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Reducción de las emisiones de gases contaminantes en el proceso de carbonización de madera proveniente de 5 especies de reforestación de Costa Rica

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ÍNDICE GENERAL

Reducción de las emisiones de gases contaminantes en el proceso de carbonización de madera proveniente de 5 especies de reforestación de Costa Rica

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2. RESUMEN.

Costa Rica produce una cantidad considerable e importante de residuos de madera. Estos residuos pueden ser pirolizados para producir carbón como producto principal, el cual puede ser utilizado como fuente de energía o para el tratamiento de suelos para diferentes cultivos. Sin embargo, existe una falta de información sobre los materiales obtenidos a diferentes temperaturas de pirólisis. Por lo tanto, este estudio determinó el rendimiento de diferentes productos de pirólisis y el desempeño de un pequeño reactor piloto para pirólisis lenta con cinco temperaturas (300, 350, 400, 450 y 500 °C) y para evaluar la calidad del carbón (física, mecánica, análisis final y análisis FTIR), las características del carbón como fuente energética (propiedades energéticas y análisis termogravimétrico—TGA) y sus características como biocarbón (conductividad, pH, ángulo de contacto inicial y tasas de humectación) producido de 5 residuos de madera. En relación con el rendimiento de los diferentes productos de pirólisis y el rendimiento del pequeño reactor piloto, los resultados mostraron que las temperaturas de 300-350 °C no son recomendables, porque la madera madre no se pirolizó completamente. Los rendimientos de carbón se mantuvieron estables entre 400-500 °C. La temperatura de 500 °C maximizó los gases condensables (vinagre de madera y bio-oil) y no condensables, pero presentó el rendimiento de carbón más bajo y este carbón era quebradizo. *Gmelina arborea* y *Dipteryx panamensis* tuvieron un rendimiento diferente al de *Hieronyma alchorneoides* y *Tectona grandis*. *G. arborea* produjo un mayor porcentaje de gases no condensables, pero la separación de vinagre de madera y bio-diesel fue difícil de llevar a cabo. *D. panamensis* produjo un bajo rendimiento de carbón, pero hubo una ventaja, se produjo el mayor porcentaje de gases condensables. *T. grandis* y *H. alchorneoides* produjeron porcentajes similares de diferentes productos y temperaturas en el reactor. La madera de *D. panamensis* fue lenta para iniciar el proceso de pirólisis, y durante este proceso tuvo una temperatura más alta que las otras especies, pero como *T. grandis* y *H. alchorneoides*. Mientras que la madera madre de *G. arborea*, el inicio de la pirólisis fue como la de las otras especies, pero tuvo un tiempo de pirólisis más largo en las diferentes temperaturas. En cuanto a la calidad del carbón, se encontró que la temperatura de pirólisis entre 450 °C y 500 °C produjo carbones con valores más bajos de densidad, contenido de humedad, resistencia a la compresión, volátiles, contenido de H y O, y valores más altos de contenido de C y cenizas, conductividad, pH, ángulo de contacto inicial y tasas de humectación. Los análisis FTIR y TGA muestran que las celulosas y la lignina se pirolizan completamente a estas temperaturas, por lo que se recomiendan estas temperaturas. El rango de temperaturas de 300–350 °C no se recomienda, ya que estos parámetros fueron inversos.

Reduction of polluting gas emissions in the carbonization process of wood from 5 reforestation species in Costa Rica

Abstract

Costa Rica produces a considerable important quantity of wood residues. This waste can be pyrolyzed to produce charcoals as main products that can be effectively used as an energy source or to immobilize carbon for soil treatment. However, there is a lack of information about the pyrogenic carbonaceous materials (PCMs), such as charcoal or biochar, obtained at different pyrolysis temperatures. Hence, this study determined the yield of different pyrolysis products and the performance of small pilot reactor for slow pyrolysis with five temperatures (300, 350, 400, 450 and 500 °C) and to evaluate the quality of PCMs (physical, mechanical, ultimate analysis, and FTIR analysis) and charcoal characteristics (energetic properties and thermogravimetric analysis—TGA) and biochar characteristics (conductivity, pH, initial contact angle, and wetting rates) for four tropical wood residues produced. In relation to the yield of different pyrolysis products and the performance of small pilot reactor, the results showed that temperatures of 300-350 °C are not recommended, because parentwood was not pyrolyzed completely. Charcoal yields were stable between 400-500 °C. Temperature 500 °C were maximized condensable (wood vinegar and bio-oil) and non-condensable gases, but there were the lowest charcoal yield and this charcoal was brittle. *Gmelina arborea* and *Dipteryx panamensis* had different performance than *Hieronyma alchorneoides* and *Tectona grandis*. *G. arborea* produced a higher percentage of non-condensable gases, but the separation of wood vinegar and bio-oil was difficult to carry out. *D. panamensis* produced a low charcoal yield, but there was an advantage, the greatest percentage of condensable gasses was produced. *T. grandis* and *H. alchorneoides* produced similar percentages of different products and temperatures into the reactor. *D. panamensis* parentwood was only slow to start the pyrolysis process, and during this process, it had a higher temperature than the other species, but like *T. grandis* and *H. alchorneoides*. While *G. arborea* parentwood, the beginning of pyrolysis was like the other species but had longest pyrolysis time at different temperatures. Into charcoal quality, it was found that the pyrolysis temperature between 450 °C and 500 °C produced charcoals with lower values of density, moisture content, compression strength, volatiles, H and O content, and higher values of C and ash contents, conductivity, pH, initial contact angle, and wetting rates. FTIR and TGA analyses show that celluloses and lignin are pyrolyzed at these temperatures, so these temperatures are recommended. The temperature range of 300–350 °C is not recommended, as these parameters were inverse.

3. PALABRAS CLAVE

biomasa, bioenergía, cambio climático, carbón vegetal, Costa Rica, energías renovables, pirólisis.

Key words: biomass, bioenergy, climate change, charcoal, Costa Rica, renewable energies, pyrolysis

4. INTRODUCCIÓN

Durante los últimos años el uso extensivo de combustibles fósiles ha causado importantes emisiones de gases de efecto invernadero y problemas ambientales (Wang et al. 2016). Sin embargo, recientemente se ha impulsado el estudio y la generación de nuevas alternativas para reemplazar los combustibles fósiles que satisfagan las demandas energéticas a nivel mundial (Wang et al. 2016). En este contexto, la biomasa para la producción de energía (bioenergía) cuenta con gran interés dada su accesibilidad, diversificación y abundancia (Lauri et al. 2019). La biomasa puede desarrollarse ampliamente con la explotación sostenible de nuevos recursos y con la mejora de tecnologías para su conversión (Tursi 2019). Así mismo el sector de producción agrícola, cada vez incorpora más tierras a la producción, con los consecuentes problemas de sostenibilidad de los suelos a largo plazo, ya que a estos deben incorporar de forma constante los macro y microelementos necesarios para que los suelos continúen su producción.

La biomasa, como se indicó, es una fuente para producir carbón, sin embargo cuenta con propiedades no deseables para ser usada en la combustión directa tales como altos contenidos de humedad, densidades bajas, alto contenido de sustancias volátiles poco aprovechables y naturaleza higroscópica, dando como resultado un poder calórico bajo en relación a otros combustibles (Singh et al. 2016). Y en la fertilización cuando se usa su forma natural el único beneficio es el de regulador de pH, y no es un aporte importante a la fertilización ya que la degradación es compleja y puede acarrear problemas a los suelos. Es por esto que se han desarrollado e implementado algunas tecnologías más eficientes para la conversión de la biomasa (Chen et al. 2015) a otro tipo de materia prima que puede ser utilizada como energía o bien que ayude a la fertilización de los suelos, en este caso es la pirolisis a baja temperatura, siendo el carbón el material sólido resultado de la carbonización.

A nivel mundial existen diferentes métodos para la carbonización de biomasa, y cada uno de ellos está orientado a diferentes tipos de materia prima. Entre los métodos más utilizados están los tradicionales como parva y tipo hueco (Adam, 2009), los métodos más tecnificados, como hornos de ladrillo, hornos metálicos y los sistemas mejorados o hornos de carbón (Cha et al., 2019). Sin embargo, el tradicional método de la carbonera (covered earth pit) sigue siendo el más utilizado en Costa Rica y en otros países en vías de desarrollo, ya que la inversión es menor y no requiere de gran conocimiento (Coomes y Milther, 2017). Este método consiste en aislar la leña del oxígeno cubriéndola con tierra y vegetación en una semi-excavación, para luego realizar la pirolisis o carbonizarla (Coomes y Milther, 2017). Durante el proceso, los gases calientes, producidos por la quema parcial de la carga de madera, secan lentamente la tierra y calientan el resto de la madera al punto de carbonización, de alrededor de 280°C (Robert, 2019). A pesar de la facilidad de este método de producción de carbón, se obtienen rendimientos bajos y el carbón puede ser de mala calidad, debido a que el material no se carboniza uniformemente y al extraerlo el carbón se mezcla con la tierra (Coomes y Milther, 2017).

Es un proceso de conversión termoquímica que funciona en condiciones inertes y en un rango de temperatura moderado (menor a 500°C), su objetivo es convertir la biomasa en carbón, este proceso puede denominarse carbonización de baja velocidad de calentamiento (Antal and Grønli 2003). El proceso de conversión de la biomasa leñosa en carbón incluye desvolatilización, despolimerización y la carbonización (Manyà 2012; Tripathi et al. 2016). Los productos de este proceso de carbonización son carbón, bio-petróleo y gases (Tripathi et al. 2016). Cuando se carboniza a temperaturas moderadas entre 400 y 500°C, una parte importante de la masa de biomasa seca se retiene como un producto sólido, el resto se convierte en gases y vapores (Qian et al. 2015).

En el Instituto Tecnológico de Costa Rica existe un trabajo previo a este, tanto en el diseño, construcción y uso de reactores de carbonización de bajo costo, como en el uso del carbón producido para el mejoramiento de suelos, principalmente en sus propiedades hidrológicas, así como en la caracterización de bio-carbones elaborados en el ITCR (Quesada Kimzey, 2012; Masís-Meléndez et al., 2020; Villagra-Mendoza et al., 2021). Ha habido una serie de proyectos apoyados por la VIE, en los que la temática ha sido la carbonización de biomasas en vistas a su aplicación energética o en suelos.

Diferentes estudios en la literatura han señalado que la biomasa convertida en carbón comparada con la biomasa cruda presenta muchas ventajas tales como, menores contenidos de volátiles y radios molares de O/C (oxigeno/carbono) y H/C (hidrogeno/carbono) bajos, lo que provoca una disminución de la emisión y pérdida de energía durante la combustión (Wang et al. 2016) o bien no puede ser incorporado al suelo. A su vez se reportan contenidos de carbono fijo más altos, así como valor de calentamiento (por unidad de masa) y mayor densidad de energía (cuando está comprimida) y excelente componente para la nutrición de plantas. También en el proceso de carbonización se pierden gran cantidad de impurezas de combustibles no deseados como nitrógeno, azufre, cloro y álcalis (Abdullah and Wu 2009; Abdullah et al. 2010).

Entre las fuentes de materia prima más utilizadas para la producción de carbón se encuentran los residuos forestales provenientes de las industrias primarias y secundarias de la madera (Solar et al. 2016). El aprovechamiento de residuos de procesos industriales disminuye el costo operativo y las emisiones de carbono, y a la vez es una solución para los problemas ambientales y de salud causados cuando no se descartan apropiadamente (Solar et al. 2016). En este contexto, en el carbón vegetal de especies maderables tropicales, se reportan valores de entre un 60% y 85% de carbón fijo (Vafaeenezhad et al. 2013), contenidos de volátiles del 32% al 12% (Nisgoski et al. 2014), contenidos de cenizas por debajo del 8% (Saiz et al. 2014), valores energéticos aproximados 26.46 MJ/kg (Anupam et al. 2016). Las ventajas del uso de carbón como fertilizante en el suelo han mostrado su eficacia en diferentes cultivos agrícolas (Medina & Alex, 2019). Por ejemplo, en diferentes dosis de biocarbón proveniente de la mazorca de maíz, cáscara de café y exoesqueleto de langostino sobre proceso de germinación y crecimiento de semillas de *Capparis scabrida* en etapa de vivero, mostró que reduce el tiempo de germinación y aumenta la masa foliar de las plantas (Herrera et al., 2018). Otro estudio realizado en Perú, evaluó el efecto del biocarbón a partir de residuos orgánicos y demostró que hubo efecto positivo en la germinación de Ceiba trichistandra (Medina & Alex, 2019). Existen abundantes estudios enfocados al efecto favorable del carbón sobre las propiedades hidrológicas de los suelos, entre ellos algunos con impotante participación del ITCR (Villagra-Mendoza & Horn, 2018a; Villagra-Mendoza & Horn, 2018b; Villagra-Mendoza & Horn, 2019; Masís-Meléndez *et al*., 2020; Villagra-Mendoza *et al.*, 2021).

Por otro lado, en Costa Rica se usan especies de reforestación de rápido crecimiento con períodos de rotación menores a los 25 años como *Acacia mangium, Alnus acuminata, Bombacopsis quinata, Cordia alliodora, Cupressus lusitanica, Dipteryx panamensis, Enterolobium cyclocarpum, Gmelina arborea* (especies exóticas), *Hieronyma alchorneoides, Samanea saman, Swietennia macrophylla* (especies nativas), *Tectona grandis, Terminalia amazonia, Terminalia oblonga, Vochysia ferruginea* y *Vochysia guatemalensis,* que han demostrado excelentes resultados como especies de reforestación en plantaciones forestales de Costa Rica (Roque 2004; Petit and Montagnini 2004). Los principales usos de la madera de estas especies en Costa Rica se dan en la industria primaria, en la construcción y en la manufactura secundaria (Serrano and Moya 2011). En estos procesos se estima que los rendimientos de la madera aserrada comercializable rondan el 25% del volumen en la plantación forestal, evidenciando poca eficiencia y la producción de un alto porcentaje de residuos (Espinoza-Durán and Moya 2013). Por lo que debería de ser de alta importancia la renovación de la industria mediante la valorización y utilización de los residuos generados en estos procesos, útiles para la producción de energía eléctrica y calórica, cogeneración, producción de carbón y leña para cocinar, producción de abono orgánico, entre otros (Serrano and Moya 2011).

Actualmente en Costa Rica, aunque se dispone de información sobre las características de la madera y su comportamiento en diferentes procesos industriales de las especies utilizadas en plantaciones forestales (Moya et al. 2019), se cuenta con pocos datos sobre las propiedades físico-químicas y energéticas del carbón producido con residuos provenientes de esta materia prima. Por otra parte, el diseño de reactores de carbonización que sean de construcción local, de bajo costo y con emisiones mínimas, son escasos o inexistentes. Es por esto que el presente proyecto de investigación tiene como objetivo determinar las condiciones experimentales óptimas para la carbonización de 5 especies de plantaciones forestales (G*melina arborea, Tectona grandis, Hieronyma alchorneoides, Cupressus lusitanica y Dipteryx panamensis*) y evaluar su comportamiento y rendimiento mediante la fabricación de un reactor industrial de 2 m^3, diseñado, construido y optimizado localmente en cuanto a costo, eficiencia y emisiones

5. ARTÍCULOS CIENTÍFICOS:

Artículo 1: Charcoal production from four tropical woods through slow pyrolysis under different temperatures: yield of different products and condition of pyrolysis into the reactor

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ORIGINAL ARTICLE

Charcoal production from four tropical woods through slow pyrolysis under different temperatures: yield of different products and condition of pyrolysis into the reactor

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Abstract

Costa Rica produces an extensive amount of forest residues, which can be pyrolyzed slowly to produce by-products like charcoal, wood vinegar, bio-oil, and non-condensable that can be effectively used in agricultural crops, providing a comprehensive approach to leveraging forest resources for finding renewable sources for agriculture production. However, there is a lack of information about the processes and products obtained with slow pyrolysis of forest residues in Costa Rica. Hence, this study aims to ascertain the yield of a diverse range of pyrolysis products and assess the performance of a small pilot reactor for slow pyrolysis of four tropical woods at five varying temperatures (300, 350, 400, 450, and 500 °C). The results showed that charcoal yields ranged from 28.2 to 56.6%, bio-oil from 2.8 to 8.1%, whereas yields of non-condensable varied from 14.0 to 33%, and wood vinegar yields ranged between 25.6 to 40.8%. Another significant finding indicated that due to incomplete pyrolysis of parentwood, the temperatures of 300–350 °C were deemed suboptimal and are thus not recommended. Charcoal yields were consistent between 400 and 500 °C. Condensable (wood vinegar and bio-oil) and non-condensable gases were at their maximum at 500 °C; however, the production of charcoal was the lowest, and the charcoal was brittle. The four tropical wood species exhibited divergent performances, as *Gmelina arborea* and *Dipteryx panamensis* performed differently than *Hieronyma alchornoides* and *Tectona grandis*. Though *G. arborea* produced a higher percentage of non-condensable gases, challenges were encountered in the separation of wood vinegar and bio-oil. While *D. panamensis* produced a low charcoal yield, it benefitted from the highest percentage of condensable gases. *T. grandis* and *H. alchornoides* produced similar percentages of different products and temperatures within the reactor. *D. panamensis* parentwood exhibited a slower initiation of the pyrolysis process, maintaining higher temperatures than the other species during this process, just like *T. grandis* and *H. alchornoides*. *G. arborea* parentwood showcased a beginning of pyrolysis similar to the other species but exhibited the longest pyrolysis time at varying temperatures.

Keywords Carbonization · Tropical wood · Pyrolysis liquids · Biochar · Pesticide · Biocide

1 Introduction

Pyrolysis entails a thermochemical technique employed on biomass, under which the biomass is subjected to a decomposition of the organic matrix in non-oxidizing atmospheres. This transformative process yields solid biochar with two types of liquid, which can be separated into bio-oil (biodiesel) or wood vinegar and non-condensable gases [1]. The diverse uses of these products include fuel (more traditional use), bio-oil, soil management, activated carbon, chemical products, and many other applications [2].

The pyrolysis process transpires in a closed chamber (reactor) in the absence of oxygen, wherein the heat injected into the system replaces the absent oxygen in

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diverse reactions occurring within the chamber [3]. The biomass decomposition process unfolds through different mechanisms encompassing dehydration, depolymerization, isomerization, aromatization, decarboxylation, and charring of cellulose, lignin, and hemicellulose [4]. Each of these undergoes decomposition at different temperatures and stages: hemicellulose decomposition mainly occurs between 250 and 350 °C, followed by cellulose decomposition, which primarily occurs in the temperature range of 325 and 400 °C and lignin is the most resilient component undergoing decomposition at a higher temperature range of 300–550 °C [5, 6].

Cellulose, characterized by relatively weak glycosidic bonds linking the glucose units, undergoes breakdown at high temperatures, and the products of cellulose pyrolysis include acids, alcohols, anhydrous sugars, charcoal, and gases. Additionally, furans and laevoglucose can also be formed by alternative mechanisms in the cleavage of $\beta-1$, 4-glycosidic bonds [7]. On the other hand, hemicellulose undergoes decomposition at low temperatures, leading to high CO_2 and charcoal production [6]. Lignin is a more intricate polymer [8], and according to Gómez-Monedero et al. [9], it is constituted by almost all kinds of structural units formed by oxidation of noniferyl alcohol, synapyl alcohol, and p-coumaryl alcohol. However, the decomposition of cellulose, hemicellulose, and lignin is affected by pyrolysis temperature, potentially altering the end products of this process [3, 4].

Based on the heat rate, temperature, and residence of solids in the reactor, the thermal degradation of lignocellulosic biomass at high temperatures without oxidants is currently classified into three types: slow pyrolysis, fast pyrolysis, and flash pyrolysis [1, 10]. Slow pyrolysis is characterized by relatively low temperatures (<500 °C) with a long residence time and is generally called carbonization. This method is widely used for charcoal production with an additional focus on maximizing solid product yield [11]. The production of the liquid or condensable phase (wood vinegar) is maximized, while the production of bio-oil is low [12]. This type of pyrolysis is recognized for its robustness and energy efficiency, aiming to maximize biochar production compared to gaseous and liquid products [13]. Temperature and heating rate are pivotal factors that influence the quality of biochar [3, 4]. This type of pyrolysis involves a low heating rate, which reduces secondary pyrolysis and the thermal cracking process in both cellulosic polymers (cellulose and hemicellulose) and lignin, thus resulting in biochar as the predominant product [14].

Slow pyrolysis, a technique applicable under conditions demanding little technological advancement in pyrolysis equipment, stands out as the best-recognized and widely embraced method across many regions of the world [15]. Costa Rica, a relatively small Central American country, exhibits limited development in pyrolizer equipment, owing to its energy matrix predominantly based on the production of hydroelectric energy. Despite the significant availability of biomass, other energy sources are deemed less important [16]. Besides the constraints in the development of equipment, Costa Rica witnesses a large part of its productive activities being dedicated to very important agricultural crops [17]. However, the substantial use of fertilizers and agrochemicals [18] poses challenges to a good sustainability policy for the agricultural sector [19]. Resultantly, the agriculture sector is actively exploring more appropriate approaches to crop management, which include soil management and the development of environmentally friendly agrochemicals [19, 20].

Despite the widespread recognition of this process of biomass conversion, there is a dearth of studies on the effect of temperature in slow pyrolysis on the yield of biochar and the different pyrolysis products and on the reactor's performance in various types of biomasses in Costa Rica [21]. The complexity of optimization of the temperature and the pyrolysis process can be compounded by the type of feedstock, composition, physicochemical properties, nature of the application, and other operational factors [22]. Specifically, studies on the production of different pyrolysis products and the behavior of the slow pyrolysis process at different temperatures have been limited to biomass sourced from forest plantations. To foster the effective development of pyrolysis systems in Costa Rica, it is necessary to comprehensively study the effects of temperature on this biomass conversion process.

On the other hand, forest plantations in Costa Rica currently supply about 78% of the woody market (750,000 tons year^{-1} in sawlog). The yield of marketable sawn wood from these processes is estimated to be at around 25% of the volume of the forest plantation (approx. 187,500 ton year^{-1}), highlighting inefficient production processes and a high percentage of residues [23, 24]. Therefore, the renewal of the wood industry calls for increased attention to be paid to the valorization and utilization of the residues generated from these processes which are useful in the production and cogeneration of electrical and heat energy, production of charcoal and firewood, organic compost, and other applications [25, 26]. The pyrolysis of residues from these plantations can produce biochar, wood vinegar, bio-oil, and non-condensable gases. In the case of biochar, the production can vary by 25–40% in slow pyrolysis [11]; it is currently used in soil management [27]. The wood vinegar, with a production of 20–40%, can be used as a fertilizer or pesticide [12], bio-oil constituting a production of less than 10% in slow pyrolysis is used as an alternative fuel source [28], and non-condensable gases serve as an energy source to be used in the same pyrolysis reactors [21–29].

Few studies assessed the biochar fuel qualities of certain tropical woods from Costa Rica, including energy densities, energy yields, biochar characteristics, thermal profiles, or other properties [30, 31]. However, while particularly studying the Costa Rican species in slow pyrolysis, *T. grandis*, and *G. arborea* were not given enough attention [32], and the references did not delve into the effects of temperature on slow pyrolysis [33–35]. A study carried out on *T. grandis* by Parthasarathy and Sheeba [36] explored the yield, solid residence time, and charcoal characteristics produced in different temperatures during slow pyrolysis (300, 350, 450, 500, and 550 °C) and demonstrated the reduced yield of charcoal, while the residence time remained stable. The studies of *G. arborea* reported that charcoal characteristics pyrolysis was carried out in a fabricated fixed-bed pilot-scale reactor using sawdust biomass to produce bio-oil; however, they again exhibited charcoal characteristics [37].

Considering that Costa Rica boasts four commercially important species (*Dipteryx panamensis*, *Gmelina arborea*, *Hieronyma alchorneoides*, and *Tectona grandis*) in reforestation program along with the generation of a significant quantity of residues during harvesting and sawing, which can be pyrolyzed to yield various pyrolysis products (vinegar, bio-oil, and charcoal), it necessary to comprehend the effect of temperature on different products of pyrolysis. These products can be further used in other agricultural crops in Costa Rica. Furthermore, there is a lack of information about the processes and products obtained from slow pyrolysis regarding these species. Thus, the objective of the present study was to determine the yield of different products of pyrolysis (charcoal, bio-oil, wood vinegar, and non-condensable), time of pyrolysis, and temperature in two stages of pyrolysis (inside reactor and outlet pyrolysis gases of the reactor) in the pilot-scale reactor at varying temperatures (300, 350, 400, 450, and 500 °C). The advancement of this study provides information about the pyrolysis process to assist in the integral utilization of forest resources and contribute to finding renewable sources for agriculture production.

2 Methodology

2.1 Materials and sample preparation

Four distinct species of parentwood growing in fast-growth plantations in Costa Rica were used as the raw material in this study (*Dipteryx panamensis*, *Gmelina arborea*, *Hieronyma alchornoides*, and *Tectona grandis*). *H. alchorneoides* and *D. panamensis* parentwood were sampled from previous research, having been dried in a drying kiln at 12% [38]. The *H. alchorneoides* plantation was 12 years old, whereas the *D. panamensis* plantation was 16 years old. Moya and Tenorio [38] provided more details on the conditions of the plantations of these two species. In the case of *G. arborea* and *T. grandis*, parentwood samples were extracted from an 8-year-old plantation of each species [39]. Different ages in the four species studied were selected due to the requirement that trees exhibit a diameter at breast height of approximately 22 cm. Eight boards were utilized and extracted from the basal log of each tree sampled and extracted from the heartwood zone. One hundred sixty-eight samples of heartwood with dimensions of 14.0 cm × 2.5 cm × 2.0 cm (length × width × thickness) were extracted from dried wood. Subsequently, all samples were divided into six groups of 28 samples each, with five groups designated for different temperatures and one group labeled as parentwood. The composition and characteristics of five woody species were detailed by Moya et al. [40], as displayed in Table 1.

2.2 Process of carbonization and treatment

The pyrolysis process involves the examination of five target temperatures or treatments corresponding to different phases of the pyrolysis process: low, medium, and high temperatures [13]. The selected temperatures were 300, 350, 400, 450, and 500 °C [13]. The charcoal production process utilized a 30-cm long new cylindrical pilot reactor of 12-cm diameter with a capacity of 3 l (Fig. 1). This reactor, previously designed for the pyrolysis process of different tropical species of Costa Rica [30], adheres to different recommendations detailed by Garcia-Nunez et al. [28] and is well-suited for small samples. This reactor can accommodate up to 14 samples, according to Fig. 1. Two baths were pyrolyzed for each temperature, resulting in a total of ten batches. The temperature was measured in two different stages using a probe: (1) temperature inside the reactor and (2) temperature at the outlet of the pyrolysis gas from the reactor (Fig. 1). These temperatures were measured using the datalogger Testo model 176/T4 (Testo SE & Co., Titisee-Neustadt, Germany).

