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Review

Exploring the Properties of the Torrefaction Process and Its Prospective in Treating Lignocellulosic Material

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Abstract: The main objective of this review is to present the latest research results regarding the importance of the torrefaction process for different biomass materials in the last 12-year period. Despite the fact that the potential of renewable energy sources has been analyzed, research regarding that of energy derived from waste biomass still remains in the infancy state. Torrefaction is known to be one of the most effective methods for enhancing the energy efficiency of biomass. Among different types of torrefactions, the focus in this study is mostly on dry torrefaction. The influential factors, like temperature and residence time, and physico-chemical properties of torrefied products, and the prospective of torrefaction due to its reduced impact on environment, are discussed in-depth. This review provides valuable insights into the torrefaction process, which is conducive to upgrading biomass for achieving net zero carbon emissions, as it has been stated in several works that torrefied biomass can be used instead of coal.

Keywords: torrefaction; lignocellulosic biomass; waste biomass; biomass properties

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Citation: Ivanovski, M.; Petrovič, A.; Goričanec, D.; Urbancl, D.; Simonič, M. Exploring the Properties of the Torrefaction Process and Its Prospective in Treating Lignocellulosic Material. *Energies* **2023**, *16*, 6521. https://doi.org/10.3390/en16186521

Received: 31 July 2023
Revised: 30 August 2023
Accepted: 8 September 2023
Published: 10 September 2023

1. Introduction

The beginning of torrefaction dates to 1930, when coffee beans were torrefied for the first time. Since then, the process has developed rapidly worldwide. A search of the literature for the keyword "torrefaction" yielded the following data: According to the "Scopus" database, 2942 studies were identified in scientific journals in which "torrefaction" appeared in the title, abstract, keywords or cited references. According to a "ScienceDirect" search, 4719 studies were identified, as shown in Figure 1. Finally, with "GoogleScholar" more than 24,000 studies were found. Many studies have focused on the characterization of biomass typical of a particular geographic region [1–4].

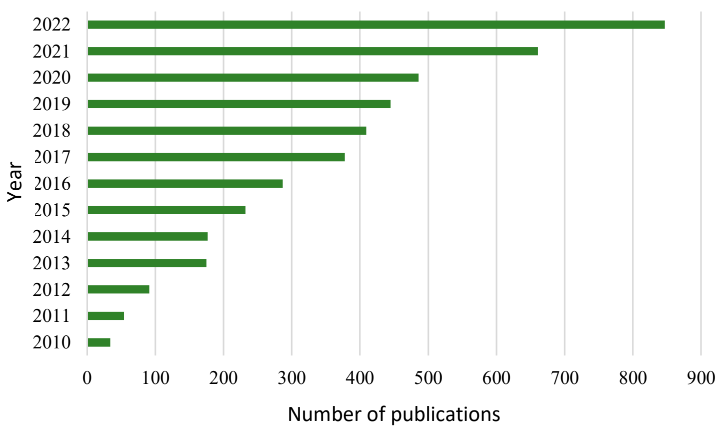


Figure 1. The number of published studies on torrefaction on ScienceDirect.

Prins et al. [5] investigated the effect of torrefaction for further application in the process of gasification. Different types of wood waste, such as beech, willow, and larch were studied under a controlled atmosphere at carefully defined temperature conditions for specific time periods. Besides the mass and energy yield calculations it was proven that preserved energy from a gasifier can drive the torrefaction reaction, increasing gasification efficiency. Bridgeman et al. [6] studied torrefaction with three different types of waste biomass, such as common grass, wheat straw and willow. It was found that willow biomass mass loss was the lowest compared with the other two types of investigated biomass. A further finding was that willow shows higher mass and energy yields. Two years later, Bridgemann et al. [6] investigated the influence of temperature in certain time periods on two different types of waste biomass, willow and miscanthus. They concluded that temperature is the more important parameter, compared with time periods, for a better torrefaction process, and that the final product has similar physico-chemical parameters to coal. Chen and Kuo [7] studied another four types of waste biomass, i.e., bamboo, willow, coconut shell, and *Ficus benjamina* L. plant. Using thermogravimetric analysis (TGA), they proved changing proportions of the main components of lignocellulosic biomass, which are hemicellulose, cellulose, and lignin, during the torrefaction process. It was found that cellulose degradation occurred first, followed by cellulose and lignin degradation. Tumuluru et al. [8] studied torrefaction in more detail, describing the main properties of torrefaction and making a comparison between torrefied biomass and the raw biomass material. Wannapeera and Worasuwannarak [9] investigated the torrefaction of wood biomass *Leucaena leucocephala* between 200 to 250 °C and under a pressure of 4 MPa. As the temperature increased, the mass and energy yields decreased, while at a constant temperature and an increased pressure, mass and energy yields increased. Batidzirai et al. [10] introduced the technical and economical yields of the torrefaction of waste biomass. Prabir [11] presented in detail the thermochemical processes, including the general characteristics, advantages, and disadvantages of torrefaction. Table 1 shows the comparison between torrefaction and other enumerated thermochemical processes. It also gives the typical range of their reaction temperature. The solid product (biochar) can be used as a soil amendment, the liquid product (bio-oil) can be processed into fuels, and the gaseous product (syngas) can be used for energy generation or further processing [12]. The process should be chosen depending on several factors, such as the feedstock available, desired end products, environmental considerations, energy efficiency, and economic feasibility. Processes like torrefaction, pyrolysis, gasification, and liquefaction are often favored, as they can offer a more efficient utilization of biomass and waste materials, and they can potentially reduce carbon emissions compared to traditional combustion. However, each process has its own challenges and limitations that need to be carefully evaluated based on the specific circumstances.

Table 1. The comparison of operating conditions between torrefaction and other enumerated thermochemical processes [11].

Thermochemical Process	Temperature (°C)	Pressure (kPa)	Pre-Drying
Liquefaction	250–330	5000–20,000	Not required
Torreaction	200–300	100	Required
Pyrolysis	300–600	100–500	Required
Gasification	500–1300	≥100	Required
Combustion	700–1400	≥100	Not required

