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The Evaluation of Torrefaction Efficiency for Lignocellulosic Materials Combined with Mixed Solid Wastes

Maja Ivanovski, Darko Goričanec * and Danijela Urbancl

Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia; maja.ivanovski@eimv.si (M.I.); danijela.urbancl@um.si (D.U.)
* Correspondence: darko.goricanec@um.si

Abstract: The paper presents the results of research aimed at evaluating the possibility of using selected biomass wastes to produce solid biofuels. In this work, the thermochemical properties of two lignocellulosic biomasses, namely, miscantshus (*Miscanthus* × *Giganteus*) and hops (Humulus *lupulus*), and non-lignocellulosic biomass, namely, municipal solid waste, and their mixtures (micanthus + municipal solid waste and hops + municipal solid waste) were studied using the torrefaction process as the main method for investigation. The effects of various torrefaction temperatures (250, 300, and 350 °C) and times (30 and 60 min) were evaluated. Proximate and ultimate analyses were performed on the torrefied samples. The following can be stated: as the torrefaction temperature and time increased, mass and energy yields decreased while the higher heating values (HHVs) and fuel ratios (FRs) increased, together with carbon contents (C). In addition, energy on return investment (EROI) was studied; the maximum EROI of 28 was achieved for MSW biochar at 250 °C for 30 min. The results of studying greenhouse gas emissions (GHGs) showed a reduction of around 88% when using torrefied biochar as a substitute for coal. In sum, this study shows that torrefaction pre-treatment can improve the physicochemical properties of raw biomasses to a level comparable with coal, and could be helpful in better understanding the conversion of those biomasses into a valuable, solid biofuel.

Keywords: torrefaction; waste biomass; renewable energy; fuel ratio; greenhouse gas emissions (GHG)

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1. Introduction

Rapid climate change and serious environmental issues today present an existential threat to Europe and the rest of the world [1]. In December 2019, the European Commission prepared and introduced an ambitious proposal called the European Green Deal to make Europe the first climate-neutral continent by 2050 [2]. This target will be reached through the European Climate Law [3] that sets climate neutrality into binding European legislation. One of the main goals stated in the European Green Deal [2] is to reduce greenhouse gas (GHGs) emissions to at least 50% by 2030. Fossils fuels (e.g., petroleum, natural gas, or coal) are still the primary reason for the high total emissions of GHGs [4], and to minimize their impact on the environment, the development of clean and renewable energy sources (RES) is coming to the fore.

Much attention has already been given to analyzing the potential of wind, solar, hydro, or geothermal energy sources, whereas energy derived from biomass is still under investigation. Several reports have been published recently explaining the benefits of using biomass-based energy sources [5,6]. For instance, Akhtar et al. [7] stated that biomass-based fuels have a better sustainability footprint when compared to fossil fuels. The same was confirmed by Kalak [8], who wrote a critical review based on the potential use of industrial biomass waste as a sustainable energy source. According to the European Union's strategy on biofuels [9], new technologies for obtaining and using renewable energy fuels must be developed, especially through the management of agricultural products and other wastes.

General definition says that biomass is an organic material obtained from plants growing through the process of photosynthesis [8]. Biomass is considered a carbon neutral source that is almost always available; in addition, it is available in large quantities [10]. It is believed that biomass energy has the potential for energy or power generation [11], despite the fact that its direct application is not always feasible due to several discovered issues [12]. Raw biomass is characterized by a high moisture content, high hygroscopy, low bulk density, low energy density, high ash content, low carbon content, and poor grindability [13]. Such qualities may cause problems in the storage, handling, and transportation of biomass; therefore, it must be processed before being used [14]. One effective way to overcome the above-mentioned issues is the torrefaction process.

Torrefaction is a thermochemical process for upgrading biomass properties for further energy applications [11], such as in thermochemical (pyrolysis, combustion, etc.), chemical (i.e., hydrolysis), or biochemical (fermentation, anaerobic digestion, etc.) conversion routes [15]. The torrefaction process is carried out in the temperature range from 200 to 350 °C in inert or semi-inert atmospheres [16], with the obtained solid biochar being the main product of the process. The torrefaction process is still not widespread on a commercial scale [17], but there have been an enormous amount of studies on the torrefaction of biomass published in the last decade. For example, torrefaction of lignocellulosic biomass such as miscanthus [18], pine wood [19], or sawdust [20] has already been extensively taken into consideration, together with non-lignocellulosic biomass, such as sewage sludge [21] or algae [22]. Doddapaneni et al. [10] studied the properties of torrefied sludge from the pulp industry. The torrefaction process was carried out at 250, 275, and 300 °C for 30 or 60 min, respectively. Physicochemical properties were investigated. Different agro-forestry (e.g., pine wood) wastes were analysed via the torrefaction process by Nunes [23]. Proximate and ultimate analyses were performed on the torrefied wastes, together with thermal analysis and grindability tests. Chang et al. [24] studied the influence of the torrefaction process on thermal degradation and chemical changes in oil palm waste through thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). Based on these studies, the following findings can be stated: when raw biomass undergoes the torrefaction process, several reactions occur, leading to the obtaining of the torrefied biomass that has reduced moisture content, increased heating value (HHV), increased carbon content, decreased oxygen content, and improved grindability [25]. In addition, such a torrefied biomass is hydrophobic [26]. With the increasing of the torrefaction temperature or torrefaction time, mass and energy yield decrease in all cases.

Lately, much attention has also been paid to municipal organic wastes (MSW), such as yard wastes, plastics, kitchen waste, paper, wood, rubber, textiles, or any other complex components from the commercial [27], industrial [28], or residential sectors [29]. MSW can cause numerous serious issues, including GHG emissions and energy instability, or even environmental and public health problems [30]. The current global annual MSW production is approximately 1.9 billion tons and it is estimated to rise up to 3.4 billion tons per year by 2050 [31]. Raw MSW is characterized as a heterogeneous material, with a high moisture content, low calorific value, and tenacious fibrous structure. Thermochemical technologies are mentioned as possible ways to treat MSW for energy purposes, with torrefaction being one of the most attractive ones [32].

The main aim of the study is to analyse the effects of torrefaction temperature (250, 300, and 350 °C) and residence time (30 and 60 min) on the physicochemical properties of biochar obtained from different lignocellulosic (i.e., miscanthus and hops) and non-lignocellulosic biomass wastes (i.e., municipal solid waste) that are typical in the Republic of Slovenia. Mass and energy yields were evaluated, together with energy density and heating values (HHVs). Moreover, energy return on investment (EROI), fuel ratios (FR), and greenhouse gas (GHG) emissions were also evaluated to determine the sustainability of the torrefied biochar. To date, only a few works have been published that describe the properties of torrefied MSW and hops, and no works on the torrefaction process of MSW mixed with miscanthus and hops have been published.

