BRUNO DE FREITAS HOMEM DE FARIA

CHARACTERIZATION AND QUALIFICATION OF TORREFIED BIOMASSES PROPERTIES DURING FUNGAL DETERIORATION FOR ENERGETIC PURPOSES

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Ciência Florestal, para obtenção do título de *Doctor Scientiae*.

Orientadora: Angélica de Cássia O. Carneiro

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Assentimento:

Bruno de Freitas Homem de Faria
Autor

Angélica de Cássia Oliveira Carneiro
Orientadora

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RESUMO

FARIA, Bruno de Freitas Homem de, D.Sc., Universidade Federal de Viçosa, novembro de 2020. **Caracterização e qualificação de propriedades de biomassas torrificadas durante a deterioração fúngica para fins energéticos**. Orientadora: Angélica de Cássia Oliveira Carneiro.

Biomassas lignocelulósicas são alternativas viáveis aos combustíveis fósseis para produzir energia ecologicamente correta, principalmente pelo seu aspecto renovável e sustentável, e pela disponibilidade mundial. O processo de torrefação pode ser uma boa forma de aprimorar algumas características da biomassa para obter melhores condições de armazenamento e aproveitamento energético. O objetivo deste estudo foi avaliar o impacto da torrefação na estocagem de diferentes resíduos de biomassas, simulado pela deterioração fúngica, para uso energético. O impacto da lixiviação e da deterioração dos fungos nas propriedades químicas e energéticas das biomassas *in natura* e torrificadas foram avaliados. Finalmente, espectros no infravermelho próximo (NIR) foram coletados para construir modelos PLS-DA e PLS para uso como uma ferramenta para o conhecimento da deterioração fúngica das biomassas. Casca de café, bagaço de cana-de-açúcar e resíduos de pinus e eucalipto foram torrificados a 290 °C em reator tipo rosca sem fim durante 5, 7,5, 10, 15 ou 20 min. Os efeitos do tipo de matéria-prima e do parâmetro do processo de torrefação (tempo de residência) sobre as características energéticas das biomassa foram investigados. As biomassas *in natura* e torrificadas foram então submetidas à lixiviação e aos fungos de podridão branca (*Trametes versicolor*) e marrom (*Coniophora puteana)* para simular as condições de armazenamento. A perda de massa após a etapa de lixiviação, teor de umidade e perda de massa devido à deterioração fúngica após 2, 4, 8, 12, 16 semanas foram obtidas. Variações no conteúdo de carbono e no poder calorífico superior foram observados durante a deterioração fúngica das biomassas *in natura* e torrificadas. A virulência do fungo de podridão marrom foi maior para o pinus em relação ao de podridão branca levando à perdas de massa próxima a 35% para o pinus torrificado por 15 minutos. Para o bagaço de cana torrificado por 7,5 e 10 minutos a perda de massa durante a deterioração por fungos foi menor do que 10% para todas semanas de avaliação sendo muito inferior à perda de massa obtida para o bagaço *in natura* em 16 semanas de exposição (aproximadamente 60%). Modelos PLS para predição do poder calorífico das biomassas apresentaram boa capacidade preditiva com RMSEP de 0,1968 e Rp de 98,17%. Os modelos PLS-DA são confiáveis para

diferenciar tipos de biomassa e então, por meio de modelos específicos, identificar o fungo de decomposição mais ativo em biomassas *in natura* e torrificadas e em qual estágio temporal de deterioração as biomassas se encontram. Os modelos PLS desenvolvidos mostraram-se eficientes na predição do poder calorífico superior de biomassas *in natura* e torrificadas de acordo com seus estágios de deterioração fúngica. A torrefação do eucalipto, pinus, bagaço de cana-de-açucar e casca de café parece ser um método viável para eliminar algumas das desvantagens dessas biomassas, pois melhora significativamente o conteúdo de energia e evita a absorção de umidade durante o armazenamento. Além disso, a casca de café parece ser uma biomassa muito promissora para conversão de energia pelo processo de torrefação, devido ao bom incremento energético.

Palavras-chave: Biocombustível. Deterioração fúngica. Espectroscopia no infravermelho próximo. Lignocelulose.

ABSTRACT

FARIA, Bruno de Freitas Homem de, D.Sc., Universidade Federal de Viçosa, November, 2020. **Characterization and qualification of torrefied biomasses properties during fungal deterioration for energetic purposes**. Advisor: Angélica de Cássia Oliveira Carneiro.

Lignocellulosic biomasses are a reliable alternative to fossil fuels to produce more environmentally friendly energy, mainly due to their renewable and sustainable characteristics, and their worldwide availability. The torrefaction process can be a good way to improve specific characteristics of biomass to achieve better storage conditions and for energetic use. The aim of this study was to evaluate the impact of torrefaction on the storage of different biomasses residues, simulated by fungal deterioration, for energetic purposes. The impact of leaching and fungal deterioration on the chemical and energy properties of raw and torrefied biomasses for energy conversion was thus evaluated. Finally, near infrared spectra were collected to build PLS-DA and PLS models to be able to better understand the fungal deterioration of biomasses. Coffee husk, sugarcane bagasse, pine residues and eucalyptus residues were torrefied at 290 °C in a screw type reactor, for 5, 7.5, 10, 15 or 20 min. The effects of feedstock type and torrefaction process parameter (holding time) on their energy characteristics were investigated. Raw and torrefied biomasses were then submitted successively to leaching and to white rot (*Trametes versicolor*) and brown rot (*Coniophora puteana*) fungi to simulate storage conditions. Mass loss after the leaching step, moisture content and mass loss due to fungal deterioration after 2, 4, 8, 12, and 16 weeks were recorded. Variations in carbon content and high heating value were observed during the fungal deterioration of raw and torrefied biomass. Brown rot fungus was more virulent than white rot fungus in pine, leading to mass losses close to 35% for pine torrefied for 15 minutes. For sugarcane bagasse torrefied for 7.5 and 10 minutes, the mass loss during fungal deterioration was less than 10% for all evaluation weeks, being much lower than the mass loss observed for raw sugarcane at 16 weeks (approximately 60%). PLS models for predicting the calorific value of biomasses showed good predictive capacity with RMSEP of 0.1968 and Rp of 98.17%. PLS-DA classification models are reliable to differentiate types of biomass and then, through specific models, identify the most active decay fungus in raw and torrefied biomasses as well as the stage of deterioration at which the biomasses are. PLS developed models appeared to be efficient to predict the high heating value of raw and torrefied biomasses according to their fungal

deterioration stages. Torrefaction of eucalyptus, pine, sugarcane bagasse and coffee husk seems to be a viable method to eliminate some of the disadvantages of these raw biomasses as it significantly improves energy content and prevents absorption of moisture during storage. In addition, coffee husk appears to be a very promising biomass for energy conversion by torrefaction process, due to its good energetic increase.

Keywords: Biofuel. Fungi decay. Lignocellulose. Near-infrared spectroscopy.

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1. INTRODUÇÃO GERAL

A composição da matriz energética brasileira difere de outros países já que 46,1% da oferta interna de energia (OIE), ano base 2019, advém de fontes renováveis, número 0,6% maior que o obtido em 2018. A biomassa de cana-de-açúcar, lenha e carvão vegetal, além de uma fração correspondente à casca de arroz, capim-elefante, entre outros, corresponde a aproximadamente 27,0% da OIE (MME, 2020). Sabe-se que os combustíveis fósseis dominam a geração de energia global. Apesar da crescente atenção dada às fontes de energia de baixo carbono, 81% do consumo global de energia em 2014 foi gerado pelo petróleo, carvão mineral e gás natural (IEA, 2016). Considerando-se os prejuízos ambientais provenientes do uso energético de combustíveis fósseis, a substituição para a biomassa lignocelulósica contribuiria para redução de emissões de gases do efeito estufa e consequentemente das mudanças climáticas (SCHULZE et al., 2012; CHERUBINI et al., 2013; ELIZONDO et al., 2017).

Maior produção energética a partir de fontes renováveis tornaria ainda mais atrativo o uso de resíduos de biomassas lignocelulósicas. Estes podem ser gerados pelos cultivos florestais e agrícolas, ou produtos residuais das cadeias agroalimentares, sendo fonte abundante e sustentável destes resíduos. Além disso, muitas vezes são obtidos a baixo custo, por meio do processo de colheita, processamento, uso industrial, entre outras formas. Entretanto, a biomassa tem algumas características que dificultam seu uso direto como combustível, tais como alto teor de umidade, baixo poder calorífico e baixo teor de carbono fixo, além da baixa densidade, principalmente quando da utilização da biomassa residual (VASSILEV et al., 2014; ZAICHENKO et al., 2020). Diante disso, é necessário buscar tecnologias que auxiliam o uso mais eficiente desse combustível heterogêneo. Para tanto, existem diversos processos, dentre os quais destaca-se a torrefação.

A torrefação é utilizada como pré-tratamento térmico da biomassa com a finalidade de melhorar características intrínsecas aos materiais lignocelulósicos de maneira a possibilitar o uso em processos de conversão térmica como gaseificação e co-combustão (*co-firing*) (VAN DER STELT et al., 2011; CHEN et al., 2015). O tratamento térmico da madeira também possibilita reduzir e estabilizar o teor de umidade da biomassa e melhorar resistência à deterioração biológica por fungos basidiomicetos (CHEN et al., 2015; COLIN et al., 2017).

O possível aumento de consumo de biomassas residuais como fonte energética ocasionaria aumento substancial na estocagem. Neste sentido, uma vez que a matéria-prima estocada passa a ser deteriorada, riscos operacionais como a geração de gases inflamáveis como o metano (CHEN et al., 2015). Além disso, biomassas lignocelulósicas armazenadas por longos períodos, devido à sua natureza higroscópica, são sujeitas à variação de umidade e deterioração biológica, resultando em consequências negativas diversas para utilização como fonte energética. A biodeterioração da biomassa durante a estocagem altera a composição química, a cor natural, causa perda de massa e resistência mecânica da matéria-prima e facilitam o ateque de insetos xilófagos reduzindo o potencial de uso da biomassa e, consequentemente, diminuem seu valor de mercado (LEPAGE, 1986). Portanto, o armazenamento é uma etapa desafiadora na cadeia de abastecimento de qualquer biocombustível sólido.

A biomassa em sua forma torrificada é considerada melhor para o armazenamento, mesmo ao ar livre, devido à sua maior hidrofobicidade e estabilidade aos efeitos predudiciais durante este processo de estocagem (BERGMAN et al., 2005; YAN et al., 2009; VAN DER STELT et al., 2011). Embora o tratamento térmico permita reduzir o comportamento hidrofílico da biomassa, é possível que a madeira torrificada atinja, durante o seu armazenamento, um nível de umidade suficiente para que os fungos apodrecedores possam se desenvolver (KYMÄLÄINEN et al., 2014). Apesar dos avanços recentes, a tecnologia de torrefação ainda está em desenvolvimento e apenas algumas avaliações técnico-econômicas sobre toda a cadeia logística, incluindo armazenamento, foram feitas (SVANBERG; HALLDÓRSSON, 2013; KYMÄLÄINEN et al., 2015). Outros estudos tem sido conduzidos para se utilizar a espectroscopia NIR para caracterização das biomassas lignocelulósicas ou como ferramenta para avaliar modificações químicas e físicas temporais durante a estocagem (LESTANDER et al., 2014; FERREIRA et al., 2018).

De acordo com o exposto, tornam-se necessários estudos sobre a influência da torrefação na estocagem de biomassas residuais no contexto brasileiro, se estendendo ao contexto mundial de substituição dos combustíveis fósseis por matérias-primas melhores do ponto de vista da sustentabilidade. Além disso, o uso da espectroscopia NIR, juntamente à métodos quimiométricos, podem ser uma excelente rota para construção de modelos de classificação e predição nas biomassas *in natura* e tratadas termicamente sob condições de estocagem.

2. OBJETIVOS

2.1. Objetivo geral

Avaliar o impacto da torrefação na estocagem de diferentes resíduos de biomassa, simulada por biodeterioração fúngica, para uso energético.

2.1.1. Objetivos específicos

- Avaliar o comportamento do resíduo de pinus e de eucalipto, bagaço de cana-de-açúcar e casca de café *in natura* e torrificados em relação a umidade e exposição à deterioração por fungos por meio de diferentes condições de estocagem para uso energético;
- Avaliar o impacto da lixiviação sobre as propriedades químicas e energéticas das biomassas torrificadas e *in natura*;
- Verificar o efeito da atividade fúngica sobre as propriedades químicas, energéticas e perda de massa das biomassas torrificadas e *in natura* após lixiviação;
- Construir modelos de calibração multivariada para resíduos de biomassas agroflorestais *in natura* e torrificadas, capazes de classificar e prever com exatidão e precisão as características relacionadas à decomposição fúngica por espectroscopia NIR e métodos quimiométricos, principalmente PLS e PLS-DA;
- Prever a evolução da perda de massa e poder calorífico superior das biomassas *in natura* e torrificadas, de acordo com a duração de exposição a fungos de podridão branca e marrom.

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CAPÍTULO I

EFFECT OF LEACHING AND FUNGAL ATTACKS DURING STORAGE ON CHEMICAL PROPERTIES OF RAW AND TORREFIED BIOMASSES

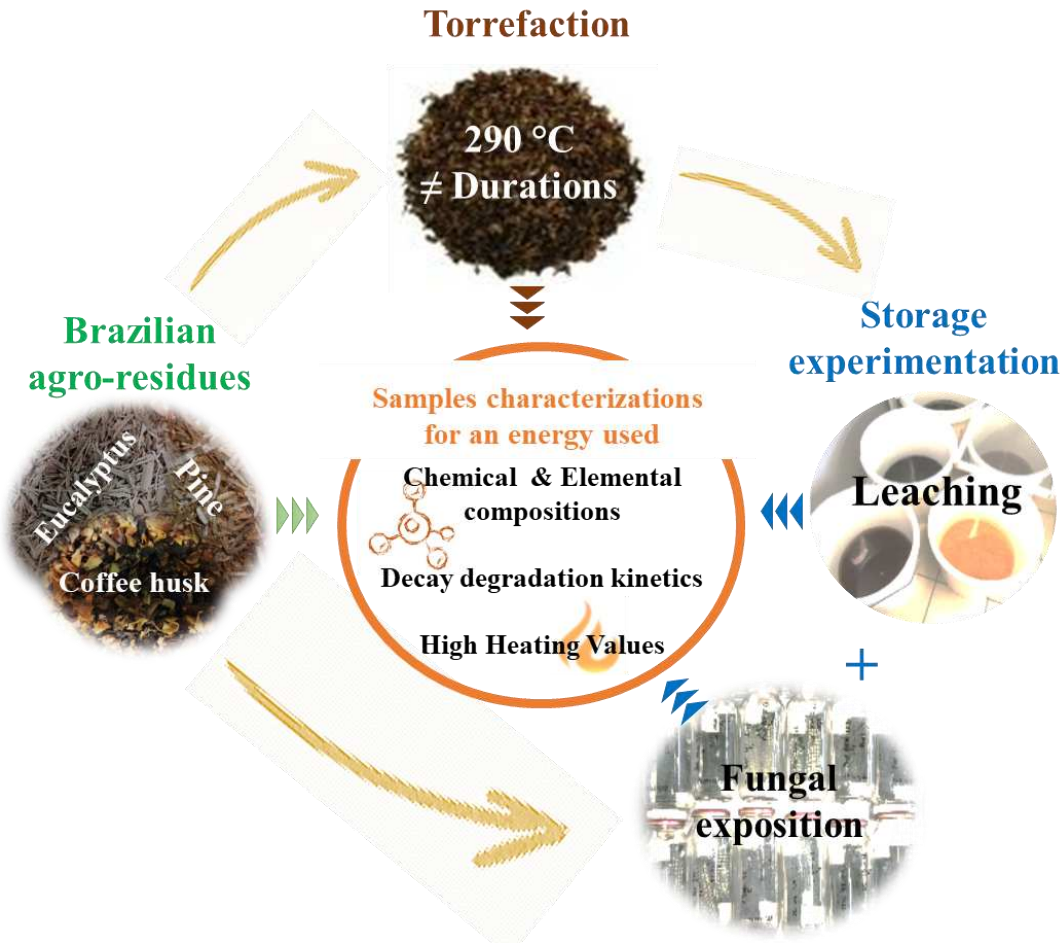
ABSTRACT

The aim of the study was to determine how the raw and torrefied biomass materials tolerate humidity and fungal decay exposure. The impact of leaching (without decay exposure) and the fungal deterioration impact on the chemical and energy properties of raw and torrefied biomasses for an energy conversion were thus evaluated. Finally, importance of the type of biomass on these different mechanisms was highlighted. Coffee husk, eucalyptus, and pine residues were torrefied at 290 °C in a screw reactor, during 5, 10, 15 or 20 min. The effects of feedstock type and torrefaction process parameters (holding time) on their energy characteristics were investigated. Raw and torrefied biomasses were then submitted successively to leaching and to white and brown rot fungi, to mimic storage conditions. Mass loss after leaching step, moisture content and weight loss due to fungal deterioration after 2, 4, 8, 12, 16 weeks were recorded. The chemical composition and High Heating Value of the torrefied samples were measured to determine the alterations compared to raw biomass during their storage. Increasing torrefaction residence time improves the decay resistance of the biomasses. Variation of carbon content (%wt., dry basis) and HHV (MJ kg^{-1}, dry basis) were observed during fungal deterioration of raw and torrefied biomasses. Carbon contents and HHV values of raw and torrefied biomasses decreased during *Trametes versicolor* exposure [49.65% > C > 44.07% and 19.71 MJ kg^{-1} > HHV > 17.19 MJ kg^{-1}, results from results from all tests combined.], whereas they increased during exposure to *Coniophora puteana* [46.15% < C < 52.70% and 17.43 MJ kg^{-1} < HHV < 20.74 MJ kg^{-1}]. Severe torrefaction is therefore a good way to improve coffee husk, eucalyptus, and pine energy properties while limiting loss of their energy properties during storage.

KEYWORDS

Biofuel, Brown-rot, Calorific value, Torrefaction, White-rot.

GRAPHICAL ABSTRACT



INDEX SUMMARY

PINE: *Pinus* sp. biomass sample

EUCA: *Eucalyptus* spp. biomass sample

CH: Coffee husk (*Coffea arabica* L.) biomass sample

CH-HT-5: Coffee husks – torrefied at 290 °C - during 5 min (given for example, the same indexing is used for the different biomass and torrefaction residence time)

CH-Ref: Coffee husks (*Coffea arabica* L.) reference (raw biomass) sample (given for example, the same indexing is used for the different biomass reference)

TV: *Trametes versicolor* fungi (white-rot)

CP: *Coniophora puteana* fungi (brown-rot)

CH-HT-5 (TV): Coffee husks – torrefied at 290 °C - during 5 min and exposed to *Trametes versicolor* fungi (given for example, the same indexing is used for the different biomass, torrefaction residence time and fungi exposures)

ML_{tf}: Mass loss of the sample due to torrefaction process (in %, dry basis)

Ext.: Extractives content of the sample (in %, dry basis)

ML_{leach}: Mass loss of the sample due to leaching process (in %, dry basis)

Moisture content: fungal metabolites and water of the sample due to fungal exposure (in %, wet basis)

WL: Weight loss of the sample due to fungal deterioration (in %, dry basis)

C: Carbon content of the sample (in %, dry basis)

H: Hydrogen content of the sample (in %, dry basis)

N: Nitrogen content of the sample (in %, dry basis)

H/C: Hydrogen / Carbon molar ratio

HHV_0: Higher Heating Value at constant volume of the dry (moisture-free) sample (in MJ kg^{-1}, dry basis)

1. INTRODUCTION

Brazil is a country using the most biomass for energy generation in the world, with approximately 16% of worldwide consumption (VAKKILAINEN et al., 2013). The Brazilian energy matrix is diversified and renewable sources contribute 83.3% of the domestic supply of electricity and particularly the varied types of biomass correspond to 9.2% of the installed energy production capacity in the country (MME, 2019). Its economic balance is strongly dependent on the agricultural and forestry sectors, and it is one of the few countries in the world that offers major potential for expansion of biomass production (ROUSSET et al., 2013). Biomasses mainly come from plantations (eg. eucalyptus and pine) dedicated to energy valorization, or as residues (eg. coffee husk) from some agricultural production chain.

Brazilian forestry is recognized due to the highest forest productivity of the world (ROUSSET et al., 2013). The Brazilian biomass production for energy is mainly supplied by plantations of eucalyptus (ROUSSET et al., 2013), due to its fast growing, high productive and adaptability characteristics (STAPE et al., 2010), followed by pine. The eucalyptus plantation was around 6.97 million ha (77% of total planted forest area) and the approximately value of annual average increment is 35.3 m^3 ha^{-1} $year^{-1}$ (IBÁ, 2020). The high productivity significantly reduces the time of forest rotation in the country compared to other countries with tradition in forestry activities in the world (IBÁ, 2020). Pine plantations are feedstock, mainly, for panels and lumber production. These areas are concentrated in south states of Brazil (Rio Grande do Sul, Santa Catarina e Paraná). In comparison with eucalyptus plantations, the average productivity for pine forests was 31.3 m^3 ha^{-1} $year^{-1}$ in 2019 (IBÁ, 2020). The productivity and facility of management practices concerning eucalyptus wood species make the market Brazilian players to prefer eucalyptus species (FIGUEIRÓ et al., 2019). This woody biomass is used directly as fuel in power generation or as raw material in the carbonization process of charcoal production (FIGUEIRÓ et al., 2019).

Past studies show the fuel potential of solid residues from the production chain of coffee (GARCÍA et al., 2018; DE RAMOS E PAULA et al., 2011). There must be a sustainable balance between the destination of crops for food and energy purposes. Moreover, this lignocellulosic residue presents chemical, physical and energetic characteristics favorable to the production of bioenergy through thermochemical processes (DE RAMOS E PAULA et al., 2011).

However, biomass has some characteristics that hinder its direct use as fuel, such as high moisture content, low calorific value and low fixed carbon content, in addition to low density, especially when using residual biomass (BATIDZIRAI et al., 2013). In addition, the storage of these biomasses before their energetic conversion can cause several damages to the material properties due to absorption and biological deterioration (KYMÄLÄINEN et al., 2015).

Some pretreatment are then necessary like torrefaction, which is a thermal treatment who improves the biomass energetic properties, including uniform physical characteristics in order to make the biofuel more homogenous and stable to biological deterioration (BATIDZIRAI et al., 2013). The modifications are strongly related to the heat treatment intensity (duration and temperature) and the nature of the biomasses (CANDELIER et al., 2016). The torrefied material is easier to handling and presents more amount of energy per volume, when compared with raw material. Thus, the transport costs of treated biomass decrease which impacts directly in the process viability (USLU et al., 2008). The utilization of torrefied biomass in existing handling and storage facilities and associated issues has been reported recently.

Torrefied biomass is considered easy to store even outside owing to its hydrophobicity and stability (VAN DER STELT et al., 2011). Although the heat treatment allows reducing the hydrophilic behavior of the biomass, it is possible that the torrefied wood nevertheless reaches, during its storage, a sufficient humidity level so that the rots can develop (KYMÄLÄINEN et al., 2014). Despite recent advances, torrefaction technology is still under development and only a few techno-economic assessments regarding the entire logistic chain, including storage, have been made (KYMÄLÄINEN et al., 2015).

The aim of the study was to determine how the raw and torrefied biomass materials tolerate humidity and fungal decay exposure, mimicking various storage conditions. Eucalyptus, pine and coffee husk were torrefied at 290 °C with four different holding times (5, 10, 15 and 20 min) for each of them, then leached and exposed to different fungal decay (brown and white rots) during five different exposure durations (from 2 to 16 weeks). Both effects of the torrefaction process and the storage conditions of the three biomasses were investigated.

The impact of leaching (without decay exposure) and the fungal deterioration impact on the chemical and energy properties of raw and torrefied biomasses for an

energy conversion were thus evaluated. Finally, importance of the type of biomass on these different mechanisms was highlighted.

2. EXPERIMENTAL SECTION

2.1. Biomass samples

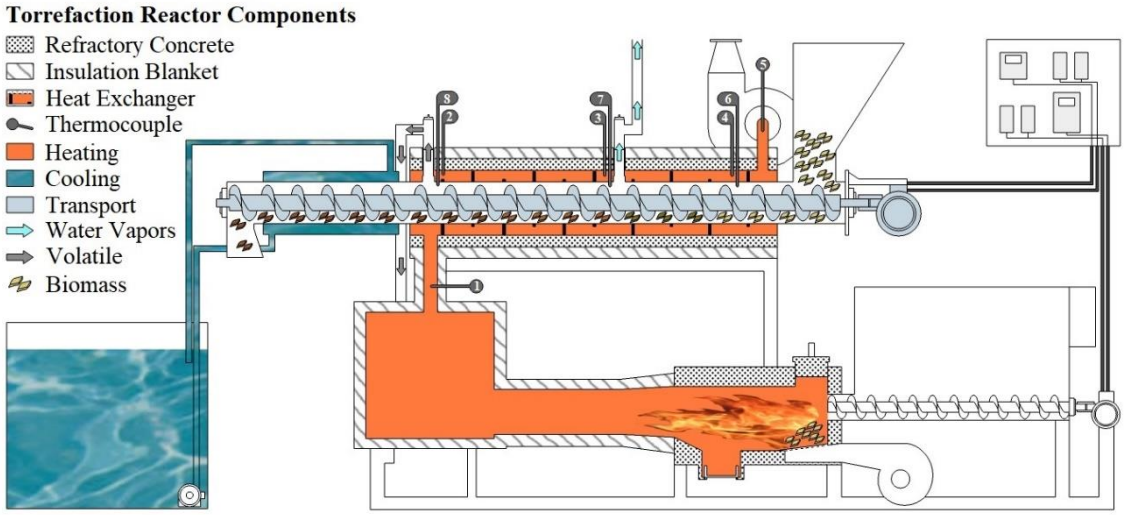
Eucalyptus wood (*Eucalyptus* spp.), pine wood (*Pinus* sp.), and coffee husk (*Coffea arabica* L.) residues were used. The three biomasses were selected due to their availability and their differences in composition and structure characteristics. These biomasses were collected in Minas Gerais state (Brazil) and were first dried outdoors in a drying yard until they reached hygroscopic equilibrium moisture (about 20%). Afterwards, milling was done in a knife mill for eucalyptus and pine wood and a classification in screen sieves with 2 mm openings was performed and particles that passed through the sieve were used, to suit the desired granulometry of the biomass samples for the heat treatment. Coffee husk was used- in granulometric form obtained after processing of the coffee bean in the industry, however before the torrefaction process a classification in screen sieves with 2 mm openings was performed to remove excess of dust. The fraction retained on the sieve was used.