During the review, various studies in the literature were considered and the major literature was used to discuss the torrefaction process. Bach and Tran [13] introduced wet torrefaction, and waste wooden biomass was taken as a sample. In another study, the changes in the higher heating values (HHV) and the enhancement factor (EF) using bamboo as a torrefaction input material were investigated [14]. Chen et al. [15] determined the physico-chemical parameters of different types of lignocellulosic materials and compared the characteristics of biomass before, between and after torrefaction. The most important result found was that when the process temperature was gradually increased from 210 °C to 300 °C, about 19.8–71.1%, 5.9–33.3% and 16.3–44.9% of oxygen was converted from hemicellulose, cellulose, and lignin, respectively, into liquid and gaseous products. It was also shown that torrefaction can be applied to pretreat biomass for pyrolysis to stabilize the bio-oil produced [16]. Yanqing et al. [17] summarized all the main results of the general properties of torrefaction products, its application in industrial purposes, and proposed some limitations and assumptions of the torrefaction process. In the above-mentioned concept, Cahyanti et al. [18] inspected the process parameters, the economic and environmental aspects of the torrefaction process, and recent progress in the field. Simonič et al. [19] compared the torrefaction of two different types of lignocellulosic and non-lignocellulosic biomass, i.e., wood waste and waste sludge, from municipal wastewater treatment plants at different temperatures and treatment times. The optimum temperature was found to be between 250 and 260 °C. Sarker et al. [20] studied the physico-chemical properties of biomass, i.e., collard greens, exposed to microwave torrefaction. The percentage of carbon increased with an increased torrefaction rate, while the oxygen and volatile compound contents decreased. Consequently, an increased content of bound carbon was detected. Xu et al. [21] established a torrefaction model for predicting the basic properties of the torrefied products. Chinese fir, corn stalks, and palm kernel shells were used as test lignocellulosic material. The simulation of torrefaction was performed in two stages: a first stage from a 200 to 250 °C temperature and a second stage under more severe conditions from 250 to 300 °C. Thengane et al. [22] gave a comprehensive review of the torrefaction process through years. Their findings were in accordance with another study by Soria-Vergudo et al. [23] based on crushed olive pits under non-isothermal and isothermal conditions. Wu et al. [24] studied a two-stage process of the pyrolysis and torrefaction of sugar cane, wherein fast pyrolysis was applied. The process was performed in a tube furnace at temperatures of 220, 260, and 300 °C for a 60 min period. Results showed an increased content of carbon and the removal of low-caloric volatile compounds.

Many investigations on using torrefaction as a technique to improve the properties of raw biomass to be similar with those for coal have been conducted. A lot of conclusions have been reached from the different studies and there are some gaps that have been identified. It has been observed that the torrefaction of raw biomass leads to a product with better physico-chemical properties, such as improved HHVs and grindability, being hydrophobic, etc. Lignocellulosic biomass is believed to be cheaper than crude oil or coal but its conversion processes are expensive and, therefore, need more research. This study will, therefore, discuss the properties of the torrefaction process, types of torrefaction, and its products. Additionally, temperature has been identified as the most important parameter in torrefaction, followed by residence time and atmosphere. This paper will also discuss different conditions that have been identified. Finally, its impact on the environment, and applications in industry will be presented.

2. Description of the Torrefaction Process

The main aim of torrefaction is to improve the qualities of raw waste biomass, i.e., to acquire a product with a higher energy density, better grindability, and lower moisture content similar to coal. The general definition is that torrefaction is a thermochemical transformation process from 200–300 °C under atmospheric pressure in the absence of oxygen [8,25,26]. Different names are found in the literature, such as roasting, slow pyrolysis, mild pyrolysis, wood cooking and high-temperature drying. It is an endothermal process, meaning that energy is needed for its performance. The general simple equation is (Equation (1)) [22]:

$$\text{Raw biomass} \rightarrow \text{Torrefied biomass} + \text{Volatile compounds} + \text{Gasses} \tag{1}$$

Figure 2 shows the conversion of raw biomass to torrefied biomass. Raw biomass has the following characteristics: (i) hydrophilicity, (ii) a high moisture content, (iii) a high O/C and H/C ratio, (iv) a low heating value (HHV), (v) a low energy density, (vi) poor grindability, (vii) high biodegradability, and (viii) in-homogeneity. When raw biomass is thermally treated, i.e., torrefied under appropriate conditions (temperature, time, pressure and atmosphere), the final product obtained has the following properties: (i) less moisture, (ii) a lower oxygen content, (iii) a higher carbon content, (iv) improved energy density, (v) a lower O/C and H/C ratio compared to raw biomass, (vi) is more friable compared to raw biomass, (vii) hydrophobic, (viii) homogeneous, (ix) contains less microbes than raw biomass, and (x) has a higher heating value (HHV) [18]. Despite all the positive effects of torrefaction, the process itself faces mainly two negative features: (i) high investment costs for setting up or establishing the technology and (ii) the biogas produced as a by-product needs a final extensive purification, which also incurs high costs. Figure 2 shows the conversion of raw biomass to torrefied biomass. The individual properties of torrefied biomass are presented below. As can be seen from Figure 2, raw biomass has the following characteristics: (i) hydrophilicity, (ii) a high moisture content, (iii) a high O/C and H/C ratio, (iv) a low heating value (HHV), (v) a low energy density, (vi) poor grindability, (vii) high biodegradability, and (viii) in-homogeneity.

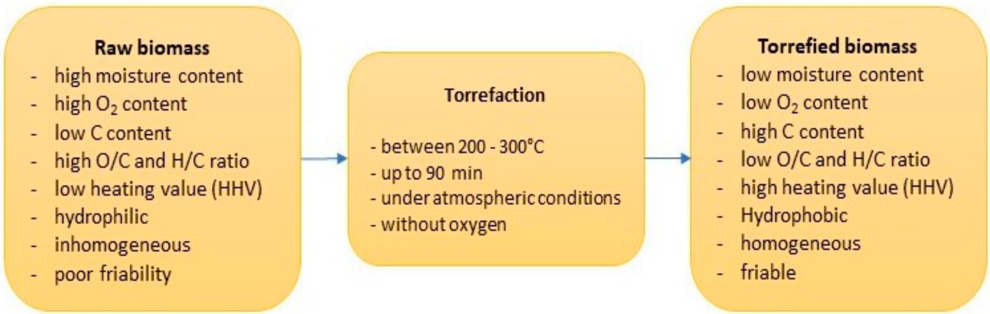


Figure 2. The properties of raw biomass and torrefied biomass.

Various types of biomasses have been, up to now, subjected to torrefaction to improve their fuel properties. Most of the studies have dealt with lignocellulosic biomass wastes, such as different wood residues [27] and agricultural residues [28], while fewer studies have been conducted on non-lignocellulosic biomass, such as waste sludge, municipal waste and algae residues. Table 2 shows the list of some studies performed with non-lignocellulosic biomass at different operating conditions.

Table 2. The list of studies dealing with non-lignocellulosic biomass.

