

## Article

# Preliminary Results of Innovative Two-Stage Torrefaction Technology Applied for Thermochemical Treatment of Sunflower Husk

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**Abstract:** This article proposes an innovative two-stage technology for biomass torrefaction generating high-quality biochar, more specifically biocoal, as solid fuel, and offering a promising solution to the challenges posed by the combustion of biomass. In particular, the higher quality of biochar as solid fuel reduces the build-up of unmanageable deposits on fired surfaces, as these deposits inhibit heat transfer and reduce the efficiency of biomass boilers. The proposed two-stage technology involves torrefaction in a hearth-type reactor at temperatures up to 250 °C, followed by a subsequent stage of cooling achieved through washing with water. The two-stage torrefaction technology is integrated within a vertical hearth reactor vessel composed of three superimposed trays serving for biomass input, torrefaction, and water washing combined with biomass cooling, respectively. Upon contact with torrefied biomass, cooling water turned into water vapor; hence, eliminating the requirement for subsequent biomass separation and drying. The system was tested on sunflower husk, and results showed a reduction in the content of problematic elements such as alkali metal chlorides or sulfur compounds in biochar ash, suggesting lower corrosion rates of convective heating surfaces of the boiler under ash sediments. It is hypothesized that, while water exited hot biomass in the form of water vapor instead of liquid water, as is typically the case in water-washing processes, a share of undesirable elements may still have been removed from biomass through vaporization, without necessitating any additional process for ash removal. Hence, the index values calculated according to the chemical analysis of biomass ash suggested that sunflower husk biochar (biocoal) resulting from the proposed two-stage torrefaction process may display fuel characteristics similar to biomasses whose combustion ash may form reduced levels of deposits on boiler surfaces. Therefore, the proposed technology holds the potential to improve solid fuel characteristics of biomass, targeting enhanced efficiency and sustainability of biomass-fired power plants.



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**Keywords:** torrefaction; biomass combustion; ash deposits

## 1. Introduction

Biomass is considered as a renewable source for sustainable energy production [1]. However, as the availability of woody biomass is declining, interest in using agricultural waste as fuel is growing. In particular, sunflower processing waste [1], the husk of which makes up 45–60% of the seed weight [2] is available in large amounts as a by-product of sunflower oil production. However, the chemical composition of sunflower husk is unfavorable for its application as solid fuel, because ash from sunflower husk combustion contains alkali (K, Na) and alkaline earth (Ca, Mg) metals, as well as Si, S, Al, P, and Cl, which increase the growth rate of ash deposits, resulting in excessive fouling of boiler heating surfaces [3].

Treatment of biomass by water washing for the improvement of fuel properties has been proposed in different configurations, either as sole treatment [4–7], or combined with

torrefaction and/or pyrolysis [8–26] for the removal of problematic elements, such as alkali metal chlorides or sulfur compounds, aiming at the reduction of corrosion, slagging and fouling of the boiler’s surface, resulting from biomass combustion [27]. Previous research works on the topic of biomass washing as a pre- or post-treatment for the improvement of the torrefaction and pyrolysis processes, as well as fuel properties of biomass, in perspective with our study, are presented in Table 1. The studies are sorted in the following order: (1) pre-wash alone [3–6] (2) pre-wash and torrefaction [7–13], (3) pre-wash, torrefaction and pyrolysis [15–17], (4) pre-wash and pyrolysis [18–23], (5) pyrolysis and post-wash [24], (6) torrefaction and post-wash [25,26], and (7) our study. Most studies focus on pre-washing of biomass prior to torrefaction and/or pyrolysis, with only few studies investigating post-washing of biomass. The removal of soluble compounds may be considered to provide a protective effect on the torrefaction and pyrolysis reactors, which would explain the focus on biomass pre-washing rather than post-washing. Nevertheless, torrefaction in particular can be performed under mild temperature conditions by means of robust technologies, so that fouling and slagging of the torrefaction reactor may not cause major operational issues, which implies that post-treatment may be considered practically feasible. Furthermore, post-washing of feedstocks after torrefaction or pyrolysis may be easier to implement due to reduced particle size, increased porosity, lower amounts of water needed and easier dewatering of feedstocks [25,26]. Additionally, in contrast with post-washing, the efficiency of pre-washing may be greatly impacted by the nature of biomass. For example, the studies have shown that pre-treatment was much more efficient for herbaceous biomass rather than woody biomass, since the latter is more recalcitrant to degradation prior to torrefaction or pyrolysis, where woody biomass is in its native state [14].