2.2. Torrefaction process

The waste biomasses were oven-dried at 103 ± 2 °C during 48 hours with constant air circulation to reach a moisture content near to 0% and allowing to eliminate the influence of water on heat treatments.

The biomasses were then torrefied using 5 kg for each sample, in duplicates at 290 °C with three different holding times as following: eucalyptus (10, 15, 20 min), pine (10, 15, 20 min) and coffee husk (5, 10, 15 min), in an endless screw type reactor (2.25 m long and 13.7 cm in diameter) (Figure 1), developed in the Laboratory of Panels and Wood Energy (LAPEM) of Federal University of Viçosa (MAGALHÃES et al., 2018). The heating section (with length of 1.3 m) was built in carbon steel main structure with an indirect heating exchange system with a combustion gas followed by an indirect water cooling system.

Two timers controlling the gear motor were used to control the residence time of the biomass sample within the reactor. The first of one was used to activate the gear motor for approximately 4 seconds (time required for one complete revolution of the worm screw), and the second timer was used to stop the gear motor for a predetermined time. The sum of these two durations recorded but the both timers, multiplied by the number of revolutions of the worm screw (without end with the roasting section) then defined the residence time of the biomass samples it torrefaction process. A Gulton Gulterm 700-10S digital thermometer, using eight type J thermocouples was used to continuously record and control the temperature of the torrefaction chamber. More information of the biomasses torrefaction process and reactor can be found in MAGALHÃES et al. (2018).



1 *to* 8 *: Thermocouples used in order to control the homogeneity of the temperature in the entire torrefaction chamber.*

Figure 1: Layout in side view of the reactor for biomass torrefaction in semi-continuous flow (MAGALHÃES et al., 2018).

2.3. Mass loss due to thermal degradation

The Mass Loss (ML%) due to the thermal degradation was determined according to the Equation 1 (Eq. 1):

$$ML_{tt}\ (\%wt., dry\ basis) = \frac{(m_0 - m_1)}{m_0} \times 100 \qquad \text{(Eq. 1)}$$

Where:

ML_{tt} = Mass loss due to thermal treatment in %wt (dry basis);

m_0 = initial oven-dried mass before torrefaction in kg;

m_1 = final oven-dried mass after torrefaction in kg.

2.4. Chemical composition of raw and torrefied biomasses samples

The structural chemical composition was obtained for the determination of the extractive, total lignin (insoluble and soluble), and holocellulose contents. The samples of the three raw and torrefied biomasses were ground and selected between the overlapping sieves with mesh of 40 (420 µm) and 60 (250 µm). The total extractive contents determination procedure were adapted, with a solution of ethanol/toluene (2:1), from procedures specified by the TAPPI 204 cm-97 (TAPPI, 1997).

Klason lignin content was determined gravimetrically as insoluble residue according to GOMIDE and DEMUNER (1986). Acid-soluble lignin was measured by UV-spectroscopy (Cary 50 Probe, Varian) at 215 and 280 nm wavelengths according to GOLDSCHIMID (1971) after a complete acid hydrolysis of the polysaccharides present in the samples. The total lignin was based on extractive-free biomass, calculated based on the sum of the Klason lignin and acid-soluble lignin.

The approximate content of structural polysaccharides, also called holocelullose, was calculated by subtracting the total lignin and total extractives content from 100%.

2.5. Fungal decay exposure

The objectives of this section was to i) evaluate the impact of fungal deterioration of biomasses on their energy properties and ii) study the influence of the nature of the biomass on the various deterioration mechanisms involved. In order to evaluate the influence on biomass species, only one torrefaction intensity whose the mass loss thermal degradation (ML_{tt}%) are close, was chosen.

All samples (raw and torrefied) were firstly submitted to leaching process according to the NF X41-568 (AFNOR, 2014) standard. This standardized procedure for accelerated ageing is commonly used for natural durability wood testing. Samples were immersed in distilled water (1 volume of biomass for 5 volumes of water) and

subjected for six leaching periods of increasing duration under continuous shaking at 20 °C. Water was replaced by fresh water after each leaching period. A first cycle of 3 leaching periods of 1, 2 and 4 hours was performed. Samples were then kept air drying for 16 hours. Leaching was pursued for 3 additional periods of 8, 16 and 48 hours, with change of water between each period. The leached samples were then dried at 103 °C and weighed (m_3). Percentage of leaching (ML_{leach}) was calculated following the Equation 2 (Eq. 2):

$$ML_{leach}\ (\%wt., dry\ basis) = \frac{(m_1 - m_2)}{m_1} \times 100 \qquad \text{(Eq. 2)}$$

Where:

ML_{leach} = Mass loss of the sample due to leaching process in % (dry basis);

m_1 = initial oven-dried mass before leaching kg;

m_2 = initial oven-dried mass after leaching in kg.

Then, raw and torrefied biomasses were placed into plastic grid bags (dimensions of 10 x 3 x 1.5 cm) in order to expose themselves to basidiomycete attacks. Before starting the fungal exposure experiment, the bags were oven dried at 103 °C for 24 h and the initial dry mass (m_3) was measured for further determination of the weight loss of the sample due to the fungal deterioration. Each sample was crafted to have an initial dried mass of sample around 3 grams. After that, all samples were sterilized, XP CEN/TS 15083-1 (CEN, 2006) standard criteria, by x-ray process carried out by the IONISOS Company (Dagneux, France).

These tests have been performed also on each raw biomass, for comparison. Namely: CH-Ref and CH-HT-5 (ML_{tt} = 8.80%), EUCA-Ref and EUCA-HT-10 (ML_{tt} = 8.50%), PINE-Ref and PINE-HT-15(ML_{tt} = 8.20%).

Decay resistance of raw (leached and not leached) and torrefied biomasses after leaching was tested according to an adaptation of the XP CEN/TS 15083-1 (CEN, 2006) standard criteria, on both fungi species required by the standard: *Trametes versicolor* (white-rot) and *Coniophora puteana* (brown-rot). The following fungal exposure duration were tested: 2, 4, 8, 12 and 16 weeks. After the different decay exposure duration, mycelia were removed and each sample was weight (m_4) and then was dried at 103 °C for 24 h and the final dried mass was determined (m_5).

The final moisture content after fungal exposure of the sample was determined according to the following formula (Eq. 3):

$$Moisture\ content\ (\%wt., as\ wet\ basis) = \frac{(m_4 - m_5)}{m_4} \times 100 \qquad \text{(Eq. 3)}$$

The Weight Loss (WL) was determined according to the following formula (Eq. 4):

$$WL\ (\%wt., dry\ basis) = \frac{(m_3 - m_5)}{m_3} \times 100 \qquad \text{(Eq. 4)}$$

The decay exposure tests were conducted as follows:

- One torrefaction intensity for eucalyptus, pine and coffee husk, after leaching, were tested in order to evaluate the impact of the torrefaction process and the influence of the biomass nature on its durability;

- For both each fungus and fungal exposure duration, 4 replicates of raw biomasses (after leaching) and for each torrefied biomasses (after leaching) were done. The evaluation of decay resistance of torrefied biomasses have been carried out only after leaching to observe results in the worst-case scenario (leaching following by fungal exposure). In fact, according to the literature, leached torrefied biomasses are more sensitive to fungal decay than un-leached biomasses (SALMAN et al., 2017).

- Beech (*Fagus sylvatica*) and pine (*Pinus sylvestris*) sapwood samples of the dimensions 50 x 25 x 15 mm (L, R, T) were used as controls for the virulence of the strains (8 tested blocks for each fungus and for each fungal exposure duration).

2.6. Sample characterization

The impacts of leaching and fungal deterioration, according to the duration of fungal exposure were evaluated on the following raw and torrefied biomasses properties according to 3 characterizations: i) the Weight Losses (WL) caused by fungal attacks, ii) the Elemental Compositions (EC) and iii) the High Heating Values (HHV). For each tested modality, the four replicated used for decay test were mixed, ground using a cutting mill Retsch SM 100 and sieved. Particle sizes fraction of 0.1 to 0.2 mm was retained. Sawdust was then conditioned at 103 °C for 24 h and stored in air-tight bottle before analysis.

2.6.1. Elemental composition

Elemental analyses were carried out with an ElementarVario Macro tube CHN analyzer according to the BS EN 15104 (EN, 2011). Atomic H/C (Eq. 5) ratios of samples were determined as following:

$$Atomic\ \frac{H}{C}ratio = \frac{\text{Number of H atoms}}{\text{Number of C atoms}} = \frac{\%\ H/1}{\%\ C/12} \qquad \text{(Eq. 5)}$$

2.6.2. High Heating Values

The calorific value was measured using an Automated Isoperibol Fixed Bomb Parr 6200 bomb calorimeter, following the CEN/TS 14918 (CEN, 2005).

2.7. Statistical analysis

The impact of heat treatment intensity compared to the raw biomasses on (i) their chemical and (ii) the elemental compositions were evaluated using ANOVA (one-way analysis of variance) and Duncan's comparison test. These statistical analyses were carried out by the JMP 10.0.2 program (SAS Institute Inc., Cary, NC, USA). Results were then ranked into several categories; from "A" to "R". Similar analyses were used to study the impact of leaching process on i) the elemental compositions and ii) HHV of the various biomasses samples. The impact of a parameter on a system not connected by the same letter was considered as significant at the 5% level.

For a better comprehension of the study approach, a scheme of the different analysis protocols are presented in Figure 2.

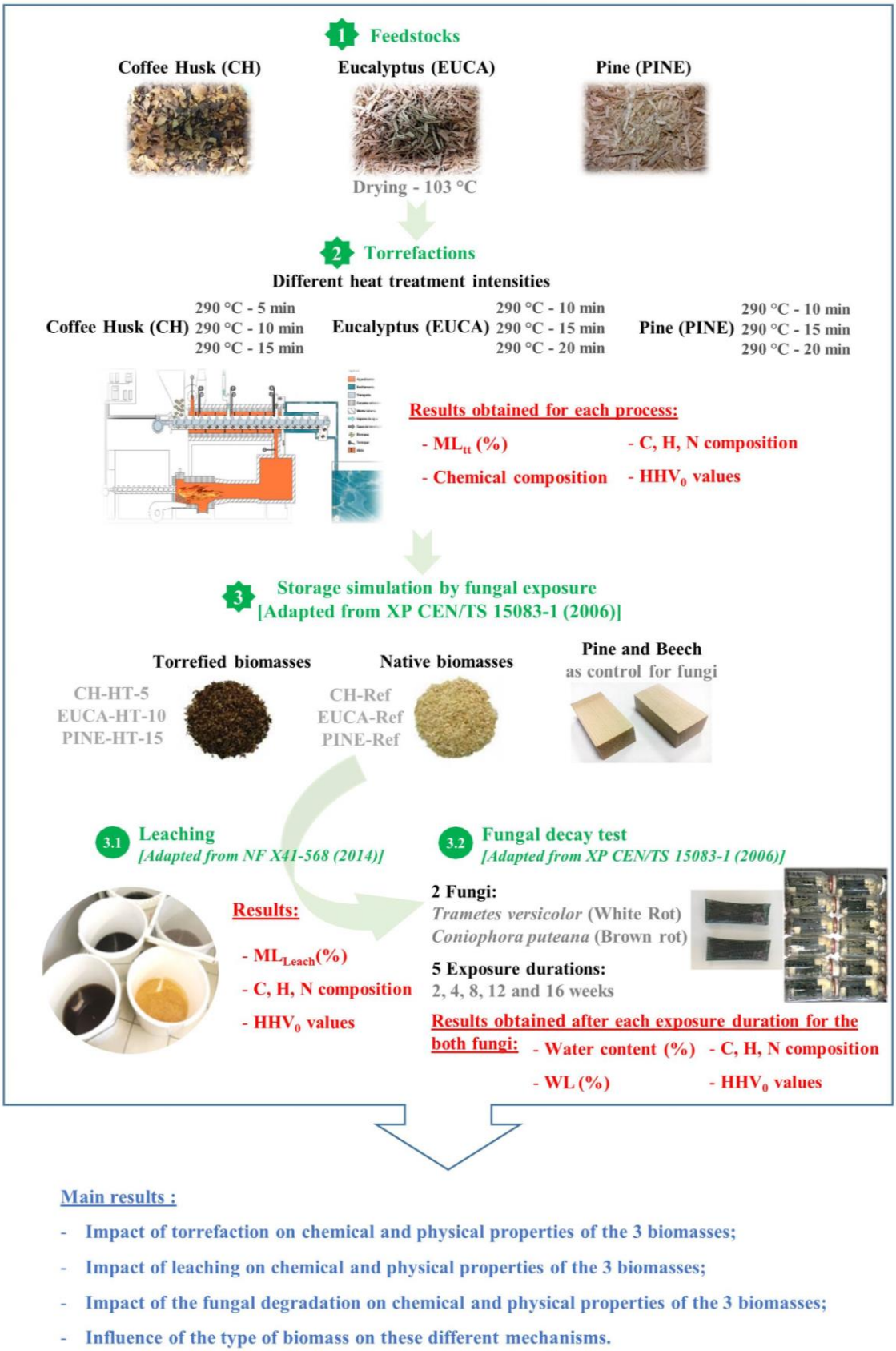


Figure 2: Synthesis of the overall approach and the different analysis protocols used for this study.

3. RESULTS AND DISCUSSION

3.1. Influence of the biomass nature on the thermal degradation kinetics

Figure 3 and Table 1 show the mass losses (ML_{tt} %) of torrefied eucalyptus, pine and coffee husk residues, according to the torrefaction process holding time. As expected, the mass loss increases with the torrefaction duration, for all kind of biomass. In addition, it appears that the nature of the biomass and their respective chemical compositions are directly correlated to thermal degradation reaction kinetic (CANDELIER et al., 2016). Eucalyptus (hardwood) is more sensitive to thermal degradation than pine (softwoods), as demonstrated by the higher mass losses recorded for a same treatment intensity (temperature-duration). The difference in hemicellulose composition between hardwood (mainly glucoroxylan) and softwood (mainly arabinoglucoronoxylan and galactoglucomannan) can explain this higher thermal sensitivity of hardwoods than those of softwoods (CANDELIER et al., 2016).

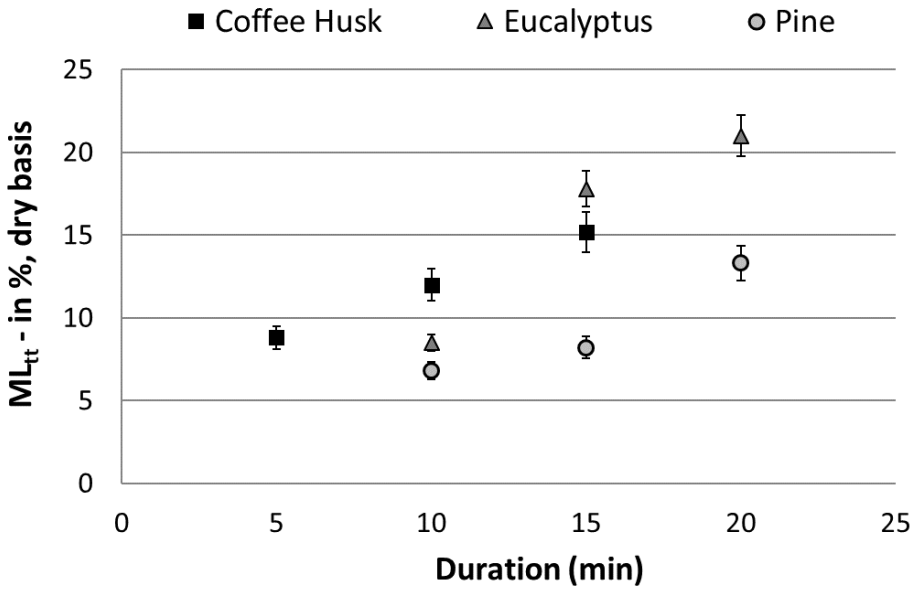


Figure 3: Mass Loss due to the biomass thermal degradation according to the torrefaction duration.

The role of the macromolecular composition of biomass on its degradation through torrefaction is confirmed. According to Figure 3 and Table 2, raw biomasses rich in holocellulose, such as pine (65.38%) and eucalyptus (68.52%), suffered a lower solid mass loss (ML_{tt} are 6.8% and 8.5% for PINE-HT-10 and EUCA-HT-10,

respectively) for than those of a raw biomass rich in lignin [e.g. coffee husk (30.61%)] (ML_{tt} is 12% for CH-HT-5), in torrefaction performed at low intensity. However, a high holocellulose content, such as for eucalyptus (68.52%), results in a more enhanced degradation up to 15 min of torrefaction at 290 °C.

The thermal degradation of ligno-cellulosic biomass is influenced by its composition. Higher extractive contents accelerate the wood thermal degradation process at low temperatures, which reduce the biomass thermal stability. The higher content in extractives (Table 2) of raw coffee husk (21.28%) than those of eucalyptus (3.38%) and pine (6.17%) woods, could explain the high thermal sensitivity at low torrefaction intensity (290 °C – 5 and 10 min), compared to that of the two other wood species. Extractives are compounds with low molecular weight, may promote ignitability of the biomass at lower temperatures because of their higher volatility and reduce the thermal stability at low temperatures (POLETTO, 2016). The high concentration of major mineral elements (i.e. Ca, K, Mg) in the coffee husk (TSAI et al., 2012) can also explain its rapid thermal degradation kinetic (MACEDO et al., 2018).

3.2. Chemical characterization of raw and torrefied biomasses

The average values of elemental composition of raw material and torrefied products are shown in Table 1, where it can be noticed that the carbon content increases with an increase in the torrefaction residence time, while hydrogen content decreases. This behavior can be explained with the removal of volatile components, containing these atoms, during the torrefaction process. Common biomass reactions during torrefaction include devolatilization, depolymerization, and carbonization of hemicellulose, lignin, and cellulose (TUMULURU et al., 2011). The elemental composition profiles are in agreement with expected changes in the biomass composition after torrefaction. Simultaneously, Table 1 shows clearly that increase in carbon content improves the combustion properties because the induced low values of H/C ratios decrease thermodynamic losses and increase the HHV value (CHEN et al., 2014). It can be seen, in Table 1, that coffee husk has the largest HHV increment (+14.79%) compared to those of eucalyptus (+10.21%) and pine (+6.05%), at the same treatment intensity of 290 °C – 15 min. This difference between the samples is probably due to the differences in the polymeric structure, causing a different reduction of low-

energy chemical bonds, such as H-C and O-C, and increase in a high-energy chemical bond (C-C) (YANG et al., 2015). Torrefaction of low-lignocellulose waste biomasses, such as coffee husk, shows that although these materials are low or free from hemicellulose (eg. 43% cellulose and 7% hemicellulose – in % dry basis, from GOUVEA et al. (2009) they also undergo an increase in energy density similar to that experienced by lignocellulose biomasses.

Table 1: Average values of Mass Losses (ML_{tt}%) due to thermal degradation, Mass Losses (ML_{leach}%) due to leaching process, and Elemental Compositions and HHV values before and after leaching of raw and torrefied Coffee Husk (CH), Eucalyptus (EUCA) and Pine (PINE) samples

Sample	Torrefaction	Before Leaching process					Leaching	After Leaching process				
	ML_{tt} (%)	**C* (%)**	**H* (%)**	**H/C***	**N* (%)**	**HHV_0** (MJ kg^{-1})**	**ML_{leach} (%)**	**C* (%)**	**H* (%)**	**H/C***	**N* (%)**	**HHV_0** (MJ kg^{-1})**
CH-Ref	**0.00** ± *0.00* (J)	**44.45** (L) (b)	**5.95** (E) (b)	**1.61** (A) (a)	**1.50** (D) (a)	**17.506** (K) (b)	**17.98** ± 0.70 (ABC)	**47.40** (K) (a)	**6.10** (D) (a)	**1.54** (C) (b)	**1.35** (D) (b)	**18.823** (HIJ) (a)
CH-HT-5	**8.80** ± *0.35* (F)	**46.40** (JK) (b)	**5.80** (H) (b)	**1.50** (D) (a)	**1.70** (B) (a)	**18.281** (GHIJ) (b)	**16.84** ± 0.22 (BCD)	**48.45** (I) (a)	**5.95** (F) (a)	**1.47** (E) (b)	**1.55** (B) (b)	**19.181** (FGHI) (a)
CH-HT-10	**12.00** ± *0.40* (CDE)	**46.50** (J) (b)	**5.70** (J) (b)	**1.47** (F) (a)	**1.60** (C) (a)	**18.497** (GH) (b)	**19.80** ± 0.70 (A)	**50.65** (G) (a)	**5.90** (G) (a)	**1.40** (H) (b)	**1.50** (C) (b)	**20.158** (CDE) (a)
CH-HT-15	**15.20** ± *0.41* (C)	**50.25** (E) (b)	**5.60** (K) (b)	**1.34** (JK) (a)	**1.75** (A) (a)	**20.095** (ABCD) (b)	**18.60** ± 0.70 (AB)	**53.60** (A) (a)	**5.90** (G) (a)	**1.32** (KL) (b)	**1.70** (A) (b)	**21.158** (A) (a)
EUCA-Ref	**0.00**± *0.00* (J)	**47.00** (HI) (a)	**6.00** (CD) (b)	**1.53** (C) (b)	**0.15** (F) (b)	**18.338** (GHI) (a)	**8.64** ± 0.13 (IJ)	**47.10** (L) (a)	**6.20** (B) (a)	**1.58** (B) (a)	**0.25** (E) (a)	**17.429** (L) (b)
EUCA-HT-10	**8.50** ± *0.27* (FG)	**49.20** (F) (a)	**5.85** (F) (b)	**1.43** (G) (b)	**0.10** (G) (b)	**19.469** (CDE) (a)	**7.98** ± 0.12 (IJK)	**49.30** (H) (a)	**6.15** (C) (a)	**1.50** (D) (a)	**0.15** (F) (a)	**19.219** (FGH) (a)
EUCA-HT-15	**17.80** ± *0.42* (B)	**51.20** (C) (b)	**5.75** (I) (b)	**1.35** (I) (b)	**0.15** (F) (a)	**20.211** (ABC) (a)	**7.60** ± 0.12 (JKL)	**52.40** (BC) (a)	**5.95** (F) (a)	**1.36** (I) (a)	**0.10** (G) (b)	**20.461** (ABCD) (a)
EUCA-HT-20	**21.00** ± *0.48* (A)	**52.50** (A) (b)	**5.75** (I) (b)	**1.31** (L) (b)	**0.15** (F) (a)	**20.324** (AB) (a)	**6.68** ± 0.12 (LM)	**53.35** (D) (a)	**5.90** (G) (a)	**1.33** (K) (a)	**0.15** (F) (a)	**20.521** (ABC) (a)
PINE-Ref	**0.00** ± *0.00* (J)	**47.15** (H) (b)	**6.30** (A) (a)	**1.60** (AB) (a)	**0.15** (G) (a)	**18.772** (EFG) (a)	**12.86** ± 0.12 (E)	**47.80** (J) (a)	**6.35** (A) (a)	**1.59** (A) (b)	**0.15** (F) (a)	**18.801** (HIJK) (a)
PINE-HT-10	**6.80** ± *0.20* (I)	**49.05** (G) (b)	**6.10** (B) (b)	**1.49** (E) (a)	**0.20** (E) (a)	**19.373** (CDEF) (a)	**10.40** ± 0.12 (GH)	**51.15** (F) (a)	**6.20** (B) (a)	**1.45** (F) (b)	**0.15** (F) (b)	**19.705** (CDEFG) (a)
PINE-HT-15	**8.20** ± *0.21* (GH)	**50.70** (D) (b)	**6.00** (C) (b)	**1.42** (GH) (b)	**0.15** (F) (a)	**19.907** (ABCD) (a)	**10.84** ± 0.12 (FG)	**51.85** (E) (a)	**6.20** (B) (a)	**1.43** (G) (a)	**0.15** (F) (a)	**19.963** (CDEF) (a)
PINE-HT-20	**13.30** ± *0.27* (CD)	**52.30** (B) (b)	**5.85** (FG) (b)	**1.34** (J) (a)	**0.10** (G) (a)	**20.372** (A) (b)	**8.80** ± 0.12 (I)	**53.45** (B) (a)	**6.00** (E) (a)	**1.35** (J) (a)	**0.10** (G) (a)	**21.107** (AB) (a)

* Each analysis has been duplicate and all the results are given with an accuracy of ± 0.20%.
**Each analysis has been duplicate and all the results are given with an accuracy of ± 5.00%.
Values (+SD) followed by the same letter are not significantly different based on one-way ANOVA followed by Duncan test at 5% (a = 0.05).
(A): Impact of biomass and torrefaction process for all samples within the same column.
(a): Impact of leaching process between columns “before leaching process” and “after leaching process”.
Bold value indicates the main results.

3.3. Elemental composition and energy properties changes of raw and torrefied biomasses after water-leaching

Water-leachates from torrefied particles result mainly in wood thermal degradation products (tannic acid, acetic acid, furfural and furfural derivatives) and extractives compounds (MEIJA-FELDMANE, 2015). This statement can explain the fact that higher mass losses due to leaching process (ML_{leach}) was observed for coffee husk than those of eucalyptus and pine woods (Table 1), due to the higher extractives contents of raw and torrefied coffee husk samples than those of the two other biomasses (Table 2). It appears, for eucalyptus and pine, that increase in torrefaction process duration reduce the amount of substances accessible to leach by water. This phenomenon could be explained by the fact of the content of hydroxyl groups decreases with thermal degradation leading to the wood hydrophobicity improvement and then its wettability is more difficult (BRITO et al., 2008). According to the results presented in Table 1, HHV of raw and torrefied CH samples were improved by water-leaching process. Leaching biomass with water has been shown to improve biomass feedstock properties for high temperature processes, by reducing the ash content and modifying the ash chemistry, increasing feedstock heating value (JENKINS et al., 1998). Water leaching undergone an oxygen content decreased of all samples, resulting in an increase in their carbon content improving their HHV values.