2. Materials and Methods

2.1. Biomass Collection

Miscanthus (*Miscanthus* × *Giganteus*) (100%, M), hops (*Humus lupulus*) (100%, H), and municipal solid waste (100%, MSW) were collected from different parts of the Republic of Slovenia, respectively. The initial moisture contents of the miscanthus, hops, and municipal solid waste were 10.58 wt.%, 12.01 wt.%, and 16.98 wt.% (wet basis), respectively. Additionally, the following mixtures were used in the work: a mixture of miscanthus and municipal solid waste (50:50%, M + MSW) and a mixture of hops and municipal solid waste (50:50%, H + MSW). The initial moisture contents of the mixtures were 13.00 wt.% and 14.33 wt.% (wet basis), respectively.

The raw materials were air-dried and pulverized or cut into similar sizes (up to 0.5 cm), respectively, and stored before being prepared for further analysis. The characteristics of the raw biomass materials, including proximate and ultimate analyses and HHVs, are summarized in Table 1. The analyses were performed as described in the following Section 2.3.

Table 1. Characteristics of raw biomass samples.

Analysis		M	H	MSW	M + MSW	H + MSW
Proximate analysis (wt.%, dry basis)	Fixed carbon	3.89	3.01	6.69	4.25	4.54
	Volatile matter	82.79	84.23	78.11	82.60	80.47
	Ash content	2.83	4.18	3.12	3.37	3.65 ± 0.18
Moisture content (wt.%, dry basis)		9.21	8.58	12.08	9.78	11.34 ± 0.57
Elemental analysis (wt.%, dry basis)	C	45.11	42.12	43.20	44.12	43.97
	H	3.71	4.54	8.10	6.19	6.42
	N	0.80	3.49	0.78	1.02	2.33
	O	50.33	49.82	47.89	48.65	47.25
	S	0.05	0.03	0.03	0.02	0.03
Energy content (wt.%, dry basis)	HHV (MJ/kg)	18.91	16.56	24.27	21.37	20.23

2.2. Torrefaction Procedure

Figure 1 presents a schematic diagram of the torrefaction set-up studied in this work. The torrefaction process was carried out in an electric lab-scale furnace, Bosio type EUP-K 6/1200, which is described in detail in the work of Jóźwiak et al. [33] and in our previous papers [34]. The materials were torrefied at three different temperatures (250, 300, and 350 °C) and two different residence times (30 and 60 min), respectively. The torrefaction temperatures and times were chosen based on the findings from our previous papers, which obtained the optimal temperature [35], optimal time [36], and severe conditions [21]. The semi-inert atmosphere was guaranteed by the lid, placed on the ceramic round crucibles specifically to create an inert atmosphere [34]. For each experimental run, around 50 g of sample was used. After torrefaction, the crucibles were removed from the furnace and placed into desiccators to cool to room temperature [34]. The obtained biochar was then collected and crushed, and again stored in hermetically sealed containers. To ensure the repeatability of the results, all experiments were repeated two times, and average values are used in the Discussion.

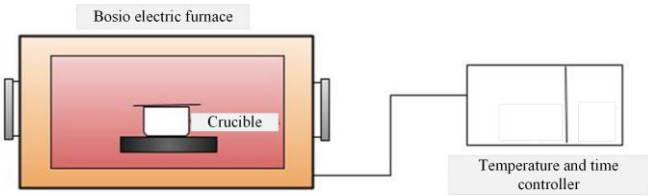

Figure 1. Experimental set-up of the torrefaction process.

2.3. Analytical Methods

2.3.1. Proximate and Ultimate Analyses

The ultimate analyses was performed using the Perkin Elmer CHNS/O 2400 elemental analyser (Billerica, MA, USA). The contents of C, H, N, and S were determined by the following international standards: UNI EN 15104:2011 ("Solid biofuels-Determination of total content of carbon, hydrogen, and nitrogen–Instrumental methods") and UNI EN 15289:2011 ("Solid biofuels-Determination of total content of sulfur and chlorine"), respectively. The content of O was calculated by the difference, as presented in the following Equation (1):

$$\text{O (\%)} = 100\% - \text{C (\%)} - \text{H (\%)} - \text{N (\%)} - \text{S (\%)} - \text{Ash (\%)} \quad (1)$$

The moisture content (MC), volatile matter (VM), ash content (Ash), and fixed carbon (FC) content were determined in accordance with the ASTM D7582:2015 ("Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis") standard.

2.3.2. HHV, Mass Yield, Energy Density, and Energy Yield Analyses

The heating values (HHVs) were measured in an IKA C6000 adiabatic bomb calorimeter (Isoperibol; Staufen, Germany) according to the UNI EN 14918:2019 ("Solid biofuels-Determination of calorific value") and ASTM DIN 51900 ISO 1928 standards ("Determining the gross calorific value of solid and liquid fuels").

Mass yield (MY), energy density (ED), and energy yield (EY) were calculated using Equations (2)–(4) to determine the impact of torrefaction.

$$\text{MY (\%)} = \frac{\text{mass}_{\text{torrefied sample}}}{\text{mass}_{\text{raw sample}}} \cdot 100 \quad (2)$$

$$\text{ED} (-) = \frac{\text{HHV}_{\text{torrefied sample}}}{\text{HHV}_{\text{raw sample}}} \quad (3)$$

$$\text{EY (\%)} = \left(\text{MY} \cdot \frac{\text{HHV}_{\text{torrefied sample}}}{\text{HHV}_{\text{raw sample}}} \right) = \text{MY} \cdot \text{ED} \quad (4)$$

Additionally, to evaluate decomposition characteristics of the torrefied biomass materials, the fuel ratios (FRs) were calculated using Equation (5) [10,37]. Contents of FC and VM were obtained from the results of the proximate analysis. As stated in the work of Lin and Zheng [38], the FR of the torrefied biomass material is usually higher than that of a raw biomass sample due to the increased FC content and decreased VM content.

$$\text{FR} (-) = \frac{\text{fixed carbon content}}{\text{volatile matter content}} \quad (5)$$

2.3.3. Energy Returns on Investment Analysis

To determine the energy benefits of the obtained solid biochars, the energy return on investment (EROI) was calculated from the ratio of the energy required during pre-drying

and the torrefaction process and the energy produced by the biochar [39] (Equation (6)). The EROI index is crucial for the evaluation of the potential energy benefit of fuel [4].

$$\text{EROI}\ (-) = \frac{\text{energy produced from biochar}}{\text{energy required during the pre-drying and torrefaction process}} \quad (6)$$

The energy produced from the biochar was calculated by multiplying the mass of the biochar by its HHV (Table 1) [40,41]. The energy required for drying and torrefaction was calculated by multiplying the reaction time and the amount of power consumed at each stage. The detailed description of the calculation method is written in the works of Lin et al. [4,38,42].

