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Research Paper

Dry vs wet torrefaction of oxytree biomass: A comparative study on fuel properties and energy yield

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ABSTRACT

This study evaluates the performance of dry torrefaction and wet torrefaction processes applied to oxytree (Paulownia Clone in Vitro 112) biomass, focusing on their effects on fuel quality and energy efficiency. Experiments were conducted at 200–260 °C for 30 and 60 min. Dry torrefaction increased the higher heating value from 16.3 to 20.5 MJ/kg, with notable carbon enrichment but at the expense of mass and energy yields. Wet torrefaction achieved a higher heating value (up to 27.9 MJ/kg) and better preservation of energy yield (>90 %), alongside favorable reductions in atomic O/C and H/C. GC–MS analysis of the wet torrefaction liquids revealed acetic acid, furfural, and phenolic compounds, highlighting value-added potential. Differential scanning calorimetry analysis showed that both the ignition temperature and activation energy (E_a) decrease with increasing torrefaction temperatures. Wet torrefaction samples consistently ignited at lower temperatures (272–302 °C) and exhibited lower activation energy (39.5–45.3 kJ/mol) than dry torrefaction samples (287–299 °C; 43.6–52.9 kJ/mol), indicating superior combustion readiness. The findings suggest that wet torrefaction offers superior carbon retention and energy densification for oxytree biomass, positioning it as a promising method for bioenergy production and biorefinery applications. By integrating solid-fuel quality, ignition behaviour, and dissolved organic content in the aquatic phase, the study provides residue-specific operating windows that support the practical choice between dry and wet torrefaction for oxytree pruning residues.

1. Introduction

Paulownia Clone in Vitro 112 (Paulowniaceae), also known as oxytree or oxygen tree, is a hybrid clone of *Paulownia elongate* and *Paulownia fortunei* [1], which is a new form of energy crop that is leading the market throughout Europe [2]. The oxytree, a fast-growing hardwood, can be harvested at least three times in its lifespan. At 6–7 years, it reaches approximately 15 m in height [3]. The wood is robust, dries quickly, has a fine grain, and is resistant to distortion, cracking, and wrapping. As a result, the oxytree has a wide range of applications and is grown for the following purposes: fuel wood, high-quality furniture, musical instruments, wood for planes and ships because it is easily carved wood, for inter-cropping in agriculture, as it can develop a suitable climate for agricultural crops, increasing yields, an organic fertilizer since the leaves are high in nitrogen, animal food, fuel pellets for heating, and so forth [4]. Higher heating values (HHV) were reported for 1-, 2-, and 3-year-old Paulownia: 19.67, 19.76, and 19.94 MJ/kg, respectively [5]. This is comparable to the energy crops currently on the market: switchgrass (14.51–15.11 MJ/kg) [6], miscanthus (18.5 MJ/kg), and willow (18.7 MJ/kg) [7]. The feedstock's biochemical composition governs its thermal response during torrefaction. Oxytree has a relatively high cellulose content (46–49 %), moderate hemicellulose (22–25 %), and low lignin (21–23 %) compared to most softwoods [8]. Cellulose, due to its crystalline structure and strong hydrogen bonds between chains, gives structural strength to both types of biomass [9]. Hemicellulose, being more amorphous and branched, is less thermally stable and breaks down at lower temperatures. Lignin's aromatic structure makes it resistant to thermal degradation, except under severe conditions (>240 °C). The first experimental plantation of oxytree was started in 2016 by the company Lasy Tlenowe and has so far planted over 600 ha of aerobic forests for its seedling customers in Poland [10]. The cultivation cycle of the oxytree includes necessary pruning in the first year to promote enhanced biomass production in subsequent years. The pruned biomass from oxytree plantations represents a significant

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portion of harvestable material, with estimates suggesting that clippings can constitute approximately 70 % of the total tree volume. This pruning generates significant waste biomass that must be effectively utilized to maximize the overall efficiency of the bioenergy production system.

The study selected torrefaction because it is a mild, sub-pyrolytic treatment (200–300 °C) that upgrades solids while limiting tar formation and preserving yield. Alternatives, such as pyrolysis (≥400 °C), offer higher deoxygenation but lower solid yields; gasification targets syngas rather than solid fuel [11]. Torrefaction is a preliminary thermochemical conversion process of biomass under an anaerobic environment, occurring at 200–300 °C [12]. The primary purpose of torrefaction is to produce biochar with characteristics similar to those of fossil-based coal [13]. Torrefaction enhances the physicochemical characteristics of biomass [14], improving its energy density, grindability, hydrophobicity, and overall combustion performance [15]. Torrefied products are utilized in various applications beyond their fuel properties. It may also be used in environmental protection to remove contaminants from water and sewage due to its well-developed specific surface area and microporosity [16]. Agriculture is another application, as adding torrefied biomass to soil enhances its properties and may help reduce fertilizer and pesticide use. It can also improve the efficacy of natural fertilizers [17]. Due to its poor thermal conductivity and absorption properties, torrefied biomass is also used in buildings for insulation [18].

Depending on the medium used, torrefaction can be broadly classified into two categories: dry torrefaction (DT) and wet torrefaction (WT), also known as hydrothermal carbonization (HTC). DT is a mild pyrolysis process typically conducted at atmospheric pressure in an inert gas (e.g., nitrogen) environment at temperatures ranging from 200 to 300 °C, with low heating rates (<50 °C·min^{-1}) and residence times less than an hour [14]. DT produces three main fractions: biochar, condensable volatiles (torrefaction liquids), and permanent gases. The solid product, biochar, is the primary output, with mass yields typically ranging from 45 to 70 % and energy yields from 65 to 85 % [15]. DT has seen extensive development and commercialization, particularly due to its ability to reduce biomass moisture content, increase calorific value, and produce a fuel suitable for co-firing in coal power plants or for gasification [14].

In contrast, WT is performed in a liquid-phase medium under subcritical water conditions, typically at 180–260 °C and elevated pressures above the saturation vapor pressure to maintain the aqueous phase [19]. The main solid product, hydrochar, is accompanied by a complex aqueous phase rich in organics and a minor gaseous fraction. WT is especially advantageous for treating high-moisture and ash-rich biomass feedstocks, as it avoids the need for prior drying and can significantly reduce ash and alkali content [20]. Hydrochars produced by WT exhibit a distinct microspherical morphology, high carbon content, low ash content, and specific surface functionalities that enhance their combustion and adsorption properties [19]. Both DT and WT offer unique advantages and limitations. While DT is better suited for dry biomass and is operationally simpler, WT enables the effective processing of wet and inorganic-rich feedstocks, producing cleaner solid fuels with enhanced properties [19,20].

Oxytree (Paulownia) plantations are expanding in Europe, generating sizeable pruning residues with favorable fuel traits (low ash content and rapid growth). To authors knowledge, there are three studies on oxytree torrefaction, focusing on dry torrefaction by Świechowski et al. [21–23], which aim to produce biochar with enhanced fuel characteristics. Previous reviews and case studies have already compared dry and wet torrefaction across various biomasses, highlighting their respective advantages and limitations [24]. However, most of these works (i) focus on stem wood or energy crops rather than pruning residues [25], (ii) rarely couple fuel properties with ignition behaviour, and (iii) rarely quantify the aqueous phase in WT. As a result, there is still a lack of residue-specific, decision-oriented data that can guide whether DT or WT is preferable for a given pruning biomass.

The present study addresses this gap by (i) applying DT and WT to oxytree pruning residues under identical severity windows (200–260 °C, 30–60 min), (ii) linking elemental composition (O/C, H/C) to HHV, energy yield and ignition indices, and (iii) quantifying the aqueous phase content in WT. From these data, we derive operating windows that inform the selection between DT and WT pathways for oxytree-based fuel chains.

2. Materials and methods

Oxytree samples were supplied from a farm in Wroclaw, Poland, Fig. 1a. The harvested plants were air-dried at ambient temperature (20 ± 2 °C) for 72 h to reduce the moisture content to approximately 15 %. Further milled using a Wiley mill (Thomas Model 4, USA) fitted with a 1 mm screen to obtain homogeneous samples suitable for characterization and torrefaction experiments. The milled samples were then passed through standard sieves to collect particles of 1 mm, which were used for all subsequent experiments. This size range was selected to ensure uniform heat transfer during torrefaction while maintaining the structural integrity of the biomass particles.

All chemicals and reagents used throughout the study were of analytical grade. For calibration of analytical instruments and preparation of standard solutions, the following chemicals were used: potassium hydrogen phthalate (99.95 %, Sigma-Aldrich), benzoic acid standard (99.9 %, Parr Instrument Company) for bomb calorimeter calibration, and BBOT standard (2,5-bis(5-*tert*-butyl-benzoxazol-2-yl) thiophene, 99.99 %, Elemental Microanalysis Ltd.) for elemental analyzer calibration.

For WT experiments, deionized water with a resistivity > 18.2 MΩ·cm (produced using a Millipore Milli-Q system) was used as the reaction medium. For pH adjustments during anaerobic digestion, sodium hydroxide (NaOH, 98 %, Sigma-Aldrich) and hydrochloric acid (HCl, 37 %, Sigma-Aldrich) solutions were used. Nitrogen 5.0 gas (99.999 % purity, Air Products) was used to create an inert atmosphere during DT.

2.1. Dry torrefaction

The torrefaction of oxytree was conducted under controlled conditions to examine the effect of different treatment temperatures on product properties. The torrefaction process was performed using a tube furnace reactor system equipped with a quartz glass reactor tube. The schematic diagram of the DT process is presented in Fig. S1a. The quartz tube, with an internal diameter of 25 mm and a sintered glass plate at the base, served as the reaction chamber. The reactor tube was heated by a 1.5 kW electrical furnace (PR-45/1350 M, Poland), with precise temperature control provided by an immersed thermocouple. The biochar production process was carried out at 200, 220, 240, and 260 °C for residence times of 30 and 60 min, with heating rates of 10 K/min and a flow rate of N_2 as an inert gas at 20 mL/min. These temperatures were selected to represent mild to severe torrefaction conditions based on previous research in the field. After the torrefaction period, the samples were cooled to room temperature under continued nitrogen flow to prevent oxidation. The torrefied samples were weighed to determine mass loss during torrefaction and stored in airtight containers until further analysis.