In the pyrolysis process, 14 samples were placed inside the reactor, and thereafter the reactor was sealed. Nitrogen was introduced at 2 MPa to create an oxygen-free environment. Subsequently, the reactor was heated at a rate of 12.5 °C/min until reaching approximately 275 °C or a pressure of 1.55 Mpa, at which point a faucet was opened (Fig. 1) for the gradual elimination of pyrolysis gases. The process continued until reaching the target temperature, and this temperature was maintained until the expulsion of gases stopped. Following this, the reactor was left to cool down to ambient temperature by constantly opening the faucet to avoid charcoal combustion and eliminate residual gases.

The gases released during pyrolysis underwent a cooling process in which they were passed through two glass allicin condensers, each 100-cm long, and circulated with water at approximately 20 °C (Fig. 1). When the flow rate of gases

Table 1 Composition and characteristics of four woody biomass tested for slow pyrolysis [40]

Wood properties	*D. panamensis*	*G. arborea*	*H. alchorneoides*	*T. grandis*
Gross caloric value (MJ/kg)	19.06 (0.74)	18.44 (1.43)	18.62 (0.52)	19.63 (1.34)
Volatile matter (%)	87.87 (0.38)	93.65 (1.21)	83.35 (0.20)	84.00 (0.23)
Ash (%)	1.53 (0.10)	1.24 (0.03)	1.59 (0.12)	1.15 (0.05)
Carbon content (%)	47.28 (0.53)	47.56 (0.20)	46.94 (1.36)	46.96 (1.44)
Hydrogen content (%)	6.57 (0.10)	6.85 (0.01)	6.53 (0.21)	6.73 (0.18)
Oxygen content (%)	44.46 (0.53)	45.46 (0.20)	46.40 (1.58)	46.18 (1.63)
Carbon/hydrogen ratio (%)	7.20 (0.13)	6.94 (0.04)	7.19 (0.03)	6.98 (0.03)
Cellulose content	46.32 (2.79)	46.34 (1.18)	49.17 (2.47)	41.41 (2.11)
Holocellulose content	77.02 (1.06)	60.38 (1.35)	60.39 (0.39)	59.65 (0.85)
Lignin content	31.76 (0.46)	25.56 (0.04)	23.06 (5.46)	30.91 (1.41)
pH	4.82 (0.02)	5.55 (0.04)	7.16 (0.06)	6.41 (0.07)
Extractives in sodium hydroxide (%)	20.96 (0.27)	26.13 (0.56)	12.80 (0.41)	11.98 (1.17)
Extractives in hot water (%)	11.38 (0.26)	8.97 (0.15)	17.70 (4.19)	3.13 (0.87)
Extractives in cool water (%)	11.87 (0.48)	7.81 (0.08)	7.83 (0.71)	3.28 (0.93)
Extractives in dichloromethane (%)	11.00 (0.43)	2.21 (0.12)	5.84 (0.20)	2.20 (0.08)
Extractives in ethanol-toluene (%)	11.20 (0.41)	0.82 (0.49)	9.58	1.18 (0.01)

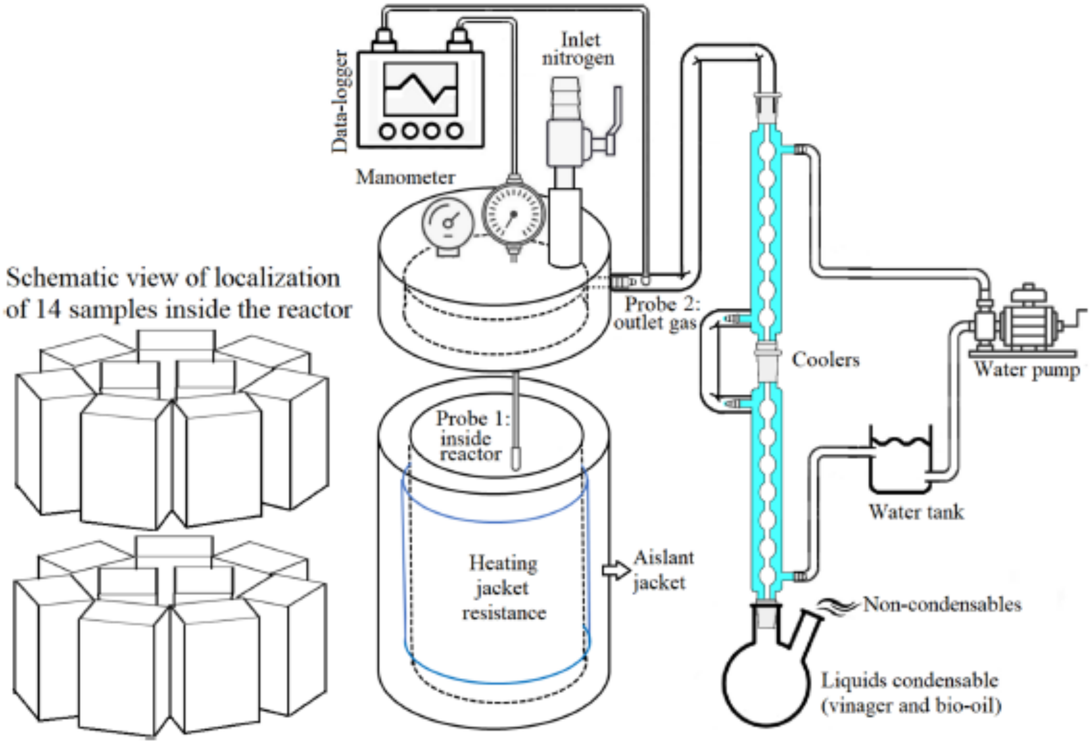

Fig. 1 Cylindrical reactor designed and utilized for evaluation of charcoal process and schematic view of localization of samples inside the reactor

and the pressure increased rapidly, the stopcock was opened fully to allow the passage of gases through the condensers. This point marks the initiation of a pyrolytic reaction. The end of the pyrolysis process was considered when no gas outlet was observed [28, 30]. At this moment, the electrical resistances of the reactor were turned off.

Water vapor, low molecular weight gases, various condensable gases at room temperature, and bio-oil combine to create the condensed gases. All these condensable products were collected in a two-neck round-bottom flask at the end of the condenser (Fig. 1) and were designated for bio-oil and wood vinegar. Non-condensable gases were eliminated by one of the necks of the flask (Fig. 1). The condensed liquid was left in the flask overnight, allowing the separation of tar and wood vinegar by density deference, followed by further segregation of these two components by decantation, after which each part was weighted.

2.3 Evaluation of pyrolysis process

Three distinct variables were used to assess the carbonization process: the yield of different types of products (charcoal, bio-oil, wood vinegar, and non-condensable), evaluation of different time points during the pyrolysis process, and evaluation of conditions in the three stages of the pyrolysis process.

2.3.1 The yield of different types of products

The yield of different types of products like charcoals, bio-oil, wood vinegar, and non-condensable was calculated according to the procedures outlined by Balaguer-Benlliure et al. [30] and Sahoo et al. [27]. The process involved weighing the parentwood of different treatments initially, and at the end of pyrolysis, the charcoal was weighed, whereas vinegar and bio-oil weight were described previously. The recovery yields of different products of pyrolysis (charcoal, vinegar, and bio-oil) were calculated according to Eq. 1 [30]. The non-condensable yield was calculated by Eq. 2 [30]. Additional parameters used in the evaluation of the pyrolysis process were the time and temperature of the different stages of the process using the graphical representation of the relation between time vs. temperature (Fig. 2).

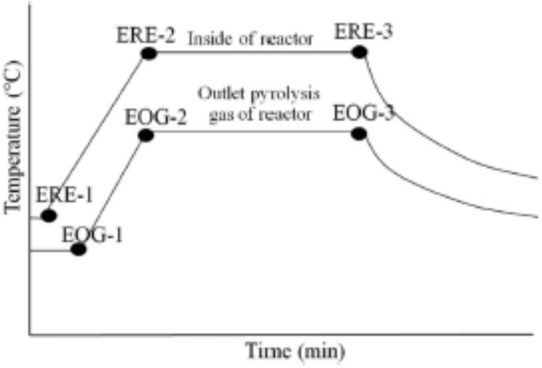

Fig. 2 Different stages in temperature inside of reactor, outlet pyrolysis gas reactor and before gases condensation during the pyrolysis process of four tropical hardwood from plantation

$$\text{Charcol, vinager or tar recovery yield (\%)} = \frac{\text{Charcol, vinager or bio} - \text{oil weigth (kg)}}{\text{Parentwod weigth (kg)}} \times 100 \quad (1)$$

$$\begin{aligned}\text{Non} - \text{condensable recovery yield(\%)} &= 100\\ &- (\text{charcol yield} + \text{vinager yield} + \text{bio} - \text{oil yield})\end{aligned} \quad (2)$$

2.3.2 Visual color, density, and moisture content charcoal characterization

Density and moisture content of charcoal were determined. For density, 20 charcoal specimens measuring 2.5 × 2.5 × 2.0 cm were cut from different samples for each pyrolysis temperature. These specimens were weighed and measured to calculate the volume and density derived from the ratio of weight/volume. Moisture content analysis of these samples was performed according to ASTM D1762-84 standard [41]. A sub-sample measuring 2.0 cm × 2.5 cm × 2.0 cm (length × width × thickness) was cut at one end of the parentwood sample measuring 16.0 cm × 2.5 cm × 2.0 cm (length × width × thickness). The 14.0-cm sample was used to calculate the density by establishing the correlation between weight and volume.

2.3.3 Evaluation of different times during the pyrolysis process

This time reference represents the time when the faucet was opened. During the heating of the reactor, gases are produced that increase the internal pressure of the reactor. To release this pressure [42], the first opening of the faucet was done at 275 °C or a pressure of 1.55 MPa. The second time reference was the total time of pyrolysis, spanning from the initial pyrolysis process to the moment when the generation of gases stopped or was not seen in one of the necks of the flask (Fig. 1).

2.3.4 Evaluation of condition in three stages of the pyrolysis process

Temperature was measured at two different stages using a probe: (1) temperature inside the reactor and (2) temperature at the outlet of pyrolysis gases from the reactor (Fig. 1). The data recorded by testo equipment was utilized for a graphical representation of the temperature variation (Fig. 2) at these three measuring points. The three slopes presented similar performance variations, leading to the establishment of three parameters for gauging the temperature inside the reactor and the temperature at the outlet of pyrolysis gas from the reactor. However, the parameters were evaluated to determine the temperature of gases before condensation. Table 2 describes the parameters, the point of measurement, and the corresponding abbreviations used in Fig. 2.

2.4 Statistical analysis

The statistical analysis confirmed the normality of the results of physical characteristics. One-way ANOVA was carried out by means of the GLM procedure of the SAS software (SAS Institute, Campus Drive Cary, NC) to confirm the effect of the pyrolysis temperature on various charcoal characteristics (density and moisture content). The Tukey test was used to discern the statistical differences between the means of the variables measured. The analysis of variance, as well as the Tukey tests, were both performed with the SAS software (SAS Institute Inc., Cary, NC). It is crucial to note that the variables obtained from the evaluation of different product yields, different pyrolysis durations, and the conditions in two stages of pyrolysis were derived from two observations or two runs. Subsequently, these values were averaged, and their standard deviations were not presented in respective figures. Besides, an additional multivariate principal component analysis (PCA) was carried out to examine the relationship between the runs of the pyrolysis process and the duration and temperatures as dependent variables. Two principal components were established for each analysis, and the type of parentwood was used to analyze the clustering of the observations.

Table 2 Time and temperature of the different stages during pyrolysis process for four tropical woods from plantation

Type of stage	Parameters	Abbreviations or point in Fig. 2
Inside of reactor	1. Time of stabilization in maximum temperature	ERE-2
	2. Temperature of stabilization in maximum temperature	ERE-2
	3. Time where temperature began to decrease	ERE-3
	4. Temperature where it began to decrease	ERE-3
Outlet pyrolysis gas of reactor	1. Time when the temperature being to increase	EOG-1
	2. Time of stabilization in maximum temperature	EOG-2
	3. Temperature of stabilization in maximum temperature	EOG-2
	4. Time where temperature maximum began to decrease	EOG-3
	5. Temperature where it began to decrease	EOG-3

3 Results

3.1 Evaluation of the yield of different products of pyrolysis

Figure 3 illustrates the different products obtained during the pyrolysis process of four distinct species at varying temperatures. In general, it was observed that bio-oil exhibited the lowest yield in all species and temperature ranges, varying from 2.8 to 8.1%. It is noteworthy to mention that it was impractical to separate bio-oil from vinegar in G. arborea, so the results for this species are not presented in Fig. 3. The yields of non-condensable constituted the second lowest percentage of products, varying from 14.0 to 33%. An additional observation highlights the variation in different types of products with the temperature. The lowest temperature (300 and 350 °C) produced a higher percentage of charcoal in comparison to the percentage of yield of vinegar, but contrary trends were observed at the temperatures of 400, 450, and 500 °C, wherein the yield of wood vinegar was higher surpassing the yield of charcoal in all species (Fig. 3).

The effects of temperature on the yields of different products are depicted in Fig. 4. The yield of charcoal (Fig. 4a) decreased with increasing temperature and varied from 45–55% at 300 °C to 30–35% at 500 °C. *D. panamensis* parentwood presented the lowest charcoal percentage for all tested temperatures, while the other three species (*G. arborea*, *H. alchornoides*, and *T. grandis*) presented similar percentages at different temperatures (Fig. 4a). Regarding the yields of condensable products (wood vinegar and bio-oil), it was found that both percentages increased with increasing temperatures (Fig. 4c, d). *G. arborea* parentwood yielded the lowest percentage of condensable and wood vinegar at all temperatures, while *D. panamensis* parentwood yielded the highest percentage of these products. The percentages

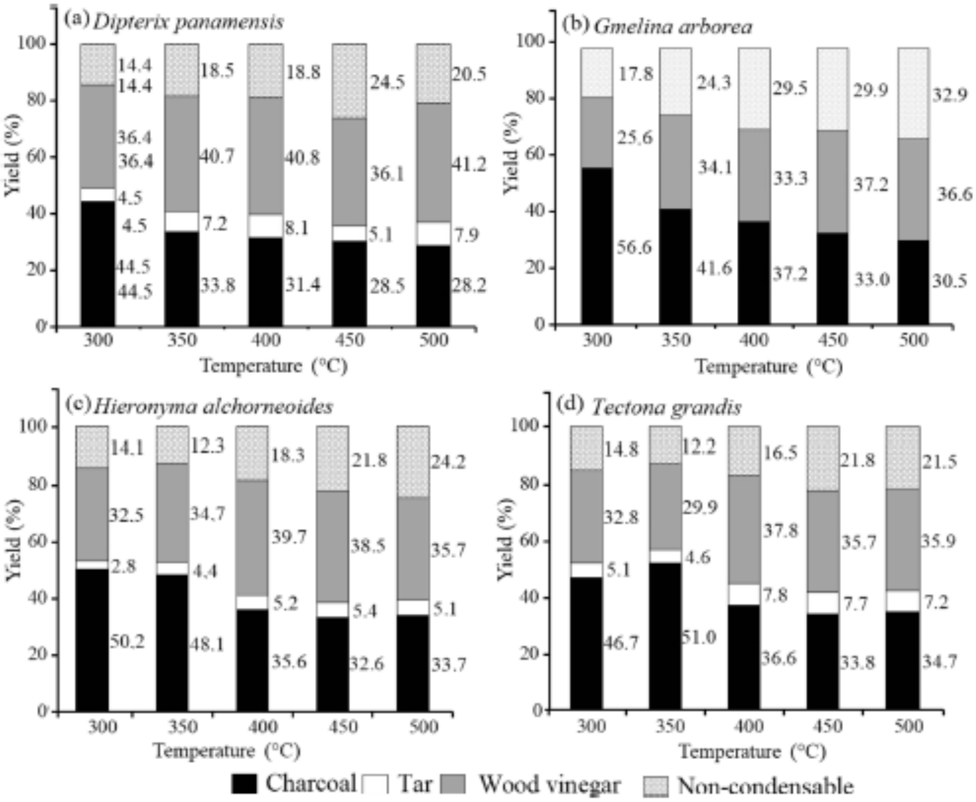

Fig. 3 Yield percentage of products obtained of *Dipteryx panamensis* (**a**), *Gmelina arborea* (**b**), *Hieronyma alchorneoides* (**c**), and *Tectona grandis* (**d**) at different pyrolysis temperatures

of yield of condensable and wood vinegar were similar in parentwood of *H. alchorneoides* and *T. grandis* (Fig. 4c), indicating potential similarity in time and conditions at the end of pyrolysis for both these species. The yields of bio-oil also increased with rising temperature, but the performance varied between species (Fig. 4d). The lowest yield of bio-oil was observed in the case of *H. alchornoides*, and a similar yield was found in *D. panamensis*, *G. arborea*, and *T. grandis* (Fig. 4d).

3.2 Visual color, density and moisture content charcoal characterization

The charcoal produced through pyrolysis for four tropical hardwoods from plantations with different temperatures exhibited variations in the shapes and dimensions of charcoal pieces. The reduction in the dimensions of the pieces of charcoal was observed with rising temperatures accompanied by partial or no pyrolysis of certain areas, particularly at temperatures of 300 °C or 350 °C. Meanwhile, the charcoal produced at 400 °C, 450 °C, and 500 °C was broken into small pieces, with a higher percentage of parentwood undergoing pyrolysis. Figure 5a, b shows the charcoal produced by *D. panamensis* at 300 °C and 350 °C, showcasing larger pieces without carbonization and charcoal pieces in the original size of the parentwood. In contrast, the size of the pieces decreases at other temperatures, and complete pyrolysis is observed (Fig. 5c–e). The color of wood vinegar varied with temperatures in distinct species; for example, the color of vinegar of *H. alchorneoides* was reddish in color, and the increasing temperature tended to produce dark red vinegar (Fig. 5f), whereas vinegar produced by *G. arborea* parentwood had a yellowish tint. The color of bio-oil was dark across all the species.

While evaluating other physical characteristics, it was observed that the parentwood presented statistically higher values of density and moisture content (Table 3). Regarding the properties of the charcoal produced at different pyrolysis temperatures, no statistical differences were observed in the density of *D. panamensis*, *G. arborea*, and *H. alchorneoides*

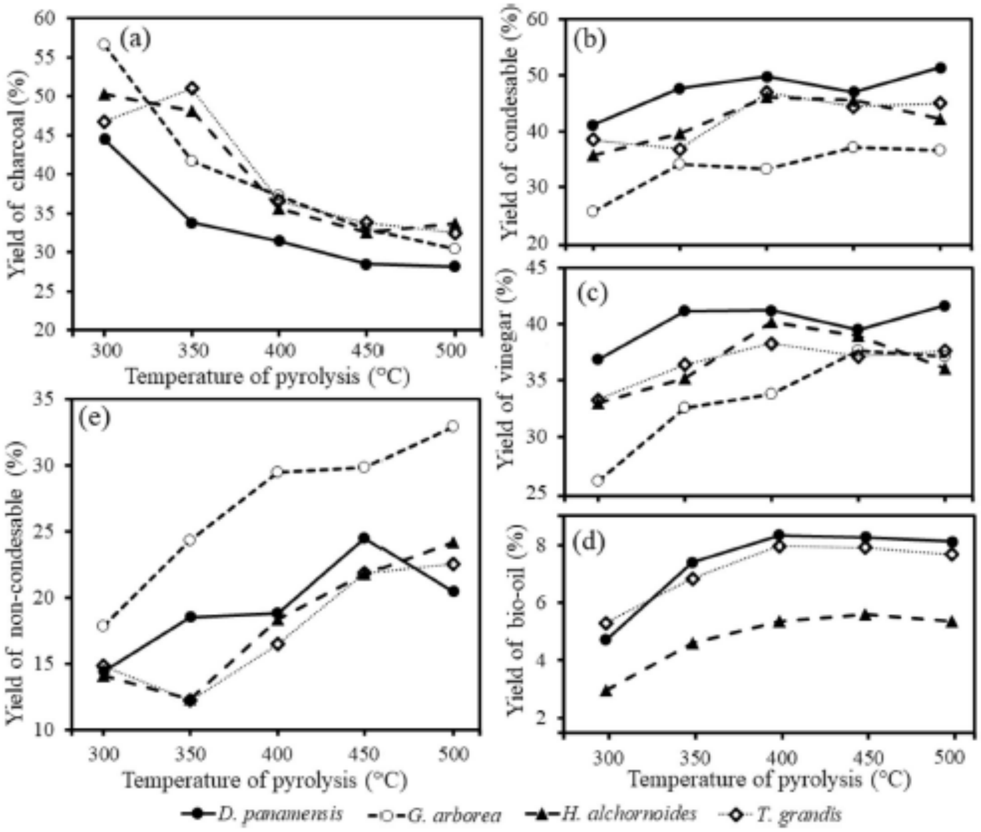

Fig. 4 Variation of yields percentage of products obtained of four tropical woods from plantation: yield of charcoal (**a**), yield of non-condensable (**e**), yield of condensable (**b**), yield of vinegar (**c**) and yield of bio-oil (**d**) at different pyrolysis temperatures

species; however, charcoal of *T. grandis* presented the statistical differences between temperatures (Table 3). Charcoal produced at 300 °C and 350 °C presented higher density than charcoal pyrolyzed at 400 °C, 450 °C and 500 °C in this species. The highest density values in charcoal produced at 300–350 °C can be attributed to partial pyrolysis of parentwood (Fig. 5a). The moisture content of charcoal produced at 400 °C and 450 °C presented higher values as compared to the other three temperatures in *D. panamensis*, *H. alchorneoides*, and *T. grandis,* with no difference in moisture content in *G. arborea* (Table 3).

Different letters between different temperatures for same species are statistically different at 99%

3.3 Evaluation of different time during pyrolysis process

The onset time of the pyrolysis process and the initial opening time of the faucet were constant in *G. arborea*, *H. alchornoides*, and *T. grandis*, without exhibiting any differences, and was approximately 10 min (Fig. 6a). However, *D. panamensis* exhibited 2 times higher timeline than the other three species. Regarding the total time of the pyrolysis process, *G. arborea*, T. *grandis*, and *H. alchornoides* presented less time than the parentwood of *G. arborea*. Analysis of the effect of the different pyrolysis temperatures revealed a reduction between 300 and 400 °C. Thereafter, the time was stable in the temperature ranges of 450 and 500 °C in *D. panamensis*, *H. alchornoides*, and *T. grandis*, but for *G. arborea*, the total time was consistent between 300 and 450 °C, unlike 500 °C, where there was a decrease in the total pyrolysis time (Fig. 6b).

3.4 Evaluation of condition in two stage of pyrolysis process

3.4.1 Inside the reactor

The temperature rise inside the reactor occurred immediately after the resistance was turned on, with the initial time being considered to be zero minutes, which is not

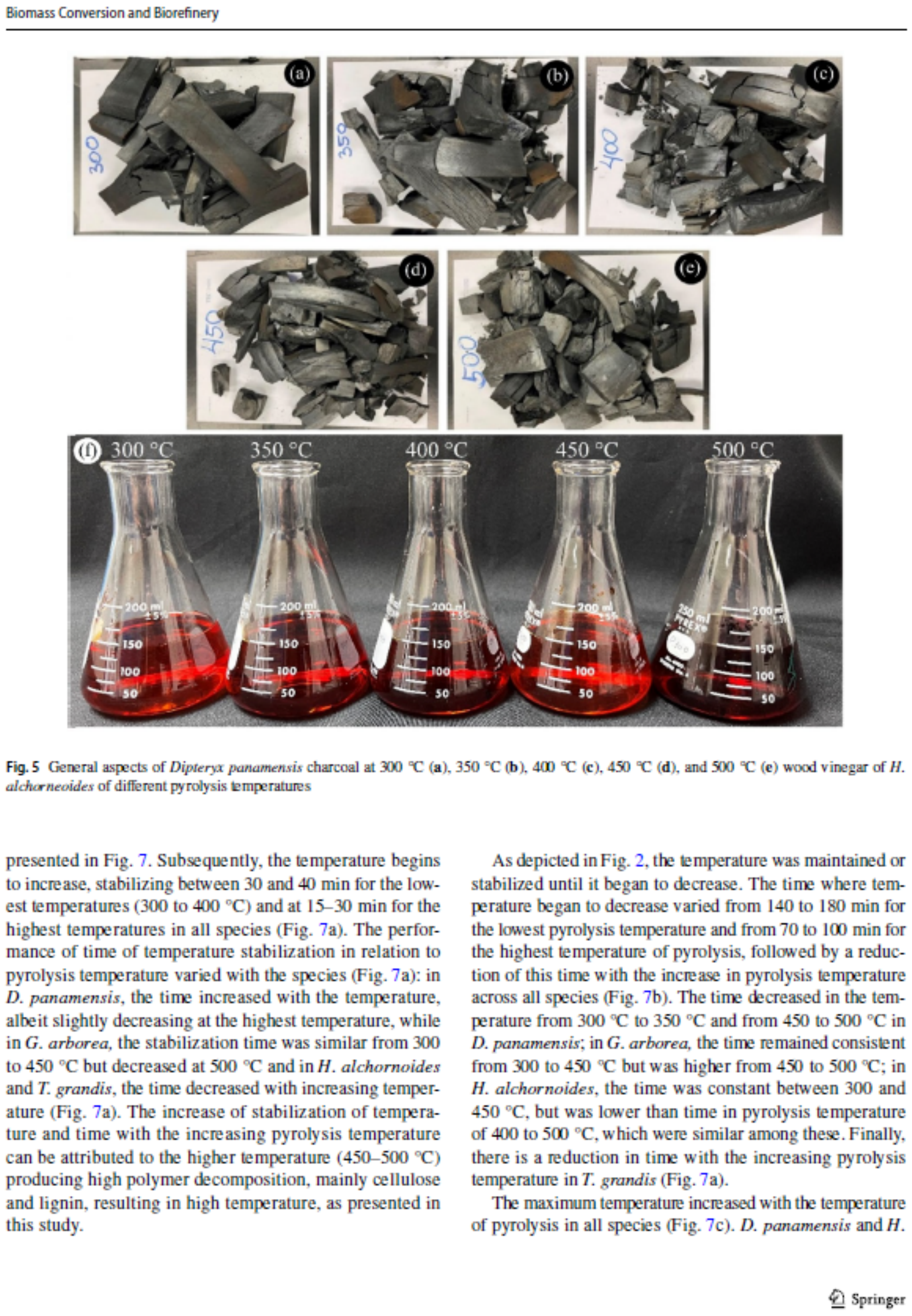

Fig. 5 General aspects of *Dipteryx panamensis* charcoal at 300 °C (**a**), 350 °C (**b**), 400 °C (**c**), 450 °C (**d**), and 500 °C (**e**) wood vinegar of *H. alchorneoides* of different pyrolysis temperatures

presented in Fig. 7. Subsequently, the temperature begins to increase, stabilizing between 30 and 40 min for the lowest temperatures (300 to 400 °C) and at 15–30 min for the highest temperatures in all species (Fig. 7a). The performance of time of temperature stabilization in relation to pyrolysis temperature varied with the species (Fig. 7a): in *D. panamensis*, the time increased with the temperature, albeit slightly decreasing at the highest temperature, while in *G. arborea*, the stabilization time was similar from 300 to 450 °C but decreased at 500 °C and in *H. alchornoides* and *T. grandis*, the time decreased with increasing temperature (Fig. 7a). The increase of stabilization of temperature and time with the increasing pyrolysis temperature can be attributed to the higher temperature (450–500 °C) producing high polymer decomposition, mainly cellulose and lignin, resulting in high temperature, as presented in this study.