2.3.4. GHG Emissions

Greenhouse gas emissions (GHGs), such as CO_2 emissions, were also determined as described in the works of Lin et al. [4,38,42]. GHG emissions achieved through substitution of biochar for coal were determined through life cycle assessment (LCA), which primarily considered the electricity consumed for pre-drying the biomass and torrefying the biochar as a renewable energy [40,41]. The GHG emissions from the torrefaction process at each life cycle stage can be used to evaluate the global warming potential (GWP) [43]. GWP was quantified using characterization factors and a classified activity inventory (e.g., electricity consumption). For the Republic of Slovenia, the characterization factor for average electricity consumption was estimated to be 0.254 kg CO_2 eq./kWh [43]. Electricity generation efficiency is around 48% [44]. In the GWP assessment, biomass was assumed to be carbon neutral and to have a minimal effect on the climate [40,41].

3. Results and Discussion

3.1. Effects of Torrefaction Temperature and Time on Obtained Biomaterial

3.1.1. Proximate and Ultimate Analyses

Firstly, Table 2 shows the results of the proximate analyses. The analyses were performed on all torrefied biomasses, respectively. As the torrefaction temperature and torrefaction time increased, the ash contents increased gradually. For miscanthus biochar, the ash contents increased from 3.50 wt.% to 4.50 wt.% when torrefying it for 30 min, and from 4.00 wt.% to 4.78 wt.% when torrefying it for 60 min. For hops biochar, the ash contents increased from 4.80 wt.% to 6.01 wt.% (when torrefied for 30 min) and from 5.23 wt.% to 6.13 wt.% (when torrefied for 60 min), respectively. Similarly, for MSW biochar, these values increased from 7.58 wt.% to 7.99 wt.% (when torrefied for 30 min) and from 7.05 wt.% to 7.99 wt.% (when torrefied for 60 min), respectively. Likewise, the ash contents of biochar in the mixtures of miscanthus and MSW, and hops and MSW, also increased. For the mixture of miscanthus and MSW, the ash contents increased from 4.56 wt.% to 5.85 wt.% (when torrefied for 30 min) and from 4.78 wt.% to 6.18 wt.% (when torrefied for 60 min), respectively, and for the mixture of hops and MSW, from 4.57 wt.% to 5.06 wt.% (when torrefied for 30 min) and from 6.50 wt.% to 7.63 wt.% (when torrefied for 60 min), respectively. The fixed carbon contents of the torrefied biomass samples presented a comparable trend: the contents increased with increasing the torrefaction temperature and torrefaction time. The fixed carbon contents of miscanthus, hops, MSW, the mixture of miscanthus and MSW, and the mixture of hops and MSW increased from 4.30 to 5.13 wt.%, 4.80 to 5.45 wt.%, 7.80 to 8.87 wt.%, 5.13 to 6.45 wt.%, and 4.93 to 5.06 wt.% for each biomass (when torrefied for 30 min), respectively, and from 4.88 to 5.33 wt.%, 3.88 to 5.47 wt.%, 7.87 to 8.93 wt.%, 6.01 to 8.93 wt.%, and 5.00 to 6.02 wt.% for each biomass (when torrefied for 60 min), respectively. On the contrary, as torrefaction temperature and time increased, volatile matter contents and moisture contents decreased. Furthermore, the volatile matter contents of the torrefied biomasses decreased from 82.20 to 81.56 wt.%, 82.80 to 80.01 wt.%, 76.45 to 74.88 wt.%, 81.24 to 79.03 wt.%, and 79.26 to 78.03 wt.% for each biomass (when torrefied for 30 min), respectively, and from 82.12 to 81.45 wt.%, 82.00 to 80.04 wt.%, 76.12 to 74.87 wt.%, 80.33 to 78.22 wt.%, and 78.09 to 77.22 wt.% for each biomass (when

torrefied for 60 min), respectively. Similarly, moisture contents decreased as shown in Table 2. In total, the obtained results were similar to those found in the literature for woody biomass, herbaceous biomass [45], and municipal solid waste [46], whereas to date, no studies on the torrefaction of mixtures of miscanthus and MSW and hops and MSW have been published. It is believed that the obtained results could also be the reason for two processes happening during the torrefaction process: devolatilization and carbonization [4]. In our previous works, it was also stated that an increase in the ash content may be a consequence of the weight loss of volatile matters that are released during the process [34,35]. In addition, the higher the torrefaction temperature, the greater the volatile release.

Table 2. Proximate and ultimate analyses of torrefied biomass samples.