Type of Biomass	The Aim of the Research	Reaction Conditions	Reference
Waste sludge from a municipal treatment plant	A study on the physio-chemical variation in sewage sludge during torrefaction in a horizontal tubular reactor under nitrogen flow	150–400 °C 50 min	[29]
Algae residue	A study on the composition, structure, and reactivity of a microalga residue after torrefaction.	200, 250 and 300 °C 15, 30 and 60 min	[30]
Municipal waste	The microwave-assisted torrefaction of construction demolition and grass clippings were studied	250, 500 and 750 W * 15, 30 and 60 min	[31]

Table 2. *Cont.*

Type of Biomass	The Aim of the Research	Reaction Conditions	Reference
Different types of waste	A study on a gas-pressurized (GP) torrefaction method to torrefy biomass wastes	200, 250 and 300 °C 15 min	[32]
Algae residue (*Arthrospira platensis* and *Chlamydomonas* sp.)	To develop a torrefaction severity factor (TSF) to account for the relationship between operating conditions, biomass nature, and torrefaction severity	200, 250, 275 and 300 °C 15, 30, 45 and 60 min	[16]
Waste sludge from municipal treatment plants	An isothermal kinetic study of the torrefaction of sewage sludge	220, 240, 260, 280 and 300 °C 5 min	[33]
Textile dyeing sludge and cattle manure	In-depth analysis of the co-pyrolytic performance between textile dyeing sludge and cattle manure using TGA apparatus	35 to 1000 °C in a N_2 atmosphere at heating rates of 5, 10, 20, and 40 °C/min	[34]
Mixture of fiber (biomass) and plastic wastes	A study on the techno-economic analysis and life-cycle assessment of an integrated torrefaction–extrusion system for solid fuel pellet production	/	[35]
Mixture of corncob and waste cooking oil	Co-torrefaction of corncob and waste cooking oil	180, 210, and 240 °C 30, 60, 90, 120 and 150 min	[36]
Textile dyeing sludge	A study on the characterization and quantification of interactions among Zn, Cd, Cl, S, and minerals and their migration and transformation behaviors in the air (N_2/O_2) versus the oxy-fuel (CO_2/O_2) co-combustions of SAH and TDS through TGA, thermodynamic equilibrium simulations, and joint optimization	650, 750, 850, and 950 °C	[37]
Spent coffee grounds and polyethylene	Co-pyrolysis performances of CG and PE, interaction effects, kinetics, and product characterization in response to the varying temperature and blend ratio, using TGA apparatus	35 to 1000 °C in an N_2 atmosphere at heating rates of 10, 20, and 40 °C/min	[38]

* Microwave power level in W.

3. Types of Torrefaction

Here, we distinguish between different types of torrefaction. In general, we differ the types into primary media phase or carrying gas or dry torrefaction, then wet torrefaction [39], then steam torrefaction [40]. The comparison of different torrefactions, their advantages and disadvantages, and a review of some recent papers is presented in Table 3.

During wet torrefaction, the process is not performed in a gas phase but in an aqueous or water phase in a temperature range from 180 to 260 °C [41]. Wet torrefaction is also known as hydrothermal carbonization [42]. Different types of biomasses have been exposed to wet torrefaction, from woody biomass [13], to residues from agriculture such as rice husk [43], olive oil cake [44] and miscanthus grass [45]. Wet torrefaction is especially appropriate for treating biomass with a high moisture content, such as sewage sludge. In addition, the liquid media (water) in the process of wet torrefaction can be replaced with some other waste liquid streams to increase sustainability and to decrease the operation costs. In one of the previous studies, sewage sludge in combination with cheese whey was successfully applied in wet torrefaction to obtain char of a high quality for various purposes [46].

Unless specified, the conventional torrefaction treatment is assumed to be dry torrefaction. Dry torrefaction can occur under two different conditions—oxidative with oxygen, or non-oxidative, i.e., inert [27,47]. In non-oxidative (inert) torrefaction, either nitrogen (N_2) or carbon dioxide (CO_2) can be used as a carrier gas, with N_2 being the most used in biomass-material processing research. As far as oxidative torrefaction is concerned, so far, attempts have been made to use air, flue gases or other gases containing different concentrations of oxygen as carrier gases for biomass pretreatment [48]. Due to the presence of oxygen and the exothermic reactions that occur during thermal decomposition, oxidative torrefaction has a higher reaction rate than non-oxidative torrefaction, which also shortens the duration of the torrefaction process [49]. Using air or flue gases for biomass torrefaction can reduce operating costs because nitrogen separation from air is not required. However, oxidative torrefaction has a lower solids yield compared to non-oxidative torrefaction [27].

In steam torrefaction, the biomass is treated by saturated or overheated steam in a temperature range from 200 to 260 °C [50]. Torrefaction under high-pressure steam conditions promoted the conversion of biomass to high-quality biochar products, but it reduced the yield of biochar. This process has not yet been applied to industrial or continuous applications [51]. In addition, laboratory experiments have been up to now conducted on various types of biomasses, including walnut oil processing wastes [50], camellia shell [51] biomass, agro-industrial residues [52], a mixture of chicken manure and sawdust [53] and many other.

Torrefaction can also be divided into light, medium or severe torrefaction. The difference between them is mainly in the temperature at which the process starts. In mild torrefaction, a temperature between 210 and 235 °C is required to start the process, in medium 235–275 °C and severe torrefaction 275–300 °C [26]. However, despite many types of torrefaction processes, this research is focused mainly on dry torrefaction.

Table 3. A list of some recent papers on different types of torrefaction, including their advantages and disadvantages.

Type of Torrefaction	Advantages/Disadvantages	Biomass Source	Reference
Dry (Non-oxidative)	*Advantages:* Low costs, fast process *Disadvantages:* Low mass and energy yields, difficult process control	Wheat straw	[54]
		Corn stalk	[55]
		Agricultural biomass	[28]
		Pine, eucalyptus, chestnut, holm oak, olive tree pruning and vine shoot	[56]
Dry (Oxidative)	*Advantages:* High mass and energy yields, simple process control *Disadvantages:* High initial energy or heat required, slow process	Microalgae	[57]
		Wood sphere	[27]
		Patula pine	[48]
		Olive stones	[23]
		Rice husk	[58]
Wet (Hydrothermal carbonization)	*Advantages:* No pre-drying necessary, suitable for wet biomass, by-products in liquid form, high quality of char with lower ash content than in dry torrefaction, possible addition of catalysts to enhance process *Disadvantages:* Lower char yield, high energy consumption due to high-pressure operation, possible corrosion of reactors, post-drying of char is required, complicated process to implement in continuous mode	Woody biomass	[13]
		Rice husk	[43]
		Olive oil cake	[44]
		Miscanthus	[45]
		Sewage sludge and cheese whey	[46]
Steam torrefaction	*Advantages:* No pre-drying necessary, suitable for wet biomass, higher pelletability of solid product *Disadvantages:* High costs and energy consumption due to high-pressure operation, complicated process to implement in continuous mode	Walnut oil processing wastes	[50]
		Agro-industrial residues	[52]
		Mixture of chicken manure and sawdust	[53]
		Camellia shell	[51]

3.1. Torrefaction Rate

The torrefaction process can be divided into five stages according to temperature: initial heating, pre-drying, drying and intermediate heating, torrefaction, and cooling (Figure 3).