Table 2: Chemical structure composition of raw and torrefied Coffee Husk (CH), Eucalyptus (EUCA) and Pine (PINE)

Sample	Total Extractive Content (%)	Insoluble Lignin (%)	Soluble Lignin (%)	Total Lignin (%)	Total Holocellulose (%)
CH-Ref	**21.28** ± 0.21 (A)	**28.96** ± 0.22 (D)	**1,65** ± 0.10 (A)	**30.61** ± 0.32 (D)	**48.11** ± 1.21 (A)
CH-HT-5	**21.27** ± 0.16 (A)	**32.41** ± 0.41 (C)	**1.32** ± 0.01 (B)	**33.53** ± 0.42 (C)	**45.20** ± 1.13 (B)
CH-HT-10	**21.16** ± 0.44 (A)	**35.28** ± 1.15 (B)	**1.23** ± 0.01 (D)	**36.51** ± 1.16 (B)	**42.33** ± 1.07 (C)
CH-HT-15	**20.43** ± 0.10 (B)	**45.32** ± 1.46 (A)	**1.28** ± 0.01 (C)	**46.60** ±1.47 (A)	**32.97** ± 0.82 (D)
EUCA-Ref	**3.38** ± 0.01 (C)	**26.52** ± 0.25 (D)	**1.58** ± 0.02 (B)	**28.10** ± 0.27 (D)	**68.52** ± 1.71 (A)
EUCA-HT-10	**5.86** ± 0.02 (B)	**27.81** ± 0.46 (C)	**2.07** ± 0.12 (A)	**29.88** ± 0.58 (C)	**64.26** ± 1.61 (B)
EUCA-HT-15	**6.55** ± 0.52 (A)	**37.92** ± 1.10 (B)	**1.45** ± 0.01 (C)	**39.37** ± 1.11 (B)	**54.08** ± 1.35 (C)
EUCA-HT-20	**6.29** ± 0.40 (A)	**39.30** ± 1.20 (A)	**0.90** ± 0.01 (D)	**40.20** ± 1.21 (A)	**53.51** ± 1.34 (D)
PINE-Ref	**6,17** ± 0.05 (C)	**28.22** ± 0.69 (D)	**0.23** ± 0.01 (D)	**28.45** ± 0.70 (D)	**65.38** ± 1.63 (A)
PINE-HT-10	**7.29** ± 0.18 (A)	**29.73** ± 0.48 (C)	**0.25** ± 0.01 (C)	**29.98** ± 0.49 (C)	**62.73** ± 1.56 (B)
PINE-HT-15	**7.07** ± 0.08 (A)	**33.53** ± 0.66 (B)	**0.34** ± 0.01 (B)	**33.87** ± 0.67 (B)	**59.06** ± 1.48 (C)
PINE-HT-20	**6.35** ± 0.09 (B)	**39.77** ± 0.49 (A)	**0.59** ± 0.02 (A)	**40.36** ± 0.51 (A)	**53.29** ± 1.33 (D)

The values (+SD) for the same biomass followed by the same letter are not significantly different based on one-way ANOVA followed by Duncan test at 5% (a = 0.05).
Bold value indicates the main results.

3.4. Deterioration according to the fungus exposure duration

3.4.1. Moisture content

Figure 4a shows the final moisture content (in %, wet basis) of control beech and pine samples as the fungal metabolites and water. Figure 4b, displays the raw and torrefied eucalyptus (290 °C – 10 min), pine (290 °C – 15 min) and coffee husk (290 °C – 5 min) samples after *Trametes versicolor* (TV) and *Coniophora puteana* (CP) fungi exposures and according to the duration of these decay expositions. The hydrophobic behavior of all samples is very similar than those of beech and pine control samples. Their moisture content levels increase highly during the first four fungi exposition weeks, and then continue to increase more slowly for longer tests durations. However, the level of water absorption due to the sample exposure to fungal decay depends on the nature of the biomass and on the type of fungus to which it is subjected.

The higher level of water uptake was recorded for coffee husk during *Trametes versicolor* exposure, following by those of pine exposed to *Coniophora puteana* and then by those of eucalyptus exposed to *Trametes versicolor.* It results that brown-rot undergoes a higher water uptake on softwood species while hardwood species are most sensitive to white-rot (ELAIEB et al., 2020). In addition, the difference of water uptake intensities between the three biomasses could be also explained by their chemical composition, mainly due to their carbohydrates and hemicellulose contents which have many hydroxyl groups (–OH) which drive biomasses to be polar and to make easily hydrogen bonds with water molecules (TUMULURU et al., 2011). However, coffee husk has a low hemicelluloses content (eg. 7%) (GOUVEA et al., 2009), and its hydrophobic behavior could be explain by its high porosity level (eg. 64.85%) (ZHANG et al., 2012) compared to those of eucalyptus (52.6%) (MOURA et al., 2005)) and pine (61.4 - 63.9%) (USTA, 2003).

The changes of lignocellulosic polymers during torrefaction lead to the formation of unsaturated non-polar structures and cause shortening of polymer chains (SUPRAMONO et al., 2015). Due to the hemicellulose degradation during torrefaction process causing a loss of hydroxyl groups (TUMULURU et al., 2011), all biomasses tend to be non-polar and hardly make hydrogen bonds with water molecules, and then their hydrophobic behavior increase compared to those of a raw biomasses, as shown by the moisture content values recorded during the fungal exposure (Figure 4b). Although

heat treatment reduces the water uptake of wood (TJEERDSMA et al., 1998) during fungal exposure, it does not prevent the occurrence of free water on the surfaces of cell lumina, and the moisture content can still increase much higher than the fiber saturation point with the fungal exposure duration (Figure 4b). Free water can therefore still serve as reactant in chemical decay processes (e.g. hydrolysis), as a diffusion medium for enzymes and solubilized substrate molecules, and as a solvent or medium for life systems within the fungal hyphae.

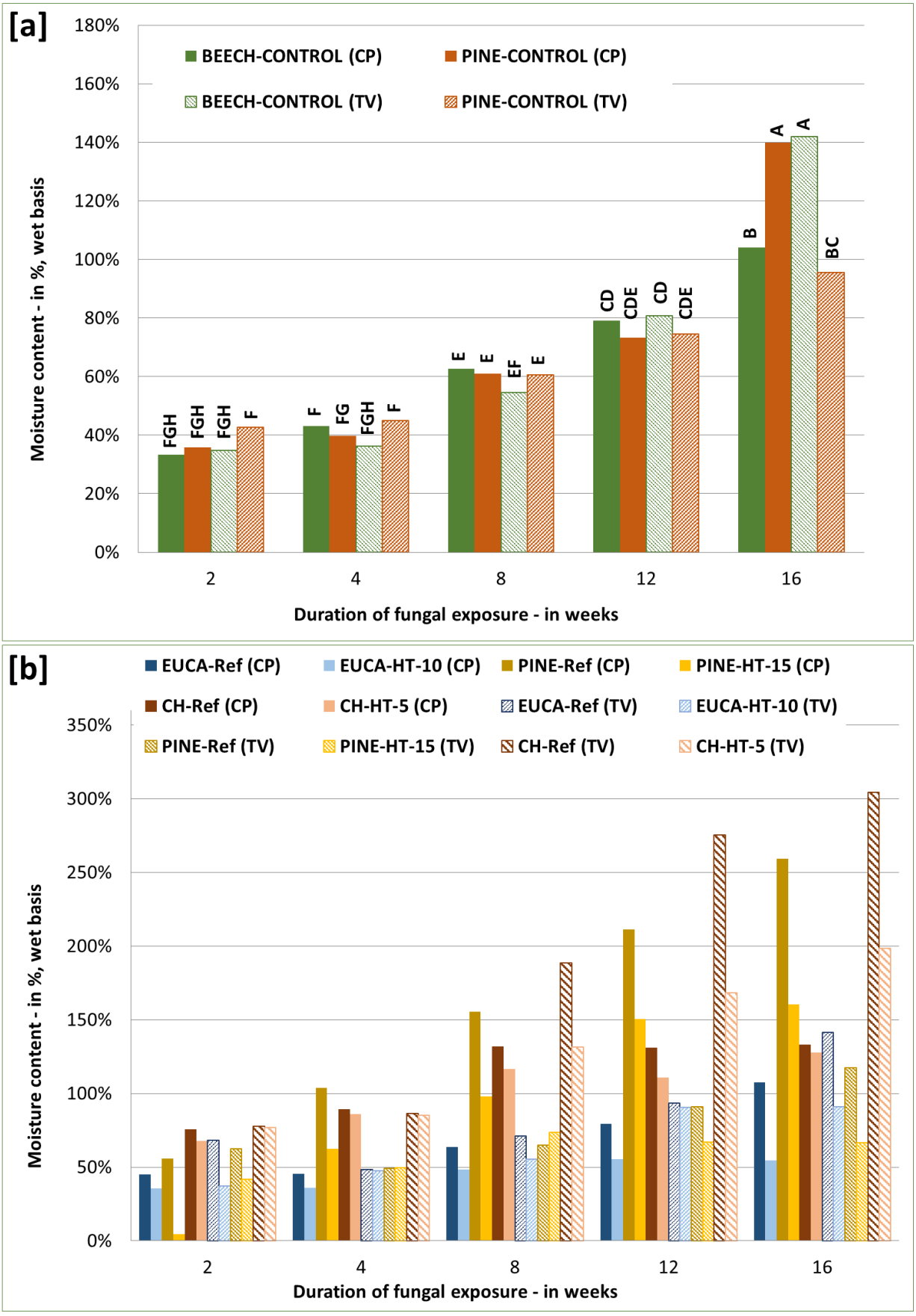


Figure 4: Moisture content (%) after *Coniophora puteana* (CP) and *Trametes versicolor* (TV) exposure of pine and beech control samples [a] and raw and torrefied Eucalyptus (EUCA), Pine (PINE) and Coffee Husk (CH) [b], according to the fungal exposure duration (bar followed by the same letter are not significantly different).

3.4.2. Fungal assay evaluation

The overall Weight Loss (WL%) due to *Trametes versicolor* and *Coniophora puteana* exposure of beech and pine control samples, raw and torrefied eucalyptus (EUCA), pine (PINE) and coffee husk (CH), are shown in Figure 5.

According to the weight loss values obtained concerning the fungal deterioration of beech and pine wood control sample after 16 weeks (Figure 5a), the decay resistance test performed through this study has been validated. Indeed, the following minimal decay levels (according to XP CEN/TS 15083-1 (CEN, 2006)) of control samples were reached:

- *Coniophora puteana* (Brown-rot) on pine: WL = 57.12% > 30%;
- *Coniophora puteana* (Brown-rot) on beech: WL = 48.18% > 30%;
- *Trametes versicolor* (White-rot) on pine: WL = 24.18% – no requirement;
- *Trametes versicolor* (White-rot) on beech: WL = 44.24% > 20%.

According to the Figure 5a, the both fungal decay of beech and pine block control samples appears to begin as early as the fourth week of rot exposure. The fungal deterioration (TV and CP) of all biomasses, under chips shape, starts as early as the second week of rot exposure.

For the both tested rots, a similar tendency concerning the decay resistance improvement of the three biomasses was observed after torrefaction.

Average values of weight loss due to fungal decay showed that *Coniophora puteana* (Brown-rot) was more aggressive on raw and torrefied PINE samples than *Trametes versicolor* (White-rot) which is more degrading on raw and torrefied EUCA samples. In addition, it appears that raw and torrefied CH samples are similar degraded by *Coniophora puteana* as by *Trametes versicolor* for the same period of exposition.

As observed in Figure 5b, the deterioration kinetics of raw eucalyptus and pine samples increased highly during the eight first weeks and tend to stabilize for longer fungal exposure duration. Whereas the deterioration kinetics of raw and torrefied coffee husk, torrefied eucalyptus and pines samples increased linearly according to the exposure duration, whatever the fungus.

The torrefaction allows reducing the WL, improving the decay resistance of all samples but the torrefaction curing intensity is not optimal to confer a great decay resistance to the three biomasses. From past studies, a mass loss due to thermal degradation higher than 12% is required to confer to woody biomasses a high level of

decay resistance [eg. durability class 3 according to the specifications of EN 350 (CEN, 2016) standard (ELAIEB et al., 2015).

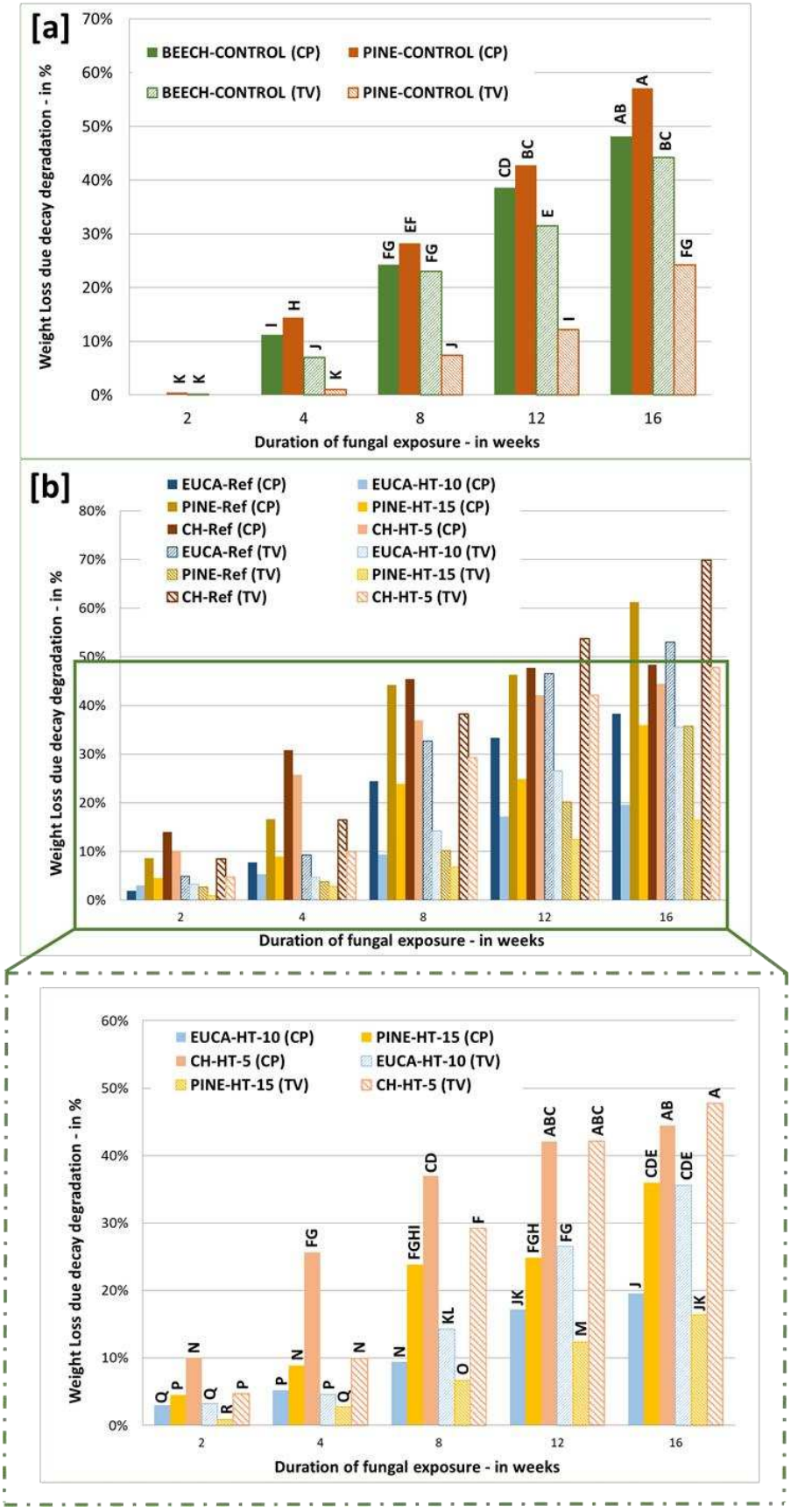


Figure 5: Weight Losses (WL%) due to CP and TV deterioration of pine and beech control samples [a] raw and torrefied biomasses [b], according to the fungal exposure duration (bar followed by the same letter are not significantly different).

3.5. Evolution of the energy properties during fungal exposure

3.5.1. Deterioration by *Trametes versicolor* (TV) – White-rot

As shown in Figure 6a, a loss of carbon was registered in all raw and torrefied biomasses with white rotter *Trametes versicolor* (TV), according to the duration of the fungal exposure of the sample. Relating to the literature, white-rot mainly degrades the lignin polymer, causing loss of carbon because carbon compounds are consumed as nutrients and respired as CO_2 during their growing (RYTIOJA et al., 2014). According to the Figure 6b, hydrogen content seems to be quite constant for raw and torrefied PINE and EUCA samples, whereas small decreases were observed during TV exposure of raw and torrefied CH samples. These changes in hydrogen contents were not statistically significant.

The nitrogen content increased in all tested materials (Figure 6c) in correlation with their TV fungi contact duration. This phenomenon was more pronounced for raw and torrefied CH samples than for PINE and EUCA samples.

It results that, for raw EUCA, PINE and CH samples, H/C ratios increased very slowly with the *Trametes versicolor* (TV) exposure duration (Figure 6d). Figure 6d shows also that the H/C ratio of torrefied EUCA, PINE and CH samples increased relating to the *Trametes versicolor* (TV) exposure duration, where the most significant evolution occurs in the first four weeks of fungal exposure. In addition, the highest growth rate of H/C ratio was obtained for CH-HT-5 sample compared to those of PINE-HT-15 and EUCA-HT-10 samples (Figure 6d).

Carbon and hydrogen are the main compounds contributing to the Heating Values of pyrolyzed woody biomasses (HUANG et al., 2009), and low H/C ratio are desirable for the use of them for energy purposes. Our results are consistent with this statement. In parallel with the observed decrease in carbon and therefore the increase in the H/C ratio, Figure 6 clearly shows that the HHV of all the tested samples (raw and torrefied) decreases during their exposure to *Trametes versicolor*. In fact, depletion of carbon will lower the calorific value and here, statistically significant changes were detected in carbon content. The heat content is related to the oxidation state of the natural fuels in which carbon atoms generally dominate and overshadow small variations of hydrogen and nitrogen content. According to the results obtained by TILLMAN (1978), founding a linear relationship between the HHV and the carbon

content of the natural fuels, chars, and volatiles, the Figure 6f highlights a linear correlation between HHV values and H/C ratio of all tested biomasses. Finally, Figure 6f shows that whatever the woody biomasses species, torrefied or not, the longer inoculation period with *Trametes versicolor*, the higher H/C ratio of the sample and hence the lower its HHV value.

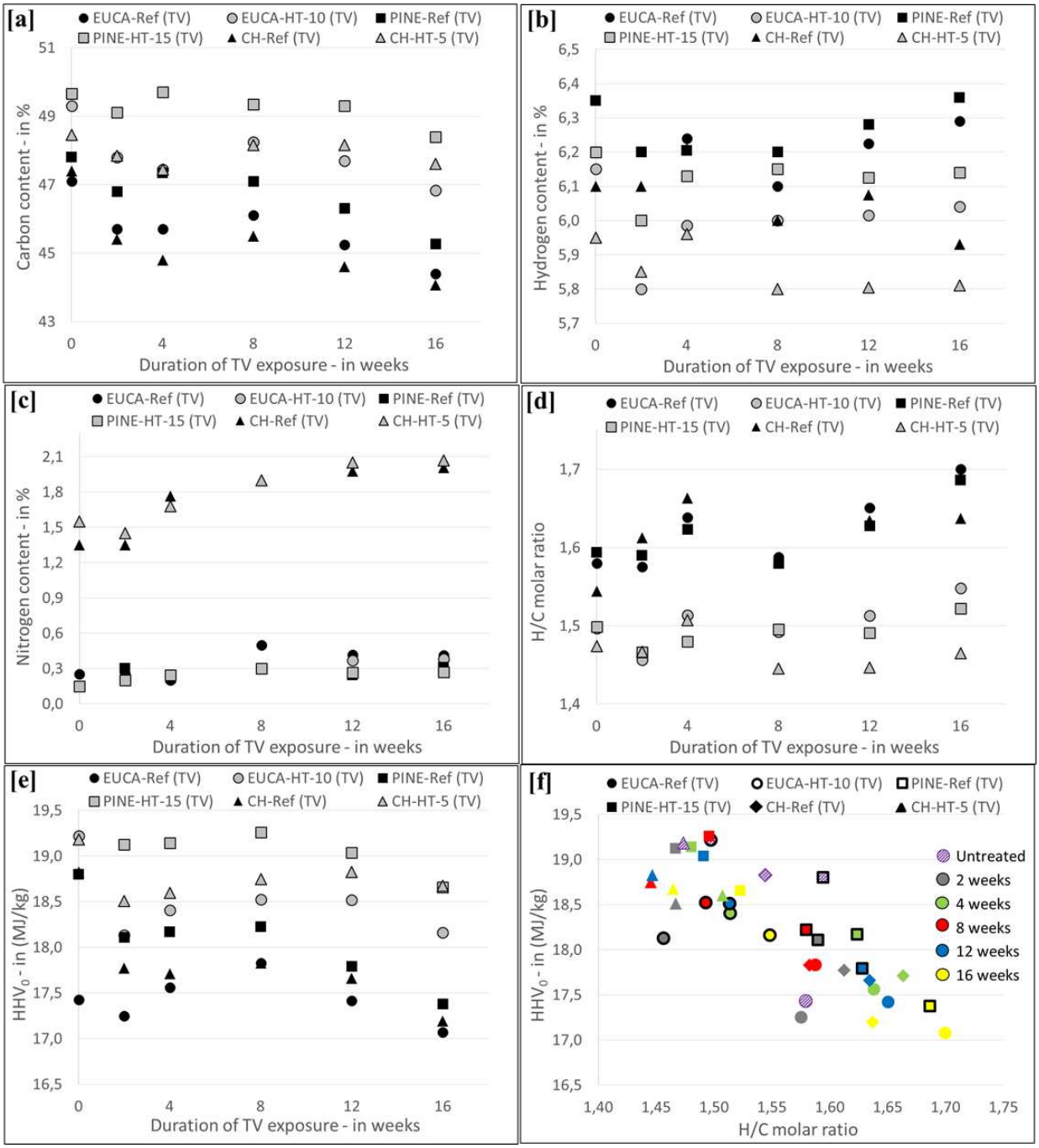


Figure 6: [a] Carbon, [b] Hydrogen and [c] nitrogen contents (%), [d] H/C molar ratio and [e] HHV_0 (MJ kg^{-1}) according to *Trametes versicolor* (TV) exposure duration; [f] Correlation between HHV_0 (MJ kg^{-1}) and atomic H/C ratio of the different raw and torrefied Eucalyptus (EUCA), Pine (PINE) and Coffee Husk (CH) samples.

3.5.2. Deterioration by *Coniophora puteana* (CP) – Brown-rot

Concerning the changes in hydrogen (Figure 7b) and nitrogen (Figure 7c) contents during fungal exposure, similar results were observed for *Coniophora puteana*

(CP) as for *Trametes versicolor* (TV). We observed different behavior of carbon content evolution, according to the type of biomass, during the samples exposure to *Coniophora puteana* (CP). It results that carbon contents increase a little for EUCA-Ref and EUCA-HT-10 relating to the *Coniophora puteana* (CP) exposition duration, whereas carbon contents of PINE-Ref,, PINE-HT-15, CH-Ref and CH-HT-5 samples increase more significantly (Figure 7a). These results could be explained by the remaining cellulose and the hemicelluloses after torrefaction at low temperature (PINE-Ref, PINE-HT-15, CH-Ref and CH-HT-5 samples) are degraded by *Coniophora puteana* (CP), increasing the relative carbon content. In fact, brown-rot fungus (*C. puteana*) causes more weight loss than the white-rot (*T. versicolor*) on these last samples, because it removes the cellulosic fraction and leaves lignin structurally modified. Brown rotter *Coniophora puteana* (CP) prefers coniferous wood species, but seems to cause also damages in CH. It uses endoglucanases to degrade cellulose and hemicelluloses, but has also been reported to produce cellobiohydrolases that erode crystalline cellulose and could therefore also utilize quite severely torrefied wood (THERASME et al., 2019).

Figure 7c shows that the nitrogen contents of raw and torrefied EUCA and PINE sample were constant during CP inhibition, whereas those of raw and torrefied CH samples increased with the CP exposure duration.

It therefore follows a decrease of H/C ratio and an increase HHV value for all the tested samples according to the *Coniophora puteana* exposure duration (Figure 7d and Figure 7e). The increase of HHV may be associated with the degradation of the low-energy content components (e.g., leaf materials or agro-food residues) that were easily accessible to the enzymatic community during storage condition (KRIGSTIN; WETZEL, 2016). The proportion of components in the biomass will affect energy content: the preferential decomposition of hemicellulose by *Coniophora puteana* (brow rot) will result in increased heating values, and the loss of extractives or the preferential fungal decomposition of lignin (eg. *Trametes versicolor* – white-rot) would tend to reduce heating values (PARI et al., 2015).

The results presented in Figure 7f confirms the linear correlation between HHV values and H/C ratio. But contrary to the results obtained with *Trametes versicolor*, the longer inoculation period with *Coniophora puteana*, the lower H/C ratio of the sample and hence the higher its HHV value for all tested biomasses.

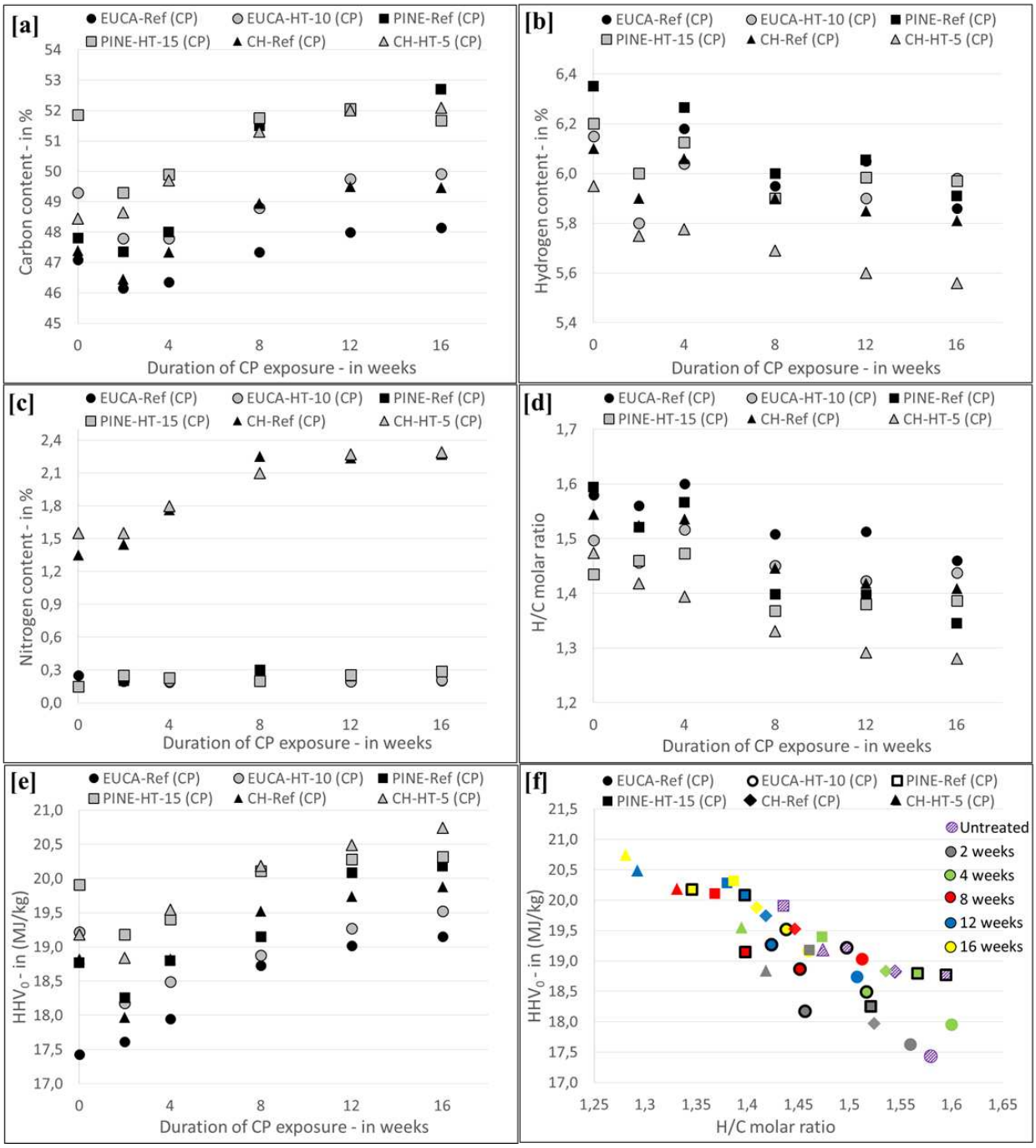


Figure 7: [a] Carbon, [b] Hydrogen and [c] Nitrogen contents (%), [d] H/C molar ratio and [e] HHV_0 (MJ kg^{-1}) according to *Coniophora puteana* (CP) exposure duration; [f] Correlation between HHV_0 (MJ kg^{-1}) and atomic H/C ratio of the different raw and torrefied Eucalyptus (EUCA), Pine (PINE) and Coffee Husk (CH) samples.