The drying procedure was conducted in the Binder 9010-0082 dryer at 105 °C for 24 h. Thermogravimetric analysis (TGA) was used to measure changes in the sample's mass as a function of analysis temperature and runtime. The NETZSCH TG 209 F3 Tarsus thermogravimeter was used for the measurements. The analysis was performed by heating approximately 10 mg of oxytree to 200, 220, 240, and 260 °C at a heating rate of 10 K min^{-1} under a N_2 flow of 20 mL/min.

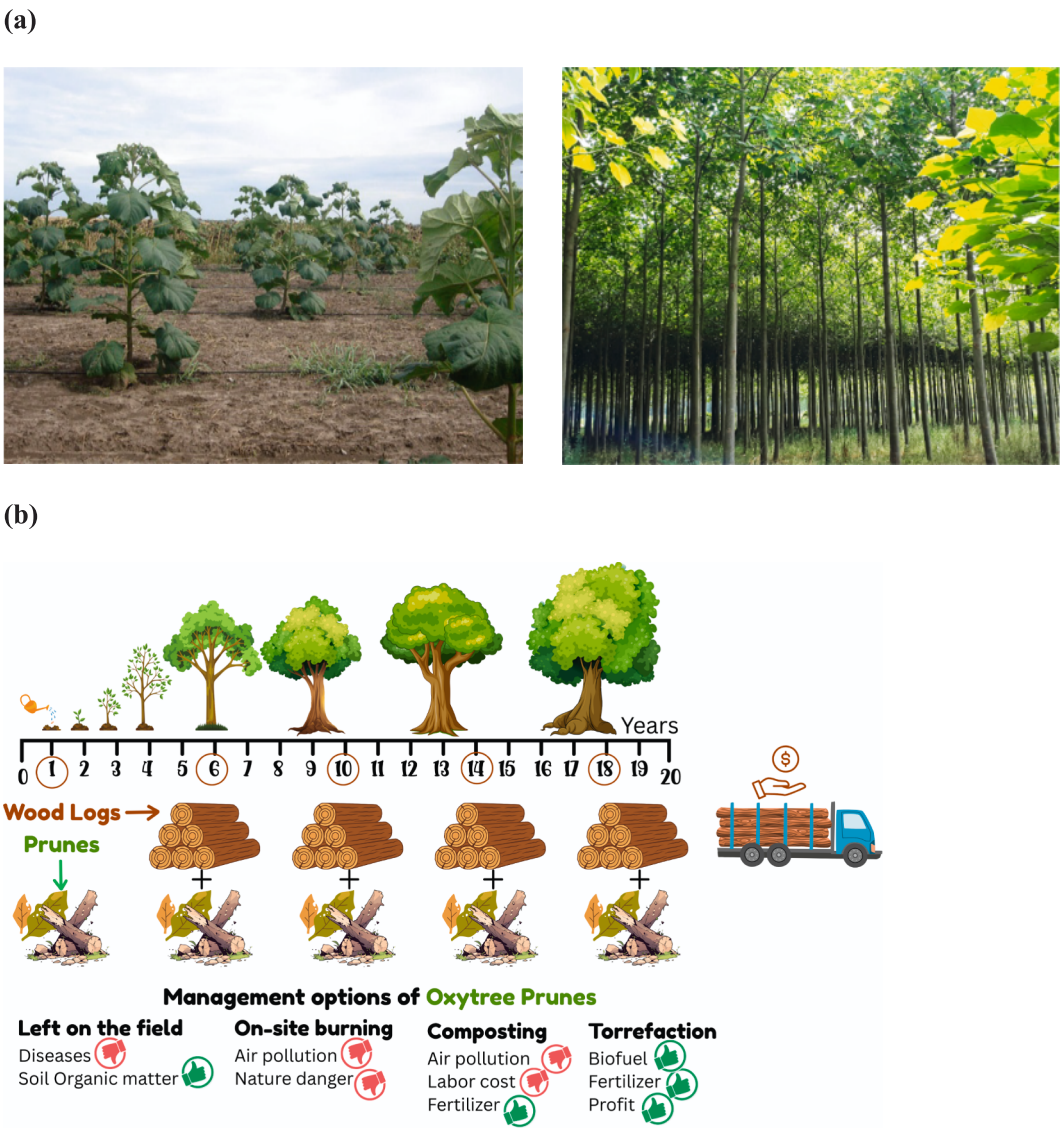

Fig. 1. Oxytree plantation after four months of growth and at the mature forest stage – (a), along with a schematic representation of the proposed utilization of biomass residues from the oxytree plantation – (b).

2.2. Wet torrefaction

WT of oxytree was carried out in 75 mL stainless-steel batch reactors (Parr) with a working volume of 30 mL (Fig. S1b). Each is fitted with online regulators for pressure and temperature control. The reactors were operated at 200, 220, 240, and 260 °C, with residence times of 30 and 60 min. Three grams of oxytree were placed in each reaction at a water/substrate ratio of 10. A magnetic stirring bar was used to stir the reaction mixture at 400 rpm to ensure proper mixing. The heating temperature was controlled by a programmed temperature controller, while an inline thermocouple directly measured the reactor temperature. The residence time was taken from the moment the target temperature was reached.

After the reaction was complete, the reactors were rapidly cooled in an ice bath, and the torrefaction process was stopped. Product solutions were then filtered through a 0.22 μm membrane filter. The hydrochars obtained were dried overnight at 105 °C. The liquid samples were analysed in duplicate using gas chromatography (GC) with an Agilent GC-7890A and an Agilent 5977B GC/MSD, achieving measurement repeatability with a relative standard deviation (RSD) of ≤5 %. Hydrogen was used as the carrier gas at a flow rate of 1 mL/min. Products were separated efficiently using a capillary column with dimensions of 30 m × 0.25 mm × 0.25 μm DB-WAX Ultra Inert. Initially, the column temperature was set to 40 °C for 4 min, then increased to 200 °C at 12 °C/min, and held for 10 min. A split ratio of 1:150 was maintained throughout. The quantification of all products was performed using an externally verified calibration method.

2.3. Analysis

Proximate analysis was performed to determine the moisture content, volatile matter, ash content, and fixed carbon of the biochar samples. These parameters are essential for evaluating fuel quality, thermal reactivity, and the suitability of biochar for thermochemical and environmental applications. The analysis was conducted according to internationally recognized standard methods: ASTM D3172, ASTM D3173, ASTM D3175, ASTM D3174, and ASTM D7582.

Biochar samples were oven-dried at 105 ± 2 °C for 24 h and ground and sieved to a particle size below 1–2 mm using a laboratory grinder and stainless-steel mesh. The processed samples were stored in airtight containers inside a desiccator to avoid atmospheric moisture uptake before analysis. Moisture content was determined gravimetrically

according to ASTM D3173 [26]. Approximately 1 g of biochar was weighed into a crucible and dried in a convection oven at 105 ± 2 °C for 24 h. The difference in mass calculated the moisture content before and after drying:

$$Moisture\% = \frac{W(initial) - W(dry)}{W(initial)} x100 \quad (1)$$

Volatile matter content was determined according to ASTM D3175 [27] and ASTM D7582 [28]. Approximately 1 g of the dry biochar was placed in a covered crucible and heated in a muffle furnace at 550 ± 10 °C for 2.5 h. The volatile content was expressed as a percentage of the original dry sample:

$$Volatile\ Matter\ \% = \frac{W(dry) - W(residue)}{W(dry)}\ x\,100 \quad (2)$$

Ash content was determined following ASTM D3174 [29]. The residue obtained from the volatile matter test was placed in an open crucible and combusted at 850 ± 25 °C in a muffle furnace for six hours under oxidizing conditions. The ash content was calculated as:

$$Ash\% = \frac{W(ash)}{W(dry)} x100 \quad (3)$$

Fixed carbon content was calculated by subtracting the moisture, volatile matter, and ash contents from 100 %, following the ASTM D3172 guideline:

$$Fixed\ Carbon\ \% = 100 - (Moisture\ \% + Volatile\ Matter\ \% + Ash\ \%) \quad (4)$$

All proximate analysis measurements were performed in triplicate, and the average values were reported. Results are presented on both a dry basis (db).

Elemental (C, H, N, and S) analysis of the raw and torrefied (DT-WT) samples was performed through a service procurement at the METU R&D Education and Measurement Center laboratory, in Ankara. The LECO CHNS-932 elemental analyzer was used for the elemental analysis.

HHV was calculated using the Dulong Equation based on elemental analysis results [30]. By determining the calorific value, this analysis helps to understand how DT enhances the energy content of biomass, making it more suitable for energy production. This data is essential for evaluating how torrefaction can improve the performance of biomass as a fuel, particularly for power generation and biofuel production.

$$HHV\left(\frac{BTU}{Lb}\right) = 145{*}C + 610{*}\left(H - \frac{1}{8}{*}O_2\right) + 40{*}S + 10{*}N \quad (5)$$

The study examines the energy and exergy analysis of the biomass torrefaction process by calculating mass yield, energy densification ratio, and energy yield using the following formulas (6, 7, and 8).

$$MY = \frac{m_b}{m_a} x100 \quad (6)$$

where MY is the mass yield (%), m_a is the mass of raw material before torrefaction (kg), and m_b is the mass of biomass after torrefaction (kg) [31].

$$DoT = \frac{HHV_b}{HHV_a} \quad (7)$$

where DoT is the energy densification ratio, which is called the degree of torrefaction, HHV_b is the high heating value of torrefied biomass (MJ/kg), and HHV_a is the high heating value of raw material (MJ/kg) [32].

$$EY = MYxDoT \quad (8)$$

where EY is the energy yield (%), MY is the mass yield (%), and DoT is the energy densification ratio [32].

$$HHV_{increase}(\%) = 100 \times \frac{HHV_{product} - HHV_{feedstock}}{HHV_{feedstock}} \quad (9)$$

where $HHV_{product}$ is the higher heating value of the produced biochar, and $HHV_{feedstock}$ is the raw material. $HHV_{increase}$ refers to the increase in HHV between raw and torrefied biomass, expressed as a percentage.