**Table 1.** Overview of biomass washing experiments for improvement of torrefaction and pyrolysis processes as well as fuel properties.

Treatment, Biomasses, Reference	Treatment Steps and Conditions	Treatment Effects
pre-wash wheat straw Singhal et al. 2021 [4]	cuttings 3, 1 or 0.05–0.08 cm → water washing (0–180 min)	max. removal rate 87% Cl, 74% S, 68% K, 46% N, and 39% ash; efficiency increases with higher washing time and lower particle size, fuel: reduced fouling and corrosion
pre-wash wheat straw Singhal et al. 2021 [5]	cuttings (3 cm) → water washing (20–80 °C), Solid: Liquid ratio 1:15–1:50 → manual pressing → drying	optimal pre-wash conditions 10 min, 40 °C and 80 °C, fuel: reduction of fouling and slagging
pre-wash wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood and rice hull Deng et al. 2013 [6]	water washing in deionized water for 3 h at 30–90 °C	removal of K, S and Cl; higher removal efficiencies of K and SiO <sub>2</sub> at higher water temperatures; fuel: increased ash fusion temperatures for some biomasses
LHW treatment poplar wood, corn stover, switchgrass, Miscanthus Runge et al. 2013 [7]	debarking, chipping, screening 2–8 mm, drying (poplar); drying, chopping, screening 25 mm → liquid hot water (LHW) treatment (30–60 min, 150–170 °C) → cooling in ice water (10 min) → vacuum filtering → rinsing (deionized water), re-filtering (twice)	reduced ash content regardless of treatment severity; fuel: up to 25% increase in energy density from higher heating value and pellet density, improved durability of pellets
pre-wash → torrefaction straw, pine Liu et al. 2022 [8]	cuttings (3 cm, 1 cm, and 0.05–0.08 cm) → water washing (2–180 min) → filtration and drying → torrefaction or hydrothermal carbonization (HTC)	both washing-torrefaction treatment and HTC treatment have beneficial effects on fuel properties of biochar

Table 1. Cont.

Treatment, Biomasses, Reference	Treatment Steps and Conditions	Treatment Effects
pre-wash → torrefaction corn stalk Cen et al. 2016 [9]	drying, grinding → water washing (6 h, 60 °C) → torrefaction in tubular furnace (250 °C, 30 min)	removal of ash and metallic species, reduced acid and water contents, increased phenol content, fuel: increased HHV
pre-wash → torrefaction waste epoxy resin Chen et al. 2020 [10]	grinding → water washing (deionized water, 10–15 min) → torrefaction (300 °C, 20 min)	salt removal, fuel: improved properties, but torrefaction had little effect
pre-wash → torrefaction waste epoxy resin Chen et al. 2021 [11]	water washing (10–15 min, with shaking) → torrefaction (tubular furnace, 300 °C, 20 min)	removal of water-soluble ash (minerals), removal of Cl, fuel: risk of increased dioxin emissions from combustion of torrefied material due to de novo synthesis
pre-wash (acid) → torrefaction rice husk Zhang et al. 2019 [12]	sieving, drying → acid washing (2 h) → water washing (deionized water) → torrefaction in tubular furnace (210–270 °C, 1 h)	increased sugars and phenols contents in bio-oil, increased bio-oil quality
pre-wash → two-stage torrefaction (pilot) road side grass, miscanthus, wheat straw and spruce bark Abelha et al. 2019 [13]	water washing with hot water (50 °C) in 2 washing bins (15 min each) → drying → milling, pelletizing (except spruce bark) → two-stage torrefaction in moving bed reactor (drying stage 150–200 °C, torrefaction stage 240–320 °C)	removal of 90% of Cl and 60–80% of K; decreased NO <sub>x</sub> emissions, fuel: slagging only slightly reduced
pre-wash (water or chemicals) → two-stage torrefaction (pilot) short-rotation coppiced willow, eucalyptus, miscanthus, wheat straw Saddawi et al. 2012 [14]	cuttings (2 × 2–4 × 4 cm for SRC willow, eucalyptus; 2 × 1–3 × 1 cm for Miscanthus, wheat straw) → washing (deionized water with stirring for 20 h, or 1 M ammonium acetate solution for 60 h, then filtration and washing with deionized water, or 1 M HCl at 70 °C for 40 h, ratio ~1 L/ 60 g) → torrefaction in tube reactor (150 °C, 50 min and 290 °C, 60 min)	high removal of alkali metal ions and chloride, more efficient for herbaceous fuels (Miscanthus and wheat straw), low Ca removal rate, fuel: water washing pretreatment yielded best results in ash fusion tests of torrefied fuel; increased ash hemisphere temperature (ash melting)
pre-wash → torrefaction → pyrolysis rice husk Zhang et al. 2016 [15]	water washing (deionized water 60 °C, 6 h with stirring) → filtration, drying → torrefaction in vertical quartz reactor (250–280 °C) → pyrolysis in TGA analyzer (700 °C)	decreased contents of acids, ketones, aldehydes and furans, increased contents of sugars, including 9-fold increase in levoglucosan in bio-oil
pre-wash (liquid torrefaction products) → torrefaction → pyrolysis cotton stalk Chen et al. 2017a [16]	washing with liquid products of torrefaction → torrefaction (250 °C, 30 min) → pyrolysis in fixed-bed reactor (500 °C, 15 min)	reduced metallic species, decreased water and acids contents, increased phenols in bio-oil, decreased ash content in biochar, fuel: increased heating value of non-condensable gas
pre-wash (aqueous phase bio-oil) → torrefaction → pyrolysis cotton stalk Chen et al. 2017b [17]	drying, grinding → washing with aqueous phase bio-oil from pyrolysis (60 °C, 2 h) → filtration, rinsing (deionized water), drying → torrefaction (260 °C, 30 min), → pyrolysis in fixed-bed reactor (500 °C, 15 min)	removal of metallic species, improved yield, quality of bio-oil, fuel: improved heating value of bio-oil
pre-wash → pyrolysis rice hulls Teng and Wei 1998 [18]	water washing (80 °C) → vacuum-drying (50 °C, 24 h) → pyrolysis in TGA (900 °C)	increased volatile yield and decreased char yield due to removal of hydrocarbons which favor char formation