As depicted in Fig. 2, the temperature was maintained or stabilized until it began to decrease. The time where temperature began to decrease varied from 140 to 180 min for the lowest pyrolysis temperature and from 70 to 100 min for the highest temperature of pyrolysis, followed by a reduction of this time with the increase in pyrolysis temperature across all species (Fig. 7b). The time decreased in the temperature from 300 °C to 350 °C and from 450 to 500 °C in *D. panamensis*; in *G. arborea*, the time remained consistent from 300 to 450 °C but was higher from 450 to 500 °C; in *H. alchornoides*, the time was constant between 300 and 450 °C, but was lower than time in pyrolysis temperature of 400 to 500 °C, which were similar among these. Finally, there is a reduction in time with the increasing pyrolysis temperature in *T. grandis* (Fig. 7a).

The maximum temperature increased with the temperature of pyrolysis in all species (Fig. 7c). *D. panamensis* and *H.*

Table 3 Physical characteristics of charcoal for four tropical woods from plantation at different pyrolysis temperatures

Species	Variable	Pyrolysis temperature (°C)					
		Parent wood	300	350	400	450	500
D. panamensis	Density (g/cm^3)	0.94^{A} (0.06)	0.42^{B} (0.08)	0.38^{B} (0.05)	0.40^{B} (0.04)	0.41^{B} (0.03)	0.40^{B} (0.07)
	Moisture content (%)	11.78^{A} (0.89)	4.10^{C} (0.47)	4.53^{C} (0.41)	5.28^{B} (0.47)	5.19^{B} (0.84)	4.47^{C} (0.54)
G. arborea	Density (g/cm^3)	0.49^{A} (0.05)	0.21^{B} (0.03)	0.18^{B} (0.03)	0.18^{B} (0.03)	0.19^{B} (0.03)	0.20^{B} (0.02)
	Moisture content (%)	12.90^{A} (0.56)	4.53^{B} (0.99)	4.89^{B} (0.53)	4.45^{B} (0.47)	4.10^{B} (0.34)	4.59^{B} (1.05)
H. alchorneoides	Density (g/cm^3)	0.56^{A} (0.16)	0.32^{B} (0.03)	0.30^{B} (0.02)	0.30^{B} (0.03)	0.31^{B} (0.04)	0.28^{B} (0.03)
	Moisture content (%)	14.92^{A} (0.61)	3.24^{C} (0.19)	3.01^{C} (0.25)	5.67^{B} (0.36)	6.17^{B} (0.75)	3.33^{C} (0.39)
T. grandis	Density (g/cm^3)	0.54^{A} (0.05)	0.26^{B} (0.04)	0.27^{B} (0.03)	0.22^{C} (0.02)	0.21^{C} (0.05)	0.19^{C} (0.03)
	Moisture content (%)	13.28^{A} (0.67)	3.85^{C} (0.53)	3.91^{C} (0.56)	5.00^{B} (0.66)	4.67^{B} (0.78)	3.80^{C} (0.77)

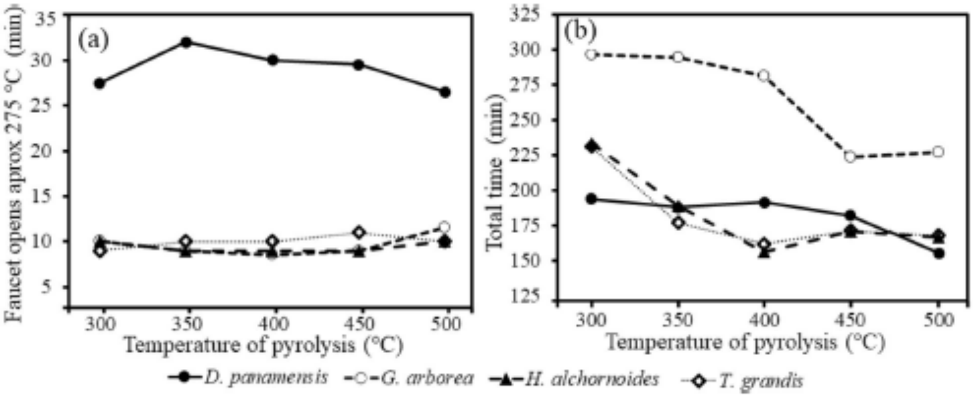

Fig. 6 Variation of time faucet opens (**a**) and time total of process of pyrolysis (**b**) for four tropical woods from plantation

alchornoides exhibited the highest maximum temperature, and *G. arborea* and *T. grandis* showcased similar performance (Fig. 7c). The temperature at which the reduction was initiated varied among species and different pyrolysis temperatures (Fig. 7d). Once again, *D. panamensis* presented the highest temperature at the point of decrease initiation with a slight increase in pyrolysis temperature after 300 °C and 350 °C followed by consistent temperature after 350 °C. *G. arborea* presented a slight increase with rising pyrolysis temperature. *H. alchornoides* and *T. grandis* presented similar performances at temperatures of 300 °C and 350 °C, respectively. Subsequently, the temperature was increased and was maintained between 400 and 500 °C, but *H. alchornoides* presented the highest temperature (Fig. 7).

3.4.2 Temperature outlet pyrolysis gases of reactor

The initiation time when the gases began to increase the temperature varied among the species (Fig. 8a); *D. panamensis* presented the highest time, followed by *T. grandis* and in both species, the time when the temperature began to increase was similar from 300 to 450 °C, after which the time decreased. Meanwhile, in *G. arborea* and *H. alchornoides*, the pyrolysis temperature at which the temperature outlet gases varied (Fig. 8a). On the other hand, the time of stabilization of the maximum temperature of gases decreased slightly with pyrolysis temperature for *D. panamensis* and *G. arborea*. In *H. alchornoides*, the time was similar in different pyrolysis temperatures, and *T. grandis* did not present

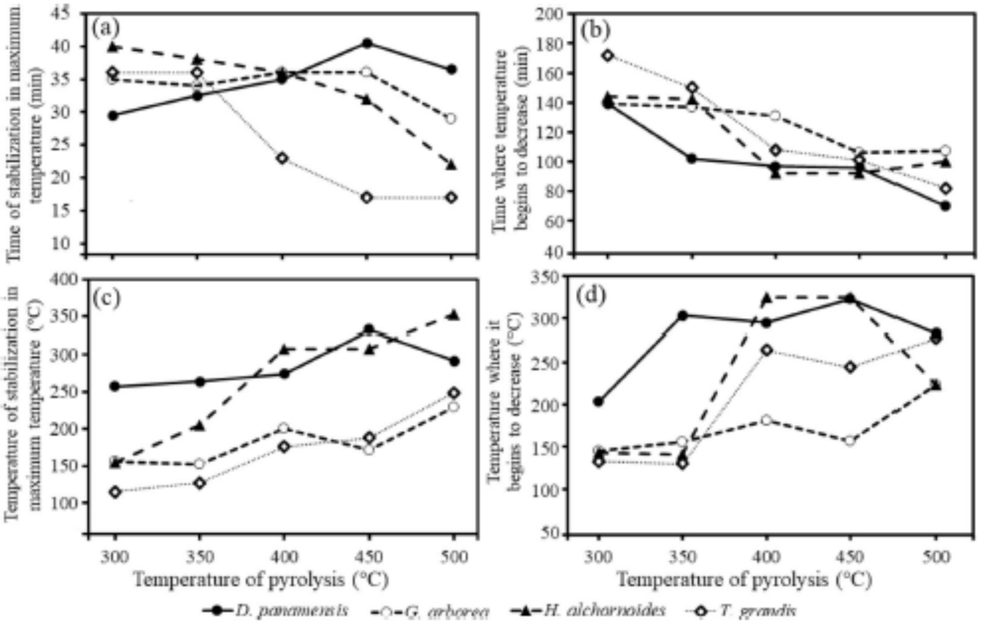

Fig. 7 Variation of temperature and time inside of reactor for process of pyrolysis for four tropical woods from plantation: **a** time of stabilization in maximum temperature, **b** time where temperature began to decrease, **c** temperature of stabilization in maximum temperature, and **d** temperature where it began to decrease

variation between 300 and 400 °C, but there was a reduction in time from 400 to 500 °C (Fig. 8b). Regarding the maximum temperature of pyrolysis, it was found that *D. panamensis* exhibited the highest temperature for all pyrolysis temperatures, and the temperature was consistent between 300 and 450 °C, followed by a decrease at 500 °C (Fig. 8c). *G. arborea* presented identical maximum temperature of gases after they exited the reactor, but *Tectona grandis* and *H. alchornoides* presented an increase in temperature of gases after 350 °C (Fig. 8c). The time when maximum temperature began to decrease reduced with temperature, with *G. arborea* exhibiting the highest time (Fig. 8d). Finally, the temperature at which it began to decrease increased with the pyrolysis temperature in *D. panamensis*, *H. alchornoides*, and *T. grandis*, mainly after 350 °C, while the temperature remained stable in *G. arborea* (Fig. 8e).

3.5 Analysis of principal component

According to the multivariate principal components analysis, the first two components justify 70.8% of the variability of the data, 50.8% for principal component 1, and 20.0% for principal component 2 (Table 4). The principal component 1 was linked with many variables measured, which included all products of pyrolysis, except non-condensable yields, density of charcoal, time of faucet opens and total time, and time and temperature inside the reactor as well as gas outlet of pyrolysis. Meanwhile, principal component 2 was exclusively related to charcoal density, the time when the temperature began to increase, and the time of stabilization in maximum temperature in outlet pyrolysis (Table 4). The scatterplot of principal component 1 and principal component 2 depicted the formation of four different groups (Fig. 9):

- First group: distinguishes between the species of *D. panamensis* and is associated with component 2, specifically charcoal density for charcoal characteristic and time of faucet opening (VP-1) and the subsequent parameters in outlet pyrolysis, including the time when the temperature began to increase (VP-7), time of stabilization in maximum temperature (VP-8) and temperature of stabilization in maximum temperature (VP-9).
- Second group: formed by low pyrolysis temperature of *G. arborea*, *T. grandis*, and *H. alchornoides* parentwood and is associated variables like charcoal yields, total time of pyrolysis (VP-2), and time of stabilization in maximum temperature (VP-3) along with the time when it begins to decrease (VP-4) inside the reactor.
- Third group: formed by different temperatures of *G. arborea* parentwood pyrolysis and is associated with non-condensable yields.

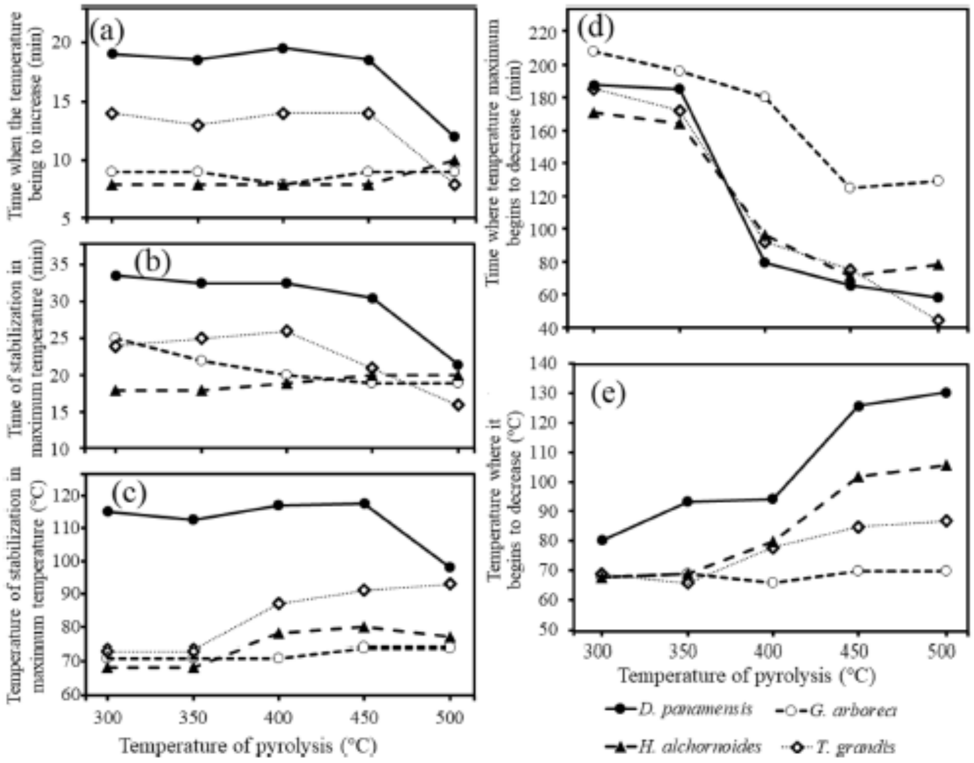

Fig. 8 Variation of temperature and time outlet pyrolysis gases of reactor for process for four tropical woods from plantation: **a** time when the temperature being to increase, **b** time of stabilization in maximum temperature, **c** temperature of stabilization in maximum temperature, **d** time where temperature maximum began to decrease and **e** temperature where it began to decrease

- Fourth group: formed by pyrolysis temperature of *T. grandis* and *H. alchornoides* parentwood ranging between 400 and 500 °C and the temperature of 500 °C of *D. panamensis* parentwood. These temperatures were associated with condensable, bio-oil, and wood vinegar yield and moisture content.

4 Discussion

The findings below indicate that each of the three aspects (charcoal characteristics, evaluation of the yield of different products, and evaluation of temperature and time in two stages of the pyrolysis process) must be analyzed independently as distinct entities. Initially, charcoal density resulting from the pyrolysis process from low temperatures (300–350 °C) exhibited lower values than higher temperatures (400–500 °C). This phenomenon is attributed to the fact that charcoal produced at 300–350 °C underwent incomplete pyrolysis in some parts of parentwood (Fig. 5a), leading to non-carbonized areas of parentwood. The multivariate analysis validated the importance of low temperatures in the different species. Figure 9 demonstrated that low temperatures were separated from other temperature ranges, especially in H. alchornoides and *T. grandis*. According to Wang et al. [5, 6], the hemicellulose decomposition occurred between 250 and 350 °C, while the highest cellulose and lignin decomposition was observed between 400 and 550 °C. Hence, parentwood subjected to the lowest temperature did not pyrolyze completely, resulting in an increase in charcoal density.

The variations in charcoal density are closely linked with the parentwood density, where species with higher density produce charcoal with high density, thus establishing a correlation between the quantity of carbon contained in the biomass and biomass porosity [43]. Subsequently, *D. panamensis* parentwood, possessing the highest density, produced charcoal with higher density (Table 3), and in contrast, *G. arborea* parentwood, characterized by the lowest density, produced charcoal with lower density

Table 4 Statistical parameters of principal components 1 and 2 and their correlations with different parameters measured for pyrolysis process for four tropical woods from plantation

Parameters	Variable	CP 1	CP 2
Statistical parameters of principal components	Eigenvalue	9.15	3.60
	% Total of variance	51.0	20.00
	Total cumulative	51.0	71.0
Correlations between principal components and different parameters measured			
Variables	Parameters	CP1	CP2
Yields of different products	Charcoal yield	−0.79**	0.45
	Condensable yields	0.93**	0.00
	Wood vinegar	0.88**	−0.06
	Bio-oil	0.81**	−0.01
	Non-condensable	−0.01	−0.59
Charcoal characteristics	Density	0.63*	0.63*
	CH	0.45	−0.13
Different time during pyrolysis process	Faucet opens approx. 275 °C (VP-1)	0.70*	0.60
	Total time of pyrolysis (VP-2)	−0.75*	0.13
Parameters inside of reactor	Time of stabilization in maximum temperature (VP-3)	−0.21	0.46
	Time where it begins to decrease (VP-4)	−0.80**	0.51
	Temperature of stabilization in maximum temperature (VP-5)	0.79**	−0.19
	Temperature where it begins to decrease (VP-6)	0.90**	−0.27
Parameter for outlet pyrolysis	Time when the temperature being to increase (VP-7)	0.57	0.72*
	Time of stabilization in maximum temperature (VP-8)	0.40	0.81**
	Temperature of stabilization in maximum temperature (VP-9)	0.82**	0.44
	Time where temperature maximum begins to decrease (V-10)	−0.75*	0.55
	Temperature where it begins to decrease (VP-11)	0.86**	−0.04

Numbers in boldface are statistically significant (The symbol "*" denotes $p<0.05$ and the symbols "**"denote $p<0.01$).

(Table 3). Decreased charcoal density can be attributed to a general expansion of the macrostructure of the charcoal caused by the release of volatiles [43].

Charcoal affinity with water is reduced during pyrolysis due to the reduction of the functional groups during the process [44], implying the anticipation of low moisture content in charcoal in the species and temperature studied (Table 3). Despite the limited affinity of charcoal with water [45], the moisture content in charcoal of the species studied is because of the presence of some functional groups, especially oxygen-containing groups, which play a crucial role in water adsorption capacity; this is likely due to involvement of hydrogen bonds in the mechanism of adsorption. The moisture content of charcoal of different species varies with temperature (Table 3) since each species generally has its own pyrolysis conditions with temperature, resulting in different effects on the functional groups [5, 6].

The density and moisture content demonstrated values of four species and different temperatures, aligning with other studies on charcoal produced from different tropical species in Costa Rica [40] or another country with tropical conditions [36, 46–48].

A reduction in charcoal yield was observed with the increase in temperature across all species (Fig. 3); however, the greatest decrease occurred between 300 and 450 °C in *D. panamensis* and *G. arborea* and at 350–450 °C in *H. alchorneoides* and *T. grandis* after which, the yield of charcoal remained constant between 450 and 500 °C across all species (Fig. 4). The decrease in yield can be attributed to greater production of vapors and gases or volatile content [49] caused by the elimination of hydrogen and oxygen by dehydrogenation and deoxygenation processes to produce CO_2, CO, H_2, and water [13]. This behavior is consistent with woody tropical species of Amazon (*T. guianensis*, *Manilkara* sp., and *D. excelsa*) as reported by Lima et al. [46], along with other types of lignocellulosic biomass reported by Parthasarathy and Sheeba [36] including sugarcane bagasse (*Saccharum officinarum*), casuarina leaves (*Casuarina equisetifolia*), coconut (*Cocos nucifera*) coir pith, groundnut (*Arachis hypogaea*) shell, rice husk (*Oryza sativa*), and wheat (*Triticum aestivum*).

In relation to condensable gases, it was challenging to separate this product in wood vinegar and bio-oil in the parentwood of *G. arborea*. Liquid condensable is formed by

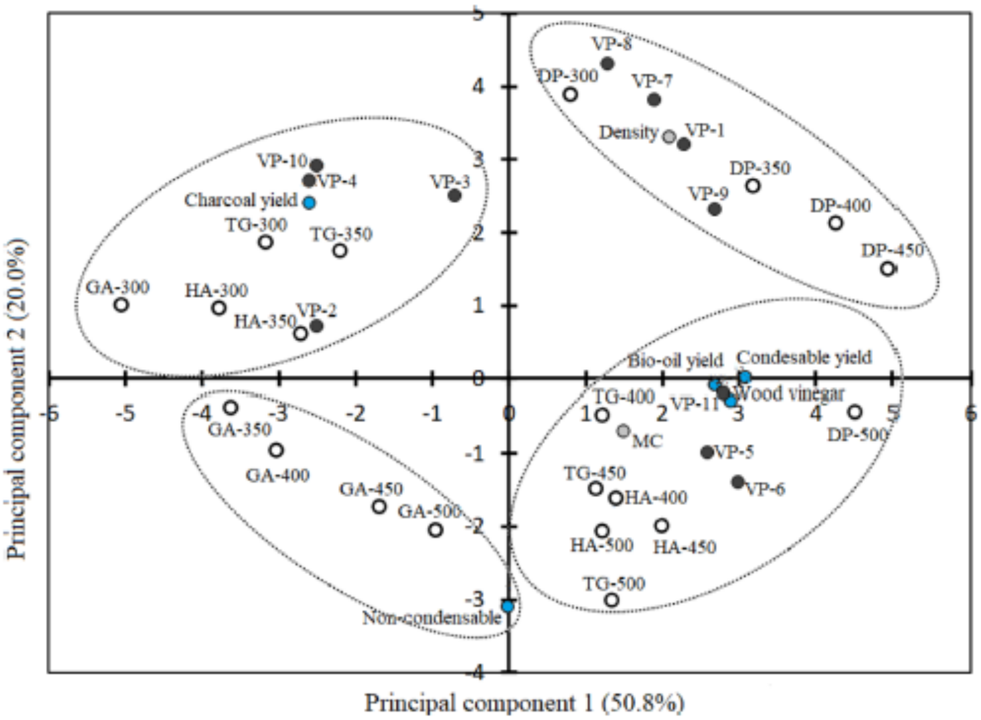

Fig. 9 Principal components analysis (PCA) for different parameters measured for pyrolysis process for four tropical woods from plantation. Note: the names of variables are detailed in Table 4

rapidly quenching and thus "freezing" the intermediate products of flash degradation of hemicellulose, cellulose, and lignin [50]. The liquid thus contains many reactive species, and the bio-oil can be considered a micro-emulsion where the continuous phase is an aqueous solution of holocellulose decomposition products, stabilizing the discontinuous phase of pyrolytic lignin macro-molecules through mechanisms such as hydrogen bonding [51]. The chemical components of bio-oil include multiples and variates, and their affinity with water mainly depends on the hemicellulose component in parentwood [1]. As a result, it is likely that the bio-oil in the liquid condensable of *G. arborea* contains chemical components comparable to water, making it hard to separate the two. However, if the separating becomes imperative and unavoidable, other techniques such as emulsification, hydrogenation, hydrodeoxygenation, catalytic pyrolysis, steam reforming, molecular distillation, and extraction using supercritical fluids can be used [51].

Condensable gases (wood vinegar and bio-oil), as expected, exhibited a behavior opposite to the biochar yield [44] and presented an increase with the pyrolysis temperature. However, a slight stability of the condensable was observed after 400 °C (Fig. 4b–d), whereas the yield of charcoal was stabilized after 450 °C (Fig. 4a). So, the decrease in the yield of charcoal does not correspond to an increase in the yield of condensable, but an increased yield of non-condensable gases increases constantly with rising temperature (Fig. 4e). However, it was indicated that the amount of bio-oil reaches its maximum point between 450 and 500 °C [1] because the gases increased due to secondary reactions, specifically the R-O-R bonds, generating water at a low amount of carbon oxides, forming polar aliphatic, and aromatic fractions [46]. During the pyrolysis of these species, the depolymerization of cellulose occurred (300–450 °C), resulting in a greater production of gases (Fig. 4b), but at higher temperatures, the defragmentation of this polymer already occurred and later turned into carboxylic acid alcohol, aldehyde, ketone and anhydrosugars, etc., which were the major components found in bio-oil [27], thus illustrating the increased bio-oil synthesis at higher temperatures (Fig. 4d). The yields of condensable (bio-oil and vinegar) become significant at temperature ranges beyond 400 °C, and these variables determined the separation of *H. alchornoides*, *T. grandis*, and *D. panamensis*, according to multivariate analysis (Fig. 9).

An important criterion to highlight was that the increase in the volume of gases during the pyrolysis of these species the agriculture sector in soil or pest management, and non-condensable gases to be used in the same pyrolysis reactors. Costa Rica presents a large part of the productive activities that are carried out by substantially vital agricultural crops, with an extensive utilization of fertilizers and agrochemicals, which are currently not considered a good sustainability policy for the agricultural sector. Thus, the agriculture sector is increasingly looking for more appropriate options for crop management, which include soil management and developing more environmentally friendly agrochemicals. Subsequently, according to the results obtained from the different products (Fig. 4a) and the measurement of different parameters in the slow pyrolysis reactor, each of the species has its advantages and disadvantages in comparison to the others. Firstly, temperatures of 300 and 350 °C are not recommended for any of the species since it was observed that the charcoal presented uncharred areas, although no difference was observed in the density values (Table 3). Furthermore, at these two temperatures, the charcoal yields were high, which indicates the lack of pyrolysis of some pieces of wood. However, the charcoal yield values were stable between 400 and 500 °C across all species (Fig. 4). In relation to the size of the charcoal, more brittle material was produced at the temperature of 500 °C (Fig. 5e), making it inconvenient from an energy point of view since larger pieces were needed. But if it was used for soil management, the charcoal was generally ground, so brittleness was not a problem. Pyrolysis temperatures of 450–500 °C maximized non-condensable and condensable gases, wherein wood vinegar and bio-oil were also maximized (Fig. 4b, c) but had the lowest charcoal yields (Fig. 4a). Thus, these two temperatures can be used as optimal conditions to carry out the slow pyrolysis of the studied species. However, *G. arborea* and *D. panamensis* exhibited different behaviors than *H. alchorneoides* and *T. grandis*. *G. arborea* produced a higher percentage of non-condensable gases that can subsequently be used in the reactor but faced challenges in separating the wood vinegar from the bio-oil, and this increase in gases resulted in a decrease in incondensable gases. Although *D. panamensis* produces a low charcoal yield, it has the merit of producing the greatest amount of wood vinegar and bio-oil. *T. grandis* and *H. alchorneoides* showed similar behaviors. Apart from the observed variations in the various products, it was also observed that *D. panamensis* needs a greater initial energy supply than the other species, but after this was achieved, pyrolysis was carried out normally, probably due to the high temperature reached in the reactor. While *G. arborea* was the species with the longest total pyrolysis time, and in general, a lower temperature was observed inside the reactor and the temperature of the gases, probably implying an incomplete production of bio-oil, therefore hindering the adequate separation of the wood vinegar in the condensable gases. Finally, the use of residues from the wood of different industrial processes of these species can be processed in slow pyrolysis, thus allowing an integral use of the forest resources, helping a circular economy since the products derived from pyrolysis can be used in other economic areas which in turn reduces dependence on imported products or products derived from non-renewable sources.