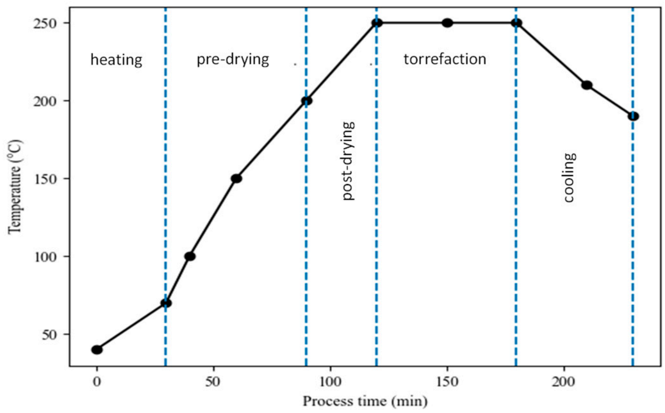


Figure 3. Schematic presentation of the torrefaction stages.

The proposal of dividing the process into five stages was given by Bergman et al. [59]. The torrefaction stages were summarized based on van der Stelt et al. [25] and are described in the following sentences:

- Initial heating: the biomass is heated to the drying stage. This usually takes place in a temperature range of between 25 and 105 °C. The temperature rises, and at the end of this stage moisture begins to evaporate.
- Pre-drying: usually takes place in a temperature range between 105 and 200 °C. The biomass begins to slowly decompose (basic components), and the free moisture begins to evaporate from the biomass at a constant rate.
- Drying and intermediate heating: the temperature of the biomass rises to approximately 200 °C, releasing physically bound water. At this stage, the biomass contains no more moisture, so the biomass begins to gradually decompose (loss of mass) and light organic matter begins to volatilize.
- Torrefaction: in this stage, the torrefaction process practically begins. The process starts when the temperature reaches exactly 200 °C and continues until the temperature decreases below 200 °C. The temperature of torrefaction is characterized by a period of constant temperature, which can be reached even only for a short time (temperature maximum). In this stage, the mass loss is the highest.
- Cooling: the obtained solid product is cooled down from 200 °C to the final desired temperature.

The degrees of torrefaction and the energy required for each stage are represented by Equations (2)–(6), given in Table 4.

3.2. Torrefaction Products

The main product of torrefaction is solid fuel, while byproducts are aqueous products and gasses [8]. Bergmann et al. identified the solid products as bio-char or newly synthesized polymeric structures and some modified sugar structures [59]. Water is almost always a by-product, as are some organic compounds, such as sugars, acids, alcohols, ketones and lipids, such as terpenes, phenolic lipids, and waxes. Among the gasses, CO_2, CO, H_2 and methane were found. Torrefied biomass retains about 70% of its initial mass, while 30% of the mass is lost in the form of gasses or volatile compounds [8]. Solid fuels also retain about 90% of their original energy value, which means that torrefied biomass has a 10% to 20% higher heating value (HHV) than raw biomass. The solid biomass can then be processed into pellets or briquettes.

Table 4. Torrefaction rate equations [22].

Stage	Heat Equation	Parameter	
Pre-heating	$Q_{PH} = \frac{m \cdot C_p \cdot (T_B - T_0)}{h_{uf}}$	m—mass (kg), Cp—heat capacity (kJ/kgK), T_0, T_B—temperatures of raw and feed biomass (K), h_{uf}—the heat utilization factor for pre-heating	(2)
Drying	$Q_D = \frac{L \cdot x_m \cdot m}{h_{ud}}$	L—latent heat (kJ/kg), x_m—the moisture (%), h_{ud}—heat utilization factor during drying	(3)
Intermediate heating	$Q_{IH} = \frac{m \cdot (1 - x_m) \cdot C_{pd} \cdot (T_{tor} - T_b)}{h_{upod}}$	C_{pd}—specific heat capacity of dry biomass (J/kgK), T_{tor}—torrefaction temperature (K) h_{upod}—heat utilization factor for intermediate heating	(4)
Torrefaction	$Q_T = H_{loss} + m \cdot (1 - x_m) \cdot X_t$	H_{loss}—the heat loss (kJ), X_t—absorbed heat during torrefaction (kJ/kg)	(5)
Cooling	$Q_C = m \cdot (1 - x_m) \cdot MY_{db} \cdot C_{pt} \cdot (T_{tor} - T_p)$	MY_{db}—mass yield (%), C_{pt}—specific heat capacity of biomass (J/kgK) T_p—temperature of torrefied biomass at the end of the process (K)	(6)

3.3. Properties of Torrefied Biomass

Changes in biomass properties during the process are related to the reactions that take place during the process. These reactions include the following [47]:

- Devolatilization reaction—the removal of oxygen and other volatile substances from the biomass. This usually occurs in the initial phase of the torrefaction process at a temperature of 200 °C. The result of devolatilization causes a loss of material mass in the initial phase of the process.
- Deoxygenation reaction—the removal of molecular oxygen, which in turn leads to an increase in the carbon content in the final product, as well as lower H/C and O/C ratios in the final product and to the formation of gases such as CO, CO_2 and H_2O.
- Depolymerization reaction—the breakdown of larger molecular compounds into smaller ones occurs, resulting in a more homogeneous and crumblier final product.
- Carbonization reaction—a thermal reaction in which an organic biomass is converted into carbon with the main objective to increase the proportion of fixed carbon and decrease the hydrocarbon content.

The physico-chemical changes during the torrefaction itself especially affect three main components of the biomass: hemicellulose, cellulose, and lignin. The proportions of the individual components vary depending on the type of biomass, and their proportions can also affect the quality of the final product after torrefaction [60].

Additionally, Tumuluru et al. [8] classified the process of biomass torrefaction into three zones or distinct stages: (i) a non-reactive stage up to 150 °C, (ii) a reactive stage up to 200 °C and (iii) a destructive stage up to 300 °C. The first stage proceeds without significant chemical transformation taking place. Towards the upper end of the non-reactive stage, lignin starts to undergo softening. In the reactive drying zone temperature range, the processes involving hydrogen and carbon bonding toward lipophilic compounds release. Concurrently, structural deformations and the depolymerization of hemicellulose also manifest at this temperature range. This hemicellulose depolymerization leads to the formation of truncated and more condensed solid polymers. In the temperature range between 200 and 300 °C, two significant processes unfold: carbonization and de-evaporation. Within this range, the complete decomposition of hemicellulose occurs.

Several analytical methods, such are Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), and others, are applied to follow biomass structural changes during torrefaction.

Table 5 shows the changes in the properties of torrefied biomass (wood pellets served as example) compared to raw biomass, charcoal and coal. An increase in fixed carbon, the heating value, and the energy density, and a decrease in the volatile mater (VM), H/C and O/C ratios and the moisture content can be observed after the torrefaction of biomass due to the occurrence of the above-mentioned reactions. However, different biomasses perform differently under the same conditions due to differences in their chemical structures and physical properties.

Table 5. Characteristics of raw biomass (wood pellets) compared to torrefied biomass, charcoal and coal [10].