Table 1. Cont.

Treatment, Biomasses, Reference	Treatment Steps and Conditions	Treatment Effects
pre-wash → pyrolysis seaweed (brown algae) Ross et al. 2009 [19]	rinsing, drying, grinding (<90 μm) → water washing (6 h) or acid washing (2 M HCl, 6 h, 60 °C) → filtration, rinsing → pyrolysis (500 °C, 20 °C/ms, hold time 20 s)	30–40% reduction of Mg, K and Na contents with water washing, >90% reduction of Mg, K, Na, Ca with acid washing
pre-wash (water or acid) → two-step pyrolysis corncob Zhang et al. 2019 [20]	crushing, sieving, drying → washing (deionized water or acid solution 5% HCl, room temperature, 3 h, stirring) → filtration, rinsing (deionized water), drying → two-step pyrolysis in quartz tube (400 °C, 5–60 s and 650 °C, 20 s)	removal of alkaline earth metals, increase in bio-oil and decrease in biochar yield, increased yields of furfural, 4-vinylphenol and levoglucosan
pre wash (acid) → two-step pyrolysis walnut shell Zhang et al. 2018 [21]	milling, sieving, drying → acid washing (5% HCl, 25 °C, 3 h, stirring) → filtration, rinsing, drying → two-step pyrolysis in quartz tube (350–550 °C, 20 s and 650 °C, 40 s)	reduced acids, ketones, alcohols, aldehydes, phenols and increased N-compounds, sugars and furans in first step; decreased hydrocarbons and further increased sugars in second step, increased value-added chemicals including furfural, levoglucosan and 2-methoxy-4-methylphenol
pre-wash (warm water, dilute acid or aqueous phase bio-oil) → pyrolysis rice straw Chen et al. 2019 [22]	grinding, drying → washing with water, dilute HCl solution, or aqueous phase bio-oil (3 g/100 mL, 50 °C, 2 h) → filtration, rinsing with distilled water → pyrolysis in TGA analyzer (50–650 °C at 10–40 °C/min)	washing with aqueous phase bio-oil yielded highest removal rate of alkaline earth metals and highest improvement of bio-oil quality, including increased content of anhydrosugars (mainly levoglucosan)
blending → pre-wash → two-step pyrolysis rice straw, groundnut shells, wheat straw Bhatnagar et al. 2022 [23]	grinding → blending of feedstocks → water washing (30–120 min, 40 °C, stirring 100 rpm) → pressing, drying (65 °C, 12 h) → two-step slow pyrolysis (20–340 and 340–600 °C at heating rate 5 °C/min, 15 min pause at 340 °C for 1st stage bio-oil recovery)	1.6–2.1 fold increase in levoglucosan yield in bio-oil, ~10% reduction in water content of bio-oil, fuel: reduced slagging and fouling, higher GCV
pyrolysis → post-wash (dilute acid) almond shells, cottonseed hulls, lignin, chicken manure Klasson et al. 2014 [24]	slow pyrolysis in box furnace (350–800 °C, 1–4 h) → dilute acid washing (0.1 M HCl, ratio 50:1 v/w, 1 h) → rinsing with deionized water (twice)	dilute acid reduces ash content in biochars, expose increased surface areas, increase biochar efficiency as adsorbent for Hg
torrefaction → post-wash → fuel blending straw Yan et al. 2021 [25]	drying, grinding → torrefaction (300 °C, 30 min) → water washing (ratio 1:40 w/w, 20 h, stirring) → filtration, drying, sieving (75–150 μm) → co-combustion with coal (ratios 1:1 and 1:4) in drop tube furnace (1400 °C)	reduced ash content reduced aluminosilicates content, fuel: ash slagging may be lower
pre-wash → two-stage torrefaction, or two-stage torrefaction → post-wash road side grass, miscanthus, wheat straw, spruce bark Abelha et al. 2018 [26]	drying (105 °C), milling (<4 mm) → water washing (liquid/solid ratios 5–40 on dry mass, shaking 1.25 Hz, 20–80 °C, 5 min–24 h) → two-stage torrefaction (drying stage 150–200 °C, torrefaction stage 240–280 °C), or water washing after torrefaction (post-washing)	removal of 90–95% Cl, 50–80% K, 30–60% S and 30% P: washing stage crucial for removal of K and P, which are not removed during torrefaction; post-washing (washing after torrefaction) yielded similar results with potential energy savings and easier dewatering of biomass