Author contribution RM and CT: methodology, investigation, formal analysis, experimental design, data analysis, and writing—original draft; JQK: experimental design, methodology, data analysis, validation, and writing—review and editing; RM: methodology and data analysis; RM: formal analysis and data analysis; JQK: formal analysis; JQK: methodology, data analysis, and validation; RM and JQK: conceptualization, supervision, and writing—review and editing; RM: conceptualization, supervision, project administration, and writing—review and editing.

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Declarations

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Artículo 2: Pyrogenic Carbonaceous Materials Production of Four Tropical Wood Produced by Slow Pyrolysis at Different Temperatures: Charcoal and Biochar Properties

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Pyrogenic Carbonaceous Materials Production of Four Tropical Wood Produced by Slow Pyrolysis at Different Temperatures: Charcoal and Biochar Properties

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Abstract: Costa Rica produces a considerable, important quantity of wood residues. This waste can be pyrolyzed to produce charcoals as main products that can be effectively used as an energy source or to immobilize carbon for soil treatment. However, there is a lack of information about the pyrogenic carbonaceous materials (PCMs), such as charcoal or biochar, obtained at different pyrolysis temperatures. Hence, this study aimed to evaluate the quality of PCMs (physical, mechanical, ultimate analysis, and FTIR analysis) and charcoal characteristics (energetic properties and thermogravimetric analysis—TGA) and biochar characteristics (conductivity, pH, initial contact angle, and wetting rates) for four tropical wood residues produced in five temperatures (300 °C, 350 °C, 400 °C, 450 °C, and 500 °C). In general, pyrolysis temperature between 450 °C and 500 °C produced charcoals with lower values of density, moisture content, compression strength, volatiles, H and O content, and higher values of C and ash contents, conductivity, pH, initial contact angle, and wetting rates. FTIR and TGA analyses show that celluloses and lignin are pyrolyzed at these temperatures, so these temperatures are recommended. The range of 300–350 °C is not recommended, as these parameters were inverse. Multivariate analysis shows that (i) PCMs obtained at lower temperatures (300–350 °C) from *Dipteryx panamensis*, *Hieronyma alchorneoides*, and *Tectona grandis* belong to a cluster with poorer properties, indicating that these temperatures are not adequate for pyrolysis of these species; (ii) all the PCMs obtained from *Gmelina arborea* were grouped into one cluster, suggesting different PCM quality; and (iii) the PCMs produced from *D. panamensis*, *H. alchorneoides*, and *T. grandis* at 400–500 °C were grouped into another cluster with better properties, suggesting this pyrolysis temperature range as the best for these species.

Keywords: carbonization; tropical wood; pyrolysis liquids; biochar

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1. Introduction

Pyrolysis is a thermochemical process that is applied to biomass, in which the main matrix polymers (cellulose, hemicellulose, and lignin) are decomposed in non-oxidizing atmospheres. This process results in solid product (charcoal or/and biochar), two types of liquid, which can be separated in bio-oil or wood vinegar, and non-condensable gases [1] with a variety of uses, including charcoal as fuel (a more traditional use), bio-oil as a soil amendment (biochar), activated carbon, chemical products, and many other uses [2]. Specially, the solid product is pyrogenic carbonaceous material (PCM), produced by thermochemical conversion of carbonaceous feedstock. If the PCM is used as a fuel, i.e., it is burned and the carbon is transformed (oxidized) into CO_2, it is classified as charcoal, but if the PCM is used for agricultural purposes or the application is a multifunctional material that can be used to address several challenges within a life cycle, the solid product of pyrolysis is called biochar [3]. Thus, in this article the term charcoal is used to refer to a fuel purpose and biochar for a soil purpose.

The pyrolysis process is carried out in a closed chamber (reactor) in the absence of oxygen and biomass decomposition process is carried out through different mechanisms that include dehydration, depolymerization, isomerization, aromatization, decarboxylation, and charring of cellulose, lignin, and hemicellulose [4,5]. Cellulose, the glycosidic bonds linking in glucose units, are not strong and break down at high temperatures and the products of cellulose pyrolysis are acids, alcohols, anhydrous sugars, charcoal, and gases, but furans and laevoglucose can also be formed by other mechanisms in the cleavage of $\beta - 1$, 4-glycosidic bonds [6]. In the case of hemicellulose, it occurs at low temperatures with high CO_2 production and high charcoal or biochar production [7]. Lignin is a more complex polymer; almost all kinds of structural units obtained during degradation are formed by oxidation of noniferyl alcohol, synapyl alcohol, and p-coumaryl alcohol [8].

The thermal degradation of lignocellulosic biomass with temperature in the absence of oxidants is currently classified into three types according to the heat rate, temperature, and residence of solids in the reactor: slow pyrolysis, fast pyrolysis, and flash pyrolysis [9]. Slow pyrolysis occurs at relatively low temperatures (<500 °C) with a long residence time, is generally called carbonization, and is widely used for PCM production in addition to maximizing this solid product. The production of the liquid or condensable phase (wood vinegar) is maximized and the production of bio-oil is low [10]. Temperature and heating rate play an important role in the quality of biochar. In this type of pyrolysis, the low heating rate reduces secondary pyrolysis and the thermal cracking process in both cellulosic polymers (cellulose and hemi-cellulose) and lignin, resulting in PCM as the main product [11].

Slow pyrolysis is a process that occurs in areas with little technological development in pyrolysis equipment, and is perhaps the best known and most popular method in regions such as the developing countries of the tropical areas of the Americas [12]. Costa Rica, a small country in Central America, has this condition of little development in pyrolizer equipment, because its energy matrix is based on the production of hydroelectric energy, so other energy sources such as biomass are less important, even though there is significant availability [13]. In addition to little development in equipment, the country has a large amount of productive activities that are carried out by very important agricultural crops, meaning a great demand for fertilizers and agrochemicals, which are currently not considered as a good sustainability policy for the agricultural sector [14,15]. Thus, the agriculture sector is increasingly looking for more appropriate options for crop management, which include soil management and developing more environmentally friendly agrochemicals [15,16].

The effect of temperature in slow pyrolysis on the yield of PCM and the different pyrolysis products and characteristics in various types of biomasses has been studied [17,18]. However, optimization of the temperature and the pyrolysis process itself is complex as it depends on the type of feedstock, composition, physicochemical properties, nature of the application, and other operational factors [18]. Specifically, studies on the production of different pyrolysis products and their behavior in the slow pyrolysis process at different temperatures have been limited to biomass from forest plantations [19].

On the other hand, in Costa Rica forest plantations supply about 78% of the wood market. The yield of marketable sawn wood from these processes is estimated at around 25% of the volume of the forest plantation, evidencing inefficient production processes and a high percentage of residues [20]. Therefore, in the renewal of the wood industry, greater importance must be given to the valorization and use of the residues from these processes, which are useful in the production and cogeneration of electrical and heat energy, production of charcoal and firewood, and organic compost, among others [21]. Therefore, the residues from these plantations can be pyrolyzed, to produce charcoal or biochar, wood vinegar, bio-oil, and non-condensable gases. In the case of biochar, the production can vary by 25–40% in slow pyrolysis [22] and is currently used in bioenergy, carbon activity, or to manage soil sustainability [23].

Main species planted in Costa Rica are *Dipteryx panamensis*, *Hieronyma alchorneoides*, and *Tectona grandis* [20,21]. The H. *alchorneoides* and *D. panamensis* species produce lumber with high density and their wood is used in structural productions [19]. In the case of *G. arborea* wood, it is used for pallet and furniture fabrication, and *Tectona grandis* is exported for international markets, flooring, and furniture fabrication. The yield of marketable sawn wood from primary sawmills is estimated to be around 25% of the volume of the forest plantation (approx. 187,500 tons per year^{-1}), highlighting inefficient production processes and a high percentage of residues, approx. 562,500 tons per year^{-1} [20]. Therefore, the renewal of the wood industry calls for increased attention to be paid to the valorization and utilization of the residues generated from these processes, which are useful in the production and cogeneration of electrical and heat energy, production of charcoal and firewood, organic compost, and other applications [21,24]. The pyrolysis of residues from these plantations can produce biochar, wood vinegar, bio-oil, and non-condensable gases [24].

Some studies evaluated the charcoal and biochar qualities of some Costa Rican tropical woods, including energy densities, energy yields, biochar characteristics, and thermal profiles, in addition to other properties [20,24–26], but when specifically studying the Costa Rican species in slow pyrolysis, *Tectona grandis* and *Gmelina arborea* lacked the same attention [27]; however, it does not refer to the effects of temperature in slow pyrolysis [28–31]. A study carried out on T. grandis by Parthasarathy and Sheeba [32] studied the yield, solid residence time, and charcoal characteristics produced at different temperatures of slow pyrolysis (300 °C, 350 °C, 450 °C, 500 °C, and 550 °C) and demonstrated that the yield of charcoal decreased, and residence time remained stable. In relation to *G. arborea* studies, it was reported that charcoal characteristics pyrolysis was carried out in a fabricated fixed bed pilot-scale reactor using sawdust biomass to produce bio-oil, but again, they presented the charcoal characteristics [33].

Considering that *Dipteryx panamensis*, *Gmelina arborea*, *Hieronyma alchorneoides*, and *Tectona grandis* are four species of commercial importance in reforestation programs, a significant quantity of residues is produced during harvesting and sawing and can be pyrolyzed to produce charcoal. However, there is a lack of information on charcoal properties obtained from slow pyrolysis. Therefore, the objective of the present study was to determine of PCM properties (physical and mechanical, ultimate, and chemical change by FTIR) and evaluate charcoal characteristics (energetic properties and thermogravimetric analysis—TGA) and biochar characteristics (conductivity, pH, initial contact angle, and wetting rates) of four wood species (*D. panamensis*, *G. arborea*, *H. alchorneoides*, and *T. grandis*) produced in a pilot-scale reactor at different temperatures (300 °C, 350 °C, 400 °C, 450 °C, and 500 °C).

2. Materials and Methods

2.1. Materials

Parent woods from four different woods (*D. panamensis*, *G. arborea*, *H. alchorneoides*, and *T. grandis*) were tested and they came from residues. *D. panamensis* and *H. alchorneoides* residues came from lumber that was dried in drying kiln, and presented a moisture content (MC) of 12% [34,35]. Lumber of *H. alchorneoides* was from a commercial plantation of 12 years of age and lumber of *D. panamensis* from a commercial plantation of 16 years of age. The information about plantation conditions of these two wood species are detailed in Moya and Tenorio [34]. *G. arborea* and *T. grandis* wood was collected from a plantation of 8 years of age [35]. Basal logs from three trees (a dimeter breast height of approximately 22 cm) from each plantation were sawn and non-commercial boards with heartwood were selected and 168 specimens of 14.0 cm × 2.5 cm × 2.0 cm (length × width × thickness) were extracted. After this, they were dried until reaching 12% MC. Subsequently, six groups of 28 samples from 160 species were separated: five groups used for PCM production with five different temperatures and one group for parent wood. The chemical and physical characteristic of parent wood can be consulted in Moya et al. [36].

2.2. Process of Carbonization and Treatment

Five target temperature were tested in each wood residue: 300 °C, 350 °C, 400 °C, 450 °C, and 500 °C. Pilot cylindrical reactor with a capacity of 3 L (12 cm in diameter and 30 cm in length) was used, according to that described by Balaguer-Benlliure et al. [19]. The reactor accommodated 14 pieces of sample wood; two batches were pyrolyzed for each temperature. The temperature was continuously measured at two points with probes: (i) inside of reactor and (ii) in gas outlet of reactor. Testo data logger, model 176/T4 (Testo SE & Co., Titisee-Neustadt, Germany), was used for recording of temperature.

After placing the 14 samples in the reactor, it was sealed and pressurized with nitrogen gas to 2 MPa, then depressurized, to create an oxygen-poor environment. Then, the reactor was heated to 12.5 °C/min until reaching 275 °C and 1.55 MPa, at which moment a valve was opened to slowly release pyrolysis gases. The target temperature was reached and maintained until no more gases were expelled. The reactor was cooled to ambient temperature. The residence time of the pyrolysis varied from 150 to 300 min according to target temperatures and this information was in Moya et al. [24].

2.3. Evaluations and Properties of Pyrogenic Carbonaceous Materials (PCMs)

The evaluation of PCMs included yield, physical properties, ultimate analysis, and chemical changes by FTIR. The properties and parameters evaluated were grouped because they are important in determining charcoal or biochar purpose.

2.3.1. Evaluation of Pyrogenic Carbonaceous Materials (PCMs) Yield

The yield of PCM was calculated according to the procedures outlined by Balaguer-Benlliure et al. [19]. Parent wood was weighed before the pyrolysis process at each temperature and PCM was weighed after cooling stage. PCM yield (charcoal or biochar) was calculated according to Equation (1).

$$Pyrogenic\ carbonaceous\ materials\ yield\ (\%) = \frac{Charcol\ or\ Biochar\ (kg)}{Parentwod\ weigth\ (kg)} * 100 \tag{1}$$

2.3.2. Physical and Mechanical Properties

PCM characteristics determined were density, MC, and compression resistance. A total of 20 charcoal specimens of 2.5 cm × 2.5 cm × 2.0 cm were extracted per temperature for density determination. After, their dimensions were measured for volume determination and were weighed too, allowing for the density to be calculated. The 20 charcoal specimens were dried until reaching constant weight in an oven at 103 °C. MC of these samples was calculated according to American Standard Testing Material (ASTM) D1762-84 Standard [37]. Compression resistance was determined in grain-parallel direction. The samples presented a dimension of 2.0 × 2.0 × 5.cm (width × thickness × length), and were tested at 0.3 mm/min load speed until rupture of sample. Compression resistance was determined in the parent woods as well using universal testing machine (Tinius Olsen, 10 kN model, Horsham, PA, USA).

2.3.3. Ultimate Analysis

Quintuplicate determination of content of C, N, H, and S was determined in 5 mg per each temperature and parent wood. These elements were measured using Elementar Analysensysteme, model Vario Macro Cube (Muchen, Germany). The determination of O content was calculated by subtracting the sum of C, H, and N content from 100. Additionally, the ratios of C/N and H/C and molar ratios of O/C and H/C were calculated [38]. Five samples per temperature/species were used for this determination.

2.3.4. FTIR Analysis

Fourier-transform infrared spectroscopy analysis (FTIR) by means of attenuated total reflection (ATR) was carried out on three samples per pyrolysis temperature and parent wood. The materials were ground and the fraction between 40 and 60 mesh selected, after drying at 105 °C to constant weight. A FTIR spectrometer (a Nicolet 380 FTIR spectrometer Thermo Scientifc, Mundelein, IL, USA) was used and configured for 32 exploration readings at 1 cm^{-1} resolution with background correction. The data were computed with Spotlight 1.5.1, HyperView 3.2, and Spectrum 6.2.0 software, developed by Perkin Elmer Inc. (Waltham, MA, USA). The vibrational bands were selected according to different studies on charcoal [39–43], as described in the following list:

- 2910 is C-H (stretching) and represents loss of hydroxyl bonds by heating;
- 2160–2170 represents CO formation due to carbonization;
- 1700 is C=O bond of hemicellulose and cellulose degradation;
- 1600 and 1630 is C=O (stretching) of the aromatic ring of lignin;
- 1434 is CH_2 and CH_3 (asymmetric charact) of aromatic nuclei in lignin, kept stable;
- 1206 is C-O (stretching) of C-O breakage;
- 1032 is C-O (stretching) and represents the bonds in acids, alcohols, phenols, ether, or ester groups;
- 1111 is C-O (stretching) and represents the bonds in acids, alcohols, phenols, ether, or ester groups;
- 900 is C-H of the out-of-plane of the aromatic ring;
- 878 is C-H of the out-of-plane glucose ring in cellulose and hemicellulose and for guaiacyl ring in lignin;
- 810 and 750 is C-H of the out-of-plane of the aromatic rings.

2.4. *Charcoal Characterization*

Characterization of the charcoals included energetic properties and thermogravimetric analysis (TGA). In addition to these, some properties associated with uses for soil amendment were assessed.

2.4.1. Energetic Properties

Energy characteristics measured were gross caloric value (GVC), ash, and volatile content. GCV was determined at 0% of moisture content according to ASTM D5865-19 standard and using Parr's calorimetric test [44]; for each material, ten samples of 300 mg per pyrolysis temperature were tested. Ash content was determined in three samples (2 g each) per material of each temperature/species, according to ASTM D3173 standard [37,45]. Three samples weighing 3 g each per temperature/species were used following the ASTM D1762 [37].

2.4.2. TGA Analysis

Thermogravimetric analyzer (TA Instruments Q500, New Castle, DE, USA) was used for TGA analysis. An inert atmosphere was provided by ultra-high purity nitrogen with glow rates of 90.0 mL min^{-1}. One sample of 5 mg of charcoal were used for each temperature and parent wood. Each analysis was developed beginning with a thermal stabilization and isothermal period at 30 °C and 10 min. The heat rate was 25 °C/min until 750 °C. TA Instruments Universal Analysis 2000 software was used in data acquired.

2.5. *Biochar Characteristics*

The charcoal was analyzed considering four parameters evaluated for agricultural applications according to Masís-Meléndez et al. [46]: electrical conductivity, pH, hydrophobicity using the initial contact angle, and wettability using wetting rate. For electrical conductivity and pH, charcoal was milled until a size of 420 µm and 250 µm, 40 and 60 mesh, respectively, and four samples of 2 g were taken temperature/species. For sample preparation, the sample was added in a 50 mL plastic flask with 30 mL of water and the mix was shaken in an orbital shaker (Hotech Instruments Corp. 720R, TPE, Taipei, Taiwan) for 1 h at 30 rpm and 25 °C. Finally, the sample was filtered.

Firstly, the pH of the filtered solution was measured using a benchtop meter (Oakton, ION 700, Environmental Express, Charleston, SC, USA). The conductivity of the solution was measured with Hanna Instruments, model HI99312 (Woonsocket, RI, USA). The sample of biochar was spread out on a double-sided adhesive tape fastened at the end of a microscope glass slide (24.4 mm × 76.2 mm) for hydrophobicity properties. Particles of biochar (size fraction < 63 μm) were pressed with a weight of 100 g onto the tape for 5 s. After, a droplet of 2 μL of water was placed on a particle of biochar and the contact angle was measured, according to Batchmann et al. [47]. The initial contact angle (θ_{initial}) was recorded every 10 s for 1200 s (20 min), using goniometer ramé-hart Model 590 (Ramé-hast instruments Co., Succasunna, NJ, USA) with DROPimage CA software (Finn Knut Hansen, OS, Norway) The wettability was determined by two contact angles measured: θ_{initial} and the contact angle at 20 min (θ_{20}). The wetting rate was calculated as the variation in the contact angle ($\theta_{20} - \theta_{\text{initial}}$) over 20 min of wetting to assess the spreading and penetration of pure water. The pH, conductivity, and wetting rate were were measured on 4 samples per treatment.

2.6. Statistical Analysis

Normality of data was confirmed, and two-way ANOVA analysis was carried out using GLM procedure of the SAS 14.1 software (SAS Institute, Campus Drive Cary, NC, USA). The effect of species and temperature on the different charcoal characteristics (density, MC, ash and volatile content, C, H, N, S, O, C/N, C/H, compression strength, conductivity, pH, and wetting rate) were tested. The statistical differences between means were determined by the Tukey test. The analysis of variance and the Tukey tests were performed with the SAS software 14.1 (SAS Institute Inc., Cary, NC, USA). Principal component multivariate analysis (PCA) was performed for the relationship between the parameters evaluated of charcoal and pyrolysis temperatures, sand two principal components were established in the cluster grouping.

3. Results and Discussion

3.1. Pyrogenic Carbonaceous Materials (PCMs) Production

The variations in yields of PCMs with temperature are presented in Table 1. The yield decreased with increasing temperature and varied from 45–55% at 300 °C to 30–35% at 500 °C. The lowest PCM percentage presented in *D. panamensis* and the other three species (*G. arborea*, *H. alchorneoides*, and *T. grandis*) presented similar values at different temperatures (Table 1). The decrease in yield with temperature can be attributed to greater production of vapors and volatile content [48,49] caused by the elimination of hydrogen and oxygen by dehydrogenation and deoxygenation processes to produce CO_2, CO, H_2, and water [50]. This behavior is consistent with other tropical wood reported by Lima et al. [51].

Table 1. Average of yield percentages of PCMs obtained for four wood residues tested in slow pyrolysis.

Species	Yield Percentages of PCMs				
	300 °C	350 °C	400 °C	450 °C	500 °C
D. panamensis	44.48	33.80	31.42	28.47	28.18
G. arborea	56.63	41.63	37.18	32.97	30.46
H. alchorneoides	50.21	48.11	35.64	32.57	33.69
T. grandis	46.74	51.00	36.56	33.78	32.47

3.2. Physical and Mechanical Properties of PCM

Values of density, MC, and compression strength were higher in parent wood than charcoal produced at different temperatures (Figure 1). In charcoal of different temperatures, no differences were found in density and compression strength, except for the density of *T. grandis* at 400 °C, 450 °C, and 500 °C and the MC of *H. alchorneoides* at 500 °C, which presented the lowest values (Figure 1a, 1c). It was observed that the MC of the charcoal produced at 400 °C and 500 °C presented higher values than the other three temperatures in all species (Figure 1b).

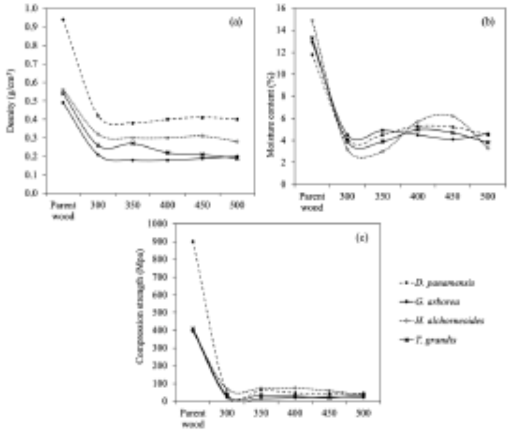

Figure 1. Variation of density (**a**), moisture content (**b**), and compression strength (**c**) for four woody biomass samples tested in slow pyrolysis. Legend: Different letters between different temperatures for same species are statistically different at 99%.

All evaluated parameters of the PCMs, and related to charcoal or biochar, were affected by species, temperature of pyrolysis, and interaction of the two factors, except initial contact angle for biochar properties (Table 1). This result shows that PCMs of the four species studied are different; however, for objective of this study, the results and discussion are focused on the relation to the temperature of pyrolysis.

According to Table 2, charcoal density pyrolyzes at low temperatures (300–350 °C) resulting, in general, in higher density values than charcoal of temperature of 400–500 °C. Moya et al. [24] attributed the higher density at 300–650 °C to incomplete pyrolysis of parent wood, leading to non-charring. Wang et al. [7] explained that parent wood using low temperatures did not completely pyrolyze the cellulose and lignin, because the decomposition of these polymers occurred between 450 and 500 °C.

On the other hand, there is positive high correlation between parent wood density and charcoal density [49]. *D. panamensis* parent wood, with the highest density, produced charcoal with a higher density, in contrast to *G. arborea* parent wood, characterized by the lowest density, which produced charcoal with a lower density (Table 2).

On the other hand, compression strength is related to density [19,49]. As expected, the species with a high density presented higher compression values.

MC ranged from 3 to 6% (Table 1), despite the limited affinity of charcoal with water [52]. This result is due to the presence of some functional groups, especially oxygen-containing groups, which present an affinity with water [52,53]. Another important observation was that the MC was different between different species and with temperature (Table 1). These results confirm that each species generally has its own pyrolysis condition with temperature, resulting in different effects on functional groups [7].

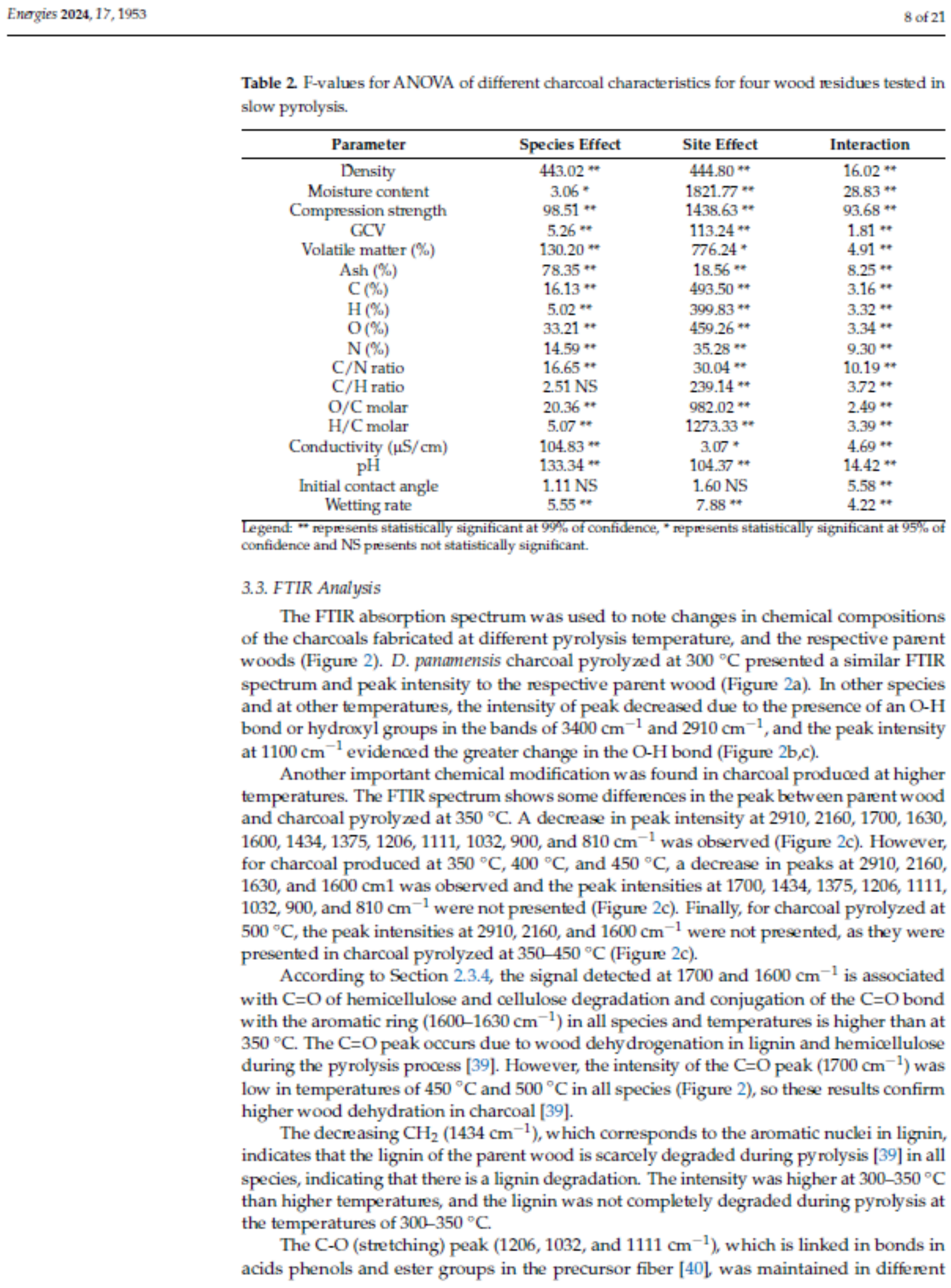

Table 2. F-values for ANOVA of different charcoal characteristics for four wood residues tested in slow pyrolysis.