Carbon enrichment measures the relative increase in carbon concentration in the product compared to the feedstock.

$$Carbon\ Enrichment = \frac{Carbon\ content_{product}}{Carbon\ content_{feedstock}} \quad (10)$$

Carbon yield (%) indicates the fraction of original carbon retained in the solid product after torrefaction.

$$Carbon\ Yield(\%) = MY \times \frac{Carbon\ content_{product}}{Carbon\ content_{feedstock}} \times 100 \quad (11)$$

Hydrogen yield (%) represents the proportion of the initial hydrogen preserved in the torrefied solid.

$$Hydrogen\ Yield(\%) = MY \times \frac{Hydrogen\ content_{product}}{Hydrogen\ content_{feedstock}} \times 100 \quad (12)$$

Decarbonization (%) reflects the extent of carbon loss from the feedstock during torrefaction.

$$Decarbonization(\%) = 100 - MY(\%) \times \frac{Carbon\ content_{product}}{Carbon\ content_{feedstock}} \times 100 \quad (13)$$

The thermal degradation behavior of raw and torrefied oxytree biomass was investigated through TGA and DTG techniques to characterize the effects of different torrefaction temperatures on biomass properties. Measurements were made using a NETZSCH TG 209 F3 Tarsus thermogravimeter under a flow rate of 20 mL/min of N_2. This section describes the experimental methodology employed in sample preparation, the torrefaction process, thermal analysis, and data interpretation. The temperature program consisted of an initial stabilization period at 30 °C for 2 min, followed by heating at a constant rate of 10 °C/min from 30 to 800 °C. This temperature range was selected to encompass all the major thermal decomposition events in lignocellulosic biomass, including moisture removal, hemicellulose decomposition, cellulose degradation, and lignin breakdown.

The TGA provided continuous measurements of sample weight as a function of temperature and time, allowing calculation of weight-loss percentages for different temperature intervals. The analytical software automatically generated the first derivative of the TGA curve (DTG) to determine the rate of weight loss (g/min) as a function of temperature, providing insights into the thermal degradation kinetics and identifying characteristic decomposition zones for different biomass components. To determine the minimum ignition temperature, biomass combustion experiments were conducted using Differential Scanning Calorimetry (DSC) under an oxygen-rich atmosphere. The Ozawa–-Flynn–Wall (OFW) kinetic method was applied to calculate activation energy (E_a) and investigate how torrefaction parameters influence minimum ignition temperatures. Below, the OFW equations are run at several heating rates for each fixed conversion level alpha, and an ln vs 1/T plot is generated, yielding the slope (m). The slope value allows for the calculation of E_a for each temperature.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} exp\left(-\frac{Ea}{RT}\right) f(\alpha) \quad (14)$$

$$\ln(\beta) = \ln\left(\frac{AEa}{g(\alpha)R}\right) - 5.331 - 1.0516\frac{Ea}{RT} \quad (15)$$

$$Ea = -\frac{R}{1.0516}m \tag{16}$$

where β = heating rate (K·min^{-1} or K·s^{-1}, be consistent), A= pre-exponential factor, E_a = apparent activation energy (J·mol^{-1}), R= gas constant (8.314 J·mol^{-1}·K^{-1}), $g(\alpha)$ = integral form of the reaction model (cancels in isoconversional slope), α = conversion fraction; T_α= temperature at that fixed α degree.

Biochar samples obtained during the torrefaction of biomass in a reactor at 200, 220, 240, and 260 °C for 30 and 60 min using two processes (WT and DT) were analyzed for ignition. A Mettler Toledo DSC Sirius 3500 differential scanning calorimeter in an oxygen atmosphere (Q-flow 50 mL/min) was used. Approximately 3 mg of each torrefied biomass was placed in an open alumina pan and heated from 50 to 500 °C at four different heating rates (HR) (10, 20, 30, and 40 °C/min). Using the Ozawa–Flynn–Wall method, which assumes complete mass conversion, the E_a of the oxidation reaction is determined without presuming a specific mechanism. The Ozawa–Flynn–Wall method assumes 100 % mass conversion, allowing the determination of the average E_a without knowledge of the exact oxidation reaction mechanism.

3. Results

This section presents the effects of DT and WT torrefaction on Oxytree pruning and compares both processes in terms of mass and energy yields, fuel properties, and product-phase distributions.

3.1. Dry torrefaction

This treatment initiates structural changes in the biomass, enhancing hydrophobicity and increasing brittleness, thereby augmenting its energy density. Table S1 and Table S2 present data demonstrating that torrefaction significantly altered the elemental composition and energy characteristics of oxytree biomass. The carbon content increased from 45.1 % in the raw sample to 54.2 % at 260 °C after 60 min of treatment. This was accompanied by a slight reduction in hydrogen content and a visible decrease in oxygen, which dropped from 44.4 % to 33.1 %. These changes show the thermal decomposition of hemicellulose and cellulose during the process. A slight increase in nitrogen and ash content was observed, most likely due to the accumulation of inorganic components as volatile substances were released during torrefaction. The HHV improved substantially from 16.4 MJ/kg in the raw biomass to 20.5 MJ/kg after torrefaction, representing a 25.1 % increase in energy content. The O/C and H/C atomic ratios decreased, indicating the development of more aromatic, carbon-rich, and hydrophobic structures. The longer residence time further enhanced these transformations, confirming the role of the thermal exposure period in devolatilization and biochar stabilization. Overall, torrefaction significantly improves the fuel quality of oxytree biomass, especially under more severe process conditions. For biochar production, it is ideal to aim for a mass reduction of 30–40 % [33]. This particular interval strikes a harmonious balance, ensuring a substantial biomass conversion while preventing excessive loss of the final product. Unlike applications such as activated carbon or chemical adsorbers, biochar production does not require an overly delicate output; rather, it produces a product that has undergone carbonization. The primary focus is on achieving a practical level of mass reduction that enables efficient conversion without compromising the usefulness of the result. Within the realm of thermochemical conversion explored in this study, the primary focus is biochar production, with particular emphasis on its energy implications.

The H/C ratio indicates the level of hydrogen content relative to carbon (Fig. 2). Higher H/C ratios suggest a more hydrogen-rich composition, while lower ratios indicate a more carbon-rich composition. The O/C ratio indicates the oxygen-to-carbon ratio. In the van Krevelen diagram, these ratios are plotted against each other to provide insights into the elemental composition of organic matter. The H/C and O/C ratios influence the fuel properties of biochar, including its calorific value, combustion characteristics, and reactivity. Higher H/C ratios generally indicate higher energy content and better combustion properties, while lower O/C ratios suggest lower ash formation and improved combustion efficiency. Torrefied oxytree products show a localization on peat and coal areas, as shown in Fig. 2.

Fig. 3 shows that torrefaction temperature (200–260 °C) and residence time (30 and 60 min) affect the energy yield and HHV of oxytree biomass under DT conditions. In both cases, there is a clear trend: as the temperature and duration of torrefaction increase, energy yield tends to decrease, while HHV increases. This outcome is expected, as higher temperatures promote thermal degradation, especially of hemicellulose, and drive off volatiles, resulting in a more carbon-rich, energy-dense solid product. For oxytree, the increase in HHV is quite pronounced, particularly at 260 °C and 60 min, where it peaks at 20.46 MJ/kg. However, this improvement in fuel quality is accompanied by a sharp drop in energy yield, especially at longer residence times. At 30 min, oxytree retains more of its original energy content while still showing a notable rise in HHV, suggesting that shorter torrefaction times may offer

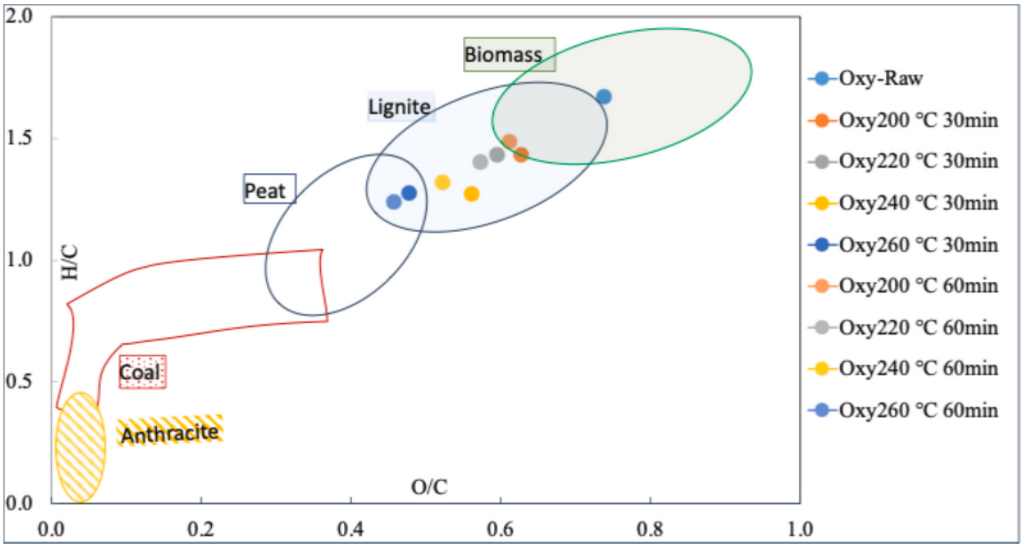

Fig. 2. The van Krevelen diagram of raw and DT oxytree prunes.