		Proximate Analysis (wt.%)			Moisture Content (wt.%)	Elemental Analysis (wt.%)					Energy Content (wt.%)
		FC	VM	Ash		C	H	N	O	S	HHV (MJ/kg)
					30 min						
250 °C	M	4.30	83.20	3.50	9.00	50.61	4.00	0.50	44.88	0.01	19.80
	H	3.45	82.80	4.80	8.95	46.35	4.10	2.80	46.74	0.01	17.12
	MSW	7.80	76.45	6.78	8.97	48.11	7.23	0.84	43.54	0.28	24.58
	M + MSW	5.13	81.24	4.56	9.07	50.71	6.78	0.84	41.46	0.21	21.45
	H + MSW	4.93	79.26	4.57	11.24	49.78	6.52	2.11	41.36	0.23	20.45
300 °C	M	4.80	82.00	4.20	9.00	55.11	3.89	0.70	40.29	0.01	19.94
	H	4.58	81.08	5.88	8.46	48.17	3.92	3.01	44.89	0.01	18.78
	MSW	8.52	75.02	7.58	8.88	52.7	6.78	0.83	39.48	0.21	24.45
	M + MSW	6.05	79.70	5.20	9.05	56.78	6.25	0.88	35.89	0.20	21.88
	H + MSW	5.23	78.58	4.86	11.33	54.22	6.48	2.14	36.96	0.20	20.58
350 °C	M	5.13	81.56	4.50	8.81	61.80	3.52	0.78	33.89	0.01	19.70
	H	5.45	80.01	6.01	8.53	55.89	3.84	3.24	37.02	0.01	17.65
	MSW	8.87	74.88	7.99	8.26	53.78	6.23	0.86	39.12	0.01	24.78
	M + MSW	6.45	79.03	5.85	8.67	60.00	5.98	0.95	32.89	0.18	21.78
	H + MSW	5.58	78.03	5.06	11.33	59.89	6.01	2.33	31.59	0.18	20.74
					60 min						
250 °C	M	4.88	82.12	4.00	9.00	53.99	3.89	0.52	41.59	0.01	20.26
	H	3.88	82.00	5.23	8.89	47.12	4.00	2.89	45.98	0.01	17.38
	MSW	7.87	76.12	7.05	8.96	50.00	7.02	0.86	41.84	0.28	24.97
	M + MSW	6.01	80.33	4.78	8.88	52.01	6.78	0.83	40.17	0.21	22.12
	H + MSW	5.00	78.09	6.50	10.41	53.96	6.35	2.11	37.35	0.23	20.79
300 °C	M	4.90	81.77	4.60	8.73	55.78	3.65	0.71	39.85	0.01	20.30
	H	5.35	81.16	5.13	8.36	48.00	3.92	3.01	45.06	0.01	20.90
	MSW	8.52	75.78	7.58	8.12	51.52	6.88	0.88	40.51	0.21	25.02
	M + MSW	6.78	78.74	5.60	8.88	56.78	6.35	0.92	35.75	0.20	22.19
	H + MSW	5.10	78.60	6.61	9.69	54.01	6.08	2.29	37.42	0.20	20.64

Table 2. *Cont.*

		Proximate Analysis (wt.%)			Moisture Content (wt.%)	Elemental Analysis (wt.%)					Energy Content (wt.%)
		FC	VM	Ash		C	H	N	O	S	HHV (MJ/kg)
					60 min						
350 °C	M	5.33	81.45	4.78	8.44	57.10	3.5	0.75	38.64	0.01	20.32
	H	5.47	80.04	6.13	8.36	55.89	3.84	3.28	36.98	0.01	19.18
	MSW	8.93	74.87	7.99	8.21	54.00	3.74	0.93	41.32	0.01	25.18
	M + MSW	6.99	78.22	6.18	8.61	60.00	6.12	0.97	32.73	0.18	22.36
	H + MSW	5.99	78.22	6.63	9.16	56.08	6.03	2.34	35.37	0.18	21.03

Secondly, the ultimate composition of the torrefied biomass sample at various temperatures for 30 and 60 min is also presented in Table 2. The increase in torrefaction temperature from 250 to 350 °C (30 and 60 min, respectively) resulted in increases in carbon content for each biomass sample, respectively. For miscanthus biochar, those values were in the range from 55.11 to 61.80 wt.% (30 min) and 53.99 to 57.10 wt.% (60 min), for hops biochar between 46.35 and 55.89 wt.% (30 min) and 47.12 and 55.89 wt.% (60 min), for MSW biochar between 45.11 and 53.78 wt.% (30 min) and 50.00 and 54.00 wt.% (60 min), for biochar obtained in the mixture of miscanthus and MSW between 50.71 and 60.00 wt.% (30 min) and 52.01 and 60.00 wt.% (60 min), and for the mixture of hops and MSW between 49.78 and 59.89 wt.% (30 min) and 53.96 and 56.08 wt.% (60 min). The nitrogen and sulphur contents remained relatively low when the torrefaction temperature and time were increased. In total, the nitrogen contents were between 0.50 and 3.24 wt.% (30 min) and between 0.52 and 3.28 wt.% (60 min), whereas sulphur contents varied up to 0.28 wt.% (30 min and 60 min, respectively). The oxygen and hydrogen contents, on other hand, decreased when the torrefaction temperature and time increased. The oxygen contents decreased from 44.88 to 33.89 wt.% (30 min) and from 41.59 to 28.64 wt.% (60 min) for miscanthus biochar. Similarly, the values also decreased for biochars of hops, MSW, and all the studied mixtures (Table 2). The hydrogen contents were between 3.52 and 7.23 wt.% (30 min) and between 3.65 and 7.02 wt.% (60 min). Such a decline could be the result of the thermal decomposition of organic compounds in the samples, such as acids and alcohols, during the torrefaction process [47]. Similar results were found in other works [48,49], together with the obtained O/C and H/C atomic ratios. Lastly, both the O/C and H/C ratios decreased as the torrefaction temperature increased. This is due to moisture and volatile removal from the samples that contain more hydrogen and oxygen content than carbon content [35].

According to the aforementioned results, both torrefaction temperature and time have a remarkable impact on the biochar produced from all the studied biomasses. Upon obtaining these results from the proximate and ultimate analyses, O/C and H/C atomic ratios could be calculated, which show that the studied feedstock presents a suitable material for producing renewable solid biofuels.

3.1.2. HHVs

Additionally, Table 2 shows the HHVs of the torrefied biomass samples as a function of temperature and time. Results are also graphically presented in Figure 2. During the torrefaction process, the HHV is increased, as a result of a decrease in oxygen content and increase in carbon and fixed carbon contents [34]. In addition, the higher the content of volatile matter, the lower the calorific value in torrefied biomass and the more reactive the fuel [34]. On the contrary, the higher the fixed carbon content, the higher the calorific value of the torrefied biomass and the less reactive the fuel [50]. In this work, as the torrefaction

temperature increased from 250 to 350 °C, the HHVs of the miscanthus, hops, MSW, and mixtures of biochars increased from the minimum values obtained at 250 °C and 30 min (i.e., 19.20 MJ/kg, 17.12 MJ/kg, 24.58 MJ/kg, 21.45 MJ/kg, and 20.45 MJ/kg, respectively) to the maximum values obtained at 300 °C and 60 min (i.e., 20.32 MJ/kg, 19.18 MJ/kg, 25.18 MJ/kg, 22.36 MJ/kg, and 21.03 MJ/kg, respectively), respectively. The raw HHVs of the studied biomasses were 18.91 MJ/kg, 16.56 MJ/kg, 24.27 MJ/kg, 21.37 MJ/kg, and 20.23 MJ/kg, respectively. The minimum HHV observed in this work was for the hops biomass sample (17.12 MJ/kg torrefied at 200 °C for 30 min), whereas the maximum observed HHV was for the MSW biomass sample (25.18 MJ/kg at 350 °C for 60 min). As already said, to date, no study on the torrefaction of hop biomass has been published elsewhere, whereas miscanthus has already been studied globally [51]. Similar HHVs for MSW were reported in other works [32,52].