Parameter	Species Effect	Site Effect	Interaction
Density	443.02 **	444.80 **	16.02 **
Moisture content	3.06 *	1821.77 **	28.83 **
Compression strength	98.51 **	1438.63 **	93.68 **
GCV	5.26 **	113.24 **	1.81 **
Volatile matter (%)	130.20 **	776.24 *	4.91 **
Ash (%)	78.35 **	18.56 **	8.25 **
C (%)	16.13 **	493.50 **	3.16 **
H (%)	5.02 **	399.83 **	3.32 **
O (%)	33.21 **	459.26 **	3.34 **
N (%)	14.59 **	35.28 **	9.30 **
C/N ratio	16.65 **	30.04 **	10.19 **
C/H ratio	2.51 NS	239.14 **	3.72 **
O/C molar	20.36 **	982.02 **	2.49 **
H/C molar	5.07 **	1273.33 **	3.39 **
Conductivity (µS/cm)	104.83 **	3.07 *	4.69 **
pH	133.34 **	104.37 **	14.42 **
Initial contact angle	1.11 NS	1.60 NS	5.58 **
Wetting rate	5.55 **	7.88 **	4.22 **

Legend: ** represents statistically significant at 99% of confidence, * represents statistically significant at 95% of confidence and NS presents not statistically significant.

3.3. FTIR Analysis

The FTIR absorption spectrum was used to note changes in chemical compositions of the charcoals fabricated at different pyrolysis temperature, and the respective parent woods (Figure 2). *D. panamensis* charcoal pyrolyzed at 300 °C presented a similar FTIR spectrum and peak intensity to the respective parent wood (Figure 2a). In other species and at other temperatures, the intensity of peak decreased due to the presence of an O-H bond or hydroxyl groups in the bands of 3400 cm^{-1} and 2910 cm^{-1}, and the peak intensity at 1100 cm^{-1} evidenced the greater change in the O-H bond (Figure 2b,c).

Another important chemical modification was found in charcoal produced at higher temperatures. The FTIR spectrum shows some differences in the peak between parent wood and charcoal pyrolyzed at 350 °C. A decrease in peak intensity at 2910, 2160, 1700, 1630, 1600, 1434, 1375, 1206, 1111, 1032, 900, and 810 cm^{-1} was observed (Figure 2c). However, for charcoal produced at 350 °C, 400 °C, and 450 °C, a decrease in peaks at 2910, 2160, 1630, and 1600 cm1 was observed and the peak intensities at 1700, 1434, 1375, 1206, 1111, 1032, 900, and 810 cm^{-1} were not presented (Figure 2c). Finally, for charcoal pyrolyzed at 500 °C, the peak intensities at 2910, 2160, and 1600 cm^{-1} were not presented, as they were presented in charcoal pyrolyzed at 350–450 °C (Figure 2c).

According to Section 2.3.4, the signal detected at 1700 and 1600 cm^{-1} is associated with C=O of hemicellulose and cellulose degradation and conjugation of the C=O bond with the aromatic ring (1600–1630 cm^{-1}) in all species and temperatures is higher than at 350 °C. The C=O peak occurs due to wood dehydrogenation in lignin and hemicellulose during the pyrolysis process [39]. However, the intensity of the C=O peak (1700 cm^{-1}) was low in temperatures of 450 °C and 500 °C in all species (Figure 2), so these results confirm higher wood dehydration in charcoal [39].

The decreasing CH$_2$ (1434 cm^{-1}), which corresponds to the aromatic nuclei in lignin, indicates that the lignin of the parent wood is scarcely degraded during pyrolysis [39] in all species, indicating that there is a lignin degradation. The intensity was higher at 300–350 °C than higher temperatures, and the lignin was not completely degraded during pyrolysis at the temperatures of 300–350 °C.

The C-O (stretching) peak (1206, 1032, and 1111 cm^{-1}), which is linked in bonds in acids phenols and ester groups in the precursor fiber [40], was maintained in different charcoals. These C-O groups are difficult to identify in carbon components because they are ascribed to acids, alcohols, phenols, ethers, and ester groups [40].

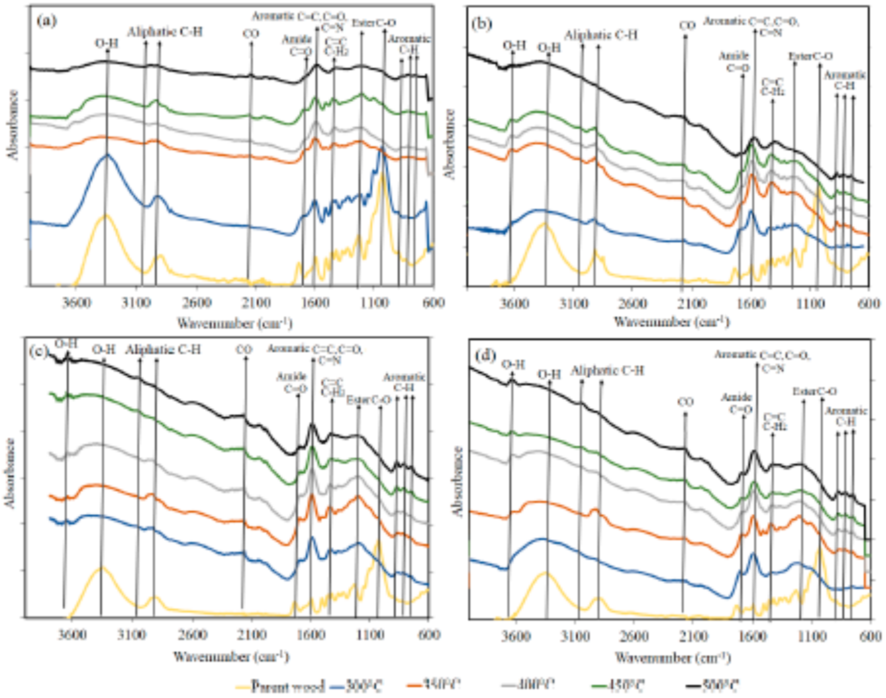

Figure 2. FTIR spectra of (**a**) *D. panamensis*, (**b**) *G. arborea*, (**c**) *H. alchorneoides*, and (**d**) *T. grandis* charcoals obtained at different pyrolysis temperatures.

Although intensity increased in the bands below 780 and 810 cm^{-1} in all species and temperatures (Figure 2), according to Section 2.3.4, there are greater changes in cellulose and lignin. The presence of these bands is attributed to complete destruction of the pyranoid rings in cellulose (band 897 cm^{-1}) [39] and complete collapse of the net structure of lignin [54], which originates in the skeletal vibration, as well as the change in the relative intensity of trio-bands at these intensities.

In all four cases, the O-H simple bond peak near 3400 cm^{-1} diminished with increasing pyrolysis temperatures, revealing a loss of the hydroxyl function during pyrolysis, which would, in turn, imply dehydration with ensuing loss of aliphatic -H. A similar trend occurred regarding the aliphatic C-H at 2900 cm^{-1}, signaling the loss of simple C-C bonds. Concomitantly, the vibrations at 1400 cm^{-1} and 1600 cm^{-1} related to C=C double bonds increasing in importance with pyrolysis temperatures. These trends confirm a gain in aromaticity and concomitant loss of other functions, with increasing pyrolysis temperatures, as discussed by Sahoo et al. [17].

In summary, according to below results, FTIR spectrum analysis shows important changes in the structure linked to the groups OH, CH_2, C=O, C-O-C, and other less important groups such as CH_3. Basically, at low temperatures (300–350 °C), the changes associated with lignin and cellulose still present in groups associated with the oxygen (OH, C=O, and C-O-C) of cellulose and aromatic rings of lignin (CH_2), which demonstrates the lack of pyrolysis of the parent wood. Nevertheless, the high temperatures and the pyrolysis completely transformed the parent woods, as revealed by the peak intensity decreases.

3.4. Energy and Chemical Properties

The parent woods presented the statistically highest values of volatile matter, H, O, and C/N and the statistically lowest values of GCV, ash content, C, N, and C/H, (Table 3). For GCV, the highest values were observed in the temperatures of 400 °C, 450 °C, and 500 °C, and no differences were observed between these temperatures (Table 3), and the charcoal from temperatures of 300 °C and 350 °C presented similar values of GCV (Table 3). The volatile matter and H and O of charcoal from temperatures of 300–350 °C have the highest values in most species, while the charcoal at 450 °C and 500 °C show the statistically lowest values. Ash and C content at 400 °C, 450 °C, and 500 °C presented the highest values, while the lowest values were presented at 300 °C and 350 °C in general for all four species (Table 3). No statistical differences were observed in N content of charcoal of *G. arborea*, while charcoal produced from *D. panamensis* and *T. grandis* presented the highest of N content at 300 °C. N content in *H. alchorneoides* was different at all temperatures tested (Table 3). The C/N ratio for *D. panamensis* and *G. arborea* was statistically similar at all temperatures, but charcoal produced from *H. alchorneoides* and *T. grandis* at different temperatures showed some differences at 300 °C and 350 °C (Table 3). Finally, C/H ratio presented the lowest values at temperatures of 300 °C and 350 °C and the highest values were found in temperatures of 400–500 °C in all species (Table 3).

Energy properties evaluated reflected the variety in the species tested and variety in target temperature (Table 3). When GCV values in charcoal exceed 28–30 MJ/kg, those are considered appropriate pyrolysis conditions [52]; therefore, the temperatures of 450 °C and 500 °C can be interpreted as the optimum temperature levels. On the contrary, the temperatures of 300–350 °C produce charcoal with GCV lower than 28–30 MJ/kg, showing that these temperatures are not adequate for charcoal production. The determination of volatile matter confirms that the low pyrolysis temperature (300–350 °C) is not recommended, as this parameter presents the highest values in most species, while the charcoal produced at 450 °C and 500 °C shows the statistically lowest values.

Ash is formed by inorganic matter and in small percentages by organic matter, and the variation in the structural components and inorganic constituents is due to the pyrolysis temperature and intrinsic chemical composition of a species [7,55]. According to Table 3, a higher ash content is found at the higher temperatures. A high percentage of ash is not desirable for energy purposes, but it can be beneficial if the ash is used as biochar, due to the high content and variety of macro- and micro-elements [55]; therefore, ash from high pyrolysis temperatures can be convenient for its higher ash content.

The variation in chemical composition shows the effect of temperature of pyrolysis. As expected, carbon content increased with temperature, but O and H content decreased; therefore, C/H increased with increasing pyrolysis temperatures and O/C molar and H/C molar decreased with temperature (Table 3). Sahoo et al. [17] mentioned that these chemical changes with temperature occurred by improvement in the carbonization and aromatization processes, meaning that the O/C and H/C ratios decreased, as presented in this study (Table 3). In addition, the chemical changes of C, H, and O produced changes in O/C molar and H/C molar ratios [55], as was observed in the present study (Table 3).

The van Krevelen diagram presents the importance of H and O ratio on GVC (Figure 3. The parent wood is similar to different types of biomasses, but during pyrolysis, the wood produces physicochemical changes in C, H, N, and O content (Table 3), which can be observed in the different feedstocks of energy present in the van Krevelen diagram. First, the pyrolysis temperature increase produces a decrease in H/C and O/C ratios, then the charcoal is closer to lignite and coal according to the van Krevelen diagram. Second, for the lowest temperature (300–350 °C), although charcoal of these temperatures is closer to coal, it is also closer to lignite, but charcoal produced at 450–500 °C appears closer to anthracite (Figure 3). This diagram confirms that higher temperatures are better for energy purposes.

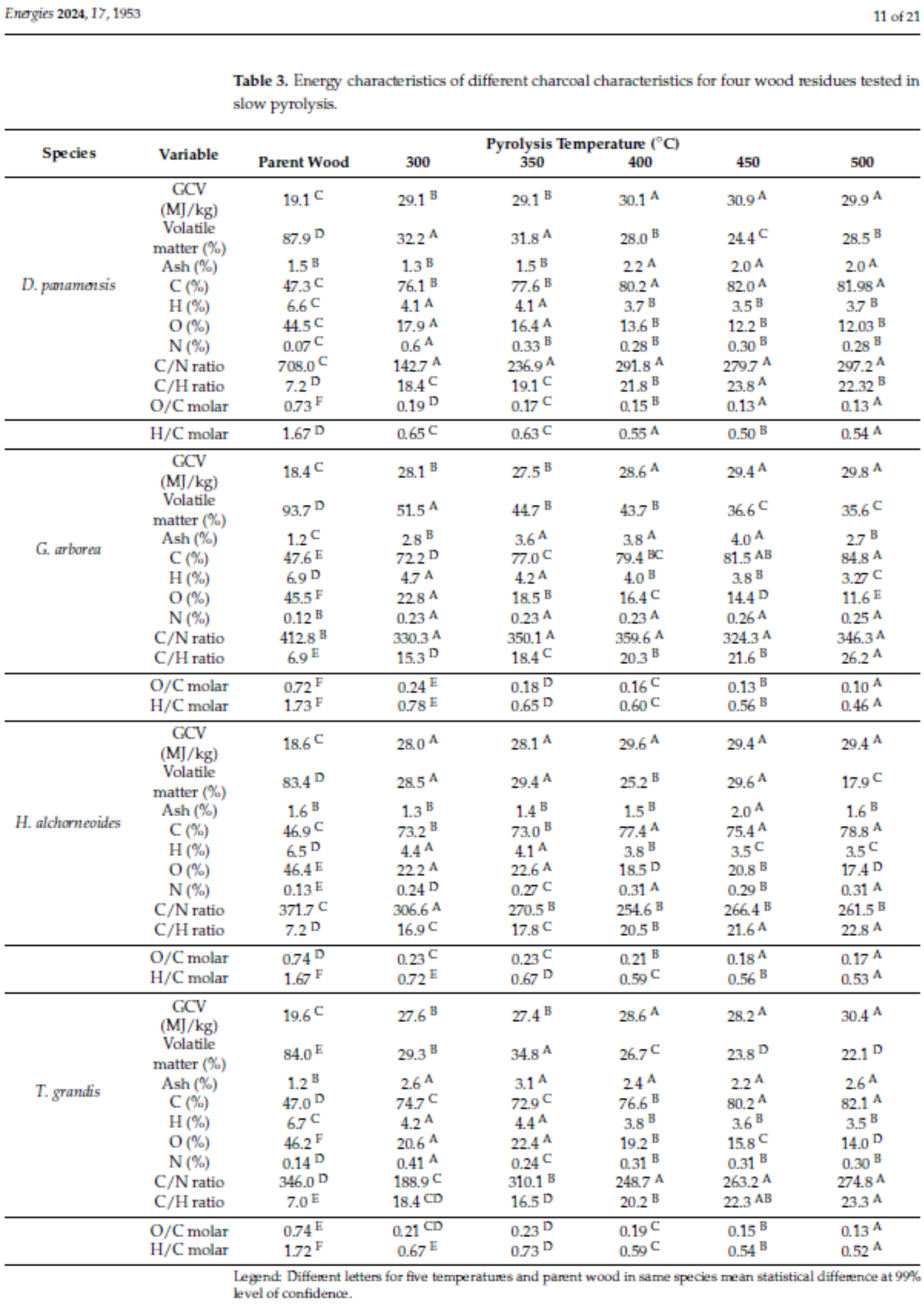

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Table 3. Energy characteristics of different charcoal characteristics for four wood residues tested in slow pyrolysis.

Species	Variable			Pyrolysis Temperature (°C)			
		Parent Wood	300	350	400	450	500
D. panamensis	GCV (MJ/kg)	19.1^{C}	29.1^{B}	29.1^{B}	30.1^{A}	30.9^{A}	29.9^{A}
	Volatile matter (%)	87.9^{D}	32.2^{A}	31.8^{A}	28.0^{B}	24.4^{C}	28.5^{B}
	Ash (%)	1.5^{B}	1.3^{B}	1.5^{B}	2.2^{A}	2.0^{A}	2.0^{A}
	C (%)	47.3^{C}	76.1^{B}	77.6^{B}	80.2^{A}	82.0^{A}	81.98^{A}
	H (%)	6.6^{C}	4.1^{A}	4.1^{A}	3.7^{B}	3.5^{B}	3.7^{B}
	O (%)	44.5^{C}	17.9^{A}	16.4^{A}	13.6^{B}	12.2^{B}	12.03^{B}
	N (%)	0.07^{C}	0.6^{A}	0.33^{B}	0.28^{B}	0.30^{B}	0.28^{B}
	C/N ratio	708.0^{C}	142.7^{A}	236.9^{A}	291.8^{A}	279.7^{A}	297.2^{A}
	C/H ratio	7.2^{D}	18.4^{C}	19.1^{C}	21.8^{B}	23.8^{A}	22.32^{B}
	O/C molar	0.73^{F}	0.19^{D}	0.17^{C}	0.15^{B}	0.13^{A}	0.13^{A}
	H/C molar	1.67^{D}	0.65^{C}	0.63^{C}	0.55^{A}	0.50^{B}	0.54^{A}
G. arborea	GCV (MJ/kg)	18.4^{C}	28.1^{B}	27.5^{B}	28.6^{A}	29.4^{A}	29.8^{A}
	Volatile matter (%)	93.7^{D}	51.5^{A}	44.7^{B}	43.7^{B}	36.6^{C}	35.6^{C}
	Ash (%)	1.2^{C}	2.8^{B}	3.6^{A}	3.8^{A}	4.0^{A}	2.7^{B}
	C (%)	47.6^{E}	72.2^{D}	77.0^{C}	79.4^{BC}	81.5^{AB}	84.8^{A}
	H (%)	6.9^{D}	4.7^{A}	4.2^{A}	4.0^{B}	3.8^{B}	3.27^{C}
	O (%)	45.5^{F}	22.8^{A}	18.5^{B}	16.4^{C}	14.4^{D}	11.6^{E}
	N (%)	0.12^{B}	0.23^{A}	0.23^{A}	0.23^{A}	0.26^{A}	0.25^{A}
	C/N ratio	412.8^{B}	330.3^{A}	350.1^{A}	359.6^{A}	324.3^{A}	346.3^{A}
	C/H ratio	6.9^{E}	15.3^{D}	18.4^{C}	20.3^{B}	21.6^{B}	26.2^{A}
	O/C molar	0.72^{F}	0.24^{E}	0.18^{D}	0.16^{C}	0.13^{B}	0.10^{A}
	H/C molar	1.73^{F}	0.78^{E}	0.65^{D}	0.60^{C}	0.56^{B}	0.46^{A}
H. alchorneoides	GCV (MJ/kg)	18.6^{C}	28.0^{A}	28.1^{A}	29.6^{A}	29.4^{A}	29.4^{A}
	Volatile matter (%)	83.4^{D}	28.5^{A}	29.4^{A}	25.2^{B}	29.6^{A}	17.9^{C}
	Ash (%)	1.6^{B}	1.3^{B}	1.4^{B}	1.5^{B}	2.0^{A}	1.6^{B}
	C (%)	46.9^{C}	73.2^{B}	73.0^{B}	77.4^{A}	75.4^{A}	78.8^{A}
	H (%)	6.5^{D}	4.4^{A}	4.1^{A}	3.8^{B}	3.5^{C}	3.5^{C}
	O (%)	46.4^{E}	22.2^{A}	22.6^{A}	18.5^{D}	20.8^{B}	17.4^{D}
	N (%)	0.13^{E}	0.24^{D}	0.27^{C}	0.31^{A}	0.29^{B}	0.31^{A}
	C/N ratio	371.7^{C}	306.6^{A}	270.5^{B}	254.6^{B}	266.4^{B}	261.5^{B}
	C/H ratio	7.2^{D}	16.9^{C}	17.8^{C}	20.5^{B}	21.6^{A}	22.8^{A}
	O/C molar	0.74^{D}	0.23^{C}	0.23^{C}	0.21^{B}	0.18^{A}	0.17^{A}
	H/C molar	1.67^{F}	0.72^{E}	0.67^{D}	0.59^{C}	0.56^{B}	0.53^{A}
T. grandis	GCV (MJ/kg)	19.6^{C}	27.6^{B}	27.4^{B}	28.6^{A}	28.2^{A}	30.4^{A}
	Volatile matter (%)	84.0^{E}	29.3^{B}	34.8^{A}	26.7^{C}	23.8^{D}	22.1^{D}
	Ash (%)	1.2^{B}	2.6^{A}	3.1^{A}	2.4^{A}	2.2^{A}	2.6^{A}
	C (%)	47.0^{D}	74.7^{C}	72.9^{C}	76.6^{B}	80.2^{A}	82.1^{A}
	H (%)	6.7^{C}	4.2^{A}	4.4^{A}	3.8^{B}	3.6^{B}	3.5^{B}
	O (%)	46.2^{F}	20.6^{A}	22.4^{A}	19.2^{B}	15.8^{C}	14.0^{D}
	N (%)	0.14^{D}	0.41^{A}	0.24^{C}	0.31^{B}	0.31^{B}	0.30^{B}
	C/N ratio	346.0^{D}	188.9^{C}	310.1^{B}	248.7^{A}	263.2^{A}	274.8^{A}
	C/H ratio	7.0^{E}	18.4^{CD}	16.5^{D}	20.2^{B}	22.3^{AB}	23.3^{A}
	O/C molar	0.74^{E}	0.21^{CD}	0.23^{D}	0.19^{C}	0.15^{B}	0.13^{A}
	H/C molar	1.72^{F}	0.67^{E}	0.73^{D}	0.59^{C}	0.54^{B}	0.52^{A}

Legend: Different letters for five temperatures and parent wood in same species mean statistical difference at 99% level of confidence.

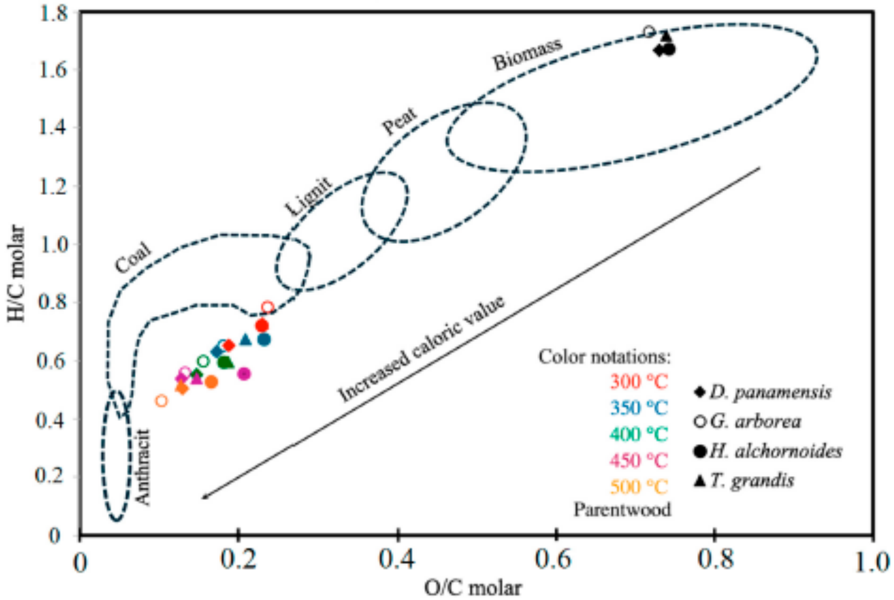

Figure 3. Van Krevelen of different charcoal characteristics for four wood residues tested in slow pyrolysis.

3.5. Thermogravimetric Analysis

The DTG/TG diagram for parent wood and charcoals produced at different pyrolysis temperatures is presented in Figure 4. DTG (Figure 4a,c,e,g) and TG (Figure 4b,d,f,h) for charcoal show the complete transformation of parent wood to charcoal. The maximum decomposition rates occurred between 150 °C to 480 °C, with a shoulder at 325 °C and a light increment after 415 °C; these decomposition temperatures are evidence of the decomposition of cellulose, hemicellulose, and lignin, respectively [56]. When they appear in the charcoal thermograms, they show that these components of the parent wood had not been completely pyrolyzed. For the parent woods, remanent mass was around 20%; in the charcoals, remanent mass was over 60% (Figure 4b,d,f,h). For charcoals, two stages were observed: (i) from 25 °C to 130 °C, where the charcoals dehydrated [57] and other low molecular substances were removed from the surface [56]. The weight loss was approximately 3–6% for the charcoals (Figure 4b,d,f,h), in agreement with values reported in Table 2 for MC; and (ii) from 150 °C and 730 °C, the DTG/TG curves of the charcoals present some differences and trends: the maximum decomposition peak (Tmax) is displaced to higher temperatures with increasing pyrolysis temperatures (Figure 4a,c,e,g). Thus, the charcoal produced presented a Tmax at 517 °C, 575 °C, 620 °C, 620 °C, and 630 °C, for 300 °C, 350 °C, 400 °C, 450 °C, and 500 °C, respectively (Figure 4a).

(i) Remanent mass increased with increasing pyrolysis temperatures (Figure 4b,d,f,h);
(ii) Shoulders at 250 °C and 375 °C were observed in charcoal produced from *D. panamensis* (Figure 4a), *G. arborea* (Figure 4c), and *H. alchorneoides* (Figure 4e) obtained at 300 and 350 °C, signaling incomplete carbonization and, thus, evidencing the presence of celluloses, hemicellulose, and lignin in unchanged wood components [56];
(iii) A small peak appeared near 700 °C in the DTG of *D. panamensis*, *G. arborea*, and *H. alchorneoides*, and was particularly visible in the charcoals obtained at 450 and 500 °C (Figure 4a,c,e).