3.6. Balance sheet

The High Heating Values of the three biomasses species were significantly affected by their decay exposure time. There was a relationship between the HHV and

decay exposure time across torrefaction process and fungi, but the change over time was small (Figure 6 and Figure 7).

It appears that *Trametes versicolor* deterioration affects negatively the HHV of raw and torrefied Eucalyptus, Pine and Coffee Husk, whereas *Conipohora puteana* improves their energy properties. Some past studies performed on the biomasses storage have recently reported also no significant change or a decrease of the higher heating value (BRAND et al., 2011; LENZ et al., 2015), while others have highlighted a slight increase of heating value (BARONTINI et al., 2014; CANDELIER et al., 2017) of woody biomass samples at the end of their storage.

From our laboratory experiment, it was clear that fungi, and more particularly, white-rot fungi, are susceptible to settle on seemingly unfavorable material, which is said to be hydrophobic and suitable for outside storage. However, the main objective of this study was to observe the impact of the nature of the biomasses on the torrefaction and storage degradation mechanisms. Based on previous work (CANDELIER et al., 2017), it is likely that better results would have been obtained regarding the durability and hydrophobicity of torrefied biomass with higher curing intensities.

Table 3 displays a qualitative evaluation of the impact of torrefaction, leaching and decay exposure impact on the elemental composition and energy properties of the three studied Brazilian biomasses.

Table 3: Qualitative evaluation of the impact of torrefaction, leaching and decay exposure impact on the elemental composition and energy properties of the three Brazilian biomasses

Parameter	Carbon content	Hydrogen content	Nitrogen content	HHV value
Torrefaction	↑	↘	↗	↑
Leaching	↗	→	→	↗
***Trametes versiocolor* exposure (white-rot)**	↘	+/- *(it depends on the biomass nature)*	+/- *(it depends on the biomass nature)*	↘
***Coniophora puteana* exposure (brown-rot)**	↗	+/- *(it depends on the biomass nature)*	+/- *(it depends on the biomass nature)*	↗

↑ : significant increase; ↗ : moderate increase; → : low increase.
↓ : significant decrease; ↘ : moderate decrease; → : low decrease.
+/- : no significante evolution.

Therefore, torrefaction of eucalyptus, pine and coffee husk seems to be a viable method to eliminate some of the disadvantages of these raw biomasses as it significantly improves energy content and prevents absorption of moisture during storage. Even if HHV values decrease during white-rot fungal (*Trametes versicolor*) exposure, HHV values are still higher for torrefied biomass samples than those in the respective raw samples (Figure 8f and Figure 9f). In addition, coffee husk appears to be a very promising biomass for energy conversion by torrefaction process, even if for the heat treatment intensity used, CH-HT-5 still appears to be very sensitive to storage (Figure 4 and Figure 5).

4. CONCLUSIONS

The heat treatment duration has an important impact on eucalyptus, pine and coffee husk mass loss kinetic during torrefaction process. Chemical and elemental composition modifications, High Heating Values and decay resistance improvements of these three matters are directly correlated to the torrefaction process duration.

Water-leaching process seems to improve slightly the three torrefied biomasses, which occurs an oxygen content decreased and a carbon content increase resulting in a better HHV values than those of the not-leached biomasses.

The water absorptions (moisture content, in %) of wood samples due to their decay exposure, whatever the decay contact duration and the fungi type, were lower for torrefied biomass samples compared to their respective raw sample. Similar observations were done on weight loss due to fungal decay. *Coniophora puteana* (Brown-rot) was more aggressive for both raw and torrefied PINE samples compared to *Trametes versicolor* (White-rot), that it is more attack raw and torrefied EUCA and CH samples.

There was a relationship between the HHV and decay exposure time across all the thermal treatments and fungi.

Torrefaction of eucalyptus, pine and coffee Husk seems to be a viable method to eliminate some of the disadvantages of these raw biomasses as it significantly improves energy content and prevents absorption of moisture during storage. Even if HHV values decrease during white-rot fungal exposure, HHV values are still higher for torrefied biomass samples than those of the respective raw samples are. To be noted that brown-rot fungal exposure seems to improve the energy properties of torrefied eucalyptus, pine and coffee husk samples. In addition, coffee husk appears to be a very promising biomass for energy conversion by torrefaction process, due to its high HHV after torrefaction. However, higher torrefaction intensity than 290 °C – 5 min (CH-HT-5) should be used in order to improve its sensitive to storage. Future studies will be needed in order to conduct similar storage experimentation and analyses on eucalyptus, pine and coffee husk samples treated at higher heat-treatment intensities to find an optimal solution between torrefaction, storage sensitivity, energy properties and economical balance.

5. AKNOWLEDGMENTS

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CAPÍTULO II

STORAGE EXPERIMENTATIONS TO ASSESS ENERGY PROPERTIES OF TORREFIED SUGARCANE BAGASSES

ABSTRACT

Sugarcane bagasse (SCB) has some characteristics that hinder its direct use as fuel, and its storage before energetic conversion can cause several additional damages to the material properties. The aim of the study was to determine how raw and torrefied sugarcane materials tolerate leaching, humidity and fungal decay exposure (*Trametes versicolor* and *Coniophora puteana)*, simulating by various storage conditions. Energetic, chemical and biological (fungi decay) properties of raw and torrefied biomasses according to the storage conditions (leaching, fungi and decay exposure duration) and to torrefaction intensity were determined. SCB were torrefied at 290 °C in a screw reactor, during 5, 7.5 and 10 min. Then, raw and torrefied SCB samples were exposed successively to water-leaching and to white and brown rot fungi, to emulate storage conditions. Mass loss after water-leaching process, moisture content and weight loss due to fungal deterioration after 2, 4, 8, 12, 16 weeks were recorded on each SCB samples. Finally, chemical composition and High Heating Value (HHV) of the torrefied samples were measured to determine the alterations compared to raw SCB during their storage mimic. Increasing torrefaction duration improves their decay resistance. According to the fungal exposure duration, loss of carbon was recorded, however, HHV remain higher for torrefied sugarcane bagasse than those of raw bagasse. Torrefaction pre-treatment is therefore a good way to improve sugarcane bagasse energy properties while limiting lose torrefied biomass quality during storage.

KEYWORDS

Bioenergy, Biomass residue, Fungal decay, Leaching, Torrefaction.

1. INTRODUCTION

Brazil is strongly dependent to the agricultural and forestry production sectors, making it the first country using the most biomass for energy production, with approximately 16% of total world consumption, followed by the United States (9%) and Germany (7%) (VAKKILAINEN et al., 2013).

Lignocellulosic biomasses mainly come from plantations dedicated to energy valorization, or as residues from some agricultural production chain like sugarcane, which ranks first in listed products (MME, 2020), due to the huge sugarcane planting area with approximately 8.5 million hectares (CONAB, 2020). A large amounts of bagasse is available at low cost (ISLAM et al., 2010; WALTER; ENSINAS, 2010), providing raw material for energy production. Each ton of sugarcane is estimated to produce 130 kg of dry bagasse, giving a world supply of 200 million tons per year giving a potential of 19 GJ ton^{-1} (STANMORE, 2010).

Even if sugarcane bagasse (SCB) can be burnt directly to produce heat and electricity, the solid residue after pressing, has some characteristics that hinder its direct use as fuel, compared to fossil fuel, such as high fibrous (43 - 52%) and low bulk density (80 - 120 kg m^{-3}), high moisture content (46 - 52%), inconsistent particle size, heterogeneous chemical composition, hydrophilic nature, and relatively low calorific value (ARIAS et al., 2008; CHEW; DOSHI, 2011).

In addition, the storage of the bagasse in humid conditions can cause several damages due to moisture absorption and biological deterioration (KYMÄLÄINEN et al., 2015). Indeed SCB is usually stored in outdoor piles occurring moisture adsorption by wood and the resultant chemical oxidation and/or microbiological activity lead to hydrolysation. This phenomenon increases the biomass temperature thereby accelerating the biological deterioration (MEDIC et al., 2012; STELTE, 2012). Such degradations reduce the biomass potential to be processing and consequently decrease its market value.

To improve the quality of bagasse as feedstock can be done with torrefaction pre-treatment (DANIYANTO et al., 2015). The utilization of torrefied bagasse in existing handling and storage facilities and associated issues has been reported recently (VAN DER STELT et al., 2011; KIEL, 2014; VALIX et al., 2017) and could be one of the solution to preserve its energetic properties depending on the torrefaction treatment intensity (CANDELIER et al., 2016). Although the torrefaction allows reducing the

hydrophilic behavior of the biomass, it is possible that the torrefied biomass nevertheless reaches, during its storage, a sufficient humidity level so that the rots can develop (KYMÄLÄINEN et al., 2014).

The aim of the study was to determine how the various raw and torrefied SCB materials tolerate humidity and fungal decay exposure, simulating by various storage conditions. Sugarcane bagasse was torrefied at 290 °C with 5, 7.5 and 10 min holding time then leached and exposed to different fungal decay (brown and white rots) during various exposure durations (from 2 to 16 weeks). Physical (High Heating Values), chemical (Elemental Composition) and biological (Fungi Decay) properties of torrefied were determined and compared to the raw biomass. The impact of leaching (without decay exposure) and the fungal deterioration impact on the chemical and energy properties of raw and torrefied bagasses for an energy conversion were thus evaluated.

2. MATERIALS AND METHODS

2.1. Biomass samples

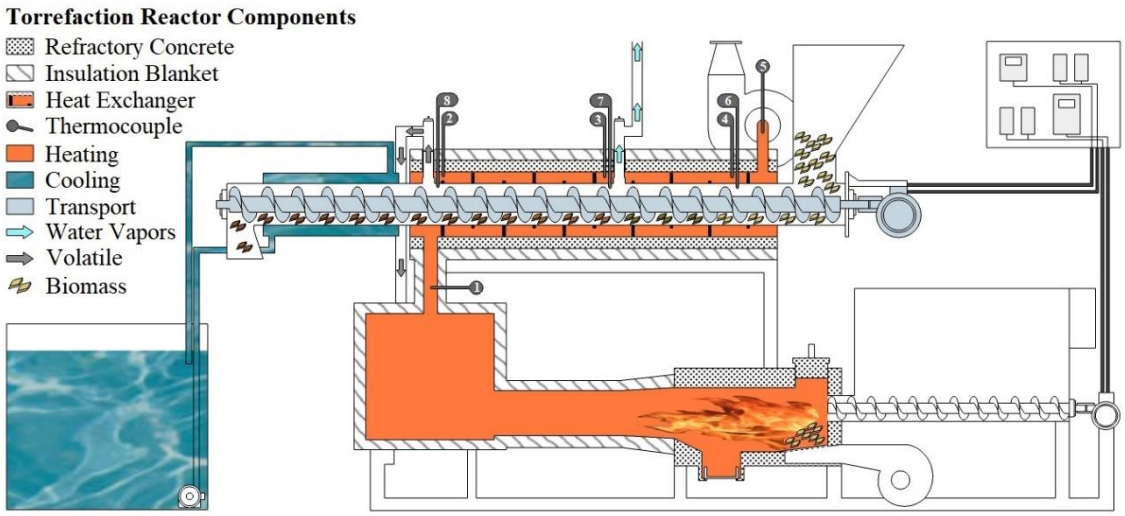
The sugarcane bagasse (*Saccharum officinarum* L.) (SCB) was collected from a sugar industry of Minas Gerais state in Brazil. Sugarcane bagasse was chosen for this study because it is produced in large quantities as a waste in sugar industries. The sugarcane bagasse was used in the common form obtained through sugarcane industrial grinding. Afterwards, the biomass was dried outdoors in a drying yard until they reached hygroscopic equilibrium moisture (about 20%). Then, a classification in screen sieves with 2 mm openings was performed, to suit the desired granulometry of the biomass samples for the heat treatment and to eliminate the excess of dust. The fraction retained on the sieve was used.

2.2. Torrefaction process

The sugarcane bagasse waste were oven-dried at 103 ± 2 °C during 48 hours with constant air circulation to reach a moisture content near to 0% and allowing to eliminate the influence of water on heat treatments.

The biomass were then torrefied using 5 kg of biomass for each sample (two replicates for each modality) at 290 °C in duplicates with three different heating times

(5, 7.5, 10 minutes), in an endless screw type reactor, developed in the Laboratory of Panels and Wood Energy (LAPEM) of Federal University of Viçosa (MAGALHÃES et al., 2018). The heating section (with length of 1.3 m) was built in carbon steel main structure with an indirect heating exchange system with a combustion gas followed by an indirect water cooling system.



1 *to* 8 *: Thermocouples used in order to control the homogeneity of the temperature in the entire torrefaction chamber.*

Fig. 1. Layout in side view of the reactor for biomass torrefaction in semi-continuous flow (MAGALHÃES et al., 2018).

2.3. Mass loss due to thermal degradation

The Mass Loss (ML%) due to the thermal degradation was determined according to the Equation 1 (Eq. 1):

$$ML_{tt}\ (\%) = \frac{(m_0 - m_1)}{m_0} \times 100 \qquad \text{(Eq. 1)}$$

Where:

m_0 = initial mass (g) before torrefaction;

m_1 = final mass (g) after torrefaction.

2.4. Chemical composition of raw and torrefied samples

The Structural Chemical Composition was obtained for the determination of the extractive, total lignin (insoluble and soluble), and holocellulose contents. The samples were ground and selected between the overlapping sieves with mesh of 40 (420 µm) and 60 (250 µm). The total extractive contents determination procedure were adapted, with a solution of ethanol/toluene (2:1), from procedures specified by the TAPPI 204 cm-97 (TAPPI, 1997).

Klason lignin content was determined gravimetrically as insoluble residue according to GOMIDE and DEMUNER (1986). Acid-soluble lignin was measured by UV-spectroscopy (Cary 50 Probe, Varian) at 215 and 280 nm wavelengths according to GOLDSCHIMID (1971) after a complete acid hydrolysis of the polysaccharides present in the samples. The total lignin was based on extractive-free biomass, calculated based on the sum of the Klason lignin and acid-soluble lignin.

The approximate content of structural polysaccharides, also called holocelullose, was calculated by subtracting the total lignin and total extractives content from 100%.

2.5. Fungal decay exposure

All samples (raw and torrefied) were firstly submitted to leaching process according to the NF X41-568 (AFNOR, 2014) standard. This standardized procedure for accelerated ageing is commonly used for natural durability wood testing. Samples were immersed in distilled water (1 volume of biomass for 5 volumes of water) and subjected for six leaching periods of increasing duration under continuous shaking at 20 °C. Water was replaced by fresh water after each leaching period. A first cycle of 3 leaching periods of 1, 2 and 4 hours was performed. Samples were then kept air drying for 16 hours. Leaching was pursued for 3 additional periods of 8, 16 and 48 hours, with change of water between each period. The leached samples were then dried at 103 °C and weighed (m_3). Percentage of leaching was calculated following the Equation 2 (Eq. 2):

$$ML_{leach}\ (\%) = \frac{(m_1 - m_2)}{m_1} \times 100 \qquad \text{(Eq. 2)}$$

Where:

m_1 = initial anhydrous mass of samples;

m_2 = anhydrous mass of leached samples.

Then, raw and torrefied biomasses were placed into plastic grid bags (dimensions of 10 x 3 x 1.5 cm) in order to expose themselves to basidiomycete attacks (Fig. 2). Before starting the fungal exposure experiment, the bags were oven dried 103 °C for 24 h and the initial dry mass (m_3) was measured for further determination of the weight loss of the sample due to the fungal decay. Each sample was crafted to have an initial dried mass of sample around 3 grams. After that, all samples were sterilized by x-ray process.

Fig. 2: Samples in contact with fungal decay.

Decay resistance of raw (leached and not leached) and torrefied biomasses after leaching was tested according to an adaptation of XP CEN/TS 15083-1 (CEN, 2006) standard criteria, on both fungi species required by the standard: *Trametes versicolor* (white-rot) and *Coniophora puteana* (brown-rot) (Fig. 2). The following fungal exposure duration were tested: 2, 4, 8, 12 and 16 weeks. After the different decay exposure duration, mycelia were removed and each sample was weight (m_4) and then was dried at 103 °C for 24 h and the final dried mass was determined (m_5).

The final moisture content after fungal exposure of the sample was determined according to the following formula (Eq. 3):

$$MC\ (\%, dry\ basis\ ) = \frac{(m_4 - m_5)}{m_5} \times 100 \qquad \text{(Eq. 3)}$$

Where :

MC = moisture content of the sample due to fungal exposure (in %, dry basis);

m_4 = wet mass of fungal decayed sample sample;

m_5 = anhydrous mass of fungal decayed sample.

The Weight Loss was determined according to the following formula (Eq. 4):

$$WL\ (\%) = \frac{(m_3 - m_5)}{m_3} \times 100 \qquad \text{(Eq. 4)}$$

Where:

WL = Weight Loss of the sample due to fungal exposure (in %, dry basis);

m_3 = initial anhydrous mass of sample before fungal exposure;

m_5 = final anhydrous mass of fungal decayed sample.

The decay exposure tests were conducted as follows:

- The three torrefaction intensities for sugarcane bagasse, after leaching, were tested in order to evaluate the impact of the heat treatment intensity on the biomasses durability;

- For both each fungus and fungal exposure duration, 4 replicates of raw biomasses (after leaching) and for each torrefied biomasses (after leaching) were done.

- Beech (*Fagus sylvatica*) and Pine (*Pinus sylvestris*) sapwood samples of the dimensions 50 x 25 x 15 mm (L, R, T) were used as controls for the virulence of the strains (8 tested blocks for each fungus and for each fungal exposure duration).

2.6. Sample characterization

The impacts of leaching and fungal deterioration, according to the duration of fungal exposure were evaluated on the following raw and torrefied biomass properties according to 3 characterizations: (i) the Weight Losses (WL) caused by fungal decay,

the Elemental Compositions (EC); and (iii) the High Heating Values (HHV). For each tested modality, the four replicated used for decay test were mixed, ground using a cutting mill Retsch SM 100 and sieved. Particle sizes fraction of 0.1 to 0.2 mm was retained. Sawdust was then conditioned at 103 °C for 24 h and stored in air-tight bottle before analysis.

2.6.1. Elemental composition

Elemental analyses were carried out with an ElementarVario Macro tube CHN analyzer according to the BS EN 15104 (EN, 2011). Prior to analysis, the samples were packed in a tin foil and two tests were performed for each sample. Atomic H/C ratios of the samples were determined following the Equation 5 (Eq. 5):

$$Atomic\ \frac{H}{C}ratio = \frac{\text{Number of H atoms}}{\text{Number of C atoms}} = \frac{\%\ H/1}{\%\ C/12} \qquad \text{(Eq. 5)}$$

2.6.2. High heating value

The calorific value was measured using an Automated Isoperibol Fixed Bomb Parr 6200 bomb calorimeter, following the CEN/TS 14918 (CEN, 2005).

1 g of oven-dried biomass, with a particle size < 0.2 mm, were required to perform the calorific test. Two replicates have been done for each sample and all the results are given with an accuracy of ± 5.00%.

2.7. Statistical analysis

The impact of heat treatment intensity compared to the raw SCB on (i) their chemical and (ii) the elemental compositions were evaluated using ANOVA (one-way analysis of variance) and Duncan's comparison test. These statistical analyses were carried out by the JMP 10.0.2 program (SAS Institute Inc., Cary, NC, USA). Results were then ranked into several categories; from "A" to "D".

Similar analyses were used to study the impact of leaching process on (i) the elemental compositions and (ii) HHV of the SCB samples.

The impact of a parameter on a system not connected by the same letter was considered as no significant at the 5% level.

For a better comprehension of the study approach, a scheme of the different analysis protocols are presented in Fig. 3.

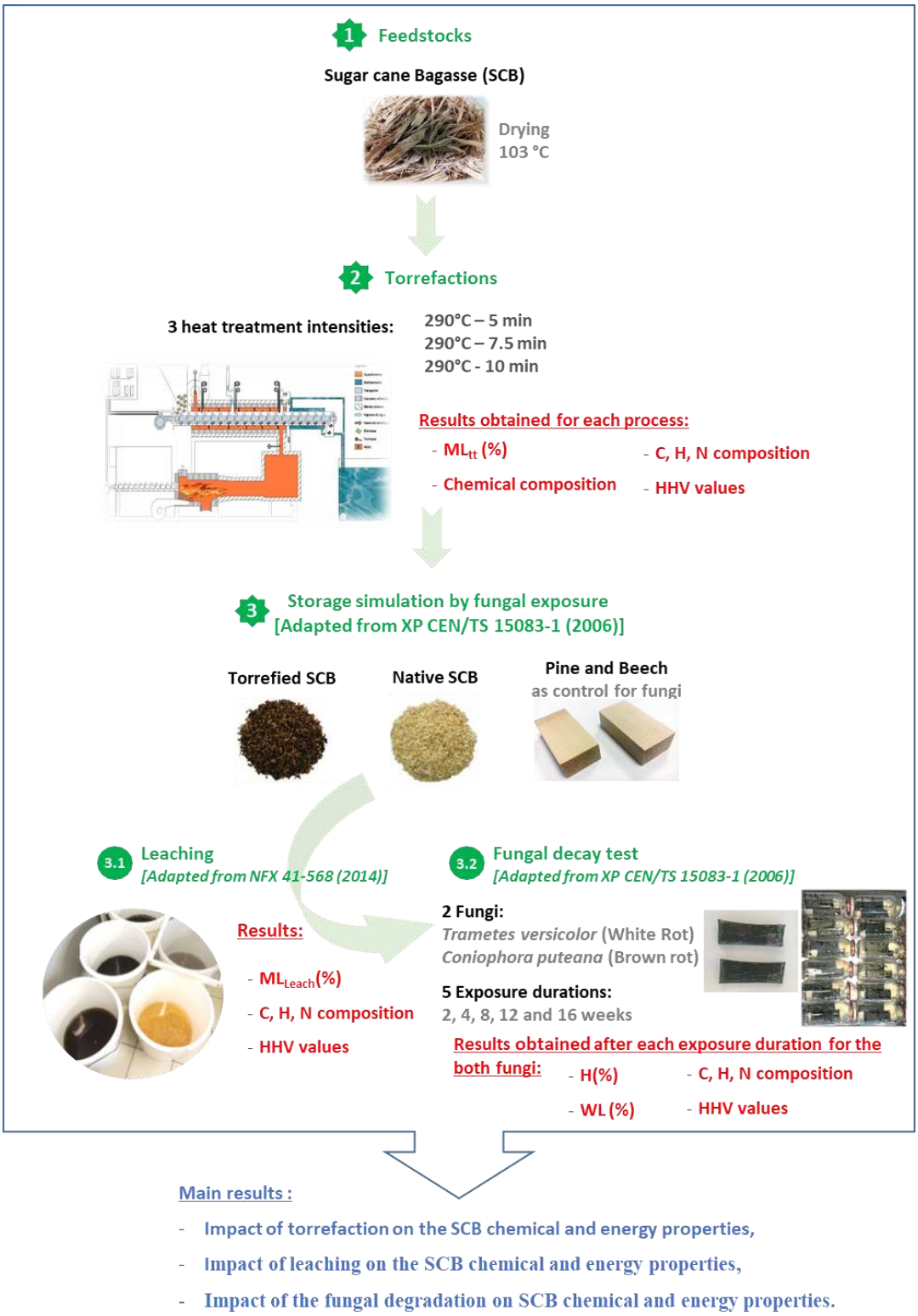


Fig. 3: Synthesis of the overall approach and the different analysis protocols used for this study.

3. RESULTS

3.1. Mass loss determination (ML_{tt} %)

According to the exponential kinetic of wood thermal degradation, the treatment duration has an impact on treatment intensity as well as on mass loss kinetic (CANDELIER et al., 2016). The results presented in Figure 4, are in accordance with this statement. For heat treatments performed at 290 °C, ML_{tt} (%) of SCB samples increased with the increasing of the process duration, from 12 ± 0.20% (t = 5 min) to 23.5 ± 0.21% (t = 10 min). This phenomenon is due to the fact of for a given temperature, the quantity of each degradation product increases progressively as the treatment duration increases (CANDELIER et al., 2013).