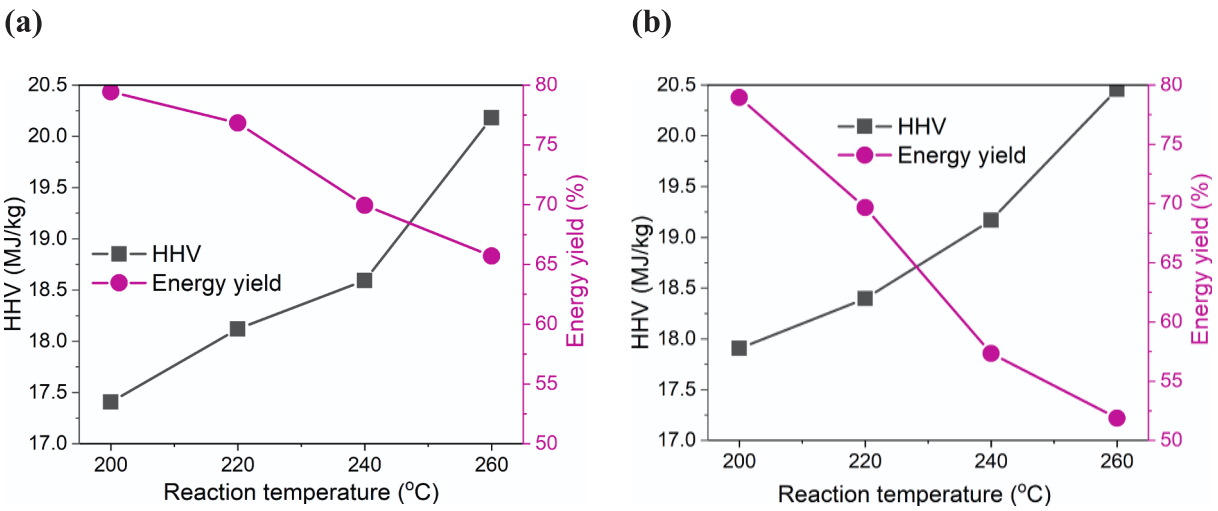

Fig. 3. Effect of torrefaction temperature and residence time on the energy yield and HHV of oxytree biomass under DT conditions: (a) – 30 min, (b) – 60 min residence time.

a better compromise between yield and quality.

The thermal degradation behaviors for raw oxytree biomass and its torrefied equivalents at different temperatures (200, 220, 240, and 260 °C) were extensively examined through the TGA and DTG plots shown in Fig. S2. The TGA profiles (Fig. S2a) show that prior torrefaction markedly increases thermal stability: the mass remaining at 900 °C rises from 5.4 % for raw oxytree to 16.7, 21.0, 28.5, and 49.5 % for samples torrefied at 200, 220, 240, and 260 °C, respectively. This reflects enhanced thermal stability and significant degradation of volatile components during higher-temperature torrefaction. TGA measures the weight loss of the material as a function of temperature, and DTG analysis yields the rate of weight loss.

The raw oxytree biomass's TGA profile shows a steep weight loss with increasing temperature, with distinct phases corresponding to water evaporation, hemicellulose decomposition, cellulose degradation, and lignin degradation. Torrefied samples exhibit progressively lower weight loss with increasing torrefaction temperature. This behavior results from the chemical changes that occur during the torrefaction process, a heat treatment that involves partial hemicellulose decomposition and an increase in the biomass's fixed carbon content. Fig. S2 shows that in the initial stage (<150 °C), raw oxytree biomass undergoes a significant weight loss due to the evaporation of water content, equivalent to the drying stage, where unbound water is eliminated from the biomass structure. Torrefied samples lose less weight during this stage because torrefaction minimizes unbound and bound water content. The hydrophobicity of the torrefied biomass is a direct consequence of this water content reduction. With increasing torrefaction temperature, water content further decreases, stabilizing the material for handling and storage. Hemicellulose, cellulose, and lignin degradation characterize the primary thermal degradation phase (200–500 °C). The most thermally unstable component, hemicellulose, degrades first (200–300 °C), followed by cellulose (300–400 °C) and lignin (400–500 °C). For raw oxytree, this phase is characterized by extensive weight loss due to high volatile content. Torrefied samples, nevertheless, experience reduced weight loss because hemicellulose is broken down either partially or totally during torrefaction. Biomass torrefied at high temperatures (240 and 260 °C) exhibits minimal hemicellulose degradation during this phase, with cellulose and lignin remaining the major constituents that undergo thermal degradation. The residual mass observed beyond 500 °C corresponds to the fixed carbon content and ash remaining after volatile components are burned off. Torrefied biomass retains more residual mass than raw biomass due to increased carbonization during torrefaction. As the torrefaction temperature increases, the fixed carbon content increases, while the volatile matter content decreases. Biomass torrefied at 260 °C exhibits the highest residual mass among all samples analyzed, indicating significant thermal treatment that enhances carbon stability.

The DTG graph provides additional insights into the rate of weight loss during thermal degradation. For raw oxytree biomass, a sharp decrease starting around 200 °C represents the rapid decomposition of hemicellulose and cellulose. Secondary peaks or shoulders arise from overlapping degradation phases of these components. As torrefaction temperature rises, these peaks shift to higher temperatures (370–450 °C), reflecting enhanced thermal stability resulting from structural changes in biomass during torrefaction. The intensity of DTG peaks decreases with increasing torrefaction temperature, indicating lower volatile content in torrefied biomass. Biomass torrefied at 260 °C exhibits a broader DTG peak with lower intensity than raw biomass. This behavior suggests slower thermal degradation due to higher carbon stability and reduced oxygen functional groups. The absence or reduction of secondary peaks in torrefied samples indicates that hemicellulose has largely decomposed during torrefaction itself.

From a scientific perspective, torrefaction alters both the chemical composition and physical structure of biomass. Wang et al. [34] discussed how hemicellulose undergoes significant depolymerization and decarboxylation during torrefaction. These reactions decrease oxygen-containing functional groups (e.g., hydroxyl groups), resulting in lower O/C and H/C ratios [35]. Increased aromaticity enhances energy density and combustion efficiency while lowering smoke emissions during burning.

Cellulose remains relatively stable under mild torrefaction conditions (<220 °C) but begins to degrade at higher temperatures (>240 °C). Lignin, being thermally stable due to its complex aromatic structure, contributes significantly to the residual mass after combustion. Torrefaction also improves structural rigidity by increasing fixed carbon content and reducing amorphous regions within cellulose fibers. Kostyniuk and Likozar [36] found that, with increasing torrefaction temperature, the content of volatile organic compounds (VOCs) decreases, while the content of fixed carbon rises. The enhanced aromaticity resulting from torrefaction leads to a higher energy density and improved combustion efficiency, making biomass more suitable for use in energy systems. In conclusion, TGA and DTG analyses show that torrefaction enhances the thermal properties of oxytree biomass by reducing moisture content, increasing fixed carbon levels, and improving thermal stability. Higher torrefaction temperatures resulted in greater carbonization and reduced volatile matter, shifting the degradation peaks toward higher temperatures. These findings show the potential of torrefied oxytree biomass as an upgraded bioenergy

feedstock with improved combustion characteristics and storage stability. Such properties make it suitable for industrial applications such as bioenergy or biochar manufacturing for soil conditioning. Further research could explore its performance in various combustion systems or its role in sustainable energy solutions.

Fig. 4 indicates significant deoxygenation and dehydration reactions within the biomass structure, reflecting the thermal decomposition of oxygen-rich components such as hemicellulose and cellulose. Fig. 4a, corresponding to 30 min torrefaction, displays a linear relationship (R^2 = 0.9606) between the O/C and H/C ratios. The equation of the trend line, y = 0.5247 + 1.52038x, suggests that hydrogen content reduces proportionally with oxygen removal, indicating effective thermal degradation that leads to higher carbon enrichment. Similarly, the right plot shows the 60 min torrefaction with an even stronger linear correlation (R^2 = 0.9957) and trend line equation y = 0.507 + 1.58077x (Fig. 4b). This notably high R^2 value emphasizes a more consistent and predictable carbonization behavior for longer reaction times.

3.2. Wet torrefaction

Fig. 5 illustrates the changes in the chemical structure of oxytree biomass during WT. As both temperature and residence time increase, the H/C and O/C atomic ratios decrease steadily. This shift means the material is losing hydrogen and oxygen mainly through dehydration and decarboxylation and becoming richer in carbon. By the time the process reaches 260 °C with 60 min residence time, the biochar's composition approaches that of peat and even lignite on the van Krevelen diagram, indicating that it's becoming more coal-like in terms of energy content and stability. This is a clear sign of successful carbonization. Compared to DT, WT is more effective at removing oxygen and improving the quality of the final product. The presence of water in the process helps break down oxygen-rich compounds more efficiently, leading to a cleaner, more energy-dense solid fuel. Table S3 presents the effects of increasing WT temperature and residence time on elemental analysis results. Additionally, Table S4 indicates that these WT conditions significantly improved energy yield and carbon enrichment, with notable decarbonization at higher torrefaction temperatures, highlighting the effective thermal upgrading of oxytree biomass.

Fig. 6 and Fig. 7 show that higher torrefaction temperatures in WT lead to a progressive increase in the HHV of oxytree biomass, regardless of residence time. The HHV of raw oxytree biomass was 16.3 MJ/kg. After WT, this value increased significantly to 27.9 MJ/kg at 260 °C for 60 min, representing a 41.4 % improvement. This boost reflects a clear trend: as temperature and time increase, carbon content rises (from 45.1 to 68.3 %) while oxygen drops sharply (from 44.4 % to 17.3 %), making the fuel more energy-dense and stable.

For samples torrefied for 30 min, the HHV rose steadily from 21.1 to 27.3 MJ/kg, but the energy yield dropped from 85.7 to 75.7 % as the torrefaction temperature increased from 200 to 260 °C. This suggests that higher devolatilization at 260 °C reduced overall energy retention. Similarly, carbon yield decreased from 80.0 to 67.5 %, while decarbonization rose from 19.9 to 32.5 %, indicating increased carbon loss despite higher HHV. In comparison, the 60 min torrefaction preserved more energy up to 240 °C, with the highest energy yield of 78.5 % and carbon yield of 71.3 % at 240 °C. At 260 °C, however, yields declined to 74.2 % (energy) and 65.8 % (C), reflecting more severe decomposition. The optimal condition appears to be 240 °C for 60 min, yielding an HHV of 24.7 MJ/kg (33.9 % increase) with good carbon retention (71.3 %) and moderate decarbonization (28.7 %). The energy yield decreases overall, but shows a slight recovery at 240 °C, suggesting this temperature offers the best trade-off between energy efficiency and HHV improvement.

Fig. S3 shows that WT is more effective at increasing oxytree biomass carbon content than DT. At identical temperatures and residence times, WT consistently resulted in higher carbon enrichment. At the highest temperature of 260 °C and 60 min residence time, WT achieved a carbon content of 68.3 %, significantly higher than the 54.2 % observed with DT under the same conditions. Additionally, extending the residence time from 30 to 60 min further enhances carbonization for both methods, although the effect is notably more pronounced in the WT process. These findings underscore the superiority of WT in enhancing the carbon-rich properties of oxytree biomass, making it potentially more suitable for energy and environmental applications than DT. Fig. S4 shows that WT leads to a more advanced degree of torrefaction than DT at all tested temperatures and times. This difference is evident at the shorter residence time (30 min), where WT accelerates biomass breakdown more effectively. The presence of pressurized water in WT likely facilitates hydrolysis, which enhances hemicellulose degradation and oxygen removal, resulting in a more carbon-rich product [37]. At 60 min, DT shows improved performance (DoT 1.25), but it still cannot match the uniform, rapid carbonization achieved by WT. The highest torrefaction degree (DoT 1.71) was observed under WT at 260 °C, demonstrating its strong thermal efficiency. Overall, these findings support WT as a more reactive and efficient method for biomass upgrading, particularly when process time and conversion depth are critical.