Charcoal decomposition or maximum devolatilization rate occurs between 200 °C and 750 °C, where functional groups of low thermal stability, such as carboxyl, carbonyl, and aliphatic hydrocarbon groups, are removed [56,58]. The maximum devolatilization rate is observed between 450 °C and 550 °C for different species, which is evidence of the formation of the aromatic ring and the splitting of more resistant side groups [39]. Tmax varies with pyrolysis temperature and species (Figure 4a,c,e,g), and this parameter increases in *D. panamensis* (Figure 4a) and *H. alchorneoides* (Figure 4e) between 300 °C and 400 °C; meanwhile, the maximum devolatilization rate (peak height) decreases with pyrolysis temperature. The charcoals obtained at 450 °C and 500 °C, in turn, present similar temperature and maximum devolatilization rates for the two species (Figure 4a,e). The DTG curves of *G. arborea* show similar Tmax values for charcoals produced between 300 °C and 450 °C, while the maximum devolatilization rate decreases with pyrolysis temperature (Figure 4c). The Tmax of the 500 °C *G. arborea* charcoal reveals a distinctive devolatilization peak in the vicinity of 650 °C (Figure 4c). Exceptionally, the *T. grandis* charcoals show a Tmax average of 625 °C, and the maximum devolatilization rates decrease with pyrolysis temperature, as in the other cases (Figure 4g).

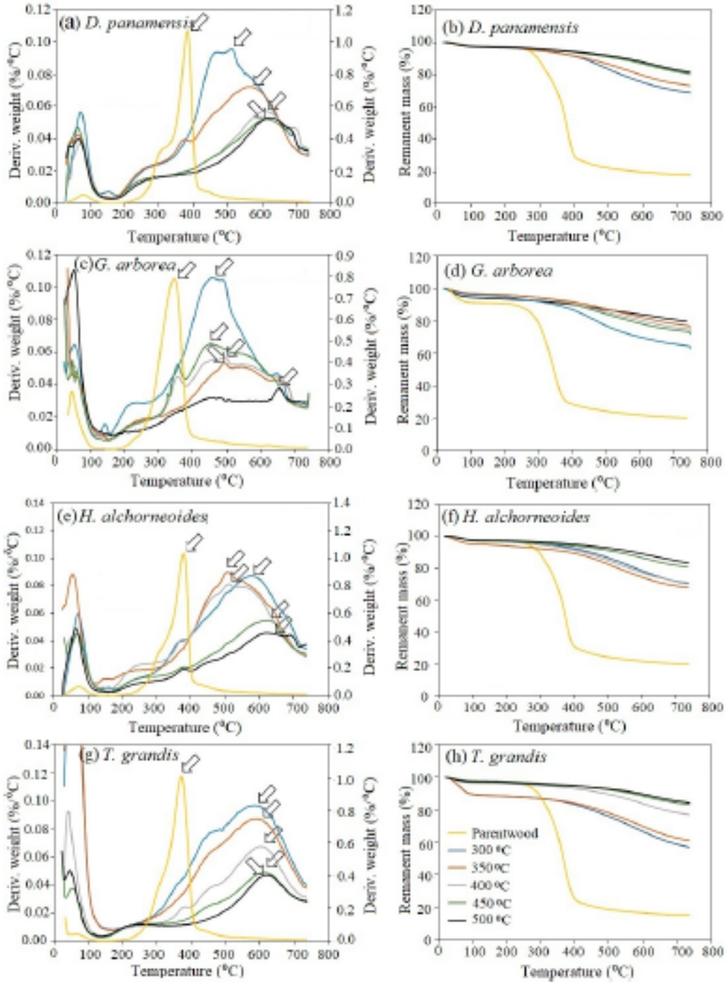

Figure 4. TGA/DTG curves of different charcoal characteristics for four wood residues tested in slow pyrolysis. Legend: Arrows show Tmax.

When comparing among the species, it becomes evident that *T. grandis* charcoals maintained a similar Tmax, while the other charcoals presented Tmax values varying between 475 °C and 630 °C. The increase in Tmax in charcoal was attributed to the fact that this charcoal produced at low temperature was relatively unreactive. Remarkable weight losses did not occur when the temperature reached 340 °C, meaning that char formation began at a higher temperature. The peaks in the devolatilization rates at these temperatures produced fixed carbon in the DTG curves and volatile matter occurred before the maximum devolatilization rate, between 100 °C and 340 °C. Thus, considering this aspect, for *D. panamensis* (Figure 4a), *H. alchorneoides* (Figure 4e), and *T. grandis* (Figure 4g), combustion of volatile matter that remains in the coal occurs mainly at temperatures from 300 °C and 400 °C, but combustion of fixed carbon occurs at temperatures between 450 °C and 550 °C.

3.6. Biochar Properties

In the evaluation of charcoal as biochar, higher conductivity was found in *G. arborea* and *D. panamensis*, but charcoal of *H. alchorneoides* and *T. grandis* presented the lowest values (Table 4). However, some differences can be found according to different temperatures of pyrolysis: (i) the conductivity was higher in charcoal of *G. arborea* produced between 300 °C and 400 °C, followed by *D. panamensis* and *H. alchorneoides* charcoal, and the lowest value of conductivity was observed in biochar of *T. grandis*. But when biochar was produced between 450 °C and 500 °C, conductivity values were different between species: the highest values were in charcoal of *D. panamensis*, and the lowest values were found in biochar of *H. alchorneoides* (Table 4).

Table 4. Electrical conductivity and pH of different biochar characteristics for four wood residues tested in slow pyrolysis.

Species	Variable	Pyrolysis Temperature (°C)				
		300	350	400	450	500
D. panamensis	Conductivity (μS/cm)	237.3^{A}	240.3^{A}	337.3^{A}	319.3^{A}	297.3^{A}
	pH	6.5^{B}	6.8^{B}	7.7^{A}	7.8^{A}	7.7^{A}
G. arborea	Conductivity (μS/cm)	286.3^{A}	308.3^{A}	299.0^{A}	163.5^{B}	291.0^{A}
	pH	6.2^{B}	9.53^{A}	9.42^{A}	8.69^{A}	9.03^{A}
H. alchorneoides	Conductivity (μS/cm)	106.8^{A}	104.0^{A}	85.0^{B}	51.0^{C}	61.0^{C}
	pH	5.7^{CD}	5.2^{D}	6.6^{BC}	7.6^{AB}	7.6^{A}
T. grandis	Conductivity (μS/cm)	107.0^{A}	91.3^{B}	71.3^{D}	73.3^{D}	71.3^{D}
	pH	5.3^{D}	5.7^{D}	6.4^{BC}	7.0^{AB}	7.6^{A}

Legend: Different letters for five temperatures and parent wood in same species mean statistical difference at 99% level of confidence.

Conductivity is a measure of the amount of salts in biochar solution and based on the principle that a solution with a higher concentration of salts has a greater ability to conduct an electrical current [59].

Therefore, when charcoal is applied in soil, for a biochar propose, with high rates of conductivity, this may adversely affect salt-sensitive plants [60] and can reduce seed germination and crop yields [61]. Therefore, biochar produced with *D. panamensis* and *G. arborea* must be managed or applied in different forms or proportions in soil than the biochar of *H. alchorneoides* and *T. grandis*.

The conductivity varied with temperatures for all species. No differences were observed among temperature in the charcoal of *D. panamensis*; the lowest conductivity was presented in biochar of *G. arborea* at a temperature of 450 °C and no differences were found in other temperatures (Table 4). *H. alchorneoides* and *T. grandis* biochar presented the highest conductivity values for temperatures of 300–350 °C, and the lowest values were observed in biochar at 450 °C and 500 °C (Table 4).

The variation in conductivity depending on species and temperature agree with the reviews presented by Singh et al. [59] and Paz-Ferreiro et al. [61], which report that this parameter is related to feedstock and temperature. However, the tendency found in our results disagrees with Singh et al. [59]. They mention that higher temperatures generally have higher conductivity values, however, our results show that the lowest values are found in the highest temperatures, or no differences were found in some species such as *D. panamensis*. Biochar conductivity is related to ash content and pH [59], chemical characteristics of parent wood [62], macro- or micro-nutrients such as potassium [61], and other factors. According to these results, the biochar from each species at each temperature must be applied in relation to its conductivity. The parent wood used presented wide variations in chemical properties [36], which can affect the biochar conductivity produced at different temperatures and other chemical properties, such as macro- or micro-nutrients, which were not measured in the present study.

In relation to pH values, biochar of *G. arborea* presented the highest values of pH, except for at the temperature of 300 °C. The biochar of *D. panamensis* presented pH values lower than *G. arborea* biochar and higher that *H. alchorneoides* and *T. grandis* biochar, which presented the lowest values observed (Table 4). The pH of biochar will positively influence soil pH [63], though its liming effect on soil will vanish over time as soil acidification is a spontaneous process, especially in the tropics. Although biochar from the other three species (*D. panamensis, T. grandis,* and *H. alchorneoides*) can be applied according to pyrolysis temperature, biochar from lower pyrolysis temperatures (300–350 °C) could increase soil acidity due to having a lower potential liming effect and to their liability to progressively decompose in the soil, increasing soil acidity. Meanwhile, biochar produced at the higher temperatures (400 °C to 500 °C) cannot affect adversely soil acidity, since the pH values are close to the ideal pH range for soils, which is from 6.0 to 6.5.

The variation in pH values with temperature in the different species studied (Table 4) is attributed to different decomposition processes of biomass with temperature [64]. Specifically, it was observed that pH values of different species sampled increased with temperature (Table 4). Ding et al. [65] mentioned that pH values were positively correlated with temperature from 300 °C to 600 °C; thereafter, pH became constant [66]. In general, it was established that pH was associated with inorganic alkalis content and the formation of carbonates, and these components increased with pyrolysis temperature [65]; in addition, higher temperatures favor functional groups and ash content [67]. For the polymer decomposition of wood with increasing temperature, acidic functional groups (-COOH) and appearance of basic functional groups are removed during pyrolysis [68] and the increasing temperature occurs due to the separation of the organic matrix, mainly alkali salts [65].

Initial contact angle is a parameter used to predict the biochar hydrophobicity; higher values of this angle means that biochar is hydrophobic [69], meaning that its surface energy is lower, therefore, the biochar has less attraction to water at the beginning of water exposure. The results found in the study show that low pyrolysis temperatures (300–350 °C) produced the highest initial contact angle (114–117°) for *T. grandis* and *H. alchorneoides* biochar. Meanwhile, biochar of *D. panamensis* presented the lowest values (112–113°) and biochar of *G. arborea* presented intermediate values (112–114°, Figure 5a). On the contrary, for biochar produced at 400 °C and 500 °C, it was found that charcoal of *T. grandis* presented the highest values (119–121°), followed by the biochar of *H. alchorneoides* and *D. panamensis* (117–119°) and the biochar of *G. arborea* presented the lowest values of initial contact angle (114–116°).

The relationship between water and biochar can be understood using different properties, and wettability is one of them [69]. Water rate was the highest in *D. panamensis* biochar at the five pyrolysis temperatures evaluated, while the other three species presented similar values at all pyrolysis temperatures, especially above 400 °C (Figure 5b). The variation in wetting rate was different in each species: this value increased with temperature in *D. panamensis* and *H. alchorneoides* biochar, but the variation was different in *T. grandis* and *G. arborea* biochar, with increasing wetting rate values from 300 °C to 350 °C and from

450 °C and 500 °C; no variation was observed between 350 °C and 450 °C (Figure 5b). Thus, according to these results, the biochar of *D. panamensis* presented lower hydrophobicity than those of other species across time, meaning this biochar could take up water faster than those of *H. alchorneoides*, *G. arborea*, and *T. grandis*, though they showed similar water absorption rates.

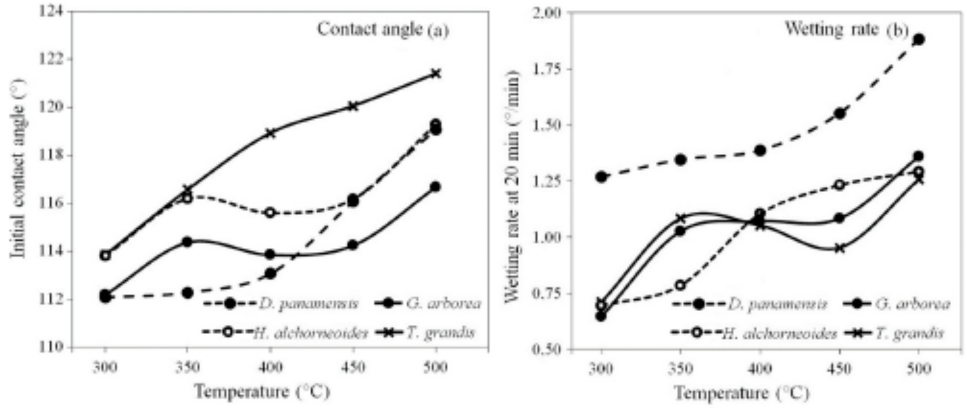

Figure 5. Initial contact angle (**a**) and wetting rate at 20 min (**b**) of different biochar characteristics for four wood residues tested in slow pyrolysis.

Figure 5 shows similar trends for all wood species; generally, higher hydrophobicity and wetting rate is observed with higher temperature. According to Rasa et al. [70], the relationship between biochar and water is a very complex phenomenon, and when the presence of aliphatic functional groups (C-H) is greater, the biochar is more hydrophobic; however, they also mention that biochar produced at temperatures lower than 500 °C present lower surface area values, lower presence of aliphatic functional groups, and increased porosity, thereby enhancing wettability of biochar [71], measured in this study by wetting rate. Besides this relationship between biochar and water, each species presents a different decomposition process of biomass with temperature during pyrolysis [68], which affects the aliphatic functional groups, with a lower presence of aliphatic groups at higher pyrolysis temperatures. This would lead to a variation in the initial contact angle or hydrophobicity and wetting rate of each species studied. Sahoo et al. [17] mentioned that increasing temperature produces an enhancement in carbonization, the aromatization process, and a decremental nature of O/C and (N + O)/ration ratios; then, biochar becomes more hydrophobic and non-polar, and there is a hydrophobicity that increases with temperature, as observed in the species studied (Figure 5a). Nevertheless, increased porosity increased wetting rate [69], as observed in the present study (Figure 5b).

3.7. Multivariate Analysis

Multivariate principal components analysis shows that the first two components explain the variability in 62.0%: 39.0% and 26.0% for principal component 1 (CP-1) and 2 (CP-2), respectively (Table 5). CP-1 was related to GCV, C, H, and O content, C/H ratio, and pH and wetting rate (Table 5). CP-2 was only related to charcoal density for physical properties, volatility and ash content for charcoal characteristics, and C/N for chemical characteristics (Table 5). Scatterplots of principal component 1 and principal component 2 show that three different groups formed (Figure 6):

- The first group groups charcoal of *H. alchorneoides* and *T. grandis* pyrolyzed at 300 °C and 350 °C (low temperatures) and that of *D. panamensis* of pyrolysis temperature 300 °C. This group is associated with pH and C/N ratio;

- The second group is formed by all the charcoals of *G. arborea*, and is associated with O and H content, C/H ratio, MC, and GCV;
- The third group includes the charcoals of *H. alchorneoides*, *T. grandis*, and *D. panamensis* pyrolyzed at 350 °C to 500 °C; it is associated with contact angle, wetting rate, ash, N and C content, compression force, conductivity, volatility, and density.

Table 5. Statistical parameters of CP-1 and CP-2 and their correlations with different characteristics measured in charcoal of four tropical wood from plantations.

Parameters	**Variable**	**CP-1**	**CP-2**
Statistical parameters of principal components	Eigenvalue	6.06	4.47
	% Total of variance	36.0	26.0
	Total cumulative	36.0	62.0
Correlations of characteristics measured and principal components			
Variables	Parameters	CP1	CP2
Physical and mechanical properties	Density	−0.01	−0.77 *
	Moisture content	0.37	0.01
	Compression strength	−0.27	−0.65
Charcoal characteristics	GCV	0.80 **	−0.38
	Volatility	−0.31	0.77 *
	Ash (%)	0.18	0.86 **
Chemical characteristics	N	−0.15	−0.68
	C	0.96 **	0.02
	H	0.89 **	0.27
	S	−0.09	−0.47
	O (%)	0.95 **	−0.03
	C/N ratio	0.26	0.83 **
	C/H ratio	0.95 **	−0.15
Biochar characteristics	pH	0.76 *	0.50
	Conductivity	0.31	0.37
	Initial contact angle	0.47	−0.12
	Wetting rate	0.77 *	−0.34

Legend: ** Denotes significance of *p*-value < 0.01 and * denotes significance of *p*-value < 0.05.

The analysis by principal components confirms important observations that were annotated individually in the variables analyzed previously. In general, it was observed that the lowest temperatures (300 °C and 350 °C) of *T. grandis* and *H. alchorneoides* and the pyrolysis temperature of 300 °C for *D. panamensis* grouped together, indicating that, probably, these conditions are not adequate for pyrolysis, considering that these temperatures present higher values of density, moisture content, compression strength, volatile matter, and H and O content, and lower higher values of C and ash content, conductivity, initial contact angle, and wetting rate and lower pH. In addition, FTIR and TGA show that celluloses and lignin were not completely decomposed at temperature of 300 °C to 350 °C. A second important observation is that the five different charcoals of *G. arborea* were grouped in one cluster, different from the cluster formed by *D. panamensis*, *H. alchorneoides*, and *T. grandis* (Figure 6), and this variation is associated with differences in O and H content, C/H ratio, MC, and GCV. Finally, charcoals produced from *D. panamensis*, *T. grandis*, and *H. alchorneoides* at 400–500 °C were grouped into one cluster, probably indicating that as the best temperature range for pyrolysis of these species.

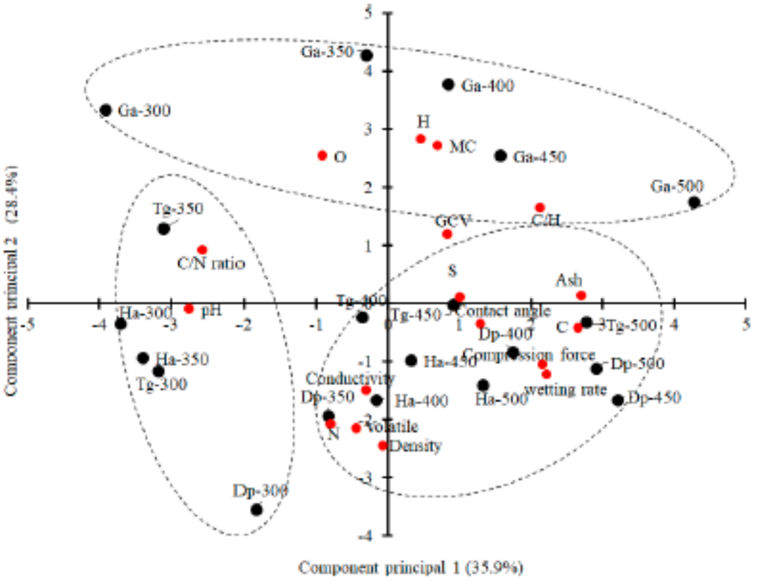

Figure 6. Relationships between principal component 1 and 2 for different biochar characteristics for four wood residues tested in slow pyrolysis. Legend: names of variables are detailed in Table 5.

4. Conclusions

According to the results obtained in the evaluation of properties of pyrogenic carbonaceous materials (PCMs) from four different tropical wood species obtained at five different temperatures, each species*temperature combination had its different effects according to PCM propose. Firstly, each species produced PCM characteristics related to intrinsic proprieties of biomass, and, second, temperatures of 300 °C and 350 °C are not recommended due to the presence of uncharred areas, as demonstrated by FTIR and TGA analysis; besides that, these charcoals present higher values of density, moisture content, compression strength, volatile matter, and H and O content, and lower values of C and ash content, conductivity, pH, initial contact angle, and wetting rate. The charcoals produced between 400–500 °C had contrasting characteristics compared to 300 °C and 350 °C across all species, so that the higher temperatures (400–500 °C) presented better conditions in slow pyrolysis of the species studied. Multivariate analysis confirms that charcoals obtained at the lowest temperatures (300–350 °C) from *D. panamensis*, *Hieronyma alchorneoides*, and *T. grandis* were separated from those obtained at other temperatures, indicating that, probably, (i) these conditions were not adequate for pyrolysis, (ii) the five different pyrolysis attempts of *G. arborea* were grouped in a cluster apart from the other species, with different charcoal/biochar properties, and (iii) the charcoal/biochar produced from *D. panamensis*, *H. alchorneoides*, and *T. grandis* at 400–500 °C were grouped into one cluster, probably indicating that to be the best temperature range for pyrolysis of those species.

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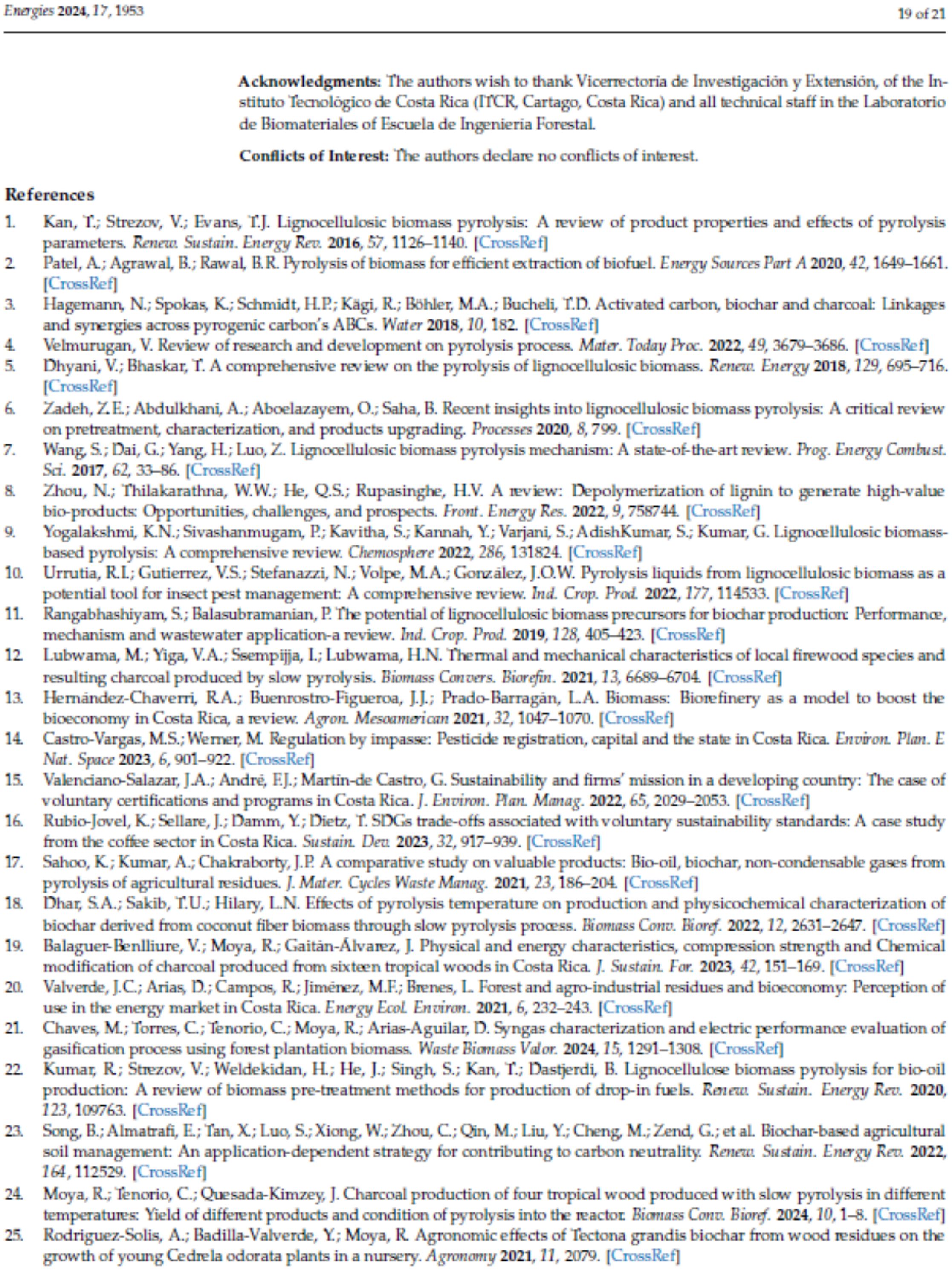

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Artículo 3: Effect of shape of residues of *Gmelina arborea* wood on yields and process of slow pyrolysis using a semi-industrial reactor prototype.

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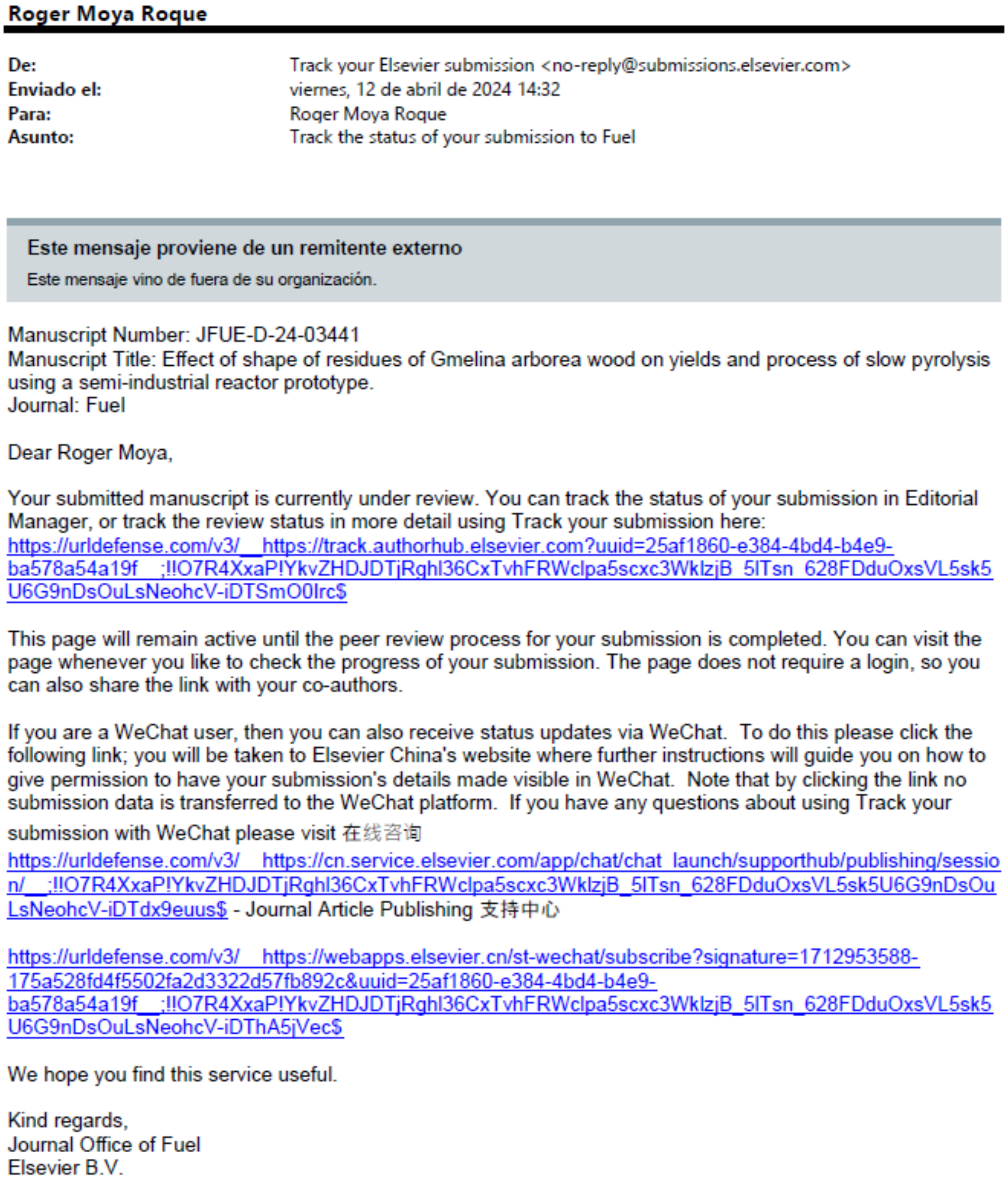

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Effect of shape of residues of *Gmelina arborea* wood on yields and process of slow pyrolysis using a semi-industrial reactor prototype.