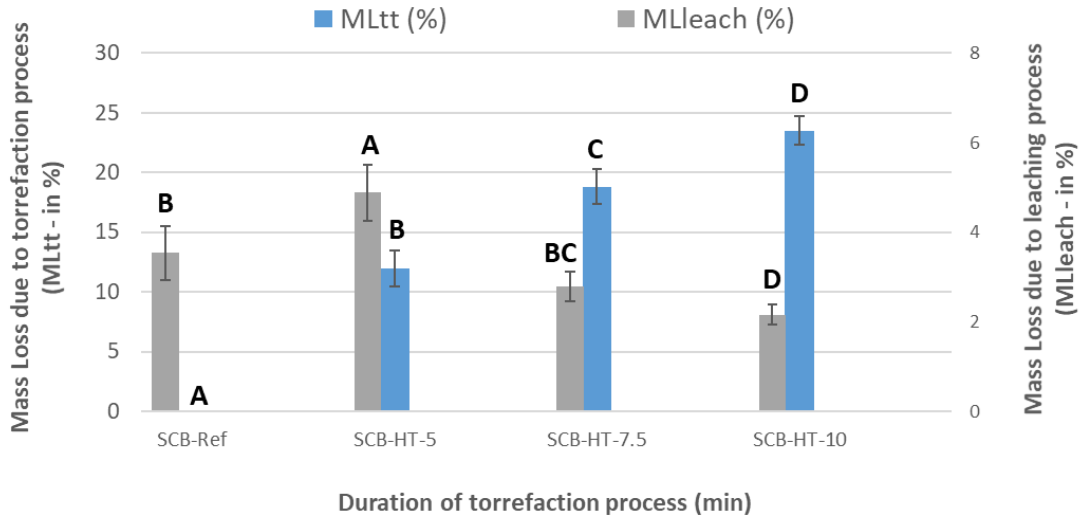


Fig. 4: Average values of raw and torrefied SCB Mass Losses (ML_{tt}%) due to thermal degradation and Mass Losses (ML_{leach}%) due to leaching process.

3.2. Chemical composition changes after torrefaction processes

As shown in Tab. 1, extractives content of SCB increased at 290 °C – 5 and 7.5 minutes and seemed to decrease at 290 °C – 10 minutes. These results are consistent with other past studies (ROSA; PEREIRA, 1994; ESTEVES et al., 2008), highlighting that the major increase at low intensity was due to water and ethanol extractives because of polysaccharide degradation. Almost all of the original extractives released and new compounds were generated by hemicelluloses and lignin thermal degradation. These mainly included monosaccharides and their dehydratation products, as well as

syringaldehyde, syringic acid and sinapaldehyde, as the most prominent lignin derived compounds (ESTEVES et al., 2008; ROUSSET et al., 2009).

Total lignin content increases considerably after thermal treatment, mainly due to the increase of insoluble lignin content, whereas soluble lignin content decreases according to the heat treatment intensity. The ether linkages of lignins are cleaved and new free phenolic hydroxyl groups and α and β-carbonyl groups arise, which are responsible for crosslinking via formation of methylene bridges (WIKBERG; MAUNU, 2004; NUOPPONEN et al., 2005; TJEERDSMA; MILITZ, 2005). The methoxyl content decreases and the new reactive sites on the aromatic ring can lead to further condensation reactions (WIKBERG; MAUNU, 2004). The decomposition of the holocellulose, mainly due to hemicellulose degradation (HASELI et al., 2011) is statistically significant as the holding time is increasing. The holocellulose is decomposed greatly and the proportion of lignin in the material increases, leaving a highly lignified material (DRUMMOND; DRUMMOND, 1996; REZENDE et al., 2011; SLUITER et al., 2016).

Tab. 1: Chemical structure composition of raw and torrefied sugarcane bagasse

Sample	Total Extractive Content (%)	Insoluble Lignin (%)	Soluble Lignin (%)	Total Lignin (%)	Total Holocellulose (%)
SCB-Ref	5.36 ± 0.09 **(C)**	24.47 ± 1.52 **(C)**	1.02 ± 0.08 **(A)**	25.49 ± 1.60 **(C)**	69.15 ± 1.73 **(A)**
SCB-HT-5	8.78 ± 0.07 **(A)**	23.78 ± 0.34 **(C)**	0.99 ± 0.01 **(A)**	24.77 ± 0.35 **(C)**	66.45 ± 1.66 **(B)**
SCB-HT-7.5	8.94 ± 0.24 **(A)**	38.07 ± 1.97 **(B)**	0.66 ± 0.01 **(B)**	38.73 ± 1.98 **(B)**	52.33 ± 1.31 **(C)**
SCB-HT-10	6.84 ± 0.14 **(B)**	45.69 ± 1.70 **(A)**	0.52 ± 0.00 **(C)**	46.21 ± 1.70 **(A)**	46.95 ± 1.17 **(D)**

The values (+SD) within the same column followed by the same letter are not significantly different based on one-way ANOVA followed by Duncan test at 5% (a = 0.05).

3.3. Elemental Composition and High Heating Values of raw and torrefied SCB samples properties before and after leaching

The objectives of this section are to (i) evaluate the influence of leaching step on the elemental composition and energy properties (HHV) of sugarcane bagasse changes, and then to (ii) determine if torrefaction process, according to the temperature and holding time, allows to improve the SCB energy properties and limit the impact of leaching for an energy use.

As shown in Tab. 2, heat treatment duration affects the element compositions of SCB materials. The carbon and nitrogen in the material increased with residence time, while the hydrogen decreased. Hydrogen and oxygen are released as water vapor and carbon dioxide emissions (GRANADOS et al., 2017). Hemicelluloses mainly generate carbon monoxide and carbon dioxide through decarboxylation reactions of acid groups linked to hemicelluloses (WERNER et al., 2014) while cellulose generates small amounts of carbon dioxide (WERNER et al., 2014).

Tab. 2: Elemental Compositions and High Heating Values (HHV), before and after leaching of raw and torrefied SCB samples

Sample	Before Leaching process					After Leaching process				
	C* (%)	H* (%)	H/C*	N* (%)	HHV_0** (MJ kg^{-1})	C* (%)	H* (%)	H/C*	N* (%)	HHV_0** (MJ kg^{-1})
SCB-Ref	47,05 (D) (a)	6,00 (A) (b)	1,53 (A) (a)	0,30 (C) (a)	18,479 (D) (a)	46,75 (D) (b)	6,20 (A) (a)	1,59 (A) (a)	0,35 (A) (a)	17,874 (D) (b)
SCB-HT-5	49,60 (C) (a)	5,80 (B) (b)	1,40 (B) (a)	0,35 (B) (a)	19,241 (C) (a)	49,20 (C) (b)	6,00 (B) (a)	1,46 (B) (a)	0,25 (C) (b)	18,975 (C) (b)
SCB-HT-7.5	53,15 (B) (a)	5,60 (C) (b)	1,26 (C) (a)	0,40 (A) (a)	20,732 (B) (a)	52,35 (B) (b)	5,75 (C) (a)	1,32 (C) (a)	0,25 (C) (b)	20,228 (B) (b)
SCB-HT-10	55,10 (A) (a)	5,40 (D) (b)	1,18 (D) (a)	0,40 (A) (a)	21,491 (A) (a)	55,20 (A) (a)	5,50 (D) (a)	1,20 (D) (a)	0,30 (B) (b)	21,260 (A) (b)

* Each analysis has been duplicate and all the results are given with an accuracy of ± 0.20%.
**Each analysis has been duplicate and all the results are given with an accuracy of ± 5.00%.
Values followed by the same letter are not significantly different based on one-way ANOVA followed by Duncan test at 5% (a = 0.05).
(A): Impact of torrefaction process within the same column.
(a): Impact of leaching process between columns "Before Leaching Process" and "After Leaching Process".

As shown in Fig. 7 and Fig. 8, HHV increased with the holding time. Overall, Fig. 7 and Fig. 8 indicate that the HHV increased with an increase of Mass Loss due to thermal degradation in SCB samples.

One of the processes in outdoor material usages is the leaching of leachates from thermally modified biomasses and it consists mainly by products from the degradation of the material constituents (tannic acid, acetic acid, furfural and furfural derivatives), but also extractives (MEIJA-FELDMANE, 2015), that may explain the higher ML_{leach}% of SCB-HT-5 than those of the three other samples. In addition, due to the thermal degradation of SCB biomass components, the content of hydroxyl groups decreases leading to increased hydrophobicity and wettability that is more difficult. According to the results obtained from sugarcane mass loss during torrefaction (Fig. 4), degradation process in SCB-HT-10 (ML_{leach} = 2.16%) occurs at greater degree than in SCB-Ref (ML_{leach} = 3.54%), SCB-HT-5 (ML_{leach} = 4.88%) and SCB-HT-7.5 (ML_{leach} =

2.78%), thereby reducing the amount of substances accessible to leach. These results are in accordance with other past studies (ESTEVES et al., 2007; BRITO et al., 2008). Finally, thermally modified SCB treated during 10 minutes (SCB-HT-10) is more environmentally friendly, than the other treatment, due to less water leachable substances (Fig. 4).

Tab. 2 highlights that the HHV of raw and torrefied SCB samples was decreased by leaching process. The decrease of HHV values could be explained by the removal of some extractives compounds during this leaching process. In fact, previous studies shown that extractives content and chemical composition are strongly correlated to the HHV of woody biomass (HOWARD, 1972; WHITE, 1987).

3.4. Fungal decay of raw and torrefied SCB samples according to the fungus exposure duration

The objectives of this section is to simulate the storage of raw and torrefied SCB in order to (i) evaluate the impact of SCB deterioration level on its energy properties and then to (ii) determine if torrefaction process, according to the temperature and holding time, allows to limit the impact of fungal deterioration on the energy properties.

3.4.1. Moisture content

Fig. 5 shows the final moisture content, as a complex of fungal metabolites and water, of the control samples of beech and pine, raw and torrefied SCB samples, after *Trametes versicolor* and *Coniophora puteana* fungi exposures and according to the duration of these decay expositions.

Whatever the fungi exposed to the SCB samples, the final moisture content of SCB sample was directly proportional to its hemicellulose content. By comparing Fig. 5 and Tab. 1, it clearly appears that the amount of water absorbed by sugarcane bagasse during fungi test increased when its hemicellulose content increased. The hydrophilic nature of bagasse is mainly due to the high content of hemicellulose. Hemicellulose polymers have many hydroxyl groups (–OH) which drive sugarcane bagasse to be polar and to make easily hydrogen bonds with water molecules (TUMULURU et al., 2011). Hemicellulose degradation during torrefaction causes the loss of hydroxyl groups in

sugarcane bagasse (TUMULURU et al., 2011). Thus, torrefied sugarcane bagasse loses its hydrophilic nature, since there are no hydroxyl groups, which tend to be polar and easily make hydrogen bonds with water molecules. In addition, the changes of lignocellulosic polymers during torrefaction lead to the formation of unsaturated non-polar structures in sugarcane bagasse.

The degradation of hemicellulose, cellulose, and lignin in sugarcane bagasse during torrefaction causes shortening of polymer chains. The changes of sugarcane bagasse properties into less fibrous, soft, and brittle is mainly caused by the degradation of hemicellulose and cellulose (SUPRAMONO et al., 2015).

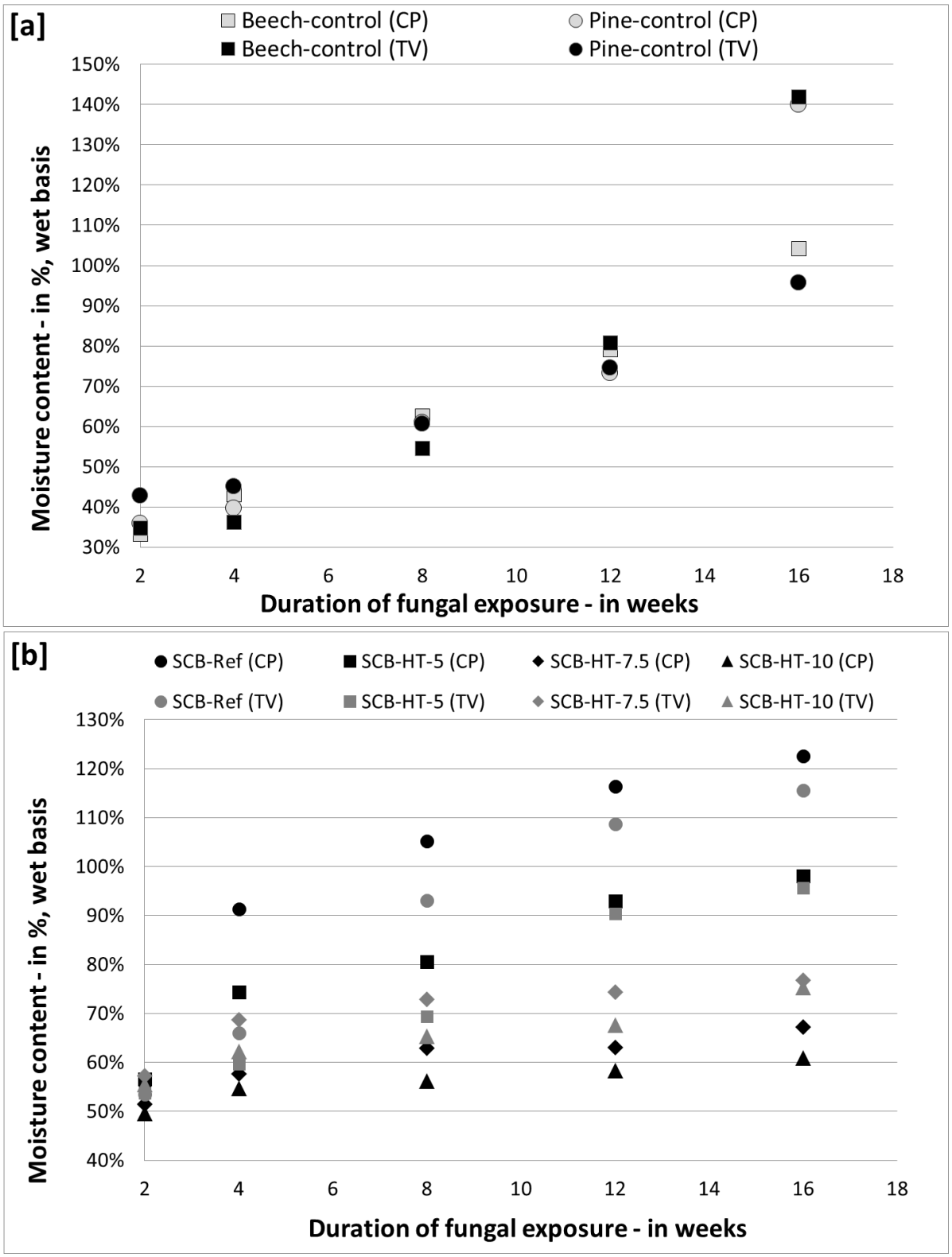


Fig. 5: Final moisture content (%) after *Coniophora puteana* (CP) and *Trametes versicolor* (TV) exposure on the pine and beech control samples [a] and raw and torrefied sugarcane bagasse (SCB) [b], according to the fungal exposure duration.

The hydrophobic behavior of raw SCB is very similar than those of beech and pine control samples. Their complex of moisture content levels increase highly during

the first four fungi exposition weeks, and then continue to increase more slowly for longer tests durations (Fig. 5).

The moisture content of torrefied SCB samples, after decay exposure, is lower than those of beech and pine control samples and raw SCB samples, whatever the decay test duration and the fungi type. In addition, we can observe a significant decrease in moisture content for SCB-HT-7.5 and SCB-HT-10 samples compared to raw and SCB-HT-5 samples. Moisture content of SCB-HT-7.5 and SCB-HT-10 seems to be increased highly during the four first weeks and tend to stabilize for longer fungal exposure duration.

3.4.2. Fungal decay

The overall Weight Loss (WL%) due to *Trametes versicolor* and *Coniophora puteana* exposure of beech and pine control samples, raw and torrefied SCB samples, is shown in Fig. 6.

According to the weight loss values obtained concerning the fungal decay of beech and pine wood control sample after 16 weeks, the decay resistance test performed through this study has been validated. Indeed, the following minimal deterioration levels (according to XP CEN/TS 15083-1 (CEN, 2006)) of control samples were reached:

- *Coniophora puteana* (Brown-rot) on Pine: WL = 57.12% > 30%
- *Coniophora puteana* (Brown-rot) on Beech: WL = 48.18% > 30%;
- *Trametes versicolor* (White-rot) on Pine: WL = 24.18% – no requirement;
- *Trametes versicolor* (White-rot) on beech: WL = 44.24% > 20%.

For the both tested rots, a similar tendency concerning the decay resistance improvement of SCB was observed after torrefaction. In addition, as for the results observed previously with respect to the moisture content levels, conferred durability to SCB by thermal modification depends on the heat treatment duration.

Average values of weight loss due to fungal deterioration showed that *Coniophora puteana* (Brown-rot) was more aggressive on raw and torrefied SCB samples than *Trametes versicolor* (White-rot), except for SCB-HT-7.5 but it is not really significant. The most obvious explanation to the observed higher colonization of white-rot in thermally modified SCB is the destructions in the cell wall due to heat, which would facilitate fungal nutrition and initial colonization of the biomass

(ALFREDSEN et al., 2008). The largely hemicelluloses degradation than the other macromolecular components (SHAFIZADEH; CHIN, 1977) which may give easier access to the lignin for the white-rot fungus *Trametes versicolor*. On the opposite, the theory of moisture exclusion via the reduction of cell wall voids provides a consistent explanation for the initial inhibition of brown-rot decay in modified biomass (JELLISON et al., 2013; RINGMAN, R. et al., 2014; RINGMAN, REBECKA et al., 2014).

According to the Fig. 6a, the both fungal deterioration of beech and pine control samples appears to begin as early as the fourth week of rot exposure. The fungal deterioration (TV and CP) of SCB-HT-5 starts as early as the second week of rot exposure, while those of SCB-HT-7.5 and SCB-HT-10 samples is delayed and begins only from the eighth week of fungal contact and then increase very slowly. Finally, SCB-HT-7.5 (WL < 5%) and SCB-HT-10 (WL < 2%) seem to be very promising treatment ways to preserve SCB properties during the biomass storage (Fig. 6b).

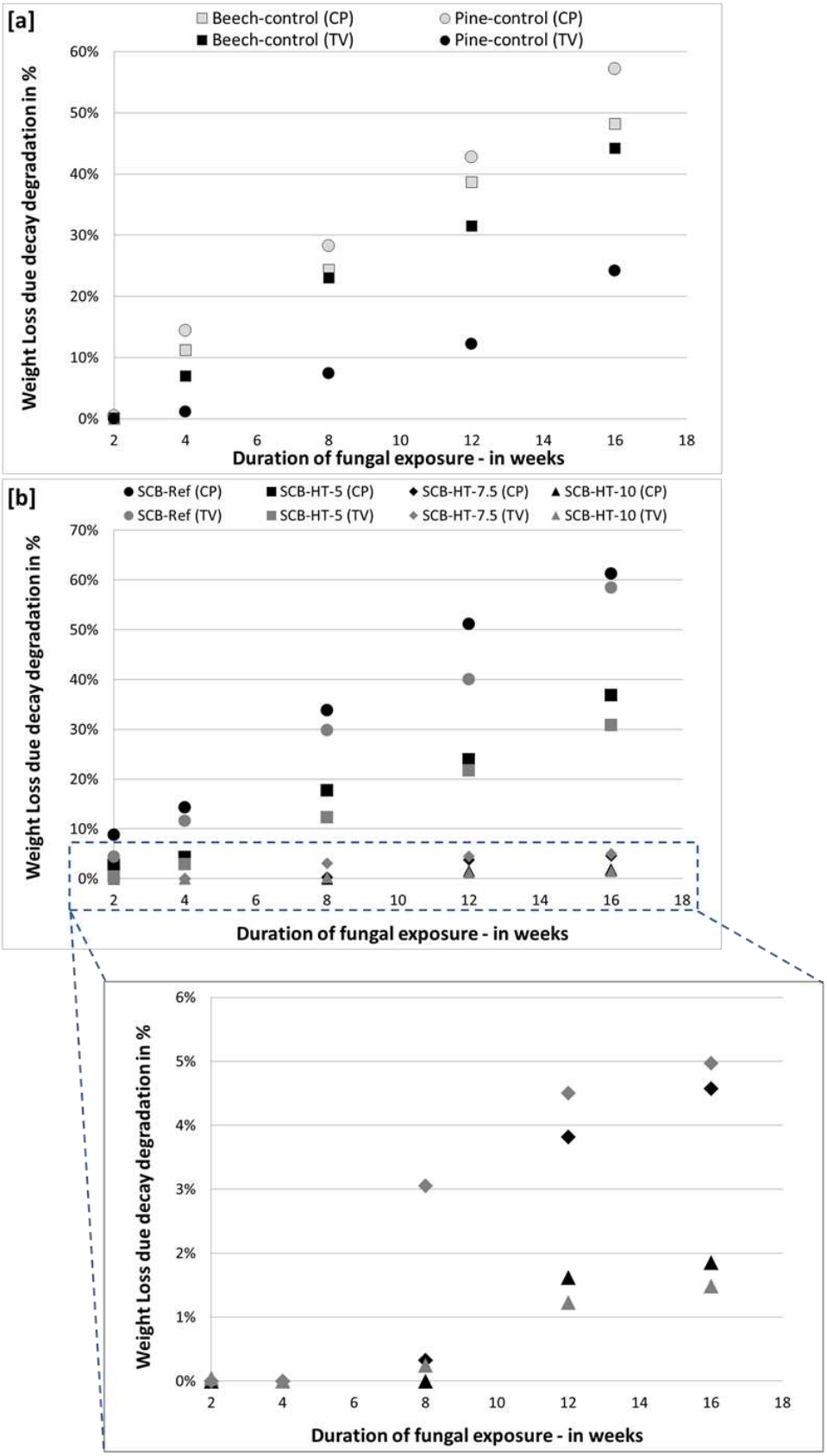


Fig. 6: Weight Losses (WL%) due to *Coniophora puteana* (CP) and *Trametes versicolor* (TV) deterioration of pine and beech control samples [a] and raw and torrefied sugarcane bagasse (SCB) [b], according to the fungal exposure duration.

4. DISCUSSION

4.1. Impact of fungal exposure on the energy properties of raw and torrefied SCB samples

4.1.1. Deterioration by *Trametes versicolor* (TV) – White-rot

Loss of carbon was recorded in all samples with white rotter *Trametes versicolor* (TV) (Fig. 7a). According to the literature, white-rot mainly degrades the lignin polymer, causing loss of carbon (JELLISON et al., 2013). Indeed, fungal activity was expected to reduce the carbon content as carbon compounds serve as nutrients and are respired as CO_2 by fungi (DIX; WEBSTER, 1995; RYTIOJA et al., 2014).

The Nitrogen content increased in all tested materials (Fig. 7c), whereas Hydrogen content decreased for SCB-HT and SCB-HT-5 and increased for SCB-HT-7.5 and SCB-HT-10 (Fig. 7b), but these changes in nitrogen and hydrogen contents were not statistically significant. It results that, for all tested samples, H/C ratio increases according to the *Trametes versicolor* (TV) exposure duration, where the most significant evolution occurs in the first four weeks of fungal exposure (Fig. 7d).

As observed in Figures 7e and 7f, the decreases of HHV values, for each SCB samples (raw and torrefied), according the fungal exposure duration are in agreement with the litterature. Depletion of carbon will lower the calorific value and here, statistically significant changes were detected in carbon content. The heat content is related to the oxidation state of the natural fuels in which carbon atoms generally dominate and overshadow small variations of hydrogen and nitrogen content (SUSOTT et al., 1975). SUSOTT et al. (1975) and TILLMAN (1978) found a linear relationship between the higher heating value and the carbon content of the natural fuels, chars, and volatiles. HUANG et al. (2009) and PROTÁSIO et al. (2012) have also put highlight that Carbon and Hydrogen are the elements that contribute most to the Heating Values of charcoal. Therefore, low H/C and O/C ratios are desirable for the use of all types of biomasses for energy, including charcoals.

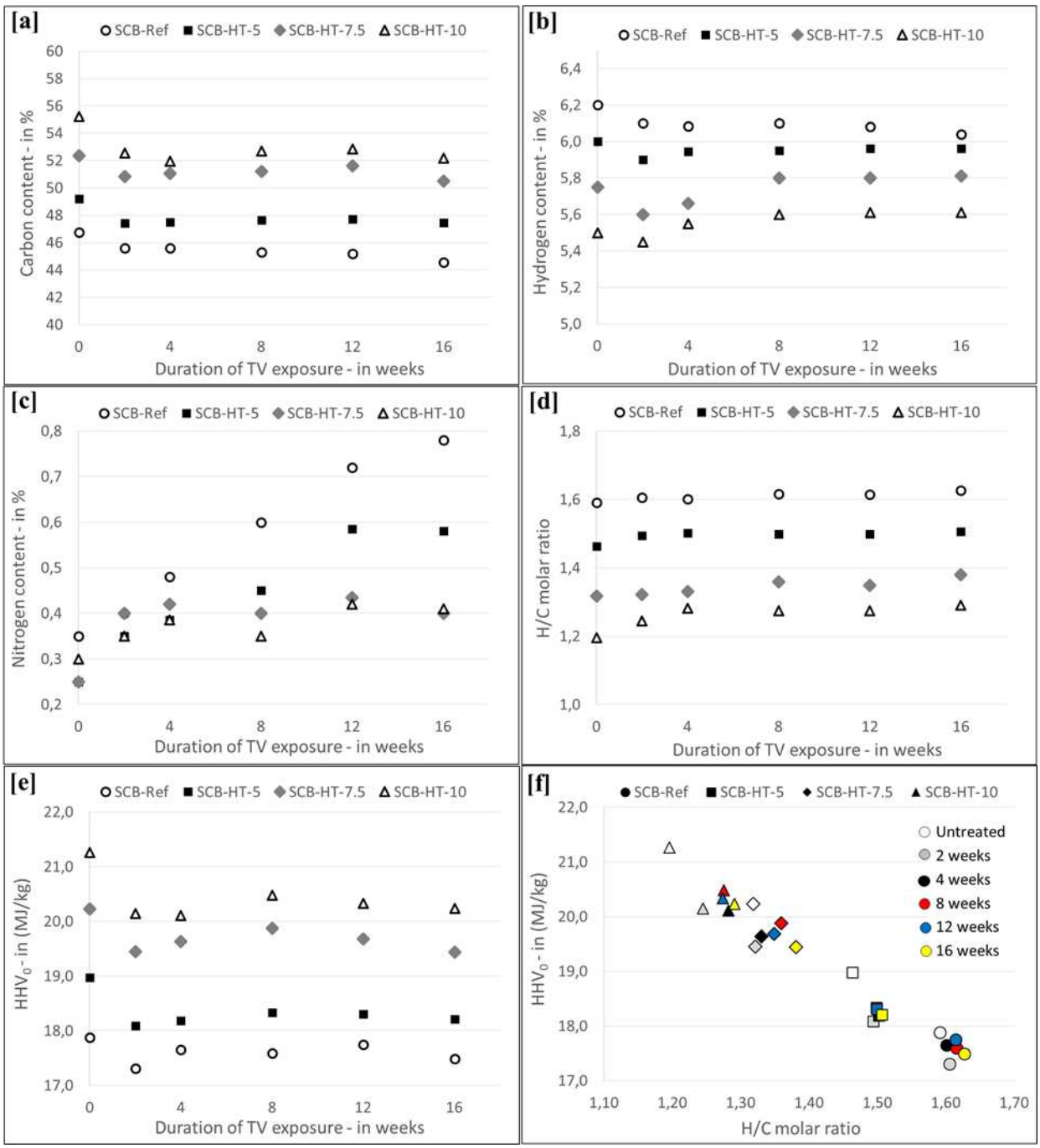


Fig. 7: [a] Carbon, [b] Hydrogen and [c] nitrogen contents (%), [d] H/C molar ratio and [e] HHV_0 (MJ kg^{-1}) of raw and torrefied sugarcane bagasse (SCB), according to *Trametes versicolor* exposure duration; [f] Correlation between HHV_0 (MJ kg^{-1}) and atomic H/C ratio of the different sugarcane bagasse (SCB) samples.