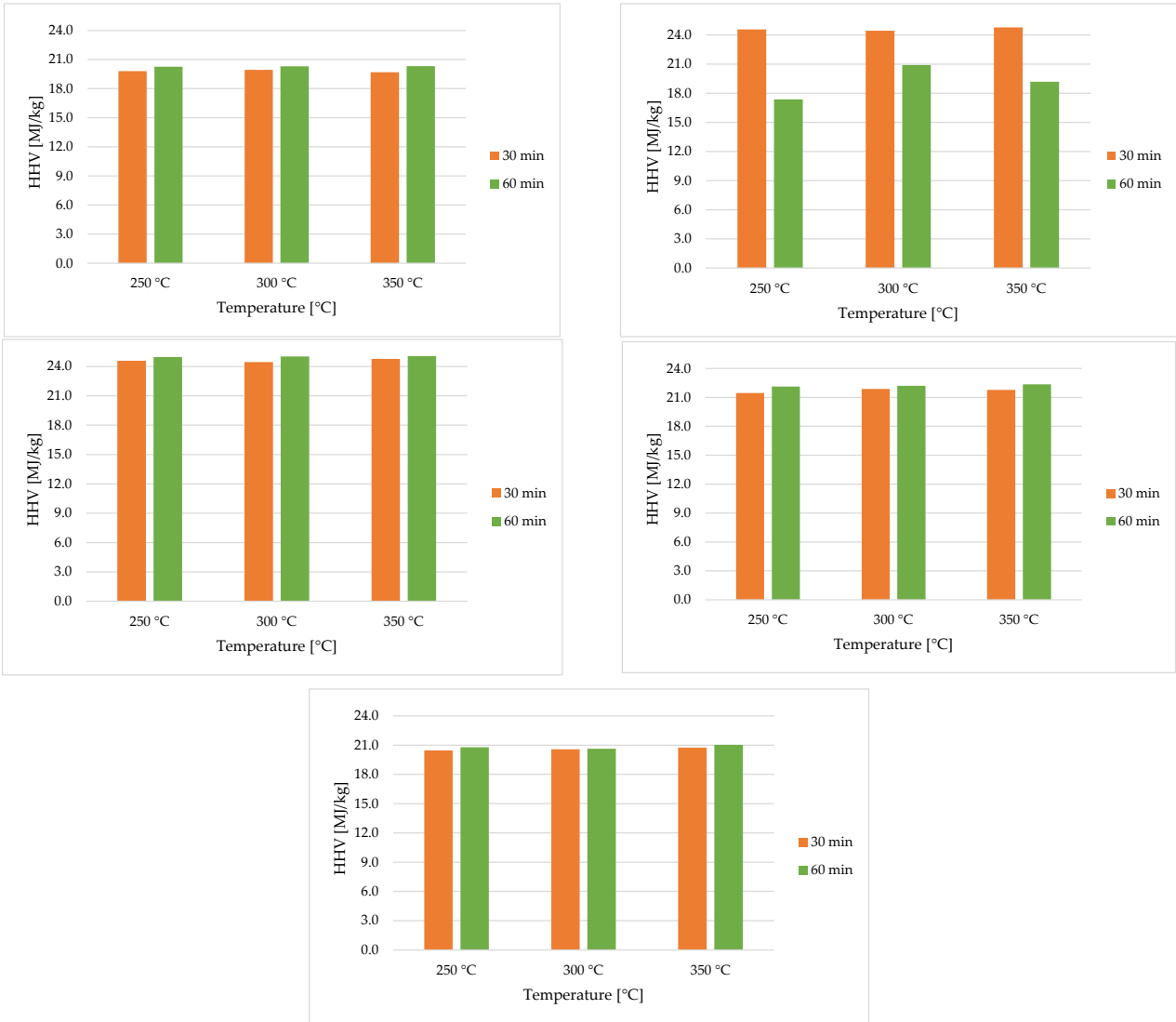

Figure 2. HHVs of torrefied biochars of miscanthus, hops, MSW, and their mixtures (from (**left**) to (**right**), (**top**) to (**bottom**)).

3.1.3. Mass Yield, Energy Yield, and Energy Density

Furthermore, Figure 3 displays the mass yield, energy yield, and energy density of miscanthus, hops, MSW, and the mixtures of biochars, respectively, as a function of temperature and time. Several research works have stated that torrefaction temperature is a more important parameter during the torrefaction process than time and may affect mass yield,

energy yield, energy density, and also HHVs [15,47,53]. When the torrefaction temperature was increased from 250 to 350 °C, the mass yields of the miscanthus, hops, MSW, and mixtures decreased continually from 79.37 to 32.91 %, 68.28 to 46.81 %, 80.87 to 57.36 %, 78.33 to 52.38, and 82.34 to 52.76 %, for each biomass, respectively (when torrefied for 30 min). Similarly, mass yields decreased when torrefying biomass for 60 min: from 75.41 to 32.10 %, 65.46 to 45.85 %, 77.10 to 56.29 %, 77.97 to 51.37 %, and 77.89 to 46.46 % for each biomass, respectively. It is believed that such a decrease is a result of the partial decomposition of volatile compounds, especially in the lignocellulosic biomass [34].