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Abstract

Pyrolysis of biomass residues can generate savings in the value chains of forest products due to the potential uses of its products in the forestry sector. The aim of this study was to know performance during slow pyrolysis process and their yields of different products (charcoal, wood vinegar, bio-oil, and non-condensable gases) of two shape of residues, wood chips and solid wood board-ends from *Gmelina arborea* wood, in a small-scale prototype of a semi-industrial reactor. Results showed that using board-ends, the parentwood presented the lowest moisture content (10.2%) and the reactor has the highest volume capacity. Furthermore, this residue reached the highest temperature during pyrolysis (262.4 °C) and the shortest pyrolysis time (93 min), requiring less energy consumption. Besides, the results showed no significant differences in yields of charcoal, wood vinegar and non-condensable gases. However, bio-oil yield was higher for the solid wood board-ends residues (7.7%). Then, results suggest that shape of parentwood provided similar charcoal, condensable and non-condensable gases yields, but solid board-ends are recommended to obtain higher yield of bio-oil and complete the process in less time.

Keywords: pyrolysis; biochar; pyroligneous acids; wood tar; wood vinegar

1. Introduction

Biomass pyrolysis is the thermal degradation of biomass in absence of oxygen and is one of the most common thermochemical biomass conversion processes for energy production (Velmurugan, 2022, Tan *et al.*, 2021). Biomass decomposition occurs at elevated temperatures (400 – 900 ºC) by breaking down the long-chain hydrocarbons in the wood biopolymers (Tan *et al.*, 2021; Dhyani & Bhaskar, 2018). Pyrolysis can be categorized as slow pyrolysis or fast pyrolysis based on the heat rate and maximum reaction temperature (Tan *et al.*, 2021). Slow pyrolysis occurs at temperatures between 300-700 °C with residence times of minutes to hours and heating rates of 0.1-10 °C min^{-1} (Tan *et al.*, 2021).

The yield of biochar is maximized (~35%) through slow pyrolysis (Tomczyk *et al.*, 2020) and when the gasses are condensed one proportion is called as bio-oil (3-5%) and is a viscous mixture of organic compounds, mostly oxygenated hydrocarbons (Oasmaa *et al.*, 2021) and other proportion of gases condensed (~25%) are called wood-vinegar (Wu *et al.*, 2015). Finally, a proportion (~35%) are not condensed and named as syngas production (Tomczyk *et al.*, 2020).

Biochar is a carbon-rich and solid product of biomass pyrolysis (Wang *et al.,* 2020). Biochar is suitable for a wide range of applications in heat and power production, metallurgy, agriculture, medical uses, among others due to its chemical and physical properties (Weber & Quicker, 2018). Wood vinegar had gained popularity in the agricultural and forestry sector, being used as biostimulant or plant growth regulator (Ofoe *et al*., 2022; Zhu *et al*., 2021), natural fungicide (Chen *et al*., 2022), and herbicide (Aguirre *et al*., 2020). On the other hand, non-condensable gases (syngas) are composed of a mixture of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), methane (CH_4), and lesser amounts of water and other gases. So, many of these gases are used as a fuel to produce heat, that can be used for pyrolysis process or other process as to generate electricity (Bajpai, 2020).

On the other hand, 88 % of the total roundwood produced in Central America and the Caribbean is used as fuel (Thiffault *et al*., 2023), showing the importance of fuel in part of the world. Moreover, in 2020, 90% of global bioenergy demand was produced in a traditional way in open fires or rustic kilns (International Energy Agency, 2021). The Central America need for a structural transition towards the valorization of forest resources is evident. According to Béland *et al.* (2020), increasing the profitability of wood energy can be obtained by managing the wood residues and generating savings in the process.

In Costa Rica, fuelwood has gained popularity in recent years as a renewable alternative to the growing energy demand and an aid to sustainable rural development (Arias, 2020). In that sense, energy production from forest biomass has been found viable for self-consumption (González *et al*., 2018). Short rotation energy plantations produce feedstock for energy production (Tenorio *et al*., 2016; Arias, 2020). However, some studies recommend the use of forest residues as an innovative solution for different thermal and thermo-chemical process for energy productions, as gasification (Chaves *et al*., 2023), torrefaction (Gaitán-Álvarez *et al*., 2017), pyrolysis (Berrocal-Méndez & Moya, 2022), besides the physical modification of this feedstock as pellet fabrication (Moya *et al*., 2015). Consequently, efforts have been made to determine the combustible characteristics of wood and charcoal produced from the most commercialized forestry species (Balaguer-Benlliure *et al.*, 2023; Moya & Tenorio, 2013, Moya *et al*., 2024).

Gmelina arborea Roxb. ex Sm (melina), is the second most reforested forest species in Costa Rica (Instituto Nacional de Estadística y Censos, 2022). It is the main species used in the manufacture of pallets, a product that dominates the national timber market (Oficina Nacional Forestal, 2022). However, sawnwood yields are low and residues of up to 78% of the standing tree volume have been reported, suggesting the need to find alternatives for the non-marketable volume (Espinoza-Durán & Moya, 2013).

On the other hand, *G. arborea* wood has desirable physical and chemical properties for pyrolysis and char production. High calorific value (20 MJ kg^{-1}), intermediate carbon fraction (48 %), and low ash fraction (1 %) has been reported (Moya & Tenorio, 2013). Charcoal from the pyrolysis of *G. arborea* has shown intermediate energy properties and a high proportion of hydrogen (H) compared to other fast-growing species (Balaguer-Benlliure *et al*., 2023). Nevertheless, *G. arborea* wood can present high moisture content and cellulose percentage (47%) (Moya & Tenorio, 2013). High moisture and cellulose lead to tar production and high cellulose influence the production of high char at low temperatures and the production of volatile products at high temperatures (Tripathi *et al*., 2016). These findings suggest that pyrolysis products of *G. arborea* can be optimized based on the parentwood and the type of pyrolysis. In fact, Moya *et al*. (2024) showed the main variables of pyrolysis process and yields of different products were affected by pyrolysis temperature.

So, *G. arborea* is a potential species for residues-based charcoal production. This study aims to (i) determine the yields of the different products (charcoal, wood vinegar, bio-oil, and non-condensable gases) and (ii) evaluate the conditions in three stages of the slow pyrolysis process of two shape of wood residues (wood chips and solid wood board-ends) of *Gmelina arborea*, from a semi-industrial prototype reactor. Results are going to be useful to estimate the production of biochar, condensable liquids (vinegar and bio-oil) and non-condensable gases from wood residues of *Gmelina arborea.*

2. Materials and methods

2.1. Materials

Wood residues with shape from the sawmill process and secondary process of *Gmelina arborea* were used. The company Maderas Cultivadas de Costa Rica (MCC) provided the wood from fast-growing plantations between 9 and 15 years old. Two shapes of wood residues were used: wood chips and solid wood board-ends (Figure 1**a-b).**

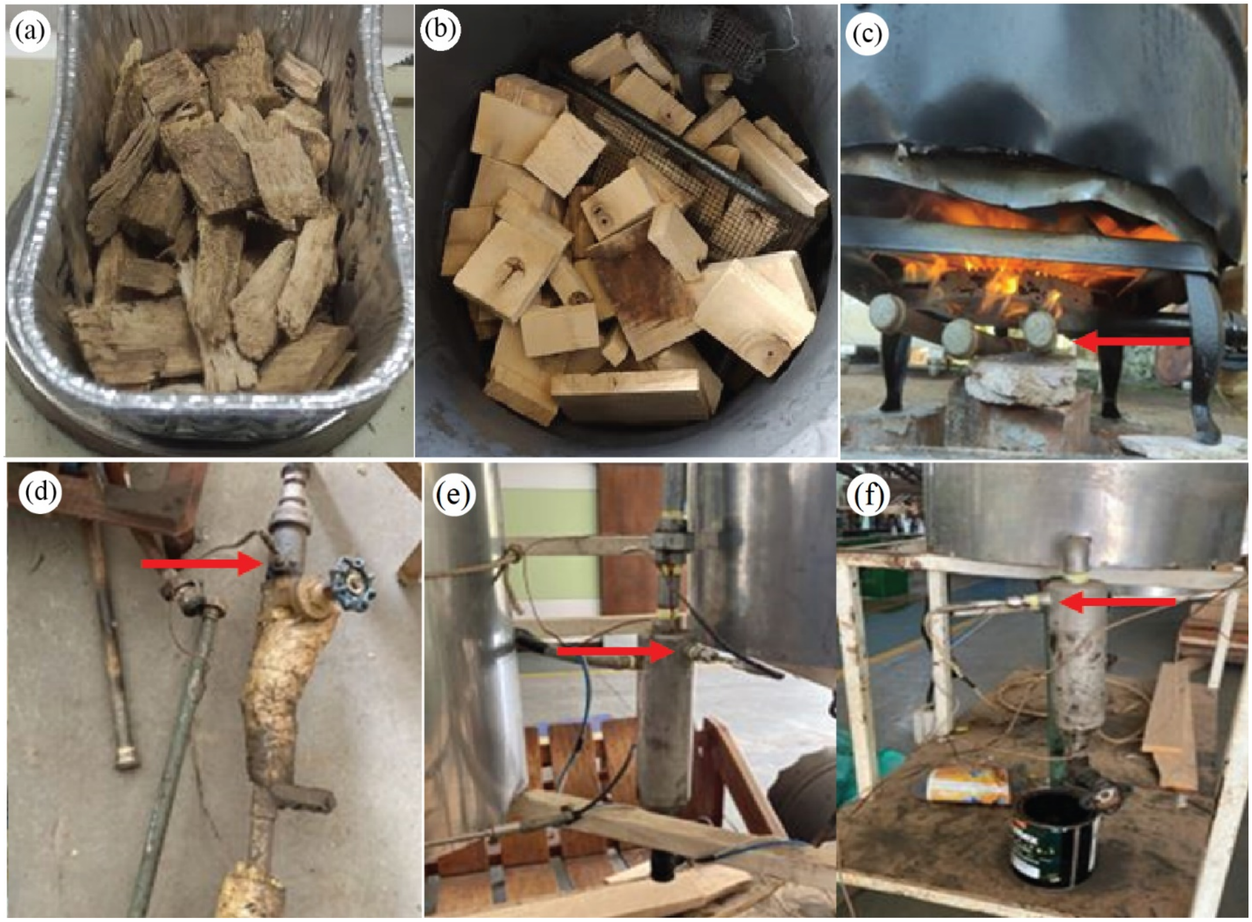

Figure 1. Wood residues of *G. arborea* used in the pyrolysis process: (a) chip parentwood and (b) board-ends solid parentwood. Different parts in the rector: Non-condensable gases outlet (c) and temperature meter probes at three stages of the wood residues pyrolysis process: pyrolizer gas outlet (d), after the first cooler (e) and after the second cooler (f).

2.2. Raw material characterization

Chip parentwood were residues from sawlog processing with dimensions of 5 to 10 cm long x 2-5 cm width and air-dried. Solid parentwood board-ends were residues from the secondary wood processing with dimensions of 4-25 cm long and 12-32 mm thick. Moisture content (MC%) was calculated according to the oven-dried secondary method of ASTM D4442-20 standard (ASTM, 2020). Three samples per batch of type of residue were extracted. Before each running of the pyrolysis process, the total weight of the residues was measured using a digital balance with 150 kg capacity.

2.3. Slow pyrolysis process

The pyrolysis of wood residues was carried out in a cylindrical reactor of 58 cm diameter, 88 cm long, and 232 L capacity (Figure 2). The reactor was covered with another cylinder with a glass fiber insulating jacket. First, the reactor was heated with liquefied petroleum gas (LPG) until pyrolysis. Then the pyrolytic gases were cooled through a system of coolers made of two helical coil heat exchangers. The first heat exchanger was cooled with air at room temperature and the second cooler with a closed water circuit moved by a pump. Liquids were collected after each cooler. Non-condensable gases (syngas) were utilized to heat the reactor (Figure 1c). The slow pyrolysis was finished when the syngas flame was over. The pyrolysis process was executed five batches or running for chip parentwood and four batches or running for solid parentwood board-ends.

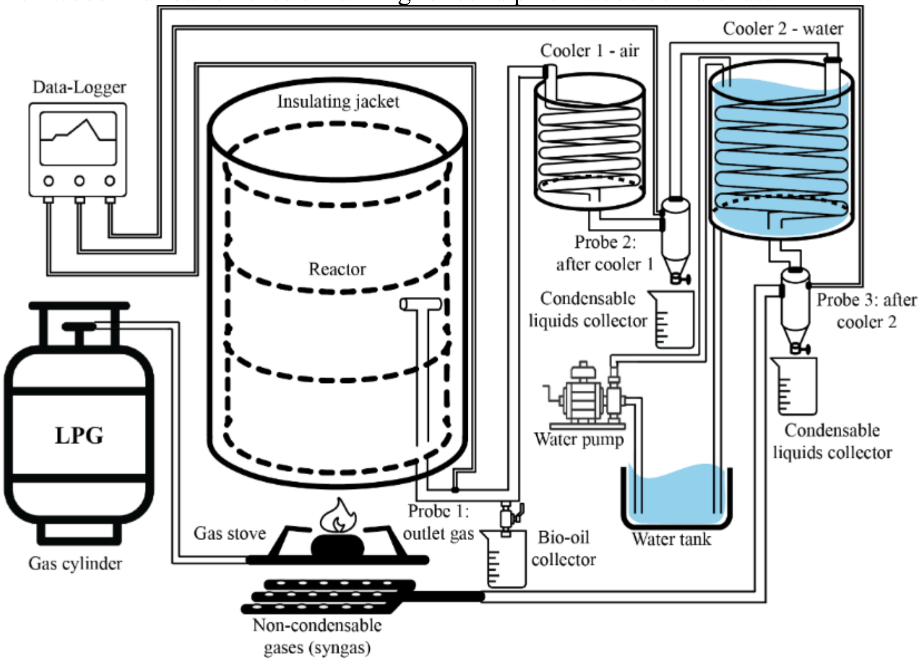

Figure 2. Cylindrical reactor designed and utilized for evaluation of the slow pyrolysis process.

Temperature was registered in three different stages of the process and are showed in the Figure 1d-f: pyrolizer gas outlet temperature (Probe 1, Figure 1d), temperature of gases after the first cooler (Probe 2, Figure 1e) and temperature of non-condensable gases after the second cooler (Probe 3, Figure 1f). Temperatures were measured each minute with a datalogger Testo model 176/T4 (Testo SE & Co., Titisee-Neustadt, Germany) and were registered for each running of the pyrolysis process.

2.4. Evaluation of the yield of pyrolysis products

The yields of the different products were calculated as Moya *et al* (2024): charcoal, bio-oil, wood vinegar and non-condensable gases. Parentwood was weighted before running the pyrolysis process and at the end of this, charcoal, bio-oil and vinegar were weighted to calculate each yield. The yields of charcoal, bio-oil and vinegar were calculated according to Eq. (1). Non-condensable gases yield was calculated according to Eq. (2)

$$Charcoal, vinegar\ or\ bio-oil\ \ yield\ (\%) = \frac{Charcoal,\ \ vinegar\ or\ bio{-}oil\ weight\ (kg)}{Parentwood\ weight\ (kg)} * 100 \quad (1)$$

$$Non-condensable\ \ yield\ (\%) = 100 - (charcoal + vinegar + tar\ yields) \quad (2)$$

2.5. Evaluation of conditions in three stages of the pyrolysis process

The temperature and time data were used to evaluate the pyrolysis process according to Moya *et al* (2024) with some modifications. Temperature was recorded in three stages using probes: (1) outlet pyrolysis gas reactor, (2) outlet pyrolysis gas of cooler 1 and (3) outlet pyrolysis gas of cooler 2 (Figure 1d-f). Four parameters for the outlet pyrolysis gas reactor and outlet pyrolysis gas of cooler 1, and three parameters for the outlet pyrolysis gas of cooler 2. Figure 3 presents the points and abbreviations of the parameters in the different stages and table 1 describes the parameters evaluated. Finally, the duration of the pyrolysis process was measured.

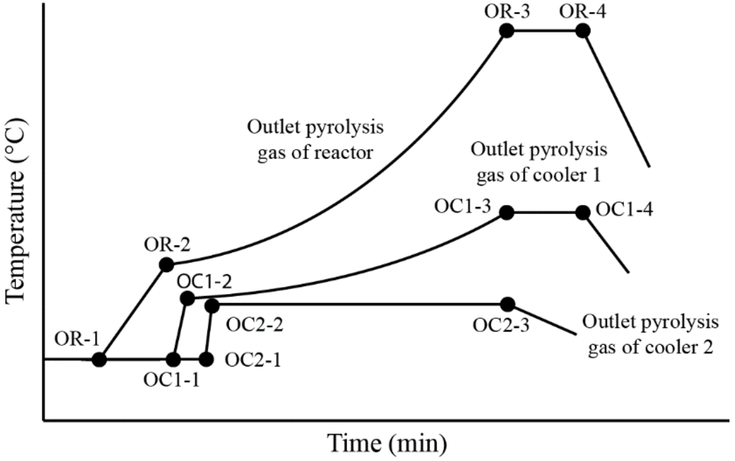

Figure 3. Different stages of the pyrolysis process of *Gmelina arborea* wood residues in four points of the outlet pyrolysis gas reactor and outlet pyrolysis gas of cooler 1, and three points of the outlet pyrolysis gas of cooler 2.

Table 1. Parameters of time and temperature of the different stages evaluated during pyrolysis process of *Gmelina arborea.*

Stage	Parameters	Abbreviations of points in figure 3
Outlet pyrolysis gas of reactor	1. Time when temperature began to increase	OR-1
	2. Time when water evaporation began	OR-2
	3. Temperature when water evaporation began	OR-2
	4. Time of stabilization in maximum temperature	OR-3
	5. Temperature of stabilization in maximum temperature	OR-3
	6. Time when temperature began to decrease	OR-4
	7. Temperature when it began to decrease	OR-4
Outlet pyrolysis gas of cooler 1	1. Time when the temperature begins to increase	OC1-1
	2. Time when water evaporation began	OC1-2
	3. Temperature when water evaporation began	OC1-2
	4. Time of stabilization in maximum temperature	OC1-3
	5. Temperature of stabilization in maximum temperature	OC1-3
	6. Time when temperature began to decrease	OC1-4
	7. Temperature when it began to decrease	OC1-4
Outlet pyrolysis gas of cooler 2	1. Time when temperature began to increase	OC2-1
	2. Time when water evaporation began	OC2-2
	3. Temperature when water evaporation began	OC2-2
	4. Time when temperature began to decrease	OC2-3
	5. Temperature when it began to decrease	OC2-3

2.6. Statistical analysis

The assumptions of normal distribution and homogeneity of variances were confirmed for the different product yields and the parameters evaluated during the pyrolysis process. Two-sample t-tests were carried out to determine statistical differences between the average of the variables measured of the wood residues. In addition, two different principal component multivariate analysis (PCA) were applied: first one was computed to explain the relationship between a first group of variables, consisting of the feedstock MC%, the pyrolyzer capacity and the yields of the different products and the second one PCA was carried out for the relationship of the time and temperature conditions and final duration of the batches of the pyrolysis process. Two PC were established for each analysis and the type of parentwood was used to analyze the clustering of the observations. The t-tests and multivariate analyses were conducted using the R programming language v.4.3.1 in the integrated development environment RStudio v.2023.16.0-421 (R Core Team, 2023).

3. Results

3.1. Pyrolizer capacity and parentwood moisture

Pyrolyzer capacity varied between two shapes of residues. The reactor had a significantly higher mass of solid wood board-ends weight, with 10.79 kg. And for chip parentwood, the pyrolizer had an average of 6.50 kg in capacity (Table 2). Furthermore, parentwood presented MC% differences as well, solid wood board-ends had a statistically lower MC% than chip parentwood.

Table 2. Moisture content (MC%) and pyrolizer capacity of parentwood.

Parentwood	MC (%)	Weight (kg)
Chips	16.11^{A}	6.50^{B}
Board-ends	10.20^{B}	10.79^{A}

Legend: Different letters between residues indicate statistical differences (p-value<0.05)

3.2. Evaluation of the yield of pyrolysis products

The different products obtained during the pyrolysis process are presented in Figure 4a. Charcoal and vinegar presented similar yields, that varied from 26 to 31% and from 27 to 32%, respectively (Figure 4b and Figure 4c). The yield of condensable (sum of vinegar and bio-oil) was statistically equal in two types of shape of parentwood, which varied between 33 and 38% (Figure 4d). Bio-oil had the lowest yield among the different products (Figure 4a), presenting the highest percentage when solid parentwood board-ends was used (7.7%) (**¡Error! No se encuentra el origen de la referencia.**e). The product with the highest yield was the non-condensable (syngas), it varied between 34 to 40% (**¡Error! No se encuentra el origen de la referencia.**f).

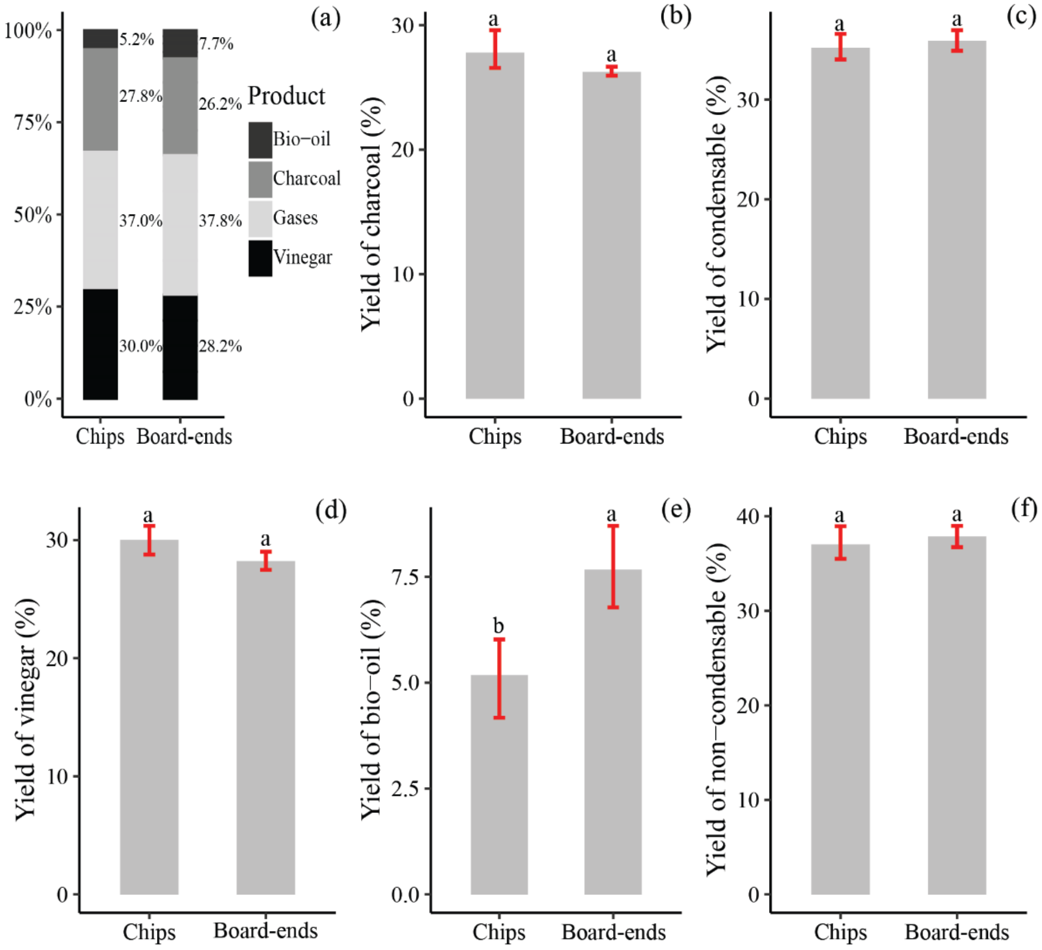

Figure 4. (a) Distribution of the products and yields of (b) charcoal, (c) condensable gases, (d) wood vinegar, (e) bio-oil (e), and (f) non-condensable gases from the pyrolysis process of two shape of wood residues of *Gmelina arborea*.
Note: Confidence limits α=0.05 and different letters between residues indicate statistical differences (p-value<0.05).

3.3. Evaluation of conditions in three stages of the pyrolysis process

The total duration of pyrolysis process presented significant differences among wood residues. Chips parentwood lasted longer with 118 min, compared to the 93 min for solid parentwood board-ends. In the three stages evaluated of the pyrolysis process, the time when the temperature started to increase (OR-1, OC1-1 and OC2-1) and time and temperature when the water started to evaporate (OR2, OC1-2 and OC2-2) did not presented significant differences between two shape of residues (

Table **3**)

Outlet of the reactor. The time when the temperature started to increase (OR-1) varied between 1 to 13 min after starting to heat the reactor and any difference was found between two types of parentwood (Table 3). The time and temperature when the water started to evaporate (OR-2) varied between 12 to 20 min and 67.5 to 89.6 °C, respectively (Table 3) and again not difference was observed between two types of parentwood. The time and temperature when the process (OR-3) reached the maximum temperature and when it began to decrease varied among two types of residues of parentwood (Table 3). Solid parentwood board-ends presented higher values of maximum temperature and shorter time than chips parentwood. After 5 min of stabilization of the maximum temperature, it began to decrease (OR-4) at between 205.5 and 273.0 °C for solid parentwood board-ends and 144.8 and 170.3 °C for wood chips, with statistical differences between two types of parentwood (

Table **3**).