Characteristic	Wood	Wood Pellets	Torrefied Wood Pellets	Charcoal	Coal
Moisture content (wt %)	30–45	7–10	1–5	1–5	10–15
LHV (MJ/kg) *	9–12	15–18	20–24	30–32	23–28
Volatile matter (wt %)	70–75	70–75	55–65	10–12	15–30
Fixed carbon (wt %)	20–25	20–25	28–35	85–87	50–55
Density (kg/dm^3)	0.2–0.25	0.55–0.75	0.75–0.85	0.2–0.4	0.8–0.85
Energy density (GJ/m^3)	2–3	7.5–10.4	15–18.7	6–6.4	18.4–23.8
Hygroscopicity	Hydrophilic	Hydrophilic	Hydrophobic	Hydrophobic	Hydrophobic
Biological decomposition	Yes	Yes	No	No	No
Grindability	Bad	Bad	Good	Good	Good

* LHV—lower heating value.

The color of the material exposed to torrefaction changes from light brown, to brown, to dark brown or even black with the increase in treatment temperature (Figure 4). The color change depends also on other operating conditions, such as the treatment time, pressure, and atmosphere. Likewise, the content of hemicellulose, cellulose, and lignin in the individual biomass affects the color of the final product. Tian et al. [61] found that the decomposition of hemicellulose occurs in a temperature range of between 220 and 315 °C, cellulose between 260 and 400 °C and lignin between 150 and 900 °C. The higher the torrefaction temperature, the darker the final product due to changes in the chemical composition of the biomass [17]. Xi et al. [21] confirmed the above-mentioned claims with the explanation that the color change is the result of the degradation of basic components and oxidation.

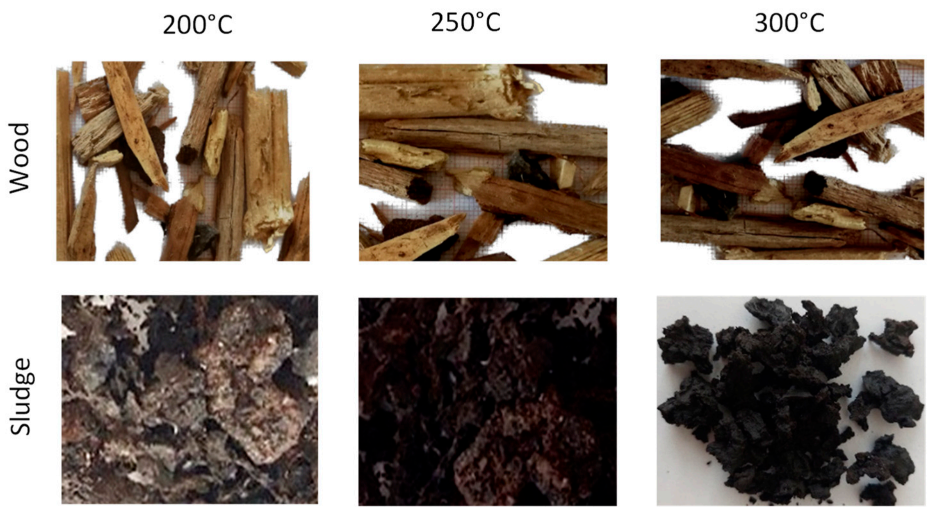


Figure 4. Color changes of biomass after its torrefaction at different temperatures.

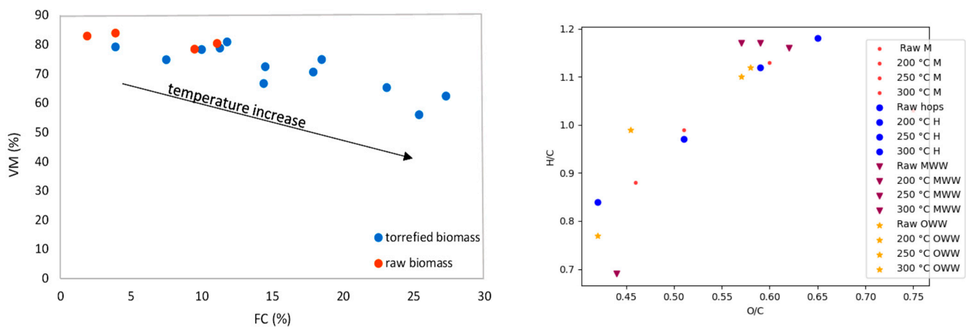
The moisture content of biomass fuels holds considerable significance, given that elevated levels of moisture in the fuel result in substantial energy losses throughout the process [18]. Also, biomass with less moisture is more stable during storage, its transport is cheaper and, in general, biomass with less moisture has less risk of biological spoilage [62]. Therefore, the goal is to lower the moisture content even before the torrefaction process itself. It makes sense that the dried biomass has a moisture content below 30% before the process, and lower than 10% after torrefaction. The drying process cannot prevent the further adsorption of moisture into the biomass, especially if it is stored in a high-moisture environment [63]. At the same time, a low moisture content is important for increasing the energy efficiency of the torrefied material, improving the quality of energy products, and reducing emissions in the thermochemical conversion process.

3.3.1. Hydrophobicity and Chemical Properties of Torrefied Biomass

Before torrefaction, the biomass is dried. Drying removes all water and moisture from the biomass, which starts the torrefaction of the already partially hydrophobic biomass. During the torrefaction process itself, hydroxyl (-OH) groups are completely decomposed, which leads to the hydrophobicity of the torrefied biomass [47]. Within lignocellulosic biomass, the hydrogen within the water molecules forms bonds with the oxygen found in the hydroxyl groups of the cell wall. The likelihood of hydrogen bonding increases as the cell wall's oxygen content rises. Torrefaction, by diminishing the presence of hydroxyl groups in the cell wall, instigates a transition toward hydrophobic properties in the biomass [18]. The equilibrium moisture content index (EMC) serves as an indicator of hydrophobicity, which is measured by exposing a solid biomass sample to an environment with constant humidity and temperature until it reaches an equilibrium value. In other words, one of the approaches for assessing EMC is dividing the percentage of relative humidity (RH) by a factor of 5. A decrease in EMC is an indicator of the increased hydrophobicity of the biomass: at a lower humidity, the torrefaction temperature does not affect hydrophobicity and the EMC remains unchanged, while at a high humidity, the EMC increases, leading to higher hydrophobicity [17]. The hydrophobic nature of biomass is intricately linked to the composition of hemicellulose, cellulose, and lignin within it. The decomposition of these constituents, particularly hemicellulose, coupled with the decrease in the H/C and O/C ratios in torrefied biomass, results in a weakening of the hydrogen bond-forming capabilities of the -OH groups.