4.1.2. Deterioration by *Coniophora puteana* (CP) – Brown-rot

Concerning the changes in Hydrogen (Fig. 8b) and Nitrogen (Fig. 8c) contents during fungal exposure, similar results were observed for *Coniophora puteana* (CP) and

Trametes versicolor (TV). Regarding the Carbon content, different behavior were observed during *Coniophora puteana* (CP) exposure, according to the heat treatment intensity. It results that Carbon content decreases for SCB-HT-7.5 and SCB-HT-10 samples relating to the *Coniophora puteana* (CP) exposition duration, whereas Carbon content increases for SCB-Ref and SCB-HT-5 samples (Fig. 8a). These results could be explained by the remaining cellulose and the hemicelluloses after torrefaction at low temperature (SCB-Ref and SCB-HT-5) are degraded by *Coniophora puteana* (CP), increasing the relative carbon content. In fact, brown-rot fungus (*C. puteana*) causes more weight loss than the white-rot (*T. versicolor*), because it removes the cellulosic fraction and leaves lignin structurally modified. Brown rotter *Coniophora puteana* (CP) prefers coniferous wood species, but seems to cause also carbon loss in SCB. It uses endoglucanases to degrade cellulose and hemicelluloses, but has also been reported to produce cellobiohydrolases that erode crystalline cellulose and could therefore also utilize quite severely torrefied wood (MANSFIELD et al., 1998). We observe a decrease of H/C ratio and an increase HHV value for SCB-Ref and SCB-HT-5 samples according to the *T. versicolor* exposure duration, whereas an increase of H/C ratio and a decrease HHV value for SCB-7.5 and SCB-HT-10 samples were observed in the same conditions (Fig. 8d and Fig. 8e). The increase of HHV in that case (SCB-Ref and SCB-HT-5), may be associated with the degradation of the low-energy content components (e.g., leaf materials or agro-food residues) that were easily accessible to the enzymatic community during storage condition (THERASME et al., 2019). KRIGSTIN e WETZEL (2016) explained in their review that changes to the proportion of components in the biomass will affect energy content. For example, the preferential decomposition of hemicellulose will result in increased heating values, but the loss of extractives or the preferential fungal decomposition of lignin would tend to reduce heating values.

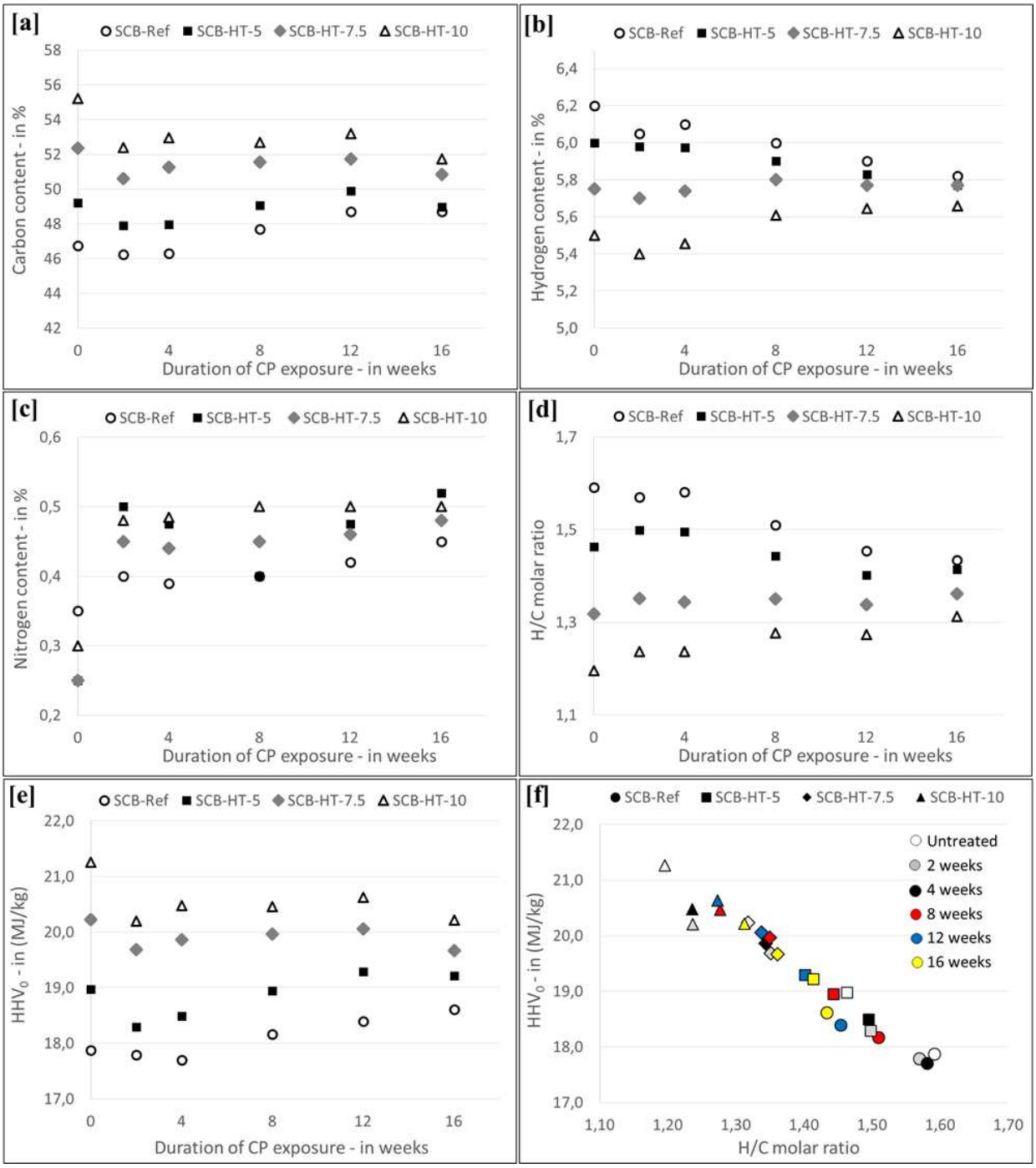


Fig. 8: [a] Carbon, [b] Hydrogen and [c] Nitrogen contents (%), [d] H/C molar ratio and [e] HHV_0 (MJ kg^{-1}) of raw and torrefied sugarcane bagasse (SCB), according to *Coniophora puteana* exposure duration; [f] Correlation between HHV_0 (MJ kg^{-1}) and atomic H/C ratio of the different sugarcane bagasse (SCB) samples.

4.1.3. Balance sheet

The High Heating Value of SCB was significantly affected by its decay exposure time. There was a relationship between the HHV and decay exposure time

across all the thermal treatments and fungi, but the change over time was small (Figure 7 and 8). Numerous studies on wood storage have recently reported no significant change or a decrease of the higher heating value (LENZ et al., 2015; PARI et al., 2015; EISENBIES et al., 2016), while others have reported a slight increase of heating value (BRAND et al., 2011; BARONTINI et al., 2014; KRZYŻANIAK et al., 2016) at the end of the storage.

From our laboratory experiment, it was clear that fungi are able to settle on seemingly unfavorable material, which is said to be hydrophobic and suitable for outside storage. The more mildly treated samples experienced more carbon loss, but took in less moisture in outside storage, contrary to the more severely treated samples (KYMÄLÄINEN et al., 2014). The loss of dry matter (WL%) and carbon (C%) as well as the increasing moisture content decrease the calorific value of the fuel and thus increase associated costs (KYMÄLÄINEN et al., 2014). Therefore, torrefaction could be a viable method to eliminate some of the disadvantages of raw biomass as it significantly improves energy content and prevents absorption of moisture during storage (PATEL et al., 2011). Even if HHV values decrease during fungal exposure, HHV values are still higher for high-intensity treated SCB samples (SCB-HT-7.5 and SCB-HT-10) than those in the raw and or slightly thermally modified (SCB-Ref and SCB-HT-5) (Fig. 7f and Fig. 8f).

5. CONCLUSION

The heat treatment duration has an important impact on sugarcane bagasse mass loss kinetic during torrefaction process. Chemical and Elemental composition modifications, High Heating Values and decay resistance improvements of SCB matter are directly correlated to the torrefaction process duration. HHV of raw and torrefied SCB samples was negatively impacted by leaching process.

The water absorption of torrefied SCB samples, due to their decay exposure, is lower than those of raw SCB samples, whatever the decay test duration and the fungi type. Similar observations were done on weight loss due to fungal decay. In addition, as for the results observed previously with respect to the moisture content levels, the improvement in decay resistance of to SCB by thermal modification depends on the heat treatment duration. *Coniophora puteana* (Brown-rot) was more aggressive for both raw and torrefied SCB samples compared to *Trametes versicolor* (White-rot). SCB-HT-

7.5 (WL < 5%) and SCB-HT-10 (WL < 2%) seem to be very promising treatment ways to preserve SCB properties during the biomass storage. There was a relationship between the HHV and decay exposure time across all the thermal treatments and fungi, but the change over time was non-significant. Even if HHV decrease during fungal exposure, these values remain higher for high-intensity treated SCB samples (SCB-HT-7.5 and SCB-HT-10) compared to the raw and or the slightly thermally modified biomass (SCB-Ref and SCB-HT-5). Torrefaction pre-treatment is therefore a good way to improve SCB's energy properties while limiting lose torrefied biomass quality during storage. Future studies will be needed in order to simulate the exact fungal deterioration dynamics of different torrefied biomasses.

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CAPÍTULO III

MODELING MASS LOSS AND HIGH HEATING VALUE OF BIOMASSES BY NIR SPECTROSCOPY DURING THE FUNGAL DECAY PROCESS

ABSTRACT

Sugarcane bagasse, coffee husk, eucalyptus, and pine residues were torrefied at 290 °C in a screw reactor, during 5, 7.5, 10, 15 or 20 min. Raw and torrefied biomasses were submitted successively to leaching and to white and brown-rot fungi, to simulate storage conditions. Mass loss (ML) due to fungal deterioration after 2, 4, 8 and 12 weeks were measured and the high heating value (HHV) of all the samples were determined. The possibility of using near infrared (NIR) spectroscopy has been investigated: (i) To classify the four different residual biomasses in raw and torrefied forms according to fungal decomposition by white-rot and brown-rot fungus, by using NIR and partial least squares for discriminant analysis (PLS-DA) models. (ii) And to predict the mass loss due to fungal exposure and the HHV value of raw and torrefied biomasses, according to the decay exposure duration, by developing PLS model with all variables and PLS model with variable selection by using ordered predictors selection (OPS). PLS-DA models appeared to be useful to classify the four different residual biomasses in raw and torrefied forms according to fungal decomposition by white-rot and brown-rot fungi. These results highlight the potential of NIR spectroscopy as a simple, fast, and efficient tool to analyze the decomposition process over the time. The results from PLS and PLS-OPS models, showed also that NIR have potential utility in an industrial context as a standardized continuous method to figure out the HHV of raw and torrefied biomasses during their fungal decay by a rapid characterization. However, such a method appeared to be not very efficient to predict the mass loss due to fungal deterioration of these samples. Further studies are required to improve and develop more efficient models to predict the fungal deterioration level of stored biomasses.

KEYWORDS

Biofuels, Fungi decay**,** Near-infrared spectroscopy**,** Ordered predictors selection**,** Partial least squares**,** Torrefaction.

INDEX SUMMARY

SCB: sugarcane bagasse

EUCA: eucalyptus

CH: coffee husk

TV: *Trametes versicolor* (white-rot)

CP: *Coniophora puteana* (brown-rot)

F1: brown-rot (*Coniophora puteana*)

F2: white-rot (*Trametes versicolor*)

T: torrefied

R: raw

ML: mass loss of the sample due to fungal decay process (in %, dry basis)

HHV: high heating value at constant volume of the dry (moisture-free) sample (in MJ kg^{-1}, dry basis)

NIR: near infrared

RMSE: root mean square error

RMSECV: root mean square error of cross-validation

RMSEC: root mean square error of calibration

RMSEP: root mean square error of prediction

PLS: partial least squares

OPS: ordered predictors selection

PLS-DA: partial least squares for discriminant analysis

CV: cross-validation

R: correlation coefficient

Rcv: coefficient of cross-validation

Rp: coefficient of prediction

Rc: coefficient of calibration

MSC: multiplicative scatter/signal correction

SNV: standard normal variate scaling

nlv: number of latent variables

N: number of samples

P: predicted samples

SD: standard deviation of the measured values

RE: relative error

1. INTRODUCTION

In the last decades, there has been a growing interest in the production of energy from renewable sources. Indeed, fossil fuels tend to lose space in energy matrices due to their greenhouse gas (GHG) emissions (CHEN et al., 2015). In this struggle against climate change, partly generated by these GHGs, the Paris Agreement (UNFCCC, 2015) promotes the use of renewable energy sources, including lignocellulosic biomasses, in order to achieve the environmental objectives established between the different countries concerned around the world.

In this sense, lignocellulosic biomasses are reliable alternatives to fossil fuels to produce more environmentally friendly energy, mainly due to their renewable and sustainable aspect, and their worldwide availability (XIANG et al., 2018; MOHAMMED et al., 2019). Forest and agricultural crops, or residual products from agro-food chains, allow generating these types of resources in abundant and sustainable way. Moreover, they are often harvested at low cost because they are mainly obtained from harvesting, processing, industrial use, among other forms.

Researches have been conducted in order to optimize the conversion processes from biomass to energy, as well as to improve their inherent characteristics (water absorption, calorific power, etc.), in such a way as to maximize efficiency of energy conversion and competitiveness compared to non-renewable and fossil resources (BOUZAROUR et al., 2018; UL HAI et al., 2019; BOUTAIEB et al., 2020; SINGH et al., 2020). One of the possible conversion process is the torrefaction, which consists in a biomass thermal pre-treatment, carried out at a low temperature range from 200 to 300 °C, in an inert environment and under atmospheric pressure that results in a lower mass losses than conventional pyrolysis processes (DA SILVA et al., 2018; KAI et al., 2019). Factors, such as process temperature, residence time, reactor type, and raw material characteristics as particle size and chemical composition have a very high impact on the final properties of the torrefied materials (NEGI et al., 2020). All these factors require a special attention in order to obtain a heat-treated biomass with the desired characteristics. The torrefaction process improves the characteristics inherent to lignocellulosic biomass for energy generation, occurring an increase in calorific value, consequently greater energy density, loss of mechanical resistance that could low energy consumption in grinding for use in co-firing systems, improvement in material

uniformity, and increases in resistance to water absorption and to biological deteriorations (TSALIDIS et al., 2014; CHEN et al., 2015; FARIA et al., 2020).

Greater demand for lignocellulosic biomass for use as an energy source leads to the storage of large quantities of this material. Depending on the storage conditions, several problems can occur during this period. An increase in moisture content of the feedstock and the development of wood-destroying fungi can occur rapidly during storage and lead to significant material losses as well as changes in certain properties of the stored biomass, mainly due to the degradation of some components of the cell wall (hemicelluloses and lignin). These phenomena, generating gaseous emissions and/or leachates, can also have adverse impacts on the environment (CANDELIER; DIBDIAKOVA, 2020) and can increase the risk of fire due to spontaneous heating (BRAND et al., 2014; TANG; ZHOU, 2020). Torrefaction pretreatment allow to reduce this phenomena occurred on torrefied biomass compared to raw biomass, during storage (FARIA et al., 2020). However, the modifications caused by biomass storage can still change the use of this material in industrial scale. In this sense, it is necessary to know the behavior of biomass under humidity and wood-destroying fungi exposures.

Conventional characterization methods of lignocellulosic materials require the use of reagents, is time-consuming, laborious, and more expensive. In this sense, near-infrared (NIR) spectroscopy has been used (PINTO et al., 2016; FERREIRA et al., 2018; LI, Y. et al., 2020) because it has advantages such as lower cost, less time to obtain results, non-destructive technique, reduced technical risk, requires minimal material preparation and can be used in real-time in the industry (ALVES; POPPI, 2013; ASSIS et al., 2017). The NIR spectroscopy technique is in the electromagnetic spectrum range from 12000 to 4000 cm^{-1} and it corresponds to an analytical technique based on vibrational spectroscopy that expresses the interaction between radiation and the material (SMITH-MORITZ et al., 2011; HEIN; CHAIX, 2014). NIR spectrum is a combination of bands formed by the overlap of vibrational transitions in the overtone region, which requires mathematical modeling that relates the spectra with one or more properties of interest qualitatively or quantitatively (PASQUINI, 2003; FERREIRA et al., 2018). Therefore, it is necessary to apply chemometric methods to extract spectral information. Partial least squares (PLS) regression and PLS for discriminant analysis (PLS-DA) are methods largely used in multivariate analysis for NIR spectra treatment (XIAO et al., 2014; SUN et al., 2020). PLS is the most applied method to build multivariate calibration models (GELADI; KOWALSKI, 1986; WOLD et al., 2001;

FERREIRA, 2015). This method is widely used to predict some properties of lignocellulosic biomasses (LESTANDER et al., 2014; FERREIRA et al., 2018; LI, Y. et al., 2020). PLS-DA is a valuable tool to evaluate changes caused by thermal treatments in biomasses (DEVOS et al., 2020), and associated with temporal changes due to biological deterioration (BARKER; RAYENS, 2003; FERREIRA et al., 2018).

This study aimed to build multivariate calibration models for residues of eucalyptus, pine, coffee husk, and sugarcane bagasse in raw and torrefied forms, able to accurately and precisely classifying and predicting characteristics related to their fungal decomposition by NIR spectroscopy and chemometric methods, mainly PLS and PLS-DA. The main objective is to predict the evolution of mass loss (ML) and high heating value (HHV) of raw and torrefied feedstocks, according to their exposure duration to wood-destroying fungi.

2. MATERIALS AND METHODS

2.1. Biomass samples

Four types of lignocellulosic biomass residues were used: sugarcane bagasse (*Saccharum* spp. hybrids), coffee husk (*Coffea arabica* L.), eucalyptus wood residues (*Eucalyptus* spp.), and pine wood residues (*Pinus* sp.). Sugarcane bagasse (SCB) was obtained from Jatiboca Sugar and Ethanol industry (Ponte Nova, Minas Gerais, Brazil). Eucalyptus wood residues (EUCA), pine wood residues (PINE) and coffee husk (CH) were collected in Minas Gerais state (Brazil). All of these biomasses were selected due to their availability and their difference in composition and structure characteristics.

SCB, EUCA, PINE and CH feedstocks were first dried outdoors in a drying yard for 30 days, until they reached their respective hygroscopic equilibrium moisture. Afterwards, all biomasses were milled in a knife mill. For SCB, a classification in screen sieves between 2 and 6 mm was done, collecting the fraction retained on the 2 mm sieves to reduce the presence of fine particles, which might compromise subsequent analysis. Finally, the particle average size was 12 mm for EUCA and PINE and 7 mm for CH samples.

2.2. Torrefaction process

The biomass residues were previously oven-dried at 103 ± 2 °C during 48 hours with constant air circulation to reach a moisture content near to 0 % and allowing to eliminate the influence of water on heat treatments. Then, each type of residue was torrefied separately in an endless screw type reactor (DA SILVA et al., 2017), developed in the Laboratory of Panels and Wood Energy (LAPEM) of Federal University of Viçosa. 5 kg of biomass was used, in duplicates, for each batch of torrefaction. Torrefaction was carried out at 290 °C, using three different holding times for each type of feedstock, as following: sugarcane bagasse (5, 7.5, 10 min), eucalyptus (10, 15, 20 min), pine (10, 15, 20 min) and coffee husk (5, 10, 15 min).

2.3. Fungal decay exposure

All samples (raw and torrefied) were firstly submitted to leaching process according to the NFX41-568 (AFNOR, 2014) standard. This standardized procedure for accelerated ageing is commonly used for wood natural durability tests. This leaching process was well detailed in FARIA et al. (2020). Then, raw and torrefied biomasses were placed into plastic grid bags of the dimensions 100 × 30 × 15 mm (L, R, T) in order to expose themselves to basidiomycete attacks. Each sample was oven-dried at 103 ± 2 °C for 24 h determining the initial dried mass (m_1). All samples were then placed in conditioned room (22 °C, 70 % relative humidity) in order to keep humidity prior to the decay exposure tests. After that, samples were sterilized by X-ray process with a dose of 25.0 (± 5.6 %) kGy, as recommended by the NFX 41-568 (AFNOR, 2014) standard, by Ionisos Compagny (France). Contrary to autoclave sterilization, X-ray does not cause significant changes in wood properties affecting the wood natural durability and X-ray is more efficient than oven drying to sterilized wood samples.

Decay resistance of raw and torrefied biomasses after leaching was tested according to the guidelines of the XP CEN/TS 15083-1 (CEN, 2006) standard criteria, with some adjustments concerning the samples size and the fungal exposure duration. As required in this standard, the both following brown and white-rot fungi, respectively, were tested: *Coniophora puteana* (F1) and *Trametes versicolor* (F2) (Fig. 1). The following fungal exposure duration were tested: 0, 2, 4, 8 and 12 weeks. After each decay exposure timeframe, the concerned test devices were kept from the climatic

chamber, mycelia were removed from the samples bags, each sample was oven dried at 103 ± 2 °C for 24 h and their final oven-dried mass was measured (m_2).

The decay exposure tests were conducted as follows:

- The three torrefaction intensities for SCB (5, 7.5 and 10 min), after leaching, were tested in order to study the impact on torrefaction duration on the decay resistance;
- One torrefaction intensity for EUCA (10 min), PINE (15 min) and CH (5 min), after leaching, were tested in order to evaluate the impact of the torrefaction process and the influence of the biomass nature on its durability;
- For each fungus and fungal exposure duration, 4 replicates of raw and torrefied biomass samples (after leaching) were done. This methodology is well described for EUCA, PINE and CH by FARIA, et al. (2020).
- Beech (*Fagus sylvatica*) and Pine (*Pinus sylvestris*) sapwood samples of the dimensions 50 × 25 × 15 mm (L, R, T) were used as controls for the virulence of the strains (8 tested blocks for each fungus and for each fungal exposure duration). This step was only used to check the great virulence of wood-destroying fungi in order to validate the decay resistance tests. The results concerning the decay resistance of these wood control samples are not discussed in this paper.

Fig. 1. Samples in contact with fungal decay.

2.4. Mass loss and high heating value

The characterization of all raw feedstocks was done by calorific power (high heating value) measurement. The impacts of leaching and fungal deterioration, according to the duration of fungal exposure were evaluated on the following raw and torrefied biomass properties according to two characterizations: (i) the mass losses (ML) caused by fungal deterioration and (ii) the high heating values (HHV). For each tested modality, the four replicated used for decay test were mixed, grinded using a cutting mill Retsch SM 100 and sieved. Particle sizes fraction of 0.1 to 0.2 mm was retained. Sawdust was then conditioned at 103 ± 2 °C °C for 24 h and stored in air-tight bottle before calorific power analyses.

2.4.1. Mass loss due to fungal deterioration

The mass loss was determined according to the following formula (Eq. 1):

$$ML \text{ (in \%, dry basis)} = ((m_1 - m_2) / m_1) \times 100 \qquad (1)$$

Where:
ML = mass loss of the sample due to fungal deterioration (in %, dry basis);
m_1 = initial oven-dried mass of sample before fungal exposure;
m_2 = final oven-dried mass of fungal decayed sample.

2.4.2. High heating value (HHV)

The calorific value was measured using an Automated Isoperibol Fixed Bomb Parr 6200 calorimeter, following the guidelines from the CEN/TS 14918 (CEN, 2005). One gram of oven-dried biomass, with a particle size smaller than 0.2 mm, were used. Two replicates have been done for each sample and all the results are given with an accuracy of ± 5.00 %.

2.5. Biomass samples for NIR spectroscopy analyses

Globally, three hundred and thirty-six biomass samples were analyzed by NIR spectroscopy. A total of seventy-two CH samples, seventy-two EUCA samples, seventy-two PINE samples and one hundred and twenty SCB samples. Each of these sample batch includes native and previously torrefied (three torrefaction intensity), leached and fungi-exposed (during 0, 2, 4, 8 and 12 weeks) samples. Then, raw and torrefied biomasses were ground in a knife-mill (SM 100, Retsch, Haan, Germany). Particle sizes fraction between 0.1 to 0.2 mm was retained and then oven- dried at 103 ± 2 °C for 24 h following by a conditioned step at 20 ± 2 °C and 65 ± 5 % of air relative humidity prior to NIR measurements.

2.5.1. Near-infrared spectroscopy analyses

Reflectance NIR spectra was collected by a Fourier transform near-infrared spectrometer Bruker Vector 22/N (Bruker Optik GmbH, Ettlingen, Germany) in diffuse reflectance mode, combined with OPUS software (v May 5, 2005). Approximately 2 g of each biomass sample was placed in a rotating cup to obtain the spectra. Data were obtained for wavelengths between 12500 to 3500 cm^{-1} (800 nm to 2850 nm), in 8 cm^{-1} increments. Thirty-two scans were performed and averaged for each sample. They were compared to the standard (sintered gold reference) in order to obtain the reflectance spectrum of the sample. Sample spectrum were collected in triplicate, and the average spectrum was used in the data analysis.

2.6. NIR spectroscopy data analysis

Data analysis was performed in two parts. The first of one concerns the quantitative analyses using partial least squares (PLS) regression with the ordered predictors selection (OPS) methods (TEOFILO et al., 2009; ROQUE et al., 2019) to select variables and the second one relates to the qualitative studies using partial least squares for discriminant analysis (PLS-DA).

All calculations were performed in MATLAB environment (MATLAB R2020a, The MathWorks Inc., Natick, USA). The OPS methods were applied using the algorithms available at http://www.deq.ufv.br/chemometrics.

2.6.1. Partial least squares method

An inverse regression model (**y** = **Xb**) was built using the PLS method (GELADI; KOWALSKI, 1986). Additionally, the OPS variable selection methods were applied to select regions that presented relevant information (TEOFILO et al., 2009; ROQUE et al., 2019). Mass loss (in %, dry basis) and HHV (in MJ kg^{-1}) were the calibrated properties. Besides the raw data, two preprocessing methods, mean center and autoscale, eight transformations, smoothing, first derivative, second derivative, multiplicative scatter/signal correction (MSC), detrend, normalize, baseline, standard normal variate scaling (SNV), and their combinations were tested to find the best regression models for each property. The dependent variables (properties) were pre-processed using centering in all calculations. The number of latent variables (*nlv*) was determined by random cross-validation with ten splits. The Kennard and Stone algorithm (KENNARD; STONE, 1969) was used to split the samples into calibration and prediction sets. Six datasets were used to build models (Table 1).