Outlet of the cooler 1. Temperature began to increase in cooler 1 (OC1-1) after 10 min later than the outlet of the reactor for two types of residues, between 12 to 18 min. Then the evaporation of water in the reactor was registered in the cooler (OC1-2) at a time between 18 and 21 min and temperature between 75.1-78.2 °C for two type of residues and any statistical differences. Later, maximum temperatures (OC1-3) were reached, and solid wood board-ends presented statistically higher temperature and shortest time than wood chips (

Table **3**).
Approximately 5 min later, the temperature began to decrease at 173 to 177.3 °C for solid wood board-ends and 90.9 to 95 °C for chips parentwood (OC1-4) and both types of residues were statistically different (

Table **3**)
Outlet of cooler 2. The time when the temperature started to increase (OC2-1) varied between 19 and 40 min, the temperature when water started to evaporate in the reactor (OC2-2) from 59.2 and 75.1 °C and the range of time of 22 to 50 min showed no statistical difference. The temperature stabilized at water evaporation (OC2-2) and then started to decrease (OC2-3) at 71-86 min for solid parentwood board-ends and this time was statistically lower than chips parentwood (Table 3). Temperatures not presented statistical differences (

Table **3**).

Table 3. Conditions of temperatures and times of the different stages during pyrolysis process of wood residues of *Gmelina arborea.*

Stage	Abbreviations of points in figure 4	Time (min)		Temperature (°C)	
		Board-ends	Chips	Board-ends	Chips
Outlet pyrolysis gas of reactor	OR-1	3.0^{A}	8.7^{A}	-	-
	OR-2	12.7^{A}	15.0^{A}	73.4^{A}	75.8^{A}
	OR-3	80.0^{B}	103.7^{A}	262.4^{A}	162.2^{B}
	OR-4	85.3^{B}	109.0^{A}	240.4^{A}	153.7^{B}
Outlet pyrolysis gas of cooler 1	OC1-1	14.3^{A}	17.0^{A}	-	-
	OC1-2	18.0^{A}	21.7^{A}	76.8^{A}	76.6^{A}
	OC1-3	82.0^{B}	104.7^{A}	182.1^{A}	97.5^{B}
	OC1-4	87.0^{B}	110.7^{A}	174.8^{A}	92.3^{B}
Outlet pyrolysis gas of cooler 2	OC2-1	21.3^{A}	31.7^{A}	-	-
	OC2-2	25.0^{A}	37.0^{A}	73.1^{A}	64.9^{A}
	OC2-3	77.3^{B}	103.0^{A}	64.8^{A}	59.9^{A}

Legend: Different letters between parentwood (board-ends and chips) of the corresponding variable (time and temperature) are statistically different at 95%.

3.4. Multivariate Analysis

The first PCA applied for the moisture content (MC%), the pyrolyzer capacity and the products yields showed the first two principal components (PC) explaining approximately 82% of the accumulated variability (
Table **4.** Proportion of variance of the principal components of the multivariate analysis for the moisture content of parentwood, pyrolyzer capacity and pyrolysis products yields (PCA 1) and for the time and temperature conditions of the pyrolysis process in three stages (PCA 2).). The PC 1 was mainly influenced by MC% and the pyrolyzer capacity, and in less proportion by the yields of vinegar and bio-oil (Note: For PCA 2 the principal components from 6 to 20 had a proportion of variance of <0.01.

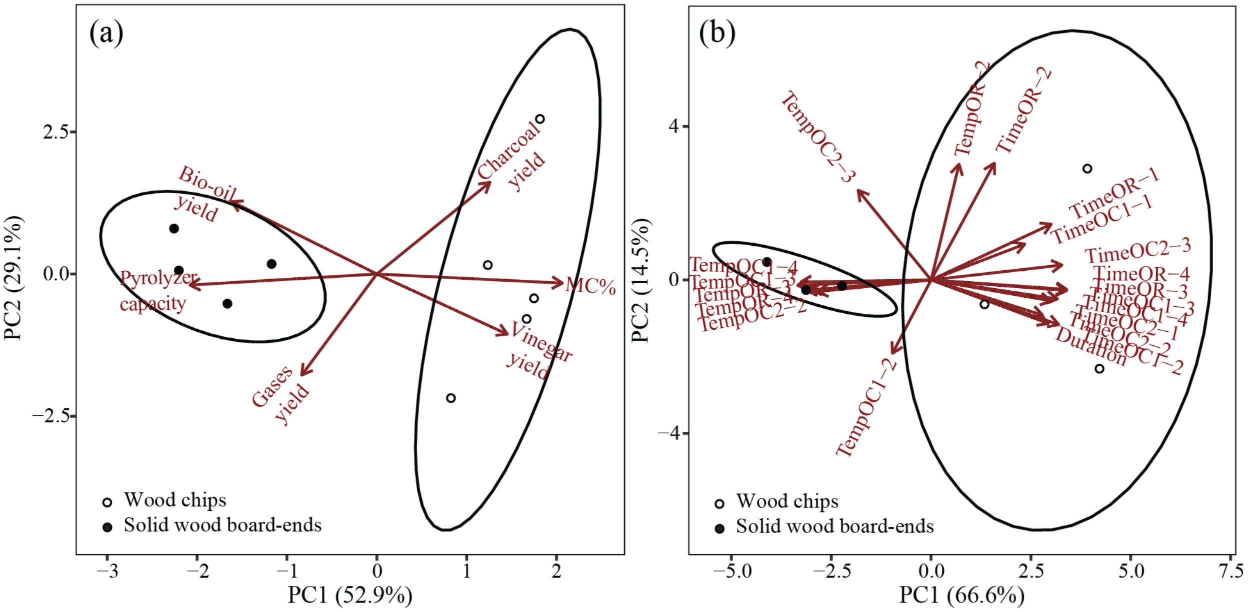

Figure 5. (a) PCA of the weight and moisture content and pyrolysis products yields for pyrolysis process and (b) PCA for the time and temperature conditions of the pyrolysis process in three stages.

Note: Ellipses at 95% of normal probability group the observations by parentwood.

). The PC 2 explained the 29% of the variation between observations (

Table **4.** Proportion of variance of the principal components of the multivariate analysis for the moisture content of parentwood, pyrolyzer capacity and pyrolysis products yields (PCA 1) and for the time and temperature conditions of the pyrolysis process in three stages (PCA 2).) and it was mostly influenced by the charcoal yield (Note: For PCA 2 the principal components from 6 to 20 had a proportion of variance of <0.01.

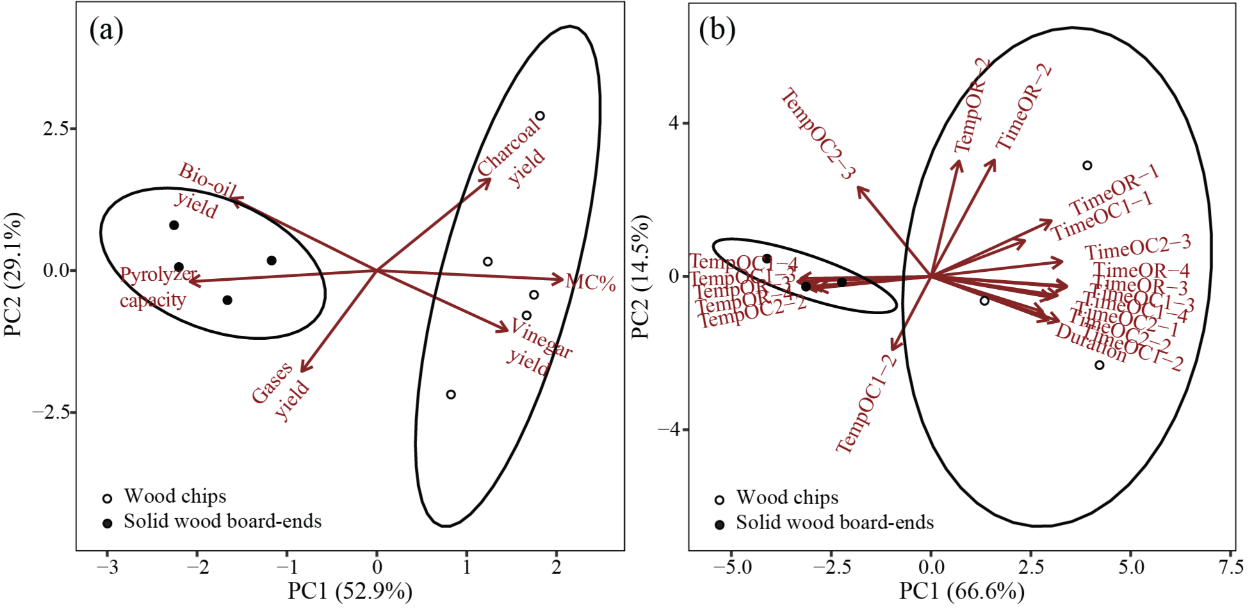

Figure 5. (a) PCA of the weight and moisture content and pyrolysis products yields for pyrolysis process and (b) PCA for the time and temperature conditions of the pyrolysis process in three stages.

Note: Ellipses at 95% of normal probability group the observations by parentwood.

). The PCA using the principal component 1 and 2 of the observations showed that the relationship between variables of the MC%, pyrolyzer capacity and pyrolysis products yields (Figure 5a). It was also possible to distinguish two groups that represent the observations: one group for solid wood board-ends and other one for chips parentwood

(Figure 5a). Solid parentwood board-ends was more correlated to PC 1, and the factors associated to this grouping were pyrolyzer capacity and bio-oil yield. On the other hand, chips parentwood are associated more with the PC 2 and the association factor were the parameter of MC%, and vinegar and charcoal yields (Figure 5a).

Table 4. Proportion of variance of the principal components of the multivariate analysis for the moisture content of parentwood, pyrolyzer capacity and pyrolysis products yields (PCA 1) and for the time and temperature conditions of the pyrolysis process in three stages (PCA 2).

PCA 1			PCA 2		
Principal component	Proportion	Accumulated proportion	Principal component	Proportion	Accumulated proportion
1	0.53	0.53	1	0.67	0.67
2	0.29	0.82	2	0.14	0.81
3	0.13	0.95	3	0.09	0.90
4	0.04	0.99	4	0.06	0.96
5	0.01	1	5	0.04	1
6	<0.01	1	6	<0.01	1

Note: For PCA 2 the principal components from 6 to 20 had a proportion of variance of <0.01.

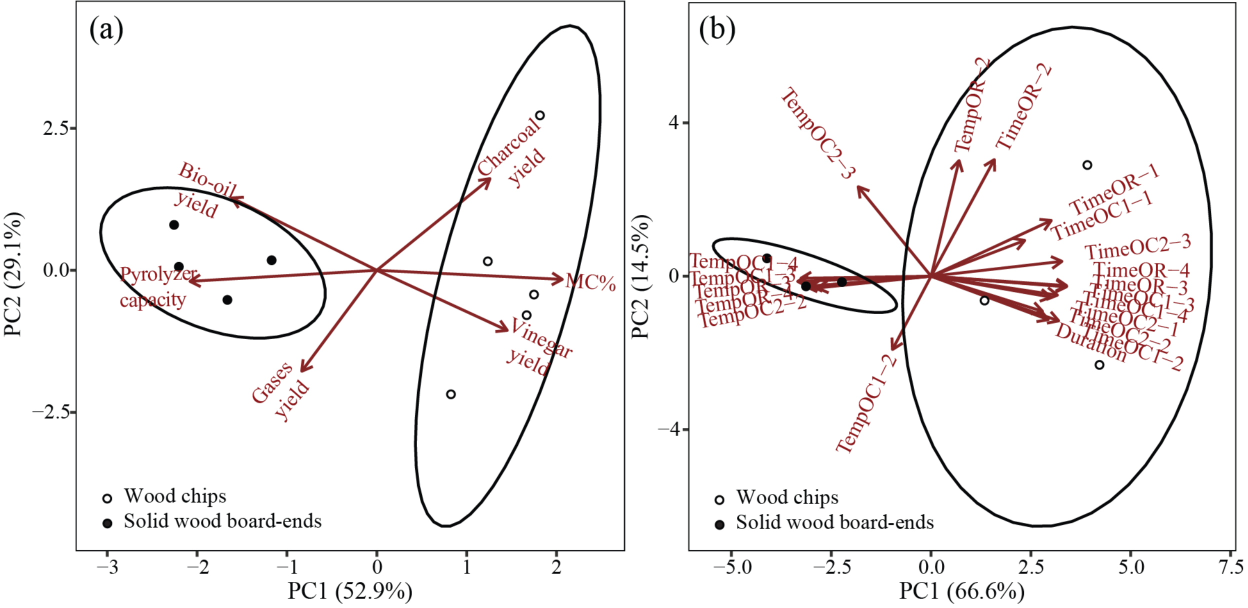

Figure 5. (a) PCA of the weight and moisture content and pyrolysis products yields for pyrolysis process and (b) PCA for the time and temperature conditions of the pyrolysis process in three stages.

Note: Ellipses at 95% of normal probability group the observations by parentwood.

The second PCA applied for the time and temperature conditions of the pyrolysis process indicated that the two first factors account for the 81% of the total variance among the observations (Figure 5b). The PC 1 captured approximately 67% of the variance (

Table **4**) and it was influenced mostly by the conditions of the three stages of the pyrolysis process when the temperature stabilized at a maximum temperature and when it started to decrease (

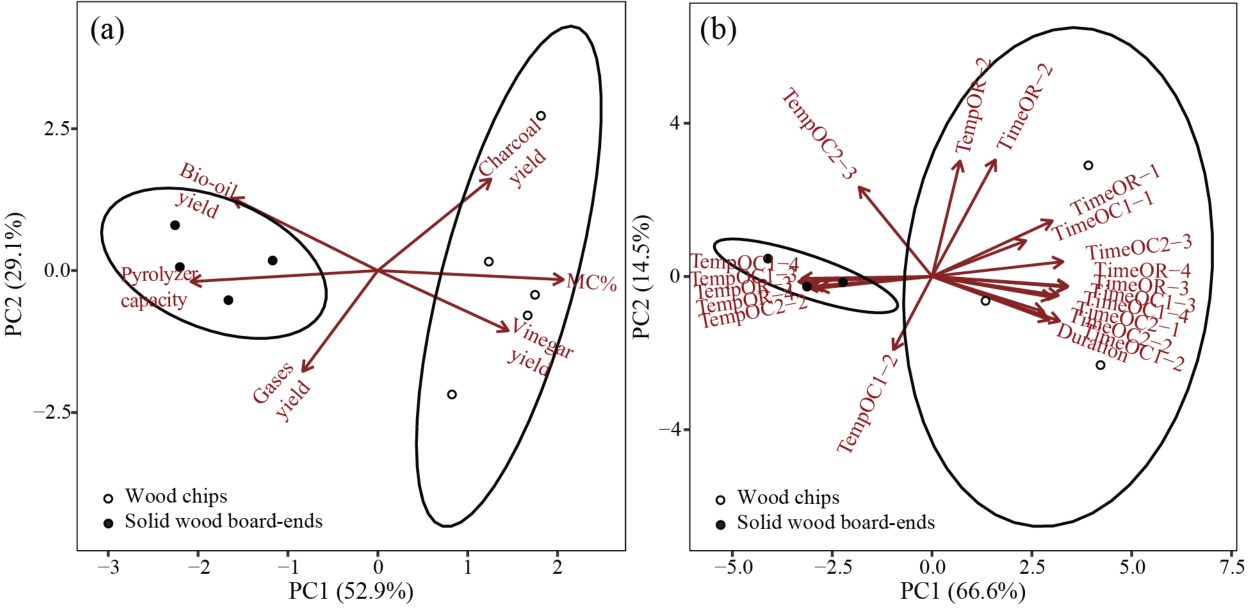

Figure 5. (a) PCA of the weight and moisture content and pyrolysis products yields for pyrolysis process and (b) PCA for the time and temperature conditions of the pyrolysis process in three stages.

Note: Ellipses at 95% of normal probability group the observations by parentwood.

Table 1). On the other hand, PC 2 accounted a variance of 14.5% (
Table **4**) and it was influenced by the time and temperature when the water evaporation began recorded in the reactor outlet (OR-2) (

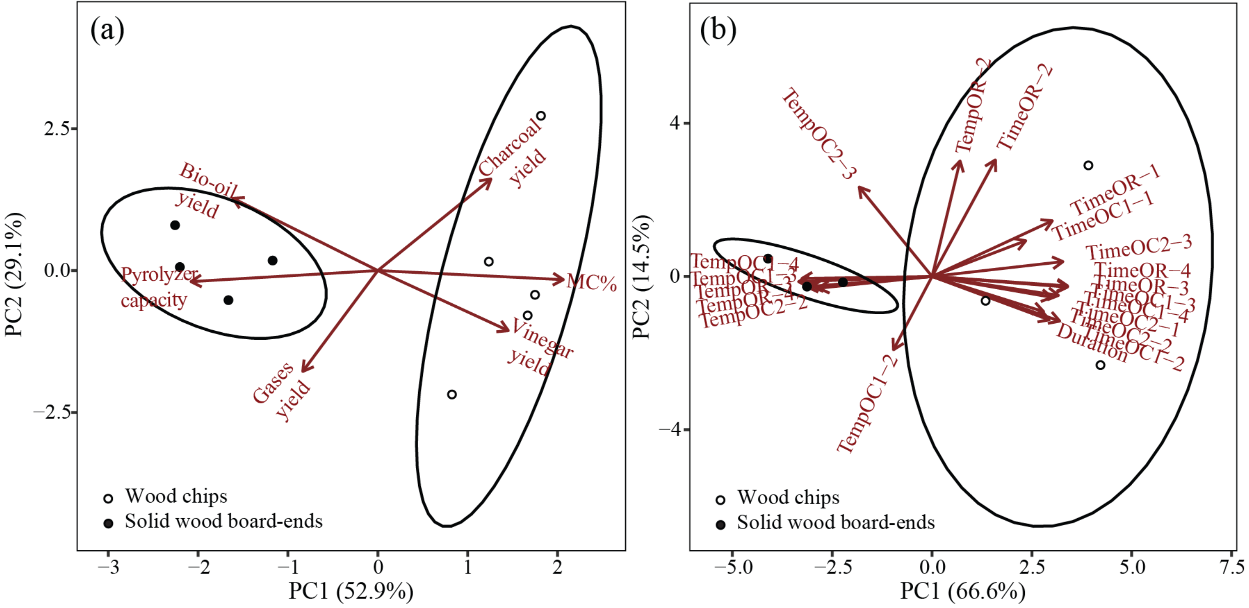
Figure 5. (a) PCA of the weight and moisture content and pyrolysis products yields for pyrolysis process and (b) PCA for the time and temperature conditions of the pyrolysis process in three stages.

Note: Ellipses at 95% of normal probability group the observations by parentwood.

). The associations between variables in two different components are presented in Figure 5b. We can observe that, in general, with some exceptions, time correlated negatively with temperature variables. One exception was identified in the reactor outlet (OR-2), time and temperature when the water evaporation presented a positive correlation with strong association (R=0.93). Furthermore, two groups are distinguished: observations of solid parentwood board-ends which are associated with high temperatures and chips parentwood associated with longer times for the parameters evaluated (Figure 5b).

Table 5. Correlation matrix for the moisture content of parentwood, pyrolyzer capacity and pyrolysis products yields (PCA 1) and for the time and temperature conditions of the pyrolysis process in three stages (PCA 2).

PCA 1		
Variable	PC 1	PC 2
Moisture content	0.93**	0.08
Pyrolyzer capacity	-0.92**	-0.31
Vinegar yield	0.74	-0.59
Bio-oil yield	-0.76*	0.03
Charcoal yield	0.42	0.83**
Gases yield	-0.52	0.48
PCA 2		
Variable	PC 1	PC 2
Time when temperature began to increase OR-1	0.86	0.42
Time when water evaporation began OR-2	0.45	0.87
Temperature when water evaporation began OR-2	0.20	0.87
Time of stabilization in maximum temperature OR-3	0.98**	-0.08
Temperature of stabilization in maximum temperature OR-3	-0.90**	-0.08
Time when temperature began to decrease OR-4	0.98***	-0.07
Temperature when it began to decrease OR-4	-0.86*	-0.07
Time when the temperature begins to increase OC1-1	0.67	0.27
Time when water evaporation began OC1-2	0.92	-0.33
Temperature when water evaporation began OC1-2	-0.28	-0.55
Time of stabilization in maximum temperature OC1-3	0.97*	-0.08
Temperature of stabilization in maximum temperature OC1-3	-0.96**	-0.04
Time when temperature began to decrease OC1-4	0.91**	-0.14
Temperature when it began to decrease OC1-4	-0.94***	-0.02
Time when the temperature begins to increase OC2-1	0.86	-0.16
Time when water evaporation began OC2-2	0.80	-0.26
Temperature when water evaporation began OC2-2	-0.82	-0.09
Time when water evaporation began OC2-3	0.94**	0.11
Temperature when it began to decrease OC2-3	-0.52	0.67
Duration of the process (min)	0.84**	-0.33

Note: * indicates statistical differences at 95% (p-value<0.05), ** at 99% (p-value<0.01) and *** at 99.9% (p-value<0.001) in Student's t-test.

4. Discussion

Different particle shape was used in this study (Figure 1a-b). It is expected to obtain higher charcoal production using larger particles due to low heat transfer rate (Tripathi *et al*., 2016). However, no significant difference of charcoal yield between the chips and board-ends were observed in this study (Figure 4b). Instead, in this study larger particles (solid wood board-ends) reached the maximum temperature faster than the smaller particles (wood chips) (

Table **3**). On the other hand, moisture content of biomass increases the energy required to reach the pyrolysis temperature (Tripathi *et al*., 2016). In this study feedstock presented MC% below the fiber saturation point (Table 2), being suitable for pyrolysis (Tripathi *et al*., 2016). However, chips presented higher moisture content (Table 2), which means that more energy supplied to the pyrolyzer through the stove is consumed to remove the moisture and less is used to raise the temperature (Tripathi *et al*., 2016) and this humidity condition probably produced longer time and lower temperatures at the different points where these parameters were measured (

Table **3**).
No differences were observed for these products among the type of residue (Figure 4a) and the yields of charcoal, condensable and non-condensable gases agreed with percentages reported by Moya *et al*. (2024) for *G. arborea* pyrolyzed at 450-500 °C. Tripathi *et al* (2016) mentioned that a high heating rate enhances biomass fragmentation and gaseous and liquid yield, and that at low temperatures contributes to high char yields while at high temperatures produce highest volatiles by cellulose decomposition and condensable products increased. But according to percentage of yield, the utilization of parentwood with two different shapes had little effects in these percentages, except for yield of bio-oil, which chips parentwood produced the lowest percentage (Figure 4e).
Wood chips pyrolysis had similar production of vapors (gases) as solid wood board-ends, probably because board-ends produced more gases by direct decomposition and less by secondary decomposition of wood tar due to a higher heating rate (Chen *et al.*, 2017), contrary to wood chips. However, wood chips did not produce higher temperatures inside of reactor (OR-2 and OR-3), that help cellulose decomposition to increase the biol-oil production. At higher surface area to volume ratio, it is expected to enhance the production of bio-oil, due to a faster decomposition of the wood and shorter transportation of tar through the hot porous solids (Chen *et al*., 2017). However, the smallest particle in this experiment (i.e. wood chips) contained higher moisture that slowed down the heating rate of feedstock (

Table **3**), which favors the production of char rather than tar. The bio-oil from solid wood board-ends (Figure 4e) can be produced from a higher volatilization of materials due to higher temperatures (

Table **3**) in this shape of feedstock (Dias Junior *et al*., 2020). In fact, PCA showed that yields of different products were related to the shaped of parentwood (Figure 5a), solid wood board-ends increased the bio-oil yield and greater weight of biomass can be placed inside the reactor, while chips parentwood increased vinegar and charcoal yields.
The temperature of stabilization in maximum temperature of the reactor outlet (OR-3;

Table **3**) for chips and board-ends parentwood presented similar performance as Moya *et al*. (2024) when pyrolysis was conducted at 450 °C and 500 °C, respectively. This behavior suggests that in this study, the maximum reached temperatures inside the reactor were higher. In addition, the temperatures and the product yields obtained (Figure 4) correspond with the slow pyrolysis values (Tomczyk *et al*., 2020). However, the time and temperatures behavior varied with shape of parentwood, especially inside the reactor in the outlet of pyrolysis gases (OR), but not when gases were cooled (

Table **3**). Wood chips extended the time of pyrolysis gas outlet, time of reaching the maximum temperature, time when temperature began to decrease, and temperatures were lower inside the reactor and for the gases produced by pyrolysis; these conditions produce different chemical reactions for different feedstock (Ateş & Işıkdağ, 2008).
Atreya *et al*., (2017) found that temperature when pyrolysis occurs influences the pyrolysis duration, which also vary with different shapes and size of the particles and follows the mass of the decomposing particle. For moisture free feedstock, large particles with cubic or spherical shapes pyrolyze slower than small and thin particles (Atreya *et al*, 2017). Similarly, Peters and Bruch (2003) indicate that the start of the pyrolysis depends on the particle size and the heating temperature, and Bennadji *et al* (2014) found that the time of heating and devolatilization increase with increasing the particle size. These findings of feedstock size and shape were conducted with moisture free

particles which can explain the contrast with our results, where the larger and like cubic shape, but drier particles (board-ends) presented the higher temperatures and the shorter pyrolysis duration.

5. Conclusion

The transformation of *Gmelina arborea* wood residues into different products through the slow pyrolysis process, offers the Costa Rican forestry stakeholders an opportunity to revalorize this material. So, it is of interest to know the products yields and performance of the pyrolysis process of different wood residues, using a small-scale reactor prototype and utilizing the non-condensable gases in the same reactor. This study suggests that wood chips and solid wood board-ends solid from *G. arborea* provide similar production of charcoal, condensable and non-condensable gases. However, the use of board-ends is recommended to obtain higher yield of bio-oil (Figure 4**¡Error! No se encuentra el origen de la referencia.**e) and complete the process in less time, making it energetically more efficient (

Table **3**).

Authorship contribution statement

Jair Granados-Chacón: data curation, formal analysis, investigation, methodology, software, visualization, writing-original draft. **Roger Moya:** conceptualization, funding acquisition, methodology, project administration, resources, supervision, validation, writing-review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

The online version does not contain supplementary material.

Data availability of data and materials

Data will be made available on request.

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