Both the WT and DT processes resulted in a steady decrease in the O/

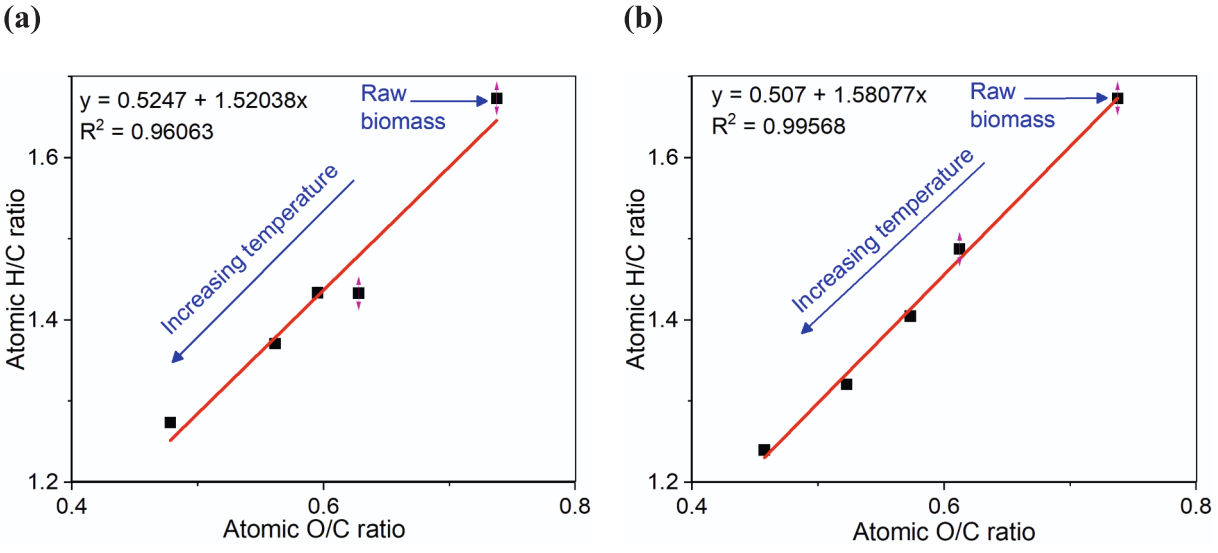

Fig. 4. The O/C and H/C atomic ratios vary with DT temperature and residence time (a) 30 min, and (b) 60 min.

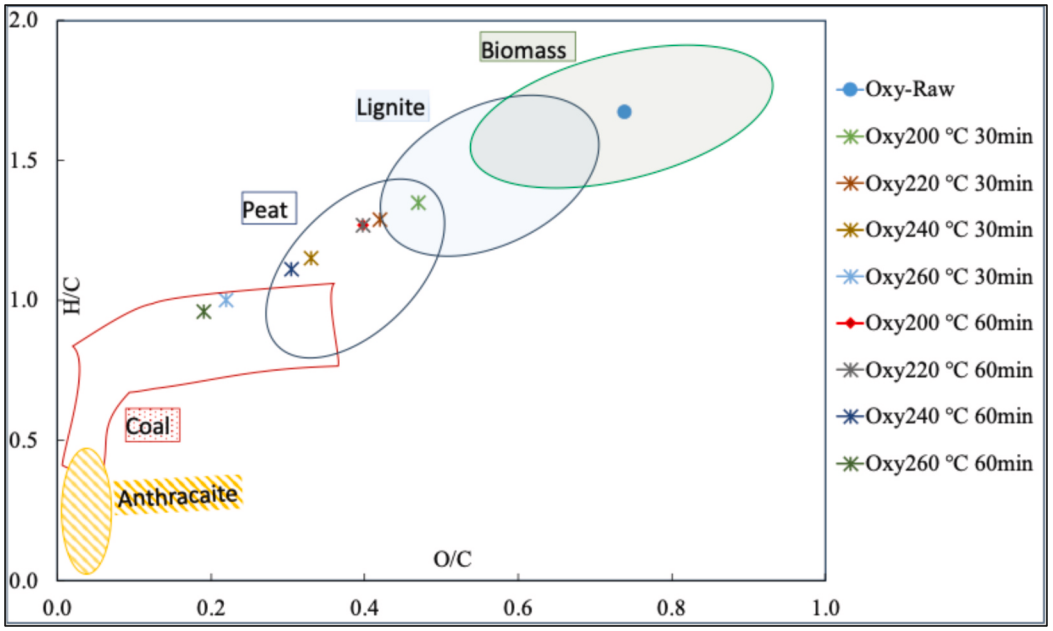

Fig. 5. The van Krevelen diagram of raw and WT oxytree prunes.

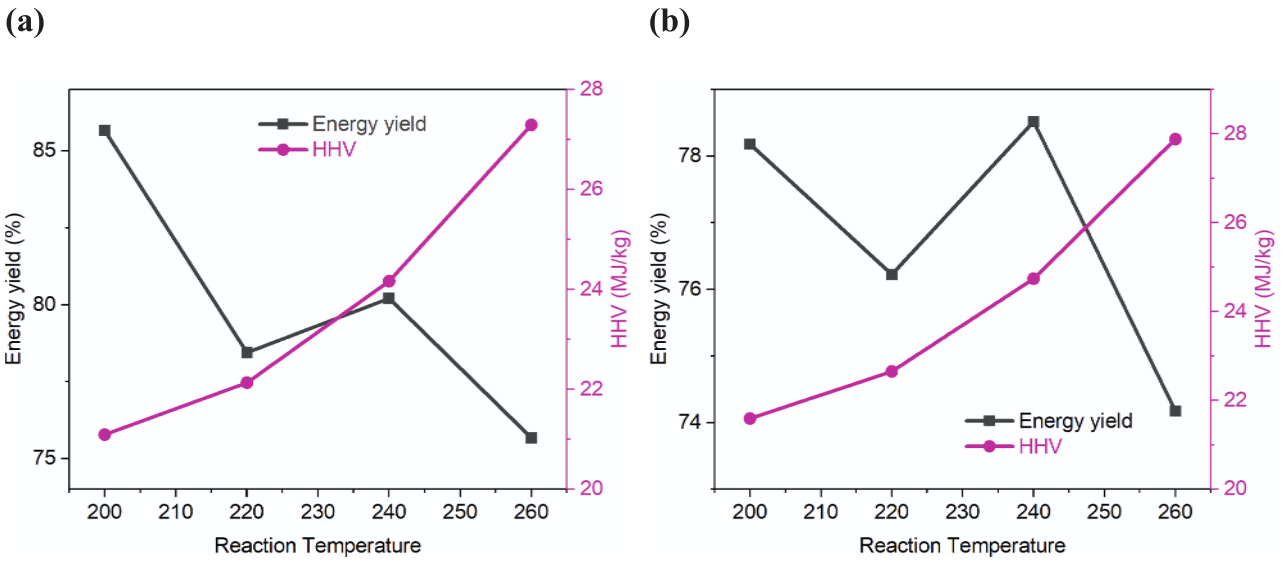

Fig. 6. Effect of torrefaction temperature and residence time (a) 30 min, and (b) 60 min., on energy yield and HHV of oxytree biomass under WT conditions.

C and H/C atomic ratios of oxytree biomass with increasing temperature and time, indicating progressive carbonization. However, the slopes and final positions differ notably between the two methods. In the WT plots, samples shift more sharply toward the lower left region of the diagram, especially at higher severity (260 °C, 60 min), suggesting more efficient removal of oxygen and hydrogen. This enhanced deoxygenation is likely due to the hydrolytic reactions in the pressurized water environment, which are absent in dry conditions [37]. By contrast, the DT samples show a more gradual shift. Although higher temperatures lower the atomic ratios, the final points remain closer to the raw biomass, especially at 30 min. This indicates less intense chemical transformation, likely because the process lacks the catalytic effects of water [38].

Also notable are the linear fits and R^2 values; both methods yield high correlations. Still, WT maintains a slightly lower slope, reflecting a more balanced dehydrogenation and decarboxylation pattern, and better reaches the path toward coal-like solid fuels (Fig. 8). WT achieves significantly lower O/C and H/C ratios than DT at all conditions. At 260 °C and 60 min, WT yields an O/C of 0.19 and H/C of 0.96, compared to DT with O/C 0.46 and H/C 1.24. This reflects that WT leads to greater deoxygenation and aromatic condensation, improving the biochar's thermal stability and energy characteristics.