Table 1. Datasets information about calibration and prediction sets of properties and biomass thermic treatment

Set	**Property**	**Biomasses *raw***	**Biomasses *torrefied***	**All biomasses**
Calibration	Mass loss (%)	77	86	164
Prediction		19	19	37
Calibration	HHV (MJ kg^{-1})	86	130	216
Prediction		22	32	54

HHV: high heating value.

Models were evaluated using statistical parameters such as the root mean square error (*RMSE*) and correlation coefficient (*R*), according to Equations 2 and 3, respectively.

$$RMSE = \sqrt{\sum_{i}^{N} (y_i - \hat{y}_i)^2} \Big/ N \qquad (2)$$

$$R = \sum_{i=1}^{N} (\hat{y}_i - \bar{\hat{y}})(y_i - \bar{y}) \Big/ \sqrt{\sum_{i=1}^{N} (\hat{y}_i - \bar{\hat{y}})^2} \sqrt{\sum_{i=1}^{N} (y_i - \bar{y})^2} \quad (3)$$

where y_i and $\hat{y}_i$ are the measured and predicted values, respectively. When calibration is used, *N* represents the number of samples in the calibration set, and the error and correlation coefficient are the root mean square error of calibration (*RMSEC*) and the correlation coefficient of calibration (R_c), respectively. When internal cross-validation (*CV*) is used, *N* represents the number of samples in the cross-validation set, and the error and correlation coefficient are the root mean square error of cross-validation (*RMSECV*) and the correlation coefficient of cross-validation (R_{cv}), respectively. When external validation is used, *N* represents the number of predicted samples (*P*) and, in this instance, the error and correlation coefficient are the root mean square error of prediction (*RMSEP*) and the correlation coefficient of prediction (R_p), respectively.

2.6.2. Variable selection

The OPS method is based on obtaining an informative vector that contains information about the location of the best response variables for prediction. The original response variables (**X** matrix columns) were differentiated according to the corresponding absolute values of the informative vector elements. The differentiated variables were sorted in descending order. Multivariate regression models were built and compared using the quality parameters calculated during cross validations (TEOFILO et al., 2009). These steps of variable selection were performed using several informative vectors, and for each interval, the best vector was chosen. This method is called *Auto*OPS. In addition, after performing the selection, the selected variables returned to a new selection, and this procedure is called *Feed*OPS. Additionally, these two methods can be applied in intervals of **X** matrix, being then called *Autoi*OPS and *Feedi*OPS (ROQUE et al., 2019).

Two optimum *nlv* are employed in this work: one representing the component number for model building (hMod) and the other representing the component number employed to generate the best informative vector in OPS method (hOPS).

2.6.3. Partial least squares for discriminant analysis

PLS-DA is a classification method based on the PLS approach (BARKER; RAYENS, 2003). In this study, samples of all biomasses (SCB, EUCA, PINE, CH) were analyzed together and separately. They were classified in relation to type of fungal exposure (1 or 2) and thermic treatment (raw or torrefied). These categorizations are better explained in Table 2. The number of latent variables (*nlv*) was determined by random cross-validation with ten splits. All datasets were split into calibration and prediction set using Kennard and Stone algorithm (KENNARD; STONE, 1969) for each class.

Table 2. Datasets information and classes of four biomasses.

			All		**SCB**		**EUCA**		**PINE**		**CH**	
		Class	**Cal**	**Pred**	**Cal**	**Pred**	**Cal**	**Pred**	**Cal**	**Pred**	**Cal**	**Pred**
Dataset 1	R	0	96	24	24	6	24	6	24	6	24	6
	T	1	173	43	72	18	34	6	34	6	34	8
Dataset 2	R	1	77	19	19	5	19	5	19	5	19	5
	T	2	115	29	58	14	19	5	19	5	19	5
Dataset 3	F1 R	0	38	10	10	2	10	2	10	2	10	2
	F1 T	1	38	10	10	2	10	2	10	2	10	2
	F2 R	2	58	14	29	7	10	2	10	2	10	2
	F2 T	3	58	14	29	7	10	2	10	2	10	2

Dataset 1: categorization in heat treated or not; Dataset 2: categorization in heat treated or not with fungus exposure (1 or 2), does not matter which; Dataset 3: categorization in heat treated or not with fungus exposure (1 or 2); R: raw; T: torrefied; F1: fungus 1; F2: fungus 2; All: all four biomasses; SCB: sugarcane bagasse; EUCA: eucalyptus wood residues; PINE: pine wood residues; CH: coffee husk; Cal: calibration set; Pred: prediction set.

Besides that, the biomasses also were classified in relation to fungal exposure overtime (0, 2, 4, 8 and 12 weeks) as showed in Table 3.

Table 3. Datasets information and categorization overtime of all biomasses.

		Dataset 4		Dataset 5		Dataset 6	
		All		R		T	
Class		Cal	Pred	Cal	Pred	Cal	Pred
0 week	1	24	6	10	2	14	4
2 weeks	2	48	12	19	5	29	7
4 weeks	3	48	12	19	5	29	7
8 weeks	4	48	12	19	5	29	7
12 weeks	5	48	12	19	5	29	7

Dataset 4: all biomasses categorized over weeks; Dataset 5: raw biomasses categorized over weeks; Dataset 6: torrefied biomasses categorized over weeks; R: raw; T: torrefied; All: all four biomasses; SCB: sugarcane bagasse; EUCA: eucalyptus wood residues; PINE: pine wood residues; CH: coffee husk; Cal: calibration set; Pred: prediction set.

The prediction from a PLS-DA model is a value of nominally zero or one. Values close to zero and one indicate that the sample either is not (0) or is (1) in the modeled class. In practice, a threshold is determined, above which the sample is considered to be in the class, and below which the sample is not in the class.

Model performance was evaluated by calculating the sensitivity, specificity, and classification error of calibration and prediction. Sensitivity is the number of samples predicted to belong to the class divided by the number of samples that belong to the class. Specificity is the number of samples predicted to not be in the class divided by the actual number that are not in the class. Sensitivity, specificity, and error were calculated according to Equations (4), (5), and (6), respectively.

$$\text{Sensitivity} = \frac{\text{TP}}{\text{TP} + \text{FN}} \qquad (4)$$

$$\text{Specificity} = \frac{\text{TN}}{\text{TN} + \text{FP}} \qquad (5)$$

$$\text{Error} = \frac{\text{FP} + \text{FN}}{\text{TP} + \text{TN} + \text{FP} + \text{FN}} \qquad (6)$$

where TP is true positive, TN is true negative, FN is false negative, and FP is false positive. TP is the number of samples that belong to the class *i* classified as belonging to the class *i*. TN is the number of samples that do not belong to the class *i* classified as not belonging to the class *i*. FN is the number of samples that belong to class *i* not classified as belonging to the class *i*. FP is the number of samples that do not belong to the class *i* classified as belonging to the class *i*.

Besides the raw data, two preprocessing methods, mean center and autoscale, eight transformations, smoothing, first derivative, second derivative, multiplicative scatter/signal correction (MSC), detrend, normalize, baseline, standard normal variate scaling (SNV), and their combinations were tested to find the best classification models for each categorization.

3. RESULTS AND DISCUSSION

Average NIR-spectra from raw biomasses showed similarity in their spectral profiles, whatever the biomass species, characterizing by common peaks of lignocellulosic materials (Fig. 2A). Chemical complexity of the biomasses might difficult to carry out an accurate distinction of the bands. However, it is possible to attribute the main signals regarding lignocellulosic biomass. In general, the region with the greatest spectral information on biomass is between 7000-4000 cm^{-1}.

The region around 6897 cm^{-1} (peak 1) is characteristic of polymeric combinations of O–H stretching attributed to cellulose (WORKMAN; WEYER, 2008). In approximately 5935 cm^{-1} (peak 2) it contains aromatic C–H lignin stretching (SHENK et al., 2007; WORKMAN; WEYER, 2008). The region between 5500-5000 cm^{-1} (peak 3) is associated with the O–H stretching and combinations of C–H (3υ) stretches related to lignin. The 5495 cm^{-1} (peak 3) signal represents the O–H and combinations of the C=O (3υ) stretching referring to cellulose and hemicellulose. Other cellulose characteristic regions were found. Around 4785 cm^{-1} (peak 4) contains polymeric O–H (2υ) stretching, between 4405 to 4261 cm^{-1} (peak 5) are the O–H and C–H bonds, and finally the 4000 cm^{-1} (peak 6) band represents C–H and C–C stretching and combinations of C–O–C stretching of the cellulose. For water, O–H stretches occur between 7000 cm^{-1} to 5100 cm^{-1} (WORKMAN; WEYER, 2008).

In Fig. 2B, the average spectra were obtained from the four different biomasses and also on subdivided into different torrefaction levels. Level 0 referring to raw

biomasses, Level 1 to biomasses in the first torrefaction stage, Level 2, intermediate stage, and Level 3 indicating the highest torrefaction times. A significant difference in torrefaction intensity can be seen, mainly when comparing Level 0 and Level 3. The results from Fig. 2B, with a focus on the peak 3, confirm the statement from others past studies highlighting that the main chemical differences between raw and torrefied biomasses are mainly attributed to the thermal modification of hemicelluloses and cellulose fractions occurred during the wood torrefaction (DEVOS et al., 2020). Hemicelluloses seem to be most reactive than cellulose and lignin and would be very sensitive to degradation and dehydration reactions at torrefaction temperatures (ROUSSET et al., 2009).

According to Fig. 2C, the spectra of raw (R) biomass is slightly higher than torrefied (T) biomass, when comparing them in the same week of biological deterioration. These results confirmed that torrefaction process affected the biomasses chemical constitution in hemicelluloses, celluloses and lignin. The second observation was about the fungal exposure duration. Within the same group of raw or torrefied biomasses, the spectrum was shifted to a region of lower absorbance with an increase in the deterioration time. These results indicated that prolonged decay exposure is a phenomenon affecting all wood compounds (ANDERSON et al., 1991). If decay is also present, physical and mechanical properties of the bulk material will be affected, as decay fungi are able to cause rapid strength losses in wood associated with a loss of weight (WANG et al., 2006).

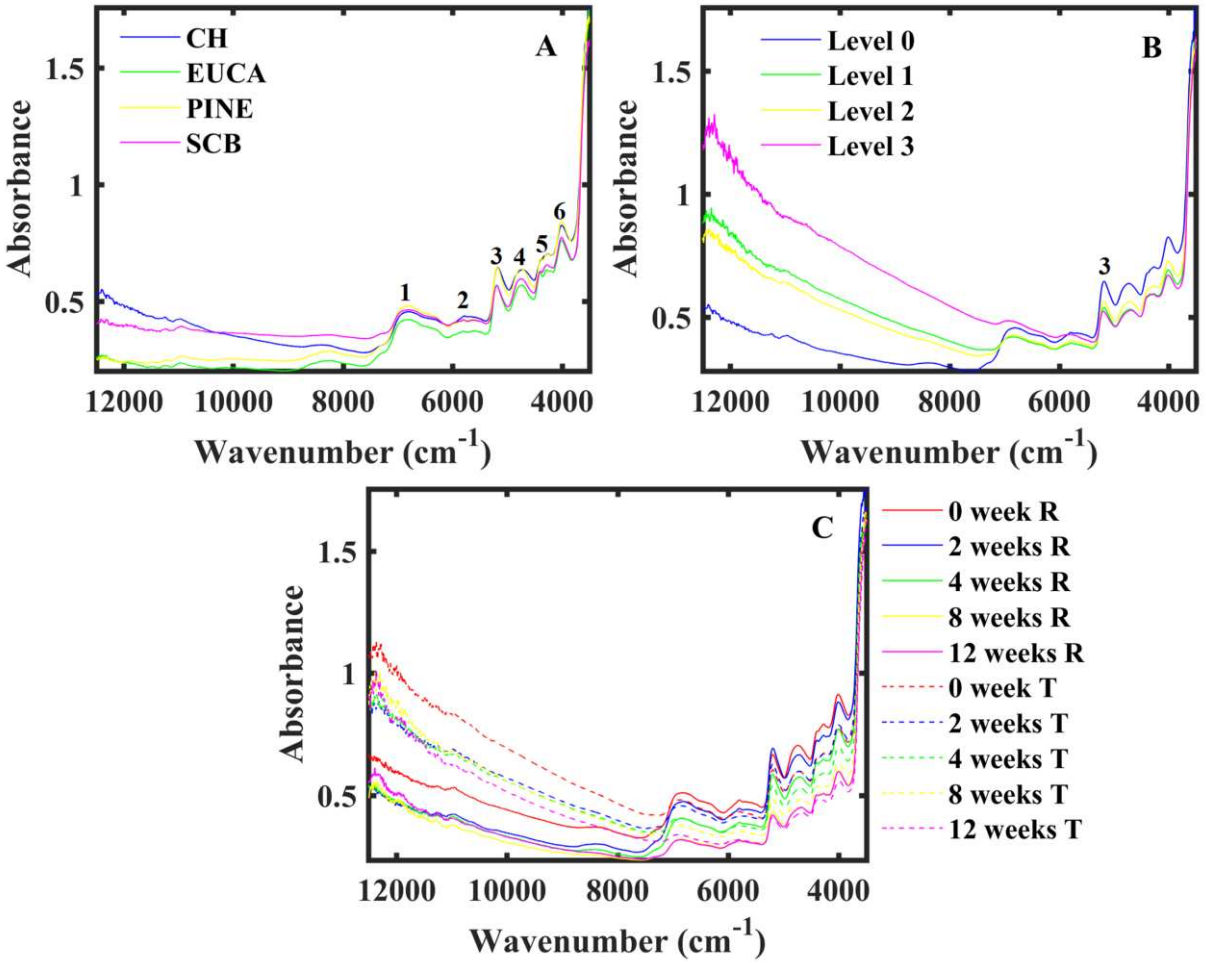

Fig. 2. NIR spectras. (A) different residual biomasses; (B) NIR spectra from the mean of the spectral values of the different torrefaction levels; (C) temporal fungal decomposition process over weeks in raw (R) and torrefied (T) biomass; Number 1 to 6 referring to peaks on the NIR spectra.

3.1. Classification models

PLS-DA models were developed for qualitative analyzes. The efficiency of these models was evaluated based on the following parameters: sensitivity, specificity and error of calibration and prediction.

3.1.1. Classification model for the different types of biomasses

The results obtained for the PLS-DA model for the different types of biomasses (EUCA, PINE, CH, SCB) are shown in Table 4 and Fig. 3. These results highlighted that this model was able to efficiently predict all biomasses in their respective classes (specificity and sensitivity (Pred.) = 1). Such a model has several applications in the

forestry and energy sector, such as the use of NIR spectroscopy for the classification of biomass residues for utilization in co-firing systems (RONI et al., 2017). TOSCANO et al. (2015) described methodology to separate different biomasses in the respective classes into coniferous and hardwoods for energy use. In addition, the EN ISO 17225-1 (ISO, 2014) standard, which requires information about solid fuels based on their origin and source, can use the classification described in this work as a tool to identify which biomass is used to produce pellets and briquettes.

Table 4. Statistical parameters of PLS-DA models for different types of biomass

	Modeled class			
Type of biomass	**CH**	**EUCA**	**PINE**	**SCB**
nlv	10	10	10	10
Sensitivity (Cal)	1.000	1.000	1.000	1.000
Sensitivity (Pred)	1.000	1.000	1.000	1.000
Specificity (Cal)	1.000	1.000	1.000	1.000
Specificity (Pred)	1.000	1.000	1.000	1.000
Class. Err (Cal)	0.000	0.000	0.000	0.000
Class. Err (Pred)	0.000	0.000	0.000	0.000

nlv: number of latent variables; Cal: calibration set; Pred: prediction set.

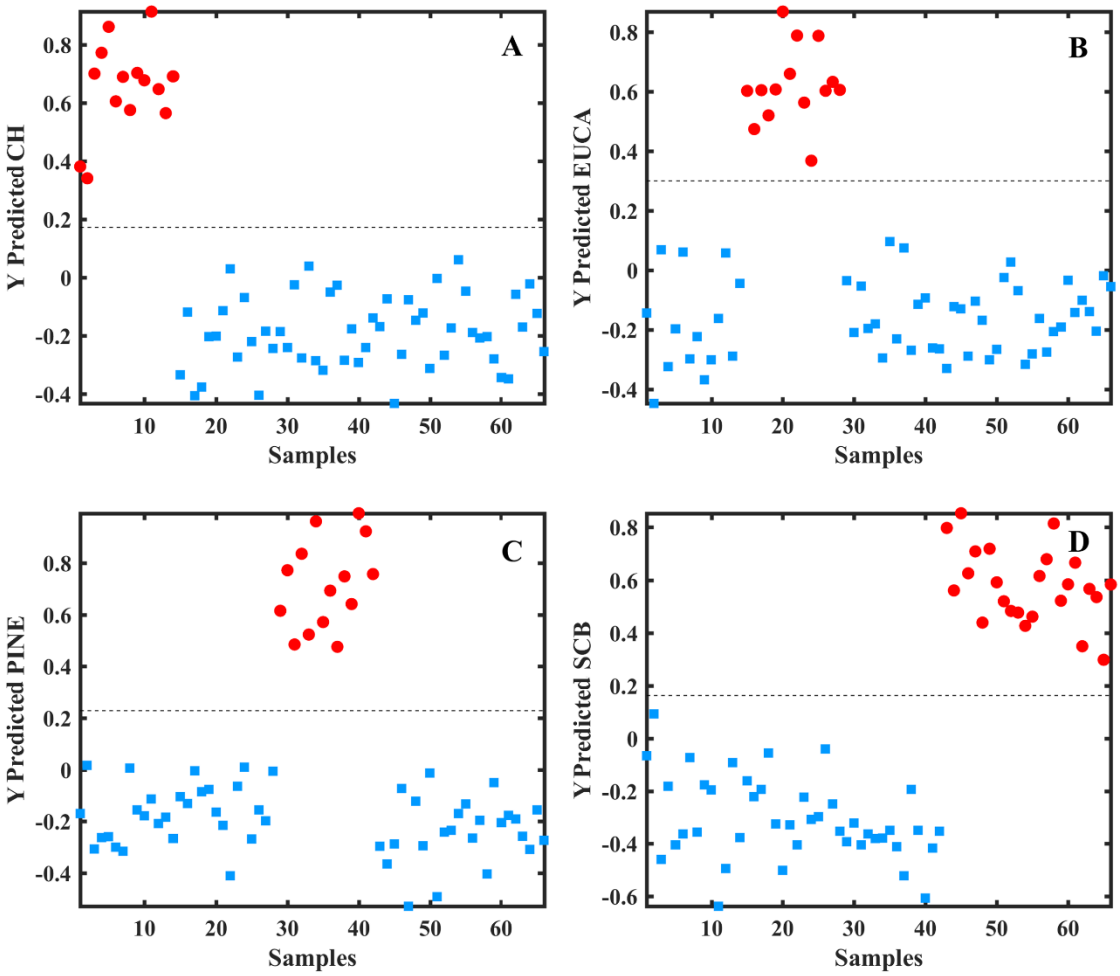

Fig. 3. Predictions of the PLS-DA model using prediction set for CH (A), EUCA (B), PINE (C) and SCB (D). (●) It corresponds to class of each type of biomass. (■) Samples of the other classes in each chart. The dashed line represents the threshold.

3.1.2. Classification model for each torrefied and raw biomass in relation to the type of fungus

The results of the PLS-DA model for each torrefied and raw biomass analysis in relation to the type of fungus are shown in Table 5 and Fig. 4. The classification was correct for the EUCA and CH models (specificity and sensitivity (Pred.) = 1). Concerning PINE and SCB models, a correct classification was observed for all variables related to raw biomasses, for both F1 and for F2. However, the classification was not correct, with prediction errors of 0.125 and 0.111 for torrefied PINE and SCB, respectively, and that considering the two types of fungi. This difficulty in separating fungi F1 and F2 in torrefied biomass can be attributed to less chemical changes in the material during the period of biological deterioration due to the resistance to the

xylophagous fungi decay generated by the torrefaction (DE CASTRO et al., 2019). Differentiation between fungi that act on biomass residues can be an important tool to understand possible changes in materials that are normally in large volumes during storage. The literature reports that white-rot fungi (F2) destroy all structural chemical constituents of biomass, including lignin. Brown-rot (F1) predominantly degrades carbohydrates (HERMOSILLA et al., 2018). Therefore, the way that each fungus acts can also cause changes in the estimated values of the energy potential of biomass, since the calorific value is highly correlated with chemical properties, mainly in the levels of carbon and hydrogen.

Table 5. Statistical parameters of PLS-DA models for raw and torrefied biomasses subjected to white and brown-rot fungus

	Modeled class				**Modeled class**			
	EUCA				**PINE**			
Fungal deterioration	BT - F1	AT - F1	BT - F2	AT - F2	BT - F1	AT - F1	BT - F2	AT - F2
nlv	9	9	9	9	7	7	7	7
Sensitivity (Cal)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Sensitivity (Pred)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.500
Specificity (Cal)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Specificity (Pred)	1.000	1.000	1.000	1.000	1.000	0.833	1.000	1.000
Class. Err (Cal)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Class. Err (Pred)	0.000	0.000	0.000	0.000	0.000	0.125	0.000	0.125

	Modeled class				**Modeled class**			
	CH				**SCB**			
Fungal deterioration	BT - F1	AT - F1	BT - F2	AT - F2	BT - F1	AT - F1	BT - F2	AT - F2
nvl	3	3	3	3	9	9	9	9
Sensitivity (Cal)	1.000	1.000	1.000	1.000	1.000	0.966	1.000	0.966
Sensitivity (Pred)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.714
Specificity (Cal)	1.000	1.000	1.000	1.000	1.000	0.980	1.000	0.980
Specificity (Pred)	1.000	1.000	1.000	1.000	1.000	0.818	1.000	1.000
Class. Err (Cal)	0.000	0.000	0.000	0.000	0.000	0.026	0.000	0.026
Class. Err (Pred)	0.000	0.000	0.000	0.000	0.000	0.111	0.000	0.111

nlv: number of latent variables; Cal: calibration set; Pred: prediction set; F1: brown-rot (*Coniophora puteana*); F2: white-rot (*Trametes versicolor*); BT: before torrefaction; AT: after torrefaction.

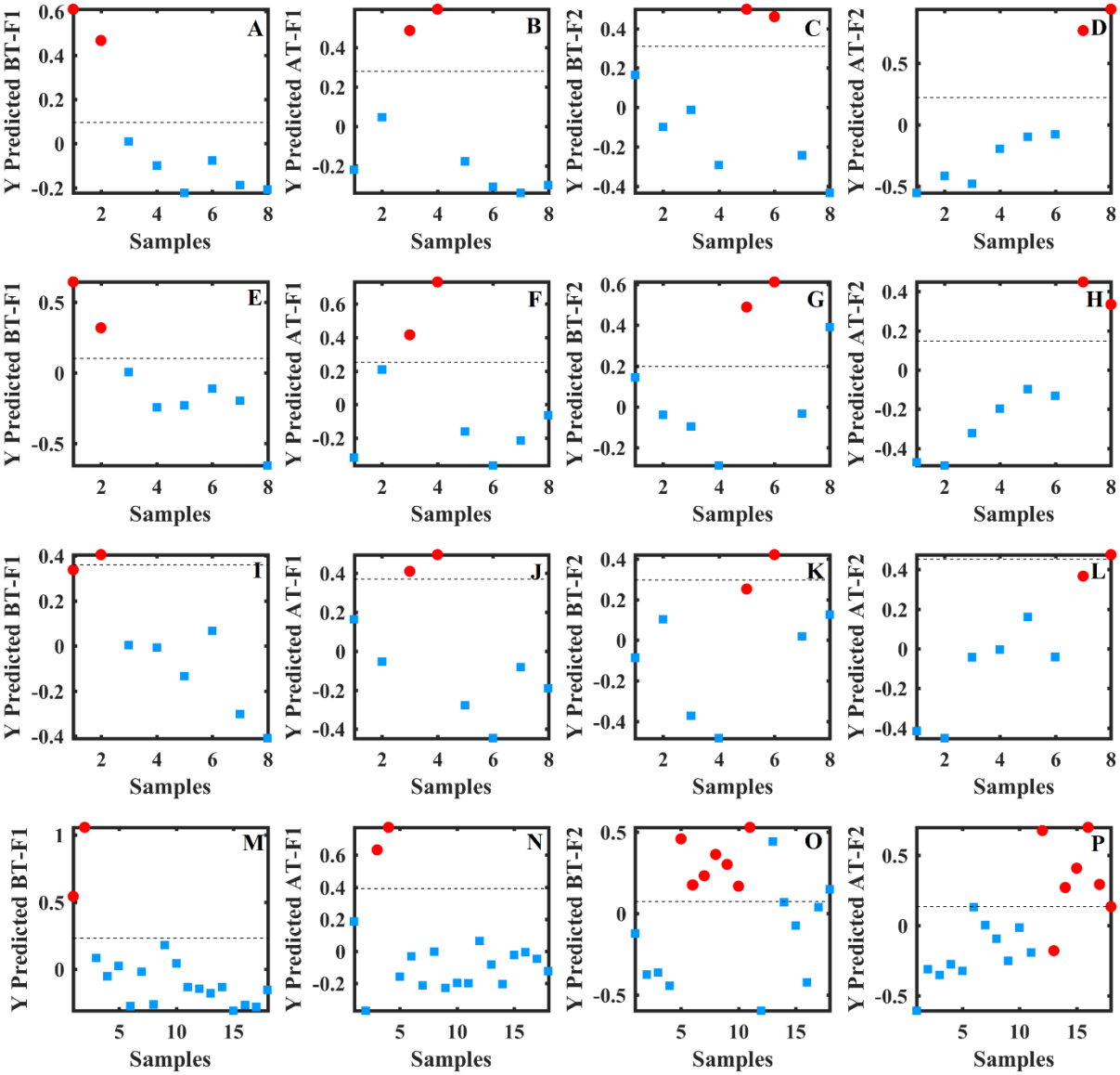

Fig. 4. Predictions of the PLS-DA model for EUCA (A – D), PINE (E – H), CH (I – F) and SCB (M – P); BT: before torrefaction; AT: after torrefaction; F1: brown-rot (*Coniophora puteana*); F2: white-rot (*Trametes versicolor*); (●) It corresponds to class of each type of biomass; (■) Samples of the other classes in each chart. The dashed line represents the threshold.