In addition to the moisture content, proximate analysis provides important information about biomass properties, which include parameters such as volatility (volatile matter, VM), and fixed carbon (FC) and ash content. Raw biomass has a high content of volatile components (between 67–88%) and a low content of fixed carbon (between 0.5–20%) [64]. This phenomenon is shown in Figure 5a. As the biomass undergoes torrefaction, more specifically dehydration during torrefaction, with an increasing temperature and torrefaction time, the content of volatile components decreases and the content of fixed carbon increases. Their contents vary between 40–85% and 13–45% separately, depending on the type of biomass being torrefied, temperature, and time. The ash content also increases with torrefaction [65]. The share of ash after torrefaction varies between 0.25–19%. It should be noted that a high ash content in the final product can lead to the accumulation of metal elements in the product itself, which in turn affects the quality of the final product [66].

Biomass primarily comprises carbon (C), oxygen (O), nitrogen (N), hydrogen (H), and sulfur (S). Carbon is the main source of heat generation during combustion. However, the presence of oxygen in biomass diminishes its heating value during the torrefaction process. A higher oxygen and ash content in the original biomass corresponds to lower heating values. In contrast to coal, biomass tends to have lower levels of carbon (C), nitrogen (N), and sulfur (S), while possessing elevated levels of oxygen (O) and hydrogen (H) [64]. In the context of torrefaction, the ratios between atomic oxygen and carbon (O/C), as well as atomic hydrogen and carbon (H/C), are of significant importance. These relationships are visually represented by the Van Krevel diagram (Figure 5b). Both ratios exhibit linear trends. Typically, the H/C and O/C ratios within untreated biomass range from 1.2 to 2.0 and 0.4 to 0.8, respectively. Post-torrefaction, the removal of moisture and low-volatile components rich in hydrogen and oxygen results in an increased proportion of carbon (C) within the biomass. This shift leads to lowered atomic ratios of H/C (0.7–1.6) and O/C (0.1–0.7), as depicted in Figure 5b. Additionally, as torrefaction conditions intensify, the carbon content within the biomass also rises [65].



(**a**) (**b**)

Figure 5. (**a**) Volatile matter vs. fixed carbon, and (**b**) Van Krevelen diagram—O/C and H/C ratios for torrefied and raw biomasses such as oak wood (OWW), mixed waste wood (MWW), hops and miscanthus [67].

During biomass combustion, the primary contributor to heat release is the oxidation of carbon. Although hydrogen plays a significant role in biomass combustion, its presence is largely confined to C-H or O-H bonds. Biomass also contains oxygen, which aids in combustion. However, an excess of oxygen within biomass can lead to a decrease in its heating value (HHV). Hence, torrefaction is employed to eliminate undesired components (hydrogen and oxygen) from the solid output, thus approximating the heating value of coal (25–35 MJ/kg) [68].

Many authors have researched the impact of grindability on the torrefaction process, and all of them have found that torrefied biomass, with a particle size reduction through pulverization, has similar properties to coal [69]. Grindability is defined as the extent to which certain solid biomass can be converted into powder form. It is defined by the Hardgrove grindability index (HGI). The higher this parameter is, the more feasible grinding is, and less energy is required.

3.3.2. Influential Factors

Operational factors like temperature, residence time, particle size, the type of reactor and heating rate exert a substantial influence on torrefaction, consequently shaping the characteristics of the resulting biochar [70,71].

3.3.3. Temperature

Of all the factors that influence the torrefaction process, temperature stands out as the foremost variable impacting the rate of chemical reactions throughout the process. This, in turn, shapes the composition of the final product, along with its mass and energy yield [22]. Depending on temperature, torrefaction can be divided into mild, medium, and strong. The general findings are that as the temperature decreases, the energy and mass yields increase while the energy density decreases. The effect of temperature on the final product can be described by changes in the proximate and elemental composition of the final product [17].

3.3.4. Residence Time

Residence time, in the context of torrefaction, refers to the duration for which biomass is exposed to a certain temperature until the end of torrefaction. Torrefaction is usually carried out from a few minutes to a few hours. Throughout torrefaction, the resultant solid fuel experiences an escalation in its heating value. With an extension of this duration, there's a corresponding augmentation in the carbon content and higher heating value (HHV) within the biomass. For instance, when wood briquettes undergo torrefaction at 250 °C for 30–90 min, the biomass's heating value increases from 20 to 23 MJ/kg. It is worth noting that lengthening the torrefaction duration necessitates greater energy input for thermal pre-treatment [47]. Various combinations of temperatures and residence times can be harnessed to attain a specified degree of torrefaction, often denoted by mass loss [22]. Alternatively, pivotal attributes of the torrefied end product, like HHV and saturated moisture uptake, can be correlated with mass loss or the intensity of biomass torrefaction [18].

3.3.5. Particle Size and Specific Area

Specific surface area and particle size distribution represent pivotal metrics in the characterization of biomass [64]. These attributes hold critical importance for gauging the flowability and combustion characteristics of biofuel. Biomass endowed with larger particle dimensions tends to exhibit a diminished surface area per unit of mass in comparison to its smaller counterparts. Consequently, the rate of convective heat transfer is curtailed. Furthermore, the extended heating duration of larger biomass particles can be attributed to their heightened resistance against mass and heat transfer. As the particle size increases, the yield of the solid product increases, while the outputs of both non-condensable and condensable as well as gas products decrease [22].

Table 6 summarizes the general findings of some recent studies dedicated to the torrefaction of specific biomass samples.

Table 6. The general findings of some recent studies dedicated to the torrefaction of different biomass samples.

Biomass	Operating Conditions (*T*, *t*, *atmosphere*)	General Remarks	Reference
Wood biomass (*Lauan*)	220, 250, 280 °C, 30–120 min	The properties of the torrefied wood improved at a temperature > 250 °C and a torrefaction time > 60 min. These conditions were recommended to increase the heating value and grinding, and to prevent the excessive loss of wood mass.	[72]
Cotton, Sugar cane	300 °C, 60 min	Torrefaction improved the gross heating value (27–41%) of research biomasses, reduced their moisture and VM contents (3–6% and 14–18%, respectively), improved their fixed carbon (9–24%) and reduced mass loss (27–46%).	[73]
Yellow poplar (*Liriodendron tulipifera*)	240, 260, 280 °C, 30 min	The carbon share increased, while the oxygen and hydrogen share decreased with increased temperature. The energy density, mass reduction and energy efficiency increased.	[74]
Stem wood and forest residue biomass	220–300 °C, 120 min, inert atmosphere (N_2)	The qualities of torrefied biomass exhibited enhancement when contrasted with those of raw biomass. However, as the temperature increased, both the mass and energy efficiency tended to diminish.	[75]
Rice husks	150, 180, 210, 240 °C, 60 min	Examination of the physicochemical attributes of untreated and pretreated samples revealed that wet torrefaction enhanced fuel properties. Additionally, a significant quantity of alkaline earth metal species were effectively eliminated. This dual benefit mirrors the advantages associated with both the dry torrefaction and demineralization processes.	[43]