The thermochemical conversion of lignocellulosic biomass through WT represents a promising pathway to produce value-added chemicals and enhanced solid fuels. This study presents a detailed analysis of the liquid-phase products obtained from the WT of oxytree biomass at varying reaction temperatures and residence times. The GC–MS results help us to understand the WT reaction mechanisms, degradation pathways, and optimization parameters. The GC–MS analysis of liquid products from the WT of oxytree biomass reveals a complex mixture of compounds derived from the hydrothermal decomposition of cellulose, hemicellulose, and lignin. Fig. 9a represents the product distribution after a 30 min residence time, while Fig. 9b depicts the distribution after 60 min of reaction time. Both datasets illustrate product evolution across four reaction temperatures: 200, 220, 240, and 260 °C. The observed

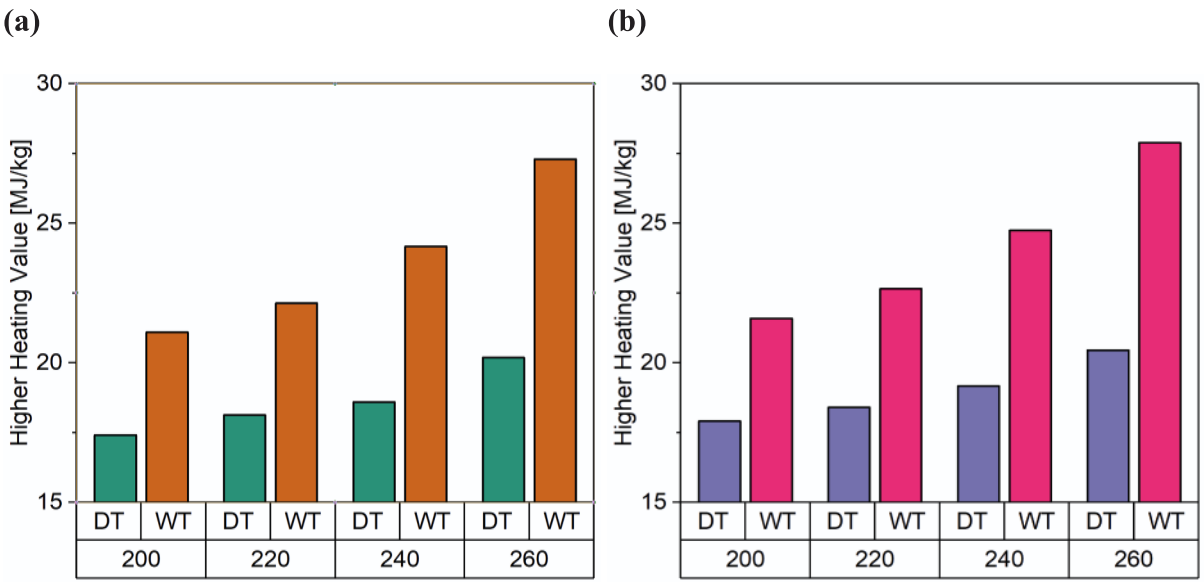

Fig. 7. Comparison of HHVs obtained from WT and DT (a) 30 min, and (b) 60 min.

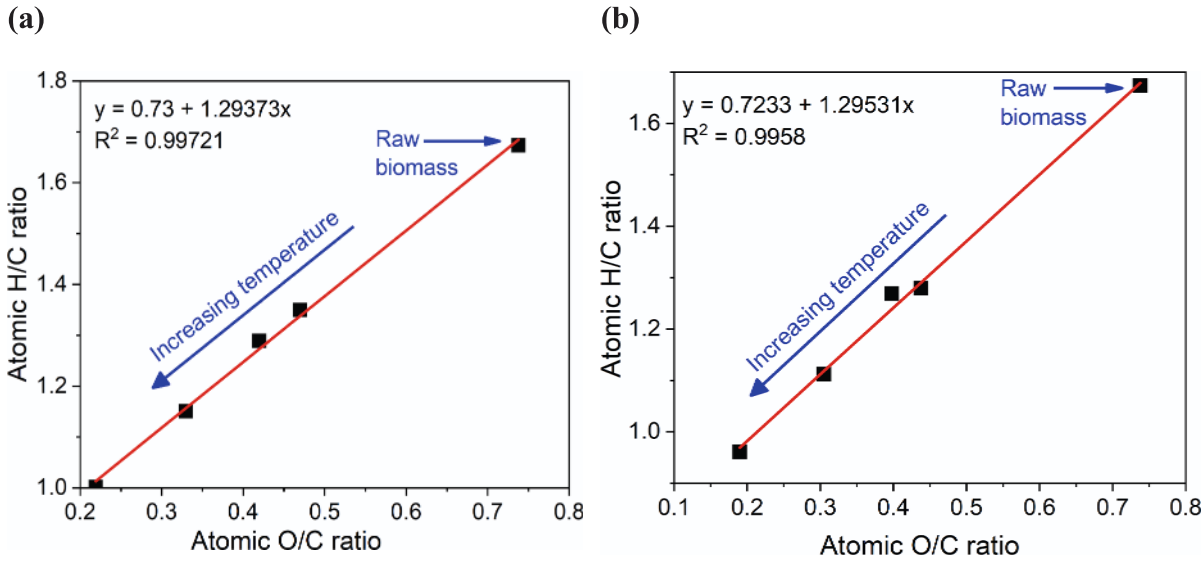

Fig. 8. The O/C and H/C atomic ratios vary with WT temperature and residence time (a) – 30 min; (b) – 60 min.

compounds can be categorized into several chemical classes, including organic acids, furans, ketones, aldehydes, alcohols, and phenolic compounds. At 200 °C, 30 min yields 17.9 % furfural and 15.9 % acetic acid, whereas 60 min produces 18.9 % and 19.8 %, respectively. Notably, a shorter residence time yields more 5-HMF (11.0 % vs. 9.1 %) and generates formic acid at 4.2 %. In contrast, compounds that form with longer residence times are barely formed, indicating that the shorter residence time limits the secondary degradation of sugar-derived intermediates. These compounds result from the dehydration of pentoses (xylose) and hexoses (glucose), respectively, indicating that hemicellulose breakdown is the primary process at this temperature [39].

Rising to 220 °C shifts both runs toward acetic acid dominance: at 30 min, it reaches 21.7 %, and at 60 min, 22.3 %. Furfural remains at 14.1 % for 30 min but falls more sharply to 9.8 % in 60 min. Likewise, 30 min maintains 5-HMF at 5.9 % versus just 4.3 % in 60 min. A 30 min reaction also resulted in the formation of 2.4 % methyl formate and 1.7 % 2,5-hexanedione. In contrast, small C_1–C_6 fragments are absent or significantly lower in the 60 min reaction, further indicating that longer residence times drive deeper fragmentation. Longer residence times typically lead to higher acetic acid concentrations while decreasing the yields of furfural and 5-HMF [40,41]. Both peak acetic acid levels were observed at 240 °C (30 min: 24.2 %; 60 min: 25.1 %). Yet, a shorter residence time still yields 3.50 % furfural and 3.46 % 5-HMF, whereas a longer residence time causes a drop to 2.10 % and 0.85 %, respectively. Kostyniuk and Likozar [41] showed that furfural (and acetic/levulinic acids) increase with temperature severity (180–260 °C), whereas 5-HMF exhibits maximum selectivity at 220 °C (73.3 % at 30 min) rather than a monotonic rise. At fixed 220 °C, extending the residence time from 15 to 60 min raised furfural (4.9 % to 8.2 %; peak 11.1 % at 30 min) while 5-HMF decreased beyond 30 min and higher temperatures than 220 °C, consistent with secondary rehydration/fragmentation at longer holds. These patterns align with oxytree results, supporting this study's findings.

Shorter residence time acetone (5.2 %) is lower than longer residence time (8.5 %), but shorter residence time accumulates more nitrogen-heterocycles (3-pyridinol 30 min: 6.9 % vs. 60 min: 4.4 %) and methoxy-phenols, showing that the shorter treatment favors preservation of certain aromatics and heterocycles. At 260 °C, acetic acid

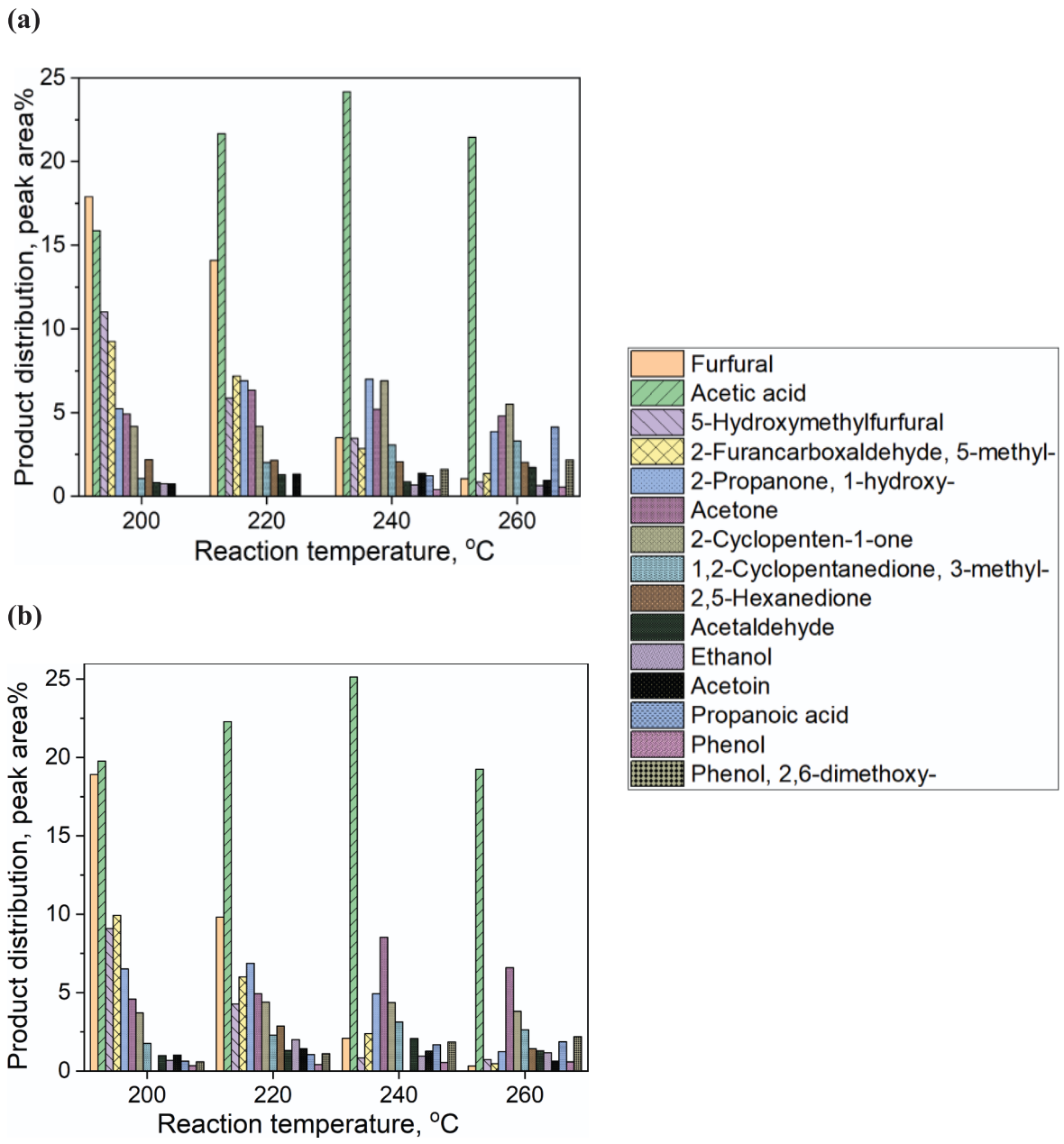

Fig. 9. GC–MS components of oxytree WT liquid products: (a) – 30 min; (b) – 60 min.

remains dominant (30 min: 21.4 %; 60 min: 19.3 %). Furfural and 5-HMF in shorter residence time are 1.05 % and 0.85 %, still double those in longer (0.3 % and 0.7 %). Shorter residence time also continues to generate light acids (propanoic acid at 4.14 %) and higher methoxy phenols (2.17 %), whereas with longer residence time, the production of these secondaries is minimal.