3.1.3. Classification model to predict fungal exposure duration

The PLS-DA classification model was also used to predict how long the material was undergoing fungal decomposition. The results are shown in Table 6 and Fig. 5 and indicate that PLS-DA is an adequate method in the prediction of the fungal deterioration duration of raw and torrefied biomass residues from EUCA, PINE, SCB and CH and also as a global model including all modalities. To be noted that there is no distinction between white-rot and brown-rot in this classification.

The model developed with all biomasses (Biomass-ALL) showed correct calibration and classification for 2, 4 and 8 weeks of decay exposure, with sensitivity (Pred. and Cal.) = 1 and specificity (Pred. and Cal.) = 1. However, the efficiency of this model was reduced for 0 and 12 weeks of fungal decay, with a prediction error of 0.018 and with specificity (Pred) and sensitivity (Pred) close to 1, as shown in Table 6 and Fig. 5.

The model based on raw biomassses (Biomass-R) showed correct classification for all decay exposure duration. When the torrefied biomass model (Biomass-T) is interpreted in 0 weeks, which corresponds to biomass without fungus inoculation, it can be observed that the model was the worst among all. This error in model predicting for biomasses between 0 and 2 weeks of biological deterioration can be attributed to the improvement in the resistance to fungi performance due to torrefaction process, which slows the deterioration level (DE CASTRO et al., 2019; FARIA et al., 2020), decreasing the difference in chemical modifications and making PLS-DA separation difficult. For 4 and 8 weeks, the classification was correct (Pred. = 1), it resulted of greater chemical modifications due to increased exposure time, which allows colonization and greater performance of enzymes related to the fungal decay process. In 12 weeks of deterioration the PLS-DA classification was adequate with specificity (Pred) close to 1.

Table 6. Statistical parameters of PLS-DA models of fungal deterioration

	Biomass-ALL					**Biomass-R**					**Biomass-T**				
	Modeled class					**Modeled class**					**Modeled class**				
Week	**0**	**2**	**4**	**8**	**12**	**0**	**2**	**4**	**8**	**12**	**0**	**2**	**4**	**8**	**12**
nlv	6	6	6	6	6	9	9	9	9	9	5	5	5	5	5
Sensitivity (Cal)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Sensitivity (Pred)	0.833	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.500	1.000	1.000	1.000	1.000
Specificity (Cal)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Specificity (Pred)	1.000	1.000	1.000	1.000	0.976	1.000	1.000	1.000	1.000	1.000	1.000	0.960	1.000	1.000	0.960
Class. Err (Cal)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Class. Err (Pred)	0.018	0.000	0.000	0.000	0.018	0.000	0.000	0.000	0.000	0.000	0.062	0.031	0.000	0.000	0.031

Biomass-ALL: prediction model of raw and torrefied biomasses in the same data set; Biomass-R: prediction model of raw biomasses; Biomass-T: prediction model of torrefied biomasses; nlv: number of latent variables; Cal: calibration set; Pred: prediction set.

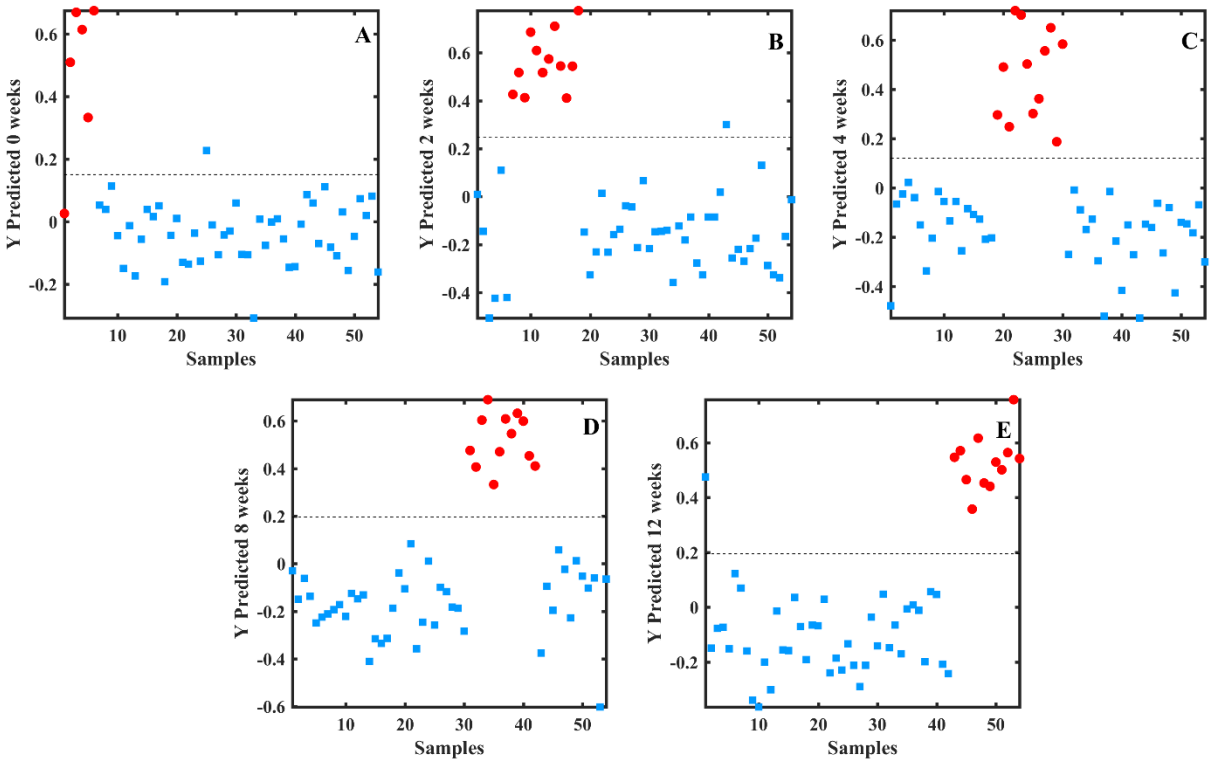

Fig 5. PLS-DA prediction model for the set of all biomasses (Biomass-ALL) over the time of fungal deterioration. 0 weeks (A), 2 weeks (B), 4 weeks (C) 8 weeks (D) and 12 weeks (E). (●) It corresponds to class of each temporal fungal decay in weeks. (■) Samples of the other classes in each graph. The dashed line represents the threshold.

This was the first study in which NIR and PLS-DA spectroscopy were used to classify four different residual biomasses in raw and torrefied forms according to fungal decomposition by white-rot and brown-rot fungus. These results highlight the potential of NIR spectroscopy as a simple, fast and efficient tool to analyze the decomposition process over the time.

3.2. Quantification models

3.2.1. Descriptive statistics of dataset

The dataset obtained in torrefaction, leaching and fungal deterioration experiments used to develop PLS models predicting HHV and ML are statistically described in Table 7. The complete description of the data (All) and the compartmentalized between the raw and torrefied biomasses data are presented separately.

Table 7. Statistical high heating value (HHV) and mass loss (ML) data of biomass residues used in model development

All biomasses					
Parameter	N	Mean	Max	Min	SD
HHV (MJ kg^{-1})	90	18.896	21.260	17.249	0.984
ML (db%)	90	15.359	53.744	0.000	15.500
Raw biomasses					
Parameter	N	Mean	Max	Min	SD
HHV (MJ kg^{-1})	36	18.192	20.385	17.249	0.787
ML (db%)	36	23.807	53.744	1.890	16.690
Torrefied biomasses					
Parameter	N	Mean	Max	Min	SD
HHV (MJ kg^{-1})	54	19.365	21.260	18.072	0.807
ML (db%)	54	9.689	42.106	0.000	11.660

N: number of samples; Min: minimum; Max: maximum; SD: standard deviation; ALL: set of raw plus torrefied biomasses; Raw: set of the raw (untreated) biomasses; Torrefied: set of the torrefied (heat-treated) biomasses.

3.2.2. High heating value

The results and statistical parameters of the PLS models for high heating value of raw (HHV-R), torrefied (HHV-T) and for all biomasses (HHV-ALL) are detailed in Table 8. The calibration models HHV-ALL and HHV-T using all data (FULL) showed excellent results for RMSEC and Rc, and also excellent results for the external prediction ($0.9817 < Rp < 0.9935$). However, for the HHV-R model, although it was satisfactory (Rp = 0.9351), it was the one that showed the higher prediction error (RMSEP = 0.2953) and the lowest Rp value, as shown in Table 8. In addition, the relative prediction error (%RE) was around 5%, as shown in Fig. 6. Then, the variable selection method - OPS was used to improve the predictive ability of the models, getting Rp = 0.9811 and reducing the RMSEP to 0.1719. Furthermore, as shown in Fig. 6, there is a reduction in the relative error to 3%. OPS was also applied to the other two models, for HHV-ALL there was no significant improvements and for HHV-T there was a slight worsening in Rp and also an increase in RMSEC. In general, the relative error values were below 3% for all models and the correlation coefficients were greater than 98%, indicating the quality of the models. The results of the calibration and prediction sets in Fig. 6 showed a straight line of 45 °, indicating excellent agreement between the values.

Recent studies have used NIR spectroscopy and PLS to predict the calorific power of different biomasses for energy use. SIRISOMBOON et al. (2020) and GILLESPIE et al. (2015) report the use of these tools in bamboo chips (Rp = 0.84; RMSEP = 0.15 MJ kg^{-1}) and pellets of biomass blend (Rp = 0.73; RMSEP = 0.912 MJ kg^{-1}), respectively, to predict the calorific value and suggest different applications for the models.

Torrefaction such as a thermal degradation process, as well as the fungal deterioration can change, in general, the chemical structure of the biomass (BARI et al., 2018; DE CASTRO et al., 2019). Some of these modifications can directly influence the calorific power of lignocellulosic feedstocks, since high levels of lignin increase the energy content (DEMIRBAS, 2001). Moreover, the moisture content in biomasses negatively affects energy properties (THIFFAULT et al., 2019). These changes can be captured by NIR spectroscopy, enabling efficient modeling with the use of chemometric methods.

Table 8. Parameters and statistical results of the evaluation of the high heating value model for the calibration, cross-validation and external prediction sets

Property	**HHV-All**		**HHV-R**		**HHV-T**	
Model	**Full**	**OPS**	**Full**	**OPS**	**Full**	**OPS**
nVars	2335	260	2335	540	2335	736
hmod	7	7	9	9	6	6
RMSEC	0.1522	0.1611	0.0718	0.1212	0.0895	0.0930
Rc	0.9870	0.9860	0.9957	0.9877	0.9935	0.9930
RMSECV	0.2061	0.1879	0.2244	0.1952	0.1500	0.1343
Rcv	0.9770	0.9809	0.9574	0.9685	0.9820	0.9854
RMSEP	0.1968	0.1761	0.2953	0.1719	0.2026	0.1566
Rp	0.9817	0.9853	0.9351	0.9811	0.9935	0.9821

nVars: number of variables; hMod: number of latent variables used to build the model; RMSEC: root mean square error of calibration; RMSECV: root mean square error of cross-validation; RMSEP: root mean square error of prediction; Rc: correlation coefficient of calibration; Rcv: correlation coefficient of cross-validation; Rp: correlation coefficient of prediction; Full: it corresponds to the complete model using all variables; HHV-ALL: high heating value of all raw and torrefied biomasses together; HHV-R: high heating value of raw biomasses; HHV-T: high heating value of torrefied biomasses.

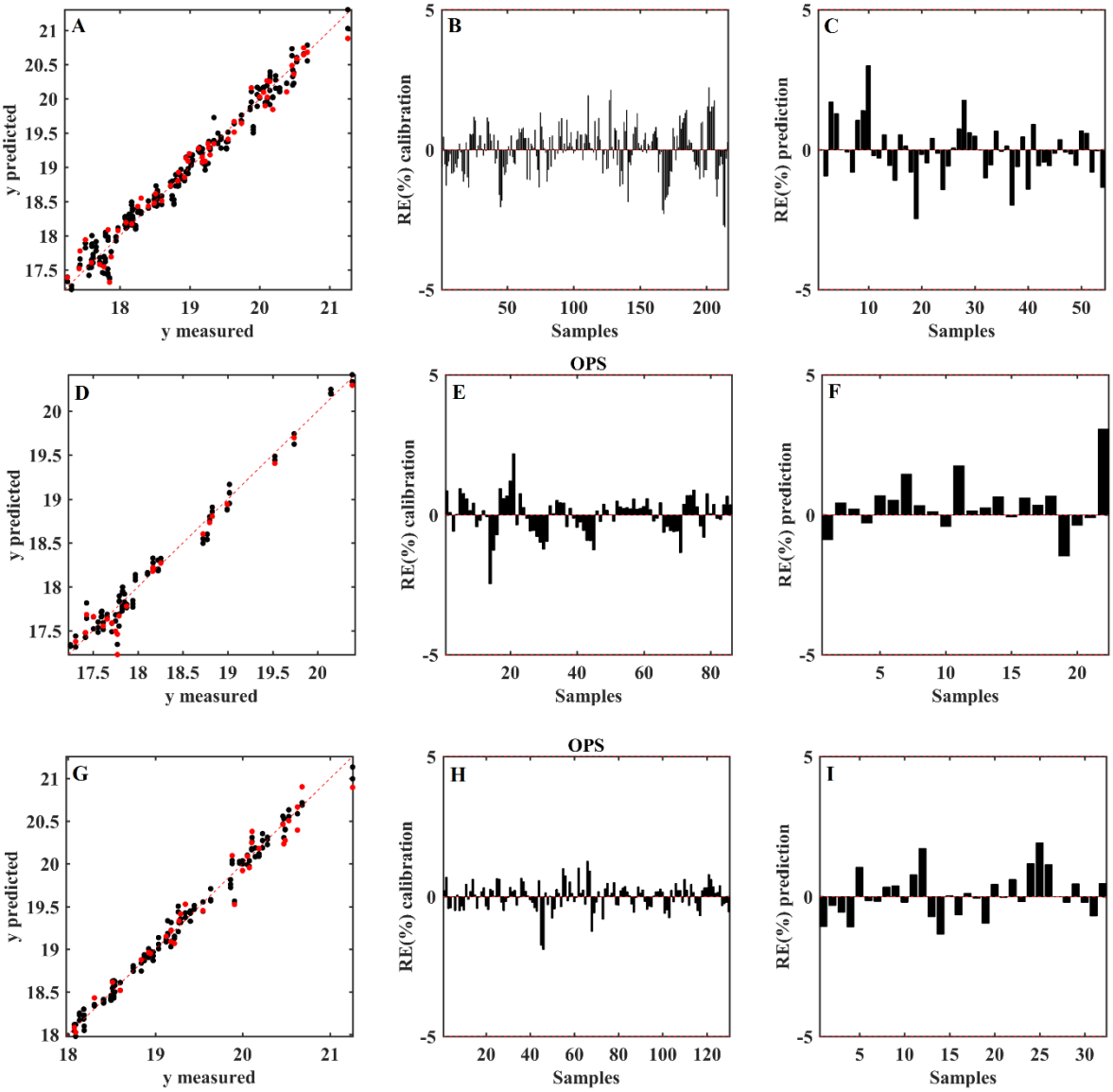

Fig. 6. Results of the PLS-OPS model HHV of all biomasses (A – C), raw biomasses (D – F) and torrefied biomasses (G – I). RE(%): relative error; (●) Calibration set; (●) Prediction set.

3.2.3. Mass loss

The results and statistical parameters of the PLS models for mass loss of raw (ML-R), torrefied (ML-T) and for all (ML-ALL) biomasses are shown in Table 9. In general, the calibration models constructed using all data (FULL) showed high prediction errors with RMSEP between 4.3789 to 8.3102 and 0.8857 < Rp < 0.974. Therefore, the variable selection method - OPS was done to improve the predictive capacity of the models. The results showed a significant reduction in the RMSEP with values between 2.9973 to 5.4542 and an improvement in the Rp. However, the PLS-OPS models still did not present a good predictive ability to assess the mass loss during

the temporal fungal deterioration. To confirm the low accuracy of the model, it is possible to observe, in Fig. 7, the high values of relative prediction error (%RE) equal to approximately 90, 60 and 70% for the PLS-OPS models of raw, torrefied and all biomasses, respectively. In addition, the results of the measured versus predicted ML values (Fig. 7) and of the calibration and prediction sets have a dispersion around the 45 ° straight line, indicating low agreement between the values. Therefore, NIR spectroscopy and PLS regression did not demonstrate a good capacity to predict the mass loss of biomass residues in relation to biological exposure duration in raw and torrefied forms, and further studies are needed to try to improve this parameter.

The quantitative modeling of mass loss values during the fungal deterioration experiment is possibly impaired due to the high dispersion of data around the mean (higher standard deviation), as shown in Table 7. The high or even low variability of the data can impair the efficiency of the prediction model (GREEN et al., 2012). This happens, firstly, because four different species of residual biomasses were studied. In addition, the effect of fungi, brown-rot and white-rot, was evaluated together, thus increasing the variability of the data. In this sense, it is possible to observe in Table 9 that the sets of raw and torrefied biomasses showed better results for RMSEP and Rp compared to the model of all biomasses together (ALL biomasses)

Similar results for mass loss predictions were found by GREEN et al. (2012), studying *Trametes versicolor* (white-rot) inoculation in samples of *Populus deltoides* (cottonwood) during eight consecutive days, as a short exposure time, and obtained Rp values equal to 0.65 and 0.57 for the NIR spectrum treated with first and second derivatives, respectively. LI, YANJIE et al. (2020) used white-rot and brown-rot for fungal decay tests on *Eucalyptus bosistoana* heartwood samples from two different sites of New Zealand. The PLS calibration models were built separately for each fungus to determine how precisely mass loss by fungi can be predicted from NIR spectra. For white-rot, the authors found Rp values around 0.72 and 8.5% for RMSEP. For brown-rot, Rp value of approximately 0.66 and 7.5% for RMSEP were found. The authors concluded that the modeling for mass loss prediction during the deterioration was efficient. In addition, it indicates the NIR spectroscopy as a tool to predict the quality of wood products like natural durability and control of wood products.

Table 9. Parameters and statistical results of the evaluation of the mass loss model for the calibration, cross-validation and external prediction sets

Property	**ML-All**		**ML-R**		**ML-T**	
Model	**Full**	**OPS**	**Full**	**OPS**	**Full**	**OPS**
nVars	2335	572	2335	548	2335	368
hmod	10	10	10	10	10	10
RMSEC	7.1956	5.3398	5.6482	4.6853	3.5430	2.6657
Rc	0.9015	0.9426	0.9411	0.9590	0.9509	0.9722
RMSECV	8.4795	5.9159	7.7461	5.6250	4.6680	3.5643
Rcv	0.8711	0.9302	0.8931	0.9400	0.9145	0.9498
RMSEP	8.3102	5.4542	4.8669	3.9128	4.3789	2.9973
Rp	0.8857	0.9428	0.974	0.9786	0.9482	0.9752

nVars: number of variables; hMod: number of latent variables used to build the model; RMSEC: root mean square error of calibration; RMSECV: root mean square error of cross-validation; RMSEP: root mean square error of prediction; Rc: correlation coefficient of calibration; Rcv: correlation coefficient of cross-validation; Rp: correlation coefficient of prediction; Full: it corresponds to the complete model using all variables; ML-ALL: mass loss of all raw and torrefied biomasses together; ML-R: mass loss of raw biomasses; ML-T: mass loss of torrefied biomasses.

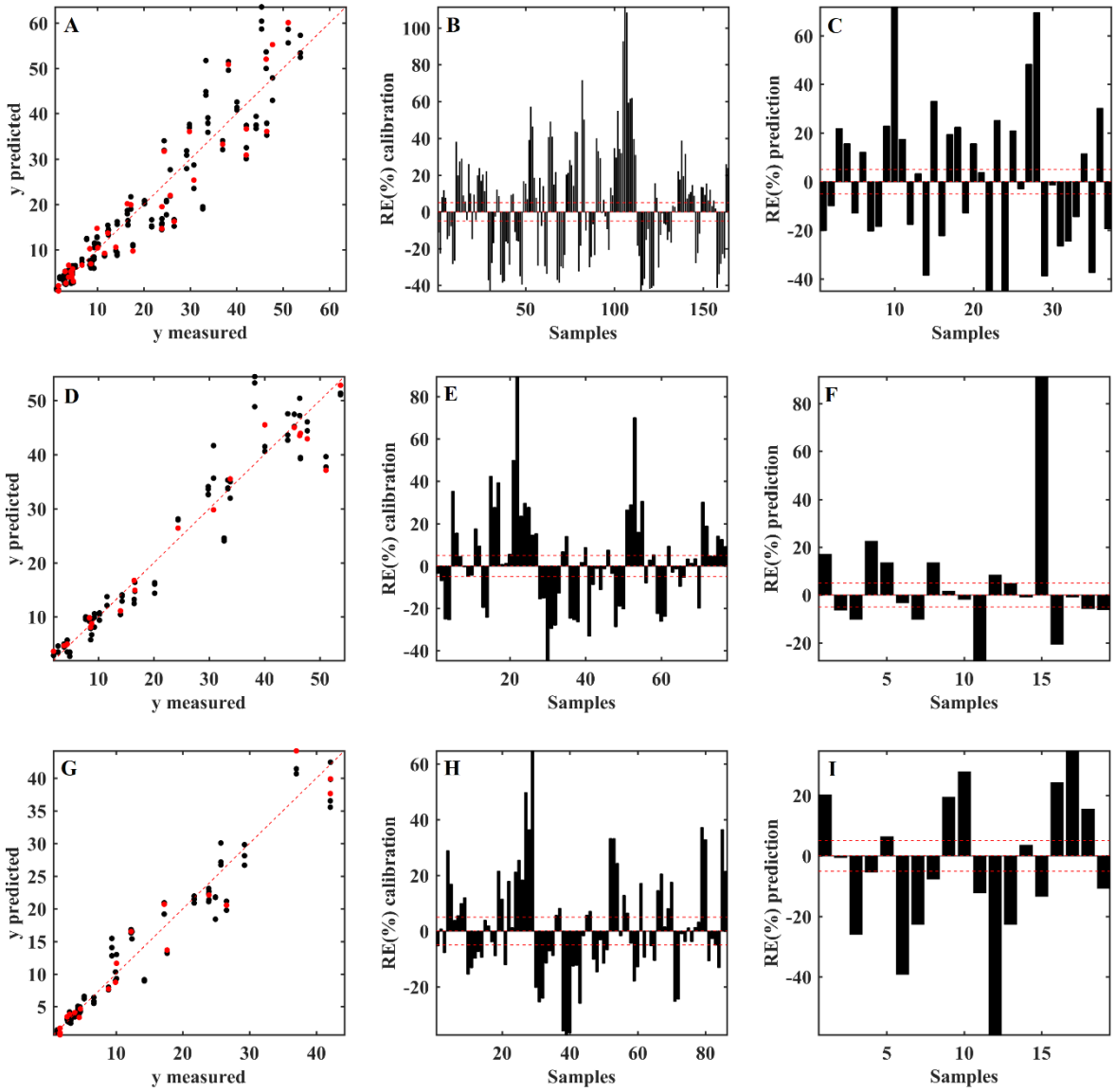

Fig. 7. Results of the PLS-OPS model ML of all biomasses (A – C), raw biomasses (D – F) and torrefied biomasses (G – I). RE(%): relative error; (●) Calibration set; (●) Prediction set.

The increasing of use of lignocellulosic biomass for energy generation requires large storage of these materials. Then, fungal colonization becomes a problem that leads to mass loss through biological deterioration. It is well established by the literature that torrefaction, as a thermal pre-treatment, makes biomass more resistant to fungi attack (DE CASTRO et al., 2019). Due to the long storage time, coupled with the mass loss process, it is feasible to determine, quickly and efficiently, the loss of material over the degradation time, according to the stored lignocellulosic residue, from the pre-heat treatment or even the type of fungus acting (brown or white-rot) on the materials.

4. CONCLUSION

This present study is one of the first to develop NIR and PLS-DA models in order to classify four different residual biomasses in raw and torrefied forms according to their white-rot and brown-rot fungal decomposition stages. The combined use of PLS-DA classification models was reliable to differentiate types of biomass and then, through specific models, identify the most active decay fungus in raw and torrefied biomasses and in which temporal stage of deterioration the biomasses are. These results highlight the potential of NIR spectroscopy as a simple, fast, and efficient tool to analyze the decomposition process over the time.

In an other hand, PLS and PLS-OPS developed models appeared to be efficient in the prediction of the high heating value of raw and torrefied biomasses according to their fungal deterioration stages. Even if the modeling did not allow predicting the fungal mass loss of biomass samples in an efficient way, this technique appeared to be a very great tool to estimate the calorific value of raw and torrefied biomasses according to their storage conditions, for an industrial energy purposes.

However, further studies need to be carried out in order to improve and develop more efficient models to predict the fungal deterioration level of stored biomasses. Considering the class of torrefied biomasses, due to less variability in the data, the model could show a better predictive capacity. The use of NIR spectroscopy combined with chemometric tools was a feasible approach to assess the effect of biological deterioration over time on lignocellulosic biomass.

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4. CONCLUSÕES GERAIS

A torrefação melhora as propriedades energéticas dos resíduos de biomassa influenciando positivamente para a estocagem, geração de energia e uso mais eficiente destes montantes de resíduos gerados em todo território nacional;

O tratamento térmico aumenta a resistência à deterioração de todas as biomassas residuais, para os dois fungos testados (*brown rot* ou *white rot*), devido à menor perda de massa durante a simulação de estocagem. Este é um ponto importante para se estender o tempo de estocagem dos resíduos que se acumulam em grande quantidade nos pontos de produção ou mesmo após o transporte até o local de uso;

O bagaço de cana mostrou-se altamente resistente à deterioração fúngica mesmo com baixas intensidades de torrefação, destacando-se o tempo de 7,5 e 10 minutos como eficientes do ponto de vista energético e de inibição da deterioração, mostrando grande potencial para uso do pré-tratamento nestes resíduos;

Vale salientar que a casca de café se mostrou uma biomassa promissora para uso energético. Entretanto, faz-se necessário novos experimentos, em diferentes intensidades de torrefação para se conhecer os reflexos que podem ser gerados na biomassa durante a estocagem;

O uso da espectroscopia NIR acoplada às técnicas quimiométricas se mostrou uma ferramenta simples, rápida e viável para avaliar o processo de deterioração fúngica das biomassas *in natura* e torrificadas ao longo do tempo. A construção de modelos PLS e PLS-OPS se mostrou eficiente para predição do poder calorífico. Por outro lado, a modelagem não foi eficiente para a predição da perda de massa durante a biodeterioração fúngica. E destaca-se a necessidade de mais experimentos para se possibilitar consenso científico de uso das modelagens tornando mais tecnológico e eficiente o uso de resíduos para geração de energia.