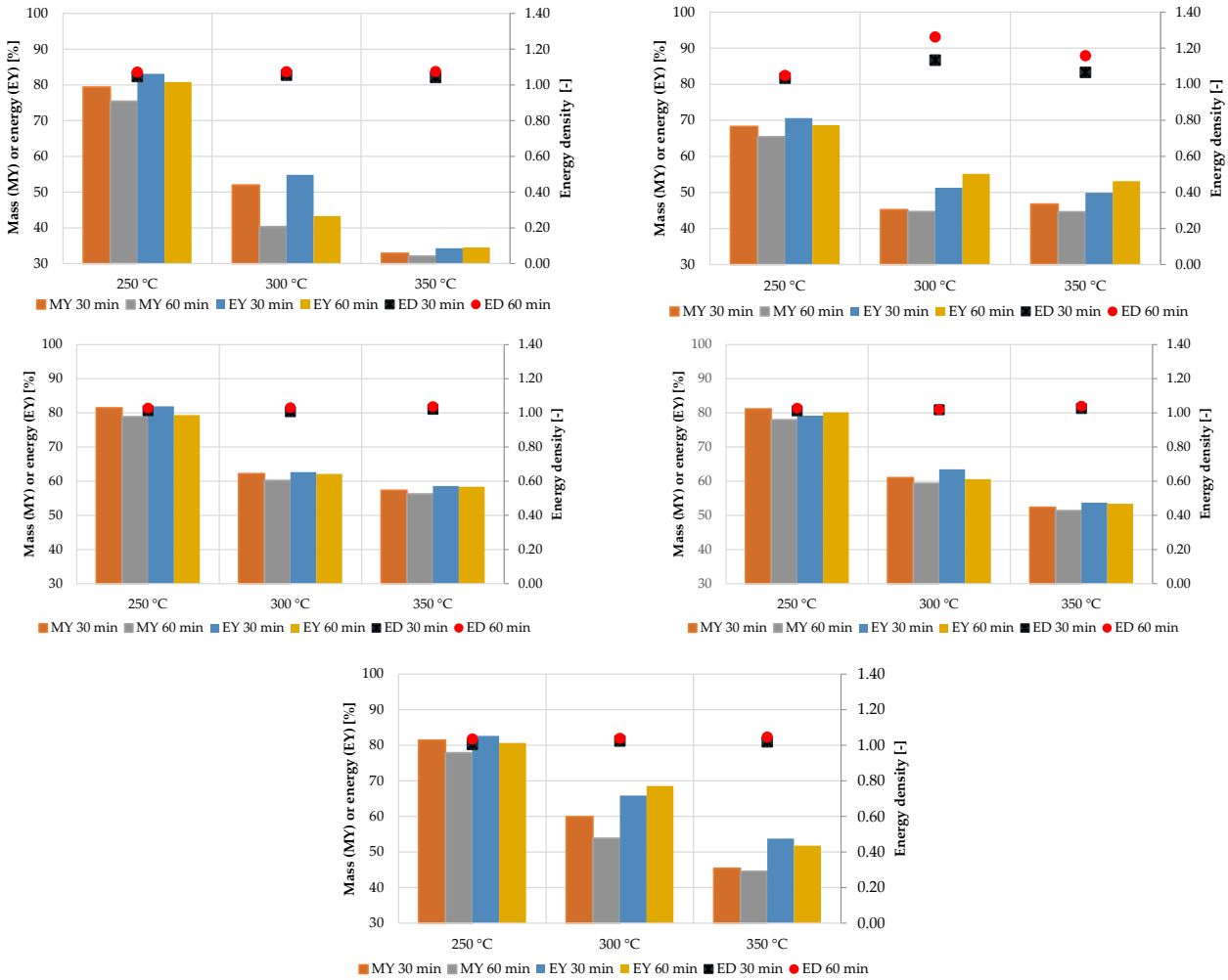

Figure 3. Mass yield, energy yield, and energy density of torrefied biochars of miscanthus, hops, MSW, and their mixtures (from (**left**) to (**right**), (**top**) to (**bottom**)).

The energy yield followed the same trend as mass yield: with increasing the torrefaction temperature and torrefaction time, energy yield decreased. The minimum energy yield was observed when the miscanthus biomass sample was torrefied at 350 °C for 30 and 60 min. The obtained energy yields were 34.28 % and 34.49 %, respectively, whereas the maximum energy yield was observed for the mixture of miscanthus and MSW at 250 °C, both for 30 and 60 min. The obtained energy yields were 82.65 % and 80.62 %, respectively. The decrease in energy yield was smaller than the decrease in mass yield, because the increased torrefaction temperature helped to improve the energy density of the torrefied biomass samples [34].

Furthermore, energy density was calculated following Equation (3). In our previous work [21], it was stated that the energy (ED) reflects the change in HHV during the torrefaction process. The results of the ED calculated in this work are listed in Table 2. The

results showed that ED increased as torrefaction temperature and time increased, which means that HHV values also improved during the torrefaction process.

3.1.4. FR Results

Figure 4 presents the fuels ratios (FRs) from this study. The FRs were calculated as shown in Equation (5) for the raw and torrefied biomass samples at various temperatures and reaction times. As stated in the work of Lin et al. [4], high fixed carbon content and low volatile matter content increase the combustibility of biochar obtained during the torrefaction process. In this work, fuel ratios increased when torrefaction temperature and time were increased. For example, FR for miscanthus increased from 0.05 to 0.06 (torrefied 30 min), for hops from 0.04 to 0.07 (torrefied 30 min), for MSW from 0.10 to 0.12 (torrefied 30 min), for the mixture of miscanthus and MSW from 0.06 to 0.08 (torrefied 30 min), and for the mixture of hops and MSW from 0.06 to 0.07 (torrefied 30 min). Similar results were obtained for all biomasses when the torrefaction time was set to 60 min (Figure 3). From the results, it was observed that the fuel ratios were especially high during torrefaction at 350 °C and 60 min. From this, it could be stated that the extreme conditions set during the torrefaction process (350 °C and 60 min) can enhance the combustibility of the studied biomass samples (biochars).

3.2. EROI Results

The EROI values were calculated as explained in Section 2.3.4 and with Equation (6). The calculation of EROI values followed exactly the same procedures described in the works of Lin et al. [4,38,42]. The EROI values of pre-dried biochar of miscanthus, hops, MSW, and their mixtures torrefied at various temperatures and times were calculated using the information presented in Table 3. Figure 5 shows the obtained EROI values. For the torrefied biomasses, EROI values decreased when both torrefaction temperature and time were increased, respectively. The minimum EROI, 7, was observed for the miscanthus biomass sample (torrefied at 350 °C for 60 min), whereas the maximum observed EROI, 28, was for the MSW biomass sample (torrefied at 250 °C for 30 min). As stated in the work of Lin et al. [4], the EROI values obtained for all biomass samples in this study are higher than the minimum EROI proposed for a sustainable society. Therefore, torrefaction of these biomass samples could be a promising method of biochar production for practical application.

Table 3. Calculation details of the EROI of torrefied miscanthus, hops, MSW, and their mixtures.