In summary, decreasing the residence time to 30 min preserves higher yields of primary dehydration products (furfural, 5-HMF) and yields additional small oxygenates and heterocycles (formic acid, methyl formate, 3-pyridinol). Extending the residence time to 60 min gives those furans an extra opportunity to break down into smaller acids and ketones (acetone and acetic acid), while losing many of the mid-weight intermediates. Adjusting the residence time gives direct control over the product mix: shorter treatments retain higher amounts of valuable furans. In comparison, longer treatments drive those furans to break down into lighter carboxylic acids and ketones. Wang et al. [42] found that increasing WT temperature from 180 to 210 °C increased the acid fraction in the ensuing pyrolysis oil, and the hydrocarbon fraction reached 71 %, indicating stronger deoxygenation at the highest temperature severity.

The ignition behavior of DT and WT biochars was quantified using DSC to obtain average ignition onset temperature (T_{onset}), average ignition temperature (T_{avg}), and activation energy (E_a) determined using the OFW method at heating rates of 10, 20, 30, and 40 °C/min. Ignition metrics govern co-firing stability and start-up requirements; comparing DT vs. WT shows how torrefaction type and severity affect char reactivity and its suitability as a solid fuel. T_{onset} was calculated using DSC signal curves analyzed with Proteus 6.1. For each heating rate, three ignition onset values were averaged over the degradation temperature range of 50–500 °C. The experimental studies carried out showed changes in the DSC signal curves. During tests of biochar at the lowest HR of the sample, a typical thermogram shape was observed, with three distinct peaks visible at approximately 290, 420, and 460 °C (Fig. 10a). It was noted that as the HR increased from 10 °C/min to 40 °C/min, a visible exothermic signal increase was observed on the Sirus 3500 DSC instrument. The strongest DSC signal was observed at 40 °C/min HR,

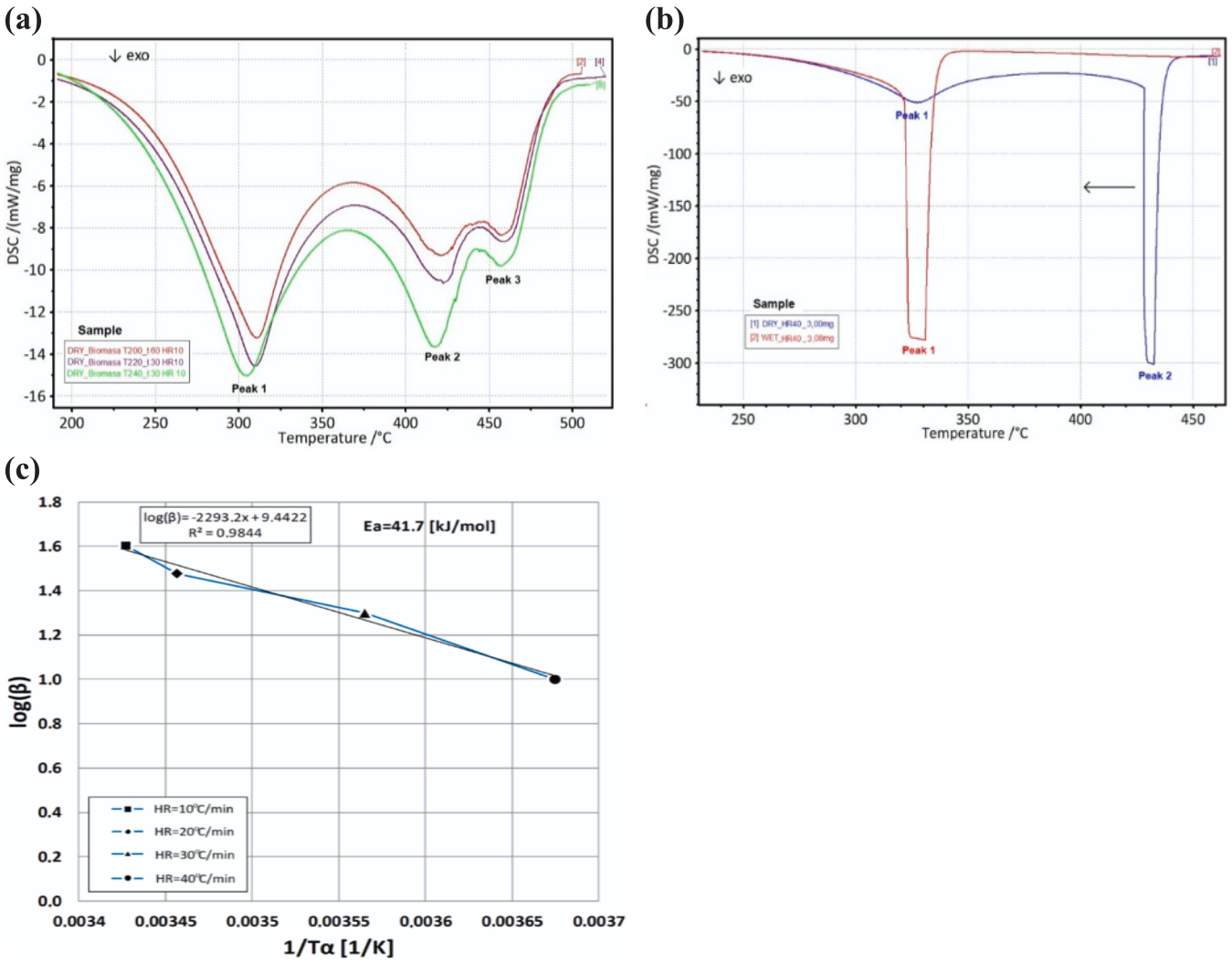

Fig. 10. (a) DSC thermograms of DT samples treated at 200, 220, and 240 °C with a heating rate of 10 °C/min; (b) Comparison of DSC thermograms for samples torrefied at 240 °C for 30 min: DT (blue) vs. WT (red); (c) Ozawa–Flynn–Wall kinetic analysis for the WT sample treated at 260 °C for 60 min.

resulting in visible combustion of biochar throughout the entire sample volume. DSC analysis of the WT biochar at a 40 °C/min HR revealed ignition temperatures between 285 and 320 °C, whereas DT biochar samples under the same conditions exhibited a lower ignition temperature of 287–315 °C. WT and DT samples at lower HRs exhibited two-stage combustion in all tested samples.

However, it was observed that increasing the HR above 30 °C/min and the heat flux to the tested samples resulted in a single peak. An increase in the heating rate led to a pronounced rise in DSC signal intensity; the exothermic effect was observed at HR = 40 °C/min. This effect reflects the acceleration of combustion kinetics and the increased heat release resulting from a faster oxidation rate.

Fig. 10b presents a comparison of DSC signal curves for two biochar samples, DT and WT, which were analyzed at 40 °C/min HR. It was observed that the DT exhibits a two-stage combustion process, characterized by a primary exothermic peak around 315 °C and the secondary peak in the range of 417–435 °C. The multi-peaked profile arises from heterogeneous surface oxidation of various carbon-rich domains and lignin-derived fragments [43]. By contrast, the WT sample at a HR of 40 °C/min (Fig. 10b, red curve) shows a single, broad exotherm at 315–320 °C, consistent with a uniform, single-stage combustion that proceeds to complete oxidation and conversion of the material to ash. The heterogeneous chemical composition of the biochar can explain the differences observed in combustion behavior [44]. At lower heating rates, the presence of light, volatile fractions promote a multi-stage combustion mechanism, as these fractions ignite earlier than more thermally stable components.

The activation energy was estimated without assuming a reaction model by the integral isoconversional model-free Ozawa–Flynn–Wall (OFW) approach. For each conversion level α (0.10–0.90), the temperature Tα was read from DSC curves at β = 10, 20, 30, 40 °C. Fig. 10c shows a representative model-free OFW analysis for the WT at 260 °C for 60 min, validating the approach for E_a calculation at a variable HR of 10–40 °C/min. Table S5 summarizes the T_{onset}, T_{avg}, and calculated E_a. A general trend was observed for both WT and DT: higher torrefaction temperature and longer residence time led to lower ignition temperatures, reflecting higher chemical reactivity and oxygen affinity. Data analysis tables showed that, for the WT chars, the lowest T_{avg} were recorded at the most severe conditions, 260 °C for both 30 min and 60 min, falling to 283.4 °C and 301.5 °C, respectively. In contrast, the DT samples showed a similar decline in ignition temperature with increasing torrefaction severity but exhibited a wider range of E_a. While the raw oxytree E_a found as 94 kJ/mol, the highest E_a after torrefaction, 52.9 kJ/mol, appeared in the 200 °C, 60 min DT sample, while DT runs at 240 °C and 260 °C fell between 46.8 and 43.6 kJ/mol.