Table 6. *Cont.*

Biomass	Operating Conditions (*T*, *t*, *atmosphere*)	General Remarks	Reference
Corn stalk	200, 230, 260, 290 °C, 30 min, inert atmosphere (N_2)	Elevating the torrefaction temperature in the range of 200–290 °C brought about a notable reduction in the oxygen share and a gradual augmentation in the carbon content in the corn stalk. During the torrefaction process, cornstalk oxygen transformed into CO_2 and CO as a gaseous product, or into H_2O and oxygen-containing compounds, such as acids and phenols. These results showed that dehydration reactions and gas generation prevail throughout the decarbonization or deoxygenation phase of torrefaction.	[76]
Wheat–barley straw	240–320 °C, 75 min, inert atmosphere (N_2)	As temperature increased, the more differentiated the structure of the torrefied biomass condensates became. Acids, aldehydes, and ketones dominated in the analyzed temperature range.	[77]
Sludge from municipal wastewater treatment plants	220–300 °C, 120 min, inert atmosphere (N_2)	Non-lignocellulosic biomass was less heat-resistant and decomposed much faster than lignocellulosic biomass. In addition, the mass yield of torrefied sewage sludge was at temperatures below 280 °C, lower than that of woody biomass.	[33]
Bamboo	200, 250, 300 °C, 60 min, inert atmosphere (N_2)	The results showed that bamboo is a suitable biomass for the torrefaction process, as the properties of the biomass improved during the process.	[78]
Microalgae *Nannochloropsis Oceanica*	200–300 °C, 15–60 min	The outcomes of this study offer valuable insights into evaluating the fuel characteristics of solid microalgae biofuel. These insights hold the potential to expedite the advancement of industrial-scale oxidative torrefaction processes.	[57]
Municipal waste	/	Review of the torrefaction of municipal waste in Malezia.	[79]
Remains penicillin mycelium	230, 260, 290, 320 °C	Gases during torrefaction were analyzed with the aim of removing antibiotic residues and achieving antimicrobial resistance. The results showed that the gaseous products during torrefaction are mainly CO_2, CO, CH_4 and H_2. The results of gas chromatography showed that the sample mainly contains ketones, furan, ester, and phenolic and N-containing compounds, among which the relative content of N-containing compounds was the highest.	[80]
Rubberwood and Gliricidia	250, 275, 300 °C, 30, 45, 60 min	The energy–mass co-benefit index of rubber and gliricidia was calculated. The optimum residence times of 60 min at 275 °C and less than 60 min at 300 °C were determined for rubberwood. The optimum residence time of 60 min at 300 °C was favorable for Gliricidia.	[81]
Oak waste wood, mixed waste wood, municipal sludge	220–400 °C, 30–120 min	From an energy point of view, the optimal torrefaction temperature is 260 °C, and the optimal torrefaction time is 80 min.	[19]
Spent coffee grounds, Chinese medicine residue, microalgal residues	200, 250, 275, 300 °C, 15–60 min	The amounts of single biomass can be predicted with the help of the torrefaction severity index (TSI).	[82]
Miscanthus, waste hops, waste mixed wood and oak wood	200, 250, 300 °C, 90 min, semi-inert atmosphere	The results showed that the higher the torrefaction temperature, the lower the mass and energy efficiency of the torrefied samples. Significant changes in the thermo-gravimetric curves (TGA) were observed after torrefaction of the samples. The FTIR and XRD spectra showed the breaking of bonds in the cellulose molecules. The same was shown using SEM analysis.	[83]

Table 6. *Cont.*

Biomass	Operating Conditions (*T*, *t*, *atmosphere*)	General Remarks	Reference
Miscanthus, waste hops, municipal sludge and blends	250, 300, 350 °C, 10–60 min, inert atmosphere (N_2)	The results showed that the higher the torrefaction temperature, the lower the mass and energy efficiency of all the research samples. The optimal torrefaction conditions were found at 260 °C and 10 min. The degree of torrefaction index and the EMCI were calculated, and the proximate and elemental composition was determined. The FTIR spectra were recorded.	[84]
Miscanthus, waste hops, mixed municipal waste and blends	250, 300, 350 °C, 30–60 min, inert atmosphere (N_2)	Proximate and elemental composition and HHV values were determined. The FR (fuel ratio) and EROI (Energy return on investment) were subsequently calculated. The results showed that the higher the torrefaction temperature, the lower the mass and energy efficiency of all the research samples. HHV and FR, on the other hand, rose with a higher temperature. The highest EROI, 28, was calculated for the thermally treated sample of mixed municipal waste.	[85]
Mixed municipal sludge	200, 250, 300 °C, 90 min, semi-inert atmosphere	Proximate and elemental composition and HHV values were determined. TGA analyses were performed and compared with each other. The results showed that the higher the torrefaction temperature, the lower the mass and energy yield of all the research samples, and the higher the HHV.	[86]

4. Prospectives of Torrefaction Due to Reduced Impact on Environment

The research on the development of alternative fuel is mainly focused on developing environmentally friendly fuels, so it is important to understand the environmental aspects of fuel technologies. The environmental impact of torrefaction has been studied in connection to global warming potential (GWP), which can be calculated based on the carbon dioxide equivalent mass ($CO_{2,eq.}$) [18]. Most studies have used electricity produced as the basis for the functional unit of Life Cycle Assessment (LCA) work. In an LCA review, based on numerous studies, there was an attempt to compare the impact of the global warming potential (GWP) with the impact of other bioenergy products from thermochemical processes on torrefied biomass [87]. The GWP represents the equivalent impact of a given greenhouse gas to CO_2, allowing the comparison of its greenhouse effect. The average GWP results for torrefied biomass ranged from 0 g CO_2/MJ energy to 30 g CO_2/MJ energy [64], which is significantly lower than the average GWP results for raw biomass. Despite the positive impact on the emissions of torrefied biomass, it is possible to achieve a negative impact with the emissions from torrefied biomass, due to the excess electricity generated due to the increased HHV of the gas produced. Therefore, it is necessary to further investigate the impact of negative-emissions technology (NET) involving torrefied biomass. According to the results of available LCA studies on torrefaction [88,89], the effect of torrefaction on greenhouse gas emissions is relatively small compared to other technologies.

The EU is one of the leading promoters of bioenergy, of which the production and consumption has increased by 150% since 2000. The current supply of biomass from forest, agriculture and waste sources amounts to somewhere between 6 and 18 EJ/year, and it is estimated that by 2030, this share will amount to 8–17 EJ/year [22]. Also, in the process of achieving climate goals, the EU became the largest importer of biomass from Canada and the USA, mainly in the form of pellets. The torrefaction process represents a promising and cost-effective technology that could become commercially available. Torrefaction is advantageous for the supply of biomass over long distances, mainly due to lower transport costs compared to the costs of raw biomass. The current use of torrefied wood could triple in the European market if only 5% of coal use were replaced by torrefied wood [90]. Currently, wood pellets have great potential for use in thermal power plants and other energy processes, mainly due to their high heating value, water resistance and durability.