Energy Required		
Pre-drying		
	Temperature	105 °C
	Power of heating processes	2700 W (6 min)
	Power of torrefaction process	600 W (10 min)
Torrefaction		
	Temperature	250, 300, 350 °C
	Time	30, 60 min
	Power of heating processes	2700 W (6 min)
	Power of torrefaction process	600 W (30 and 60 min)
Energy Produced		
Weight of biochar obtained 4.8 kg (air-dried material) × MY of each biochar		
HHV of each biochar torrefied at specific torrefaction temperature and time		

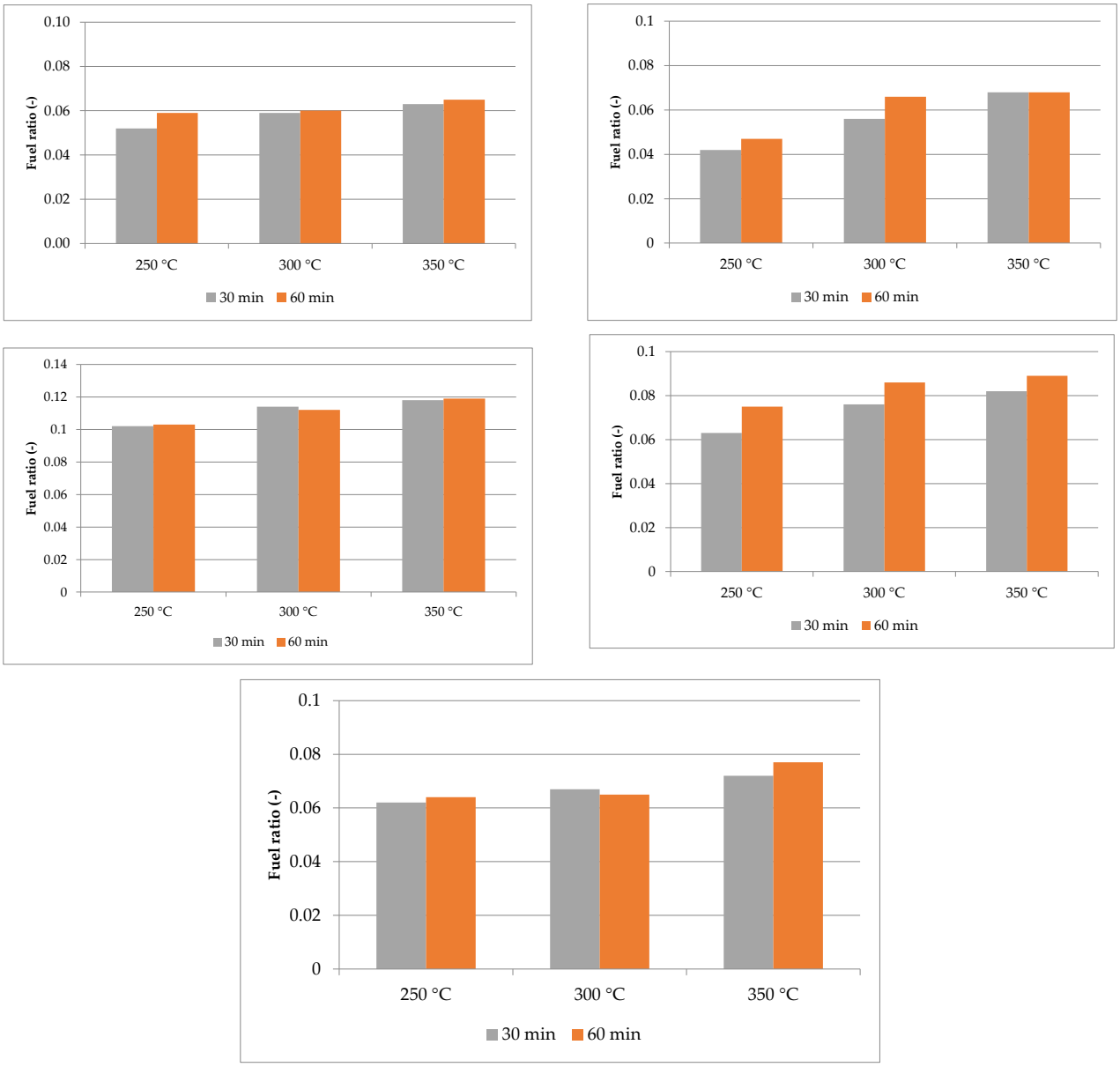

Figure 4. Fuel ratios of torrefied miscanthus, hops, MSW, and their mixtures at different torrefaction temperatures and times (from (**left**) to (**right**), (**top**) to (**bottom**)).

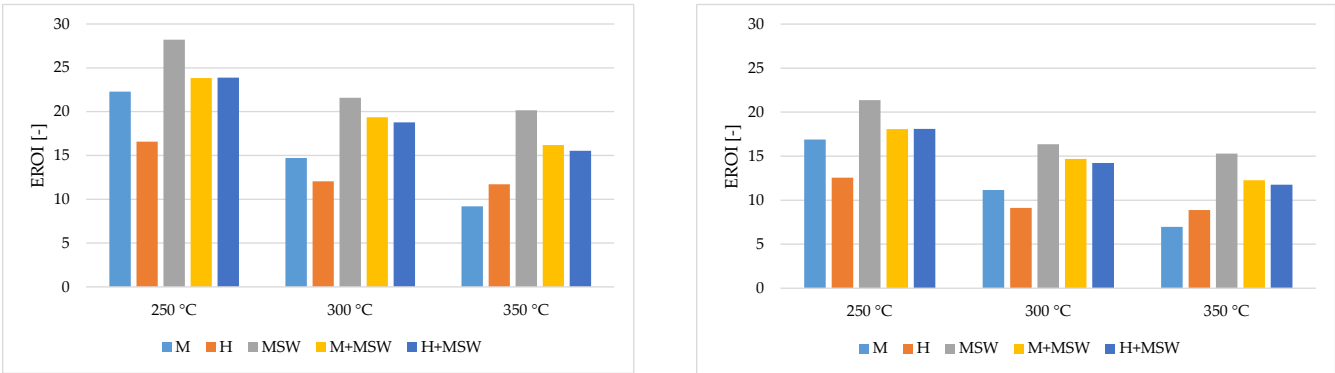

Figure 5. EROI of torrefied miscanthus, hops, MSW, and their mixtures ((**left**): torrefaction time 30 min; (**right**): torrefaction time 60 min).