This pattern, characterized by a higher E_a at milder torrefaction conditions and a lower E_a at harsher torrefaction conditions, is consistent with the results of Lu et al. [45], who showed that torrefaction

decreased the E_a value by 48 % according to raw biomass. This reflects a shift from oxidizing easily reactive fractions (hemicellulose, light organics) at lower temperatures to breaking down more stable, aromatic-rich residues (lignin, carbonized structures) as the reaction progresses [46]. In both WT and DT, increasing torrefaction temperature and time not only lowers the ignition threshold but also narrows the energy barrier needed to sustain combustion, underscoring how process severity governs char reactivity and thermal behavior. In practical terms, WT char behaves more like a highly reactive fuel: it lights quickly and burns rapidly, traits that are functional for stable flame propagation in co-firing applications. DT char, with its higher ignition barrier and slower burn, more closely shows the behavior of lower-grade coals, offering steadier heat release but requiring higher startup temperatures. Wang et al. [47] demonstrated that WT samples initiate and complete decomposition at temperatures approximately 5–49 °C lower than those of DT samples. They explain this by water opening pores and helping vapors move, which lets the material break down sooner. They also report component-specific changes in E_a: the highest change is for hemicellulose, the smallest for lignin, and water-evaporation E_a is about 49 kJ/mol in both WT and DT. These results indicate that WT chars ignite sooner and require less energy than DT chars (lower T_{onset}/T_{avg} and E_a).

4. Discussion

The process of torrefaction has been widely studied for its potential to enhance the fuel properties of various biomass types. DT and WT are two commonly employed methods, each with unique impacts on biomass characteristics such as mass yield, energy density, and chemical properties. Fig. 11 illustrates multiple performance indicators of oxytree-derived biochar produced using two torrefaction methods, summarizing the findings of this study. WT (blue area) demonstrates clear advantages over DT (pink area) in terms of:

- Carbon content and enrichment, confirming enhanced carbonization.
- Energy yield and HHV increase, indicating improved energy recovery.
- Lower O/C and H/C ratios, reflecting higher aromaticity and thermal stability.
- Higher hydrogen and carbon yields, which suggests better preservation of energy-dense elements.

Although WT shows slightly higher mass loss, this is compensated for by greater improvements in fuel quality and stability. This study suggests that WT is more effective for producing high-quality biochar suitable for both energy and environmental applications.

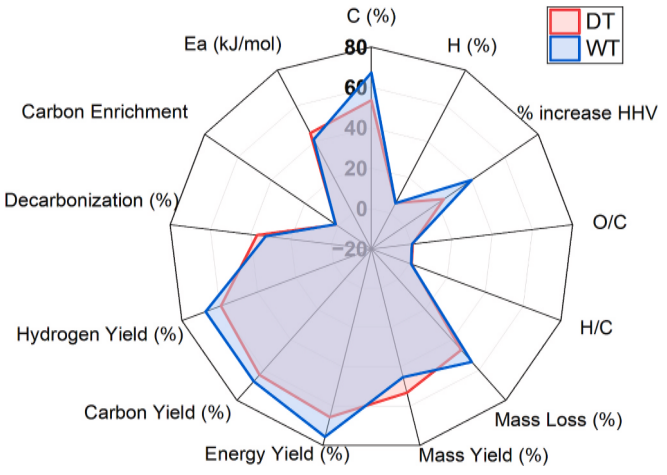

Fig. 11. Comprehensive plot comparing key properties of oxytree biochars produced via DT (pink) and WT (blue) at 260 °C for 30 min.

Comprehensive reviews by Bach et al. [48] and Chen et al. [49] conclude that, under comparable severities, WT typically provides higher energy yields, whereas DT provides higher solid yield and is often preferable at the cost of additional process energy demand. These general trends have been confirmed for a range of feedstocks, including coniferous wood, agricultural residues, and energy crops. One of the key factors in assessing the effectiveness of torrefaction is the process's energy efficiency and mass yield [11]. Ernesto Arteaga-Perez et al. [8] reported that the WT of Pinus radiata resulted in a bio-carbon with an HHV of 26.3 MJ/kg, while DT was 20.6 MJ/kg max. DT resulted in a higher energy yield of up to 90 % compared to WT, which reached a maximum of 79.7 %. In contrast, Yan et al. [9] demonstrated that WT increases the energy density of the lignocellulosic biomass at the same mass yield, mainly by removing hemicellulose and increasing hydrophobicity. This suggests that while DT may be more energy-efficient overall, WT could still provide significant improvements in energy density with similar mass yield. The torrefaction of bamboo and Japanese cedar showed superior performance under DT in terms of solid and energy yield, making it more favorable for fuel properties. However, they noted that WT was better for biomass decomposition, which might make it more suitable for processes such as gasification or biofuel production, where a more reactive product is required [50].

Loblolly pine was treated with WT using hot, compressed water at 200–260 °C, and DT in a N_2 atmosphere at 250–300 °C. The mass yield of the solid product ranged from 57 to 89 %, with energy densification ranging from 108 to 136 % of the original feedstock. Jan et al. [9] observed that hemicellulose is highly reactive in WT even at 200 °C, while cellulose and lignin begin to dissolve at higher temperatures (which improves the biomass's hydrophobicity), yielding more favorable energy outcomes in WT. In contrast, DT results in a solid that resists dissolution, as cellulose and hemicellulose are only mildly reactive, almost similar to lignin, and the solid product produced by DT was insoluble in fiber analysis. This might be particularly advantageous for biofuel applications, where hydrophobicity enhances combustion efficiency and energy production.

Inoue and Sawai [51] further emphasized that WT is particularly effective for high-moisture feedstock, as it achieves a higher net energy ratio than DT. This suggests that WT is more efficient for treating wet biomass, as the hydrothermal process maintains a higher energy output without requiring sample drying. When examining the effects of torrefaction on different biomass types, each material responds differently to the process. Corn stalks were studied for wet and dry torrefaction. They found that WT resulted in an impressive 98 % ash removal and higher yields of hydrogen, bio-oil, and sugars, making it highly suitable for biofuel applications [52]. Research with beech wood and wheat straw showed that DT yielded higher char while WT produced higher volatile content, which could be advantageous for various thermal conversion processes [53]. WT and DT corncobs were studied, and WT increased levoglucosan yield while producing less char. This suggests that WT may be more suitable for biofuel production and gasification, where the liquid fraction (such as levoglucosan) is crucial [54].

WT of corn stalk digestate led to higher crystallinity and better removal of organics and alkalis [55]. This suggests that WT may improve the chemical structure and purity of biomass feedstocks, particularly when refined biomass is required. The impact of WT on Miscanthus was studied, and a significant improvement in grindability was reported, accompanied by a 53 % reduction in ash. This makes WT Miscanthus more suitable for processing in energy systems that require fine grinding, such as pelletization or combustion systems [56]. The reduced ash content is also crucial for improving the performance of biomass in energy production, as excessive ash can lead to operational challenges. Table S6 gives the results of HHV values under WT with various substrates.

WT of oxytree raised the HHV from 16.3 MJ/kg (raw) to 21.09

(200 °C), 22.13 (220 °C), 24.16 (240 °C), and up to 27.29 MJ/kg at 260 °C. This corresponds to an energy densification of + 29, +36, +48, +67 % over raw. DT increased HHV more modestly: 17.41–20.18 MJ/kg from 200 to 260 °C (+7 to + 24 %). At similar severities, oxytree WT sits in the upper range of the literature: it is comparable to Norway birch WT (21.2–24.0 MJ/kg at 200–225 °C) and Tahoe Mix WT (22.6–28.3 MJ/kg at 215–255 °C), and clearly above Miscanthus WT at 160–200 °C (18.2–19.3) and sugarcane bagasse WT at 215–255 °C (19.6–23.4). The low values for rice hulls (16.4–17.9) are consistent with their high silica ash; the relatively high palm kernel shell value (23.4 at 220 °C) reflects its lignin-rich, low-ash character. Overall, own results oxytree WT at 260 °C (27.29 MJ/kg) approach the best-performing literature cases and outperform the DT of conifers reported near similar temperatures.

In conclusion, both DT and WT offer distinct advantages, depending on the type of biomass and the desired product or application area. DT generally provides higher energy density and solid/energy yield, making it ideal for combustion and co-firing in power plants. However, WT can enhance hydrophobicity, improve grindability, and offer higher yields of bio-oil, levoglucosan, and hydrogen, making it suitable for biofuel and gasification applications. The choice between the two methods highly depends on the feedstock's moisture content, the desired product properties, and the intended commercial application.

5. Conclusions

The comparative evaluation of DT and WT processes demonstrates that both methods significantly improve the energy characteristics and fuel quality of oxytree biomass. At the most severe condition tested (260 °C, 60 min), WT produced biochar with a carbon content of 68.3 %, a HHV of 27.9 MJ/kg, and energy yield exceeding 74 %, clearly outperforming DT under identical conditions. Additionally, WT led to a higher degree of torrefaction and carbon enrichment, highlighting its enhanced thermal degradation of oxygenated compounds and more effective carbon retention.

By combining a strictly matched-severity DT/WT matrix with detailed characterisation of both the solid char and, for WT, the aqueous phase, this study provides several specific contributions:

1. The study shows that oxytree WT at 260 °C achieves HHV and energy densification values among the highest reported for WT lignocellulosic residues, while DT of the same material falls within the mid-range of literature values.
2. Linkage between elemental composition (O/C, H/C) to ignition indices derived from TGA, yielding a simple, composition-based indicator of combustion behaviour for preliminary fuel screening.
3. Derives residue-specific operating windows under which DT or WT is preferable, thereby supporting practical decisions on pretreatment routes for oxytree pruning residues in decentralised bioenergy systems.

Overall, WT emerges as a promising pretreatment strategy for producing high-performance biochar from oxytree, suitable for renewable solid biofuels, carbon sequestration and soil improvement, whereas DT remains attractive when process simplicity and maximum energy yield are prioritised. Future work should address scale-up, reactor optimisation and the environmental behaviour of oxytree DT and WT biochars in soil and anaerobic digestion systems, as well as integrate these findings into full techno-economic and life-cycle assessments of oxytree-based bioenergy chains.

The study fills the gap by utilizing WT on oxytree residues and examining their performance in terms of function (HHV, energy yield, ignition), thereby providing actionable operating windows for fuel upgrading and energy use. The results also confirm oxytree's strong performance as a feedstock for energy conversion. Future research should further explore scale-up feasibility, reactor optimization, and the environmental behavior of WT biochars in soil and/or anaerobic digestion systems.

CRediT authorship contribution statement

Hilal Unyay: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Andrii Kostyniuk:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Szymon Szufa:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Artur Lewandowski:** Writing – review & editing, Visualization, Formal analysis, Data curation. **Blaž Likozar:** Writing – review & editing, Supervision, Resources, Project administration. **Grzegorz Wielgosinski:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

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 data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.enconman.2025.120974.

Data availability

Data will be made available on request.

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