Even though initial input prices are higher when using torrefied pellets compared to using raw pellets, the total cost of production, transportation, and overall logistics may be lower. It is often mentioned in the literature that the cost of torrefied pellets in Europe is about 4.7 EUR/GJ, while the price of raw pellets is about 5.8 EUR/GJ [64,91]. Strong torrefied pellets, i.e., those with a high mechanical strength, are obtained at temperatures higher than 200 °C. The EU also has an established International Biomass Torrefaction Association (IBTC) in Brussels, which was founded in 2012 by Bioenergy Europe and a group supporting the development of torrefied biomass and its technologies. Biomass can potentially replace coal in the steel industry and reduce the use of fossil fuels. A very important issue in the iron industry is CO_2 emissions, caused by the considerable consumption of coal. The steel industry accounts for 5–7% of total CO_2 emissions, of which about 70% of emissions are produced in the production of iron in blast furnaces [91].

5. Application of the Torrefaction Process

The use of technology for the torrefaction process is increasing [8,11]. The key to this is, among other things, patents that allow the process to be researched at the laboratory and pilot level. According to statistics from the European Patent Office (EPO), 393 patents related to torrefaction were published worldwide from 1 January 1970, to 21 January 2020. Most patents were published in Europe (51%), followed by the USA (34%), China and Canada (16%). Torrefied biomass can be co-fired with coal in existing coal-fired power plants. This can reduce greenhouse gas emissions and the environmental impact of coal combustion. The energy-rich nature of torrefied biomass enables its efficient blending with coal and contributes to cleaner power generation [18]. Torrefied biomass can be directly combusted in specialized biomass power plants to generate electricity. The higher energy density and improved grindability of torrefied biomass make it a more efficient fuel for electricity production compared to raw biomass [18]. Industries that require heat for processes such as drying, steam generation, and heating can use torrefied biomass as a sustainable alternative to fossil fuels. Torrefied biomass's uniform properties and higher calorific value make it suitable for various industrial heating applications [11]. Torrefaction can enhance the quality of biomass pellets by improving their durability and energy content. These upgraded pellets can have improved handling and combustion properties, making them more attractive for residential heating and small-scale industrial applications [91]. Torrefaction can be used to treat and upgrade organic waste materials, such as agricultural residues, sewage sludge, and organic waste from municipalities. Torrefaction can be integrated with gasification processes to produce syngas, a mixture of hydrogen and carbon monoxide that can be used for various applications, including power generation and chemical synthesis [91]. The liquid fraction resulting from torrefaction, known as bio-oil, can be further refined by processes such as hydrodeoxygenation to produce advanced biofuels. These biofuels can be used as substitutes for fossil fuels in the transportation and heating sectors [91]. By converting biomass into a more energy-rich and cleaner-burning fuel, torrefaction can help reduce the emissions of pollutants such as particulate matter, sulfur dioxide, and nitrogen oxides, contributing to better air quality [18]. Torrefaction supports the transition to a more sustainable energy landscape by providing an alternative to fossil fuels, reducing dependence on non-renewable resources, and providing an efficient way to utilize biomass resources [18].

6. Torrefaction Reactors

There are several reactors that are used for biomass torrefaction. Some of the reactors fall under one of the following types: (i) rotary kilns, (ii) fluidized beds (iii) moving beds, (iv) microwaves, and (v) fixed beds. In all these technologies, there are advantages and disadvantages of their use, which can assist decisions when selecting a reactor type for torrefaction purposes. These technologies aim to optimize the torrefaction process for various feedstocks and applications [8,11,26].

- Rotary kilns are cylindrical, rotating furnaces used for thermal processing, which provide a controlled environment for biomass heating. The biomass feedstock is introduced at one end of the kiln, and as it rotates, it moves through different temperature zones, undergoing torrefaction.
- Fluidized-bed reactors suspend biomass particles in an upward-flowing gas stream, offering good heat-transfer and mixing characteristics suitable for torrefaction. The fluidized bed can be adjusted to maintain a uniform temperature and residence time, resulting in consistent torrefied biomass properties.
- Moving-bed reactors involve passing biomass through a series of temperature-controlled chambers on a conveyor belt or other moving system. Each chamber exposes the biomass to progressively higher temperatures, achieving torrefaction as the biomass moves along the bed.
- Microwave torrefaction uses electromagnetic waves to generate heat within biomass. This technology offers rapid and efficient heating, resulting in shorter processing times. However, it requires careful control to ensure uniform heating and prevent overheating.
- Fixed-bed reactor: after the raw biomass is fed into the reactor, it is dried and torrefied in the furnace. Torrefied biomass is collected at the end after the torrefaction process and the reactor has cooled down.

7. Conclusions

This literature review clearly shows the increased interest in torrefaction, as the number of published papers in 2022 had increased significantly compared to previous years. The studies suggest that torrefaction is a promising technology and even more publications on this process can be expected in the coming years. The review has also shown that torrefaction improves the suitability of raw biomass for further processing. The raw materials are all usable natural sources that are generally not part of the food chain. Because of the improved properties of torrefied biomass, such as a reduced moisture content, increased heating value, increased carbon content, decreased oxygen content, and improved grindability, torrefied biomass is a promising renewable source. As the mass and energy density increase, the hydrophobic properties of torrefied biomass improve, leading to its easier and less expensive densification into pellets or briquettes. As the properties of torrefied biomass are improved, the torrefied biomass is expected to be a more efficient feedstock for gasification than raw biomass. In addition, torrefied biomass is expected to reduce tar formation due to its high heating value and low volatile content. Torrefied biomass can potentially replace coal in the steel industry to reduce fossil fuel use. The current use of torrefied wood could increase manyfold in the European market.

As technology advances and the need for sustainable energy solutions becomes more pressing, several key future aspects of the torrefaction process are emerging. Advancements in reactor design, automation, and process optimization could play a role in achieving commercial-scale torrefaction facilities; the ability of torrefaction to produce biochar with carbon-rich properties presents opportunities for carbon capture and utilization. Integrating torrefaction with circular economy principles can help close resource loops by using waste biomass and residues to produce valuable energy products. As technology advances and global energy priorities shift, torrefaction is likely to play a significant role in the transition to a cleaner and more efficient energy landscape.

Author Contributions: Conceptualization, M.I. and A.P.; writing—original draft preparation, M.I., M.S., D.U. and A.P.; writing—review and editing, M.I., M.S., D.U. and A.P.; visualization, M.I., M.S., D.U. and A.P.; supervision, D.G. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the Slovenian Research Agency for the Research and Infrastructure programs P2-0046, P2-0421 and P2-0414.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge the Slovenian Research Agency for the Research and Infrastructure for supporting the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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