3.3. GHG Emissions

The GHG emissions of the torrefied miscanthus, hops, MSW, and their mixtures at different torrefaction temperatures and reaction times are shown in Figure 6. The parameters and all calculations were determined as described in the work of Lin et al. [4,38,42]. For producing 1 kg of biochar, the amount of GHGs released was 0.06–0.20 kg CO_2 eq. for torrefied miscanthus, 0.07–0.15 kg CO_2 eq. for torrefied hops, 0.06–0.12 kg CO_2 eq. for torrefied MSW, 0.06–0.13 kg CO_2 eq. for the torrefied mixture of miscanthus and MSW, and 0.06–0.13 kg CO_2 eq. for the torrefied mixture of hops and MSW. Similarly, emissions for kilowatt-hour electricity generated were around 0.005–0.0174 kg CO_2 eq. for torrefied miscanthus, 0.0074–0.0129 kg CO_2 eq. for torrefied hops, 0.0053–0.0080 CO_2 eq. for torrefied MSW, 0.0051–0.0099 kg CO_2 eq. for the torrefied mixture of miscanthus and MSW, and 0.0051–0.0109 kg CO_2 eq. for the torrefied mixture of hops and MSW. The GHG emissions of torrefied biomass were similar to those found in the works of Lin et al. [4,38,42].

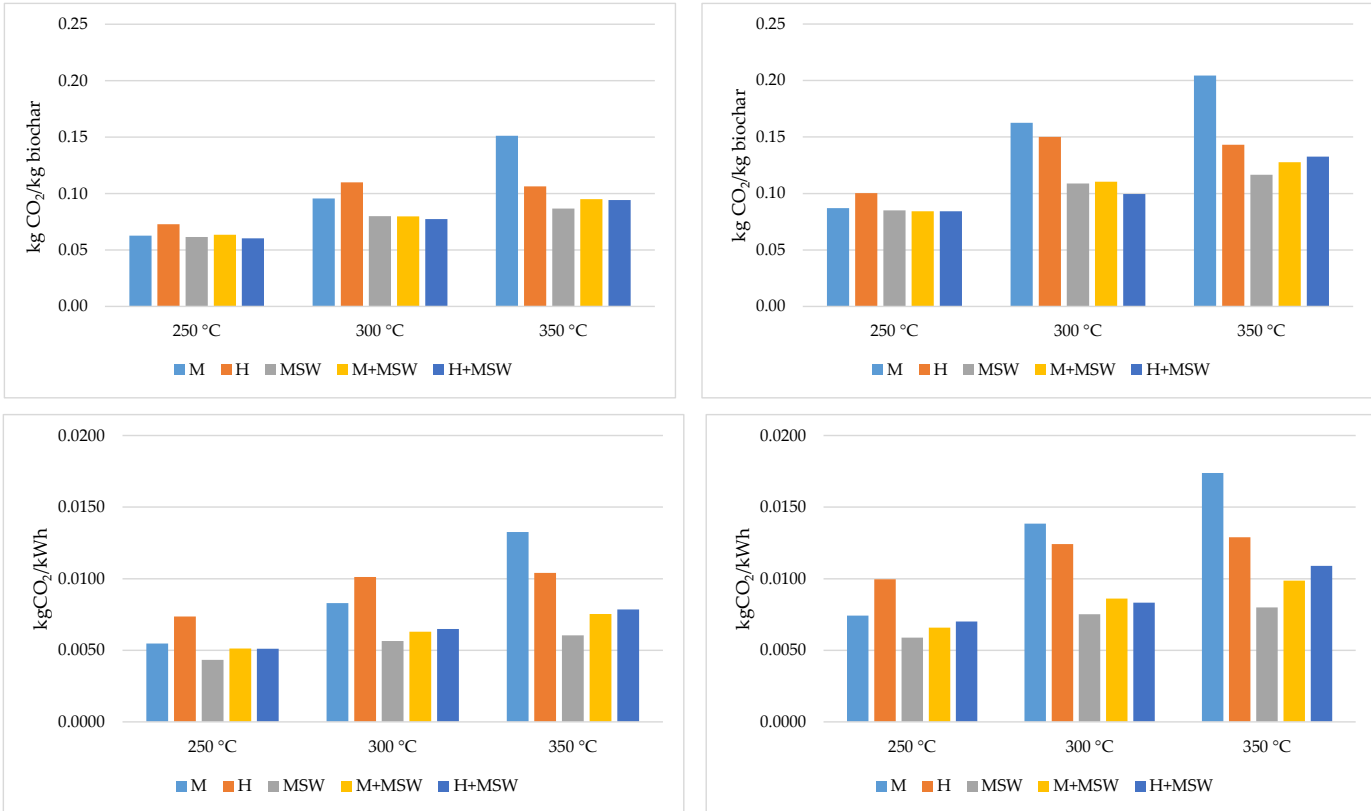

Figure 6. GHG emissions of torrefied miscanthus, hops, MSW, and their mixtures ((**above**): GHGs released per kg CO_2 eq.; (**below**): GHGs released per kWh; (**left**): torrefaction time 30 min; (**right**): torrefaction time 60 min).

4. Conclusions

In this study, the torrefaction process was investigated for two different lignocellulosic biomasses and non-lignocellulosic mixed solid wastes; additionally, their mixtures were also analysed. The torrefaction process was performed at the temperatures ranging from 250 to 350 °C and with time ranging from 30 to 60 min, respectively. Several analytical methods were used to determine the effects of torrefaction temperatures and times for miscanthus, hops, municipal solid waste, and mixtures of municipal solid waste with miscanthus and hops. The results showed that as the torrefaction temperature increased, the mass and energy yield decreased, while HHVs increased. Additionally, energy density increased. The same was observed when the torrefaction time increased for all the studied biomasses. Energy on return investment (EROI) showed the minimum value,

7, for miscanthus biochar (torrefied at 350 °C for 60 min), whereas the maximum EROI value, 28, was observed for MSW biochar (torrefied at 250 °C for 30 min). Additionally, results of studying the greenhouse gas emissions (GHGs) showed a reduction of around 88% when using torrefied biochar as a substitute for coal. According to the results, it can be confirmed that the torrefaction process improves the properties of all the studied biomass samples; therefore, adding a lignocellulosic biomass to the non-lignocellulosic samples is recommended.

In our future research, the kinetics of pyrolysis of the same materials will be evaluated, together with thermodynamic parameters, activation energy, and pre-exponential factors. Two iso-conversional methods will be used for this purpose (the Kissinger–Akahira–Sunose and Friedman methods). TGA will be performed under N_2 atmosphere in the temperature range of up to 800 °C at three different heating rates.

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Abbreviations

ED	Energy density
EF	Enhancement factor
EU	European Union
EY	Energy yield
EROI	Energy return on investment analysis
FC	Fixed carbon
FR	Fuel ratio
GHG	Greenhouse gas emissions
HHV	High heating value (MJ kg^{-1})
MC	Moisture content
MSW	Municipal solid waste
MY	Mass yield
RES	Renewable energy sources
SURS	Statistical Biro of Slovenia
VM	Volatile matter content

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