Table 1. Cont.

Treatment, Biomasses, Reference	Treatment Steps and Conditions	Treatment Effects
torrefaction → post-wash (water evaporating as water vapour > 120 °C) sunflower husk Our study	torrefaction in hearth reactor (250 °C, 1 h) → water washing (thinly sprayed water) combined with biomass cooling, while maintaining biomass temperature > 120 °C for efficient water evaporation and drying of treated biomass, along with evaporation of some minerals, not requiring additional treatment stages	biomass ash displays decreased Cl ratio (7.9-fold) and S ratio (10.7-fold), with increased CaO (3.1-fold), along with decreased K <sub>2</sub> O (2.1-fold), SO <sub>3</sub> (up to 1.6-fold), and Cl (1.9-fold) hinting at reduced slagging

Many lab-scale studies contain complex experimental protocols involving numerous steps, high dilution rates, and the use of chemicals. Hence, up-scaling of the proposed treatment steps may be an issue. Yet, some researchers propose to focus on obtaining biomaterials for high-value applications, in particular through the extraction of high-value compounds from bio-oil [12,15,20], as well as the use of biochar as an adsorbent [24].

Most previous studies have focused on the pre-washing of biomass before torrefaction and/or pyrolysis, with only a few studies investigating post-washing of biomass. However, post-washing of feedstocks may be easier to implement due to reduced particle size, increased porosity, lower amounts of water needed, and easier dewatering of feedstocks after torrefaction. Considering the limited number of studies involving post-washing, further research is required in order to validate these hypotheses and further optimize the conditions for biomass post-treatment. In particular, the recycling of liquid torrefaction and pyrolysis products has been investigated in the context of the pre-washing of biomass with condensable products from torrefaction [16], and aqueous phase bio-oil from pyrolysis [17,22]. A similar strategy may be tested for the post-washing of torrefied or pyrolyzed biomass, providing an interesting avenue of research for process optimization and simplification in view of up-scaling of the technology.

The conventional process of sunflower husk torrefaction takes up to 1 h [28]. The water washing process also requires an average of 1 h [4–23]. In addition, after washing with water, the biomass must be dried before torrefaction [5]. These aspects dramatically reduce the productivity of the process, complicate the design of equipment used for biomass processing, and increase the costs for the production of torrefied biomass.

In view of these shortcomings, we propose to reverse the order of the treatment steps by combining the process of water washing of biomass together with biomass cooling taking place after completion of the torrefaction process, as proposed in few studies [25,26]. For this purpose, finely sprayed water was applied on hot torrefied biomass, displaying a cooling effect, whereas water was removed from the treated biomass as water vapor upon contact with the hot biomass. Furthermore, the proposed process did not include any additional stages of separation, dewatering, or ash removal.

