and the degradation of hemicellulose. When biomass undergoes middle torrefaction, hemicellulose decomposition and volatiles liberation are intensified. Hemicellulose is substantially depleted and cellulose is consumed to a certain extent. With regard to severe torrefaction, hemicellulose is almost completely depleted and cellulose is largely decomposed. By virtue of substantial removal of hemicellulose and cellulose from biomass by severe torrefaction, the weight is lowered significantly but the energy density of the material is greatly intensified.

The advance of torrefaction processes can be monitored performing mass measurements, hence thermogravimetric analyses (TGA) are useful for their study [13,14]. In this type of measurements, heat and gas transfer limitations are controlled and therefore truly reflects the reactions involved during torrefaction [5,13,15]. Chen and Kuo [13,14] showed the effect of torrefaction temperature using TGA in the structure of the main components of the wood (i.e. lignin cellulose and hemicellulose). Similarly, Chen et al. [5] developed an extensive analysis of the effects of various temperatures on the components of the wood using TGA, and pointed out that with light torrefaction, hemicellulose is thermally degraded to a certain extent, whereas cellulose and lignin are only slightly affected.

Torrefaction time is another factor affecting the various components of the biomass [5]. The torrefaction process can take from several minutes to hours [16]. Then, different combinations of temperature and residence time can be used to achieve a given degree of torrefaction [17].

Wood is a type of biomass with interesting properties to be used as a source of energy [18] and the torrefaction process can increase its energy efficiency [19]. However, there is a lot of information on torrefaction of tropical woods (both from plantations and from natural forests) that need to be studied in detail [20–22].

Considering the aforementioned, the present work aims to evaluate the characteristics of torrefaction at three temperature conditions (light, middle and severe) of biomass from five tropical woody species (*Cupressus lusitanica*, *Dipteryx panamensis*, *Gmelina arborea*, *Tectona grandis* and *Vochysia ferruginea*) using TGA. The range of devolatilization, weight losses during the thermal processes and the devolatilization rate were considered. In addition, it was explored the relationship of these parameters with cellulose, lignin, extractives in different solvents as well as ash, carbon and volatiles contents of the species studied. The results obtained can help to establish optimal conditions for the torrefaction of different biomass feedstocks as well as the control of processes at larger scales.

2. Methodology

2.1. Sampling and materials used

Five woody species from fast growing forest plantations of Costa Rica were analyzed. The age of the plantations ranged between 6 and 21 years. The data of density and dasometric conditions were described in detail by Moya and co-workers in a previous report [22]. Three trees were felled and cross-sections obtained at 1.3 m height. This sample was chipped and grinded. For those species presenting sapwood and heartwood, a 50%–50% combination of each type of wood was made when possible. Sawdust was sieved through 0.25 mm and 0.42 mm meshes (40–60 meshes, respectively). The material in between these two meshes was used for torrefaction analyses by TGA and chemical analyses. All the samples were kept at 7% moisture content and the determinations were obtained from 3 different samples per species.

2.2. Determination of the chemical composition and extractives

The following components where determined for each woody biomass: lignin (TAPPI T222 om-02 [23]), cellulose (following the procedure of Seifert [24]), extractives in hot water and cold water (E_{HW} and E_{CW}) (ASTM D-1110-84 [25]), extractives in sodium hydroxide (1% NaOH) (ASTM D-1109-84 [26]), extractives in an ethanol-toluene solution (Et-To) (ASTM D-1107-96 [27]) and extractives in dichloromethane (CH_2Cl_2) (ASTM D-1108-96 [28]). In addition, carbon (C), nitrogen (N) and the C/N ratio were determined (using an Elementar Analysensysteme, model Vario Macro Cube).

2.3. Thermogravimetric analysis (TGA)

Experiments involving mass loss measurements were developed using a thermogravimetric analyzer TA Instruments SDT Q600. These were developed under atmospheric pressure in an inert environment provided by a nitrogen flow (100 mL/min of UHP N_2), using ca. 5 mg of the corresponding sample.

2.4. Torrefaction conditions

The torrefaction characteristics of the five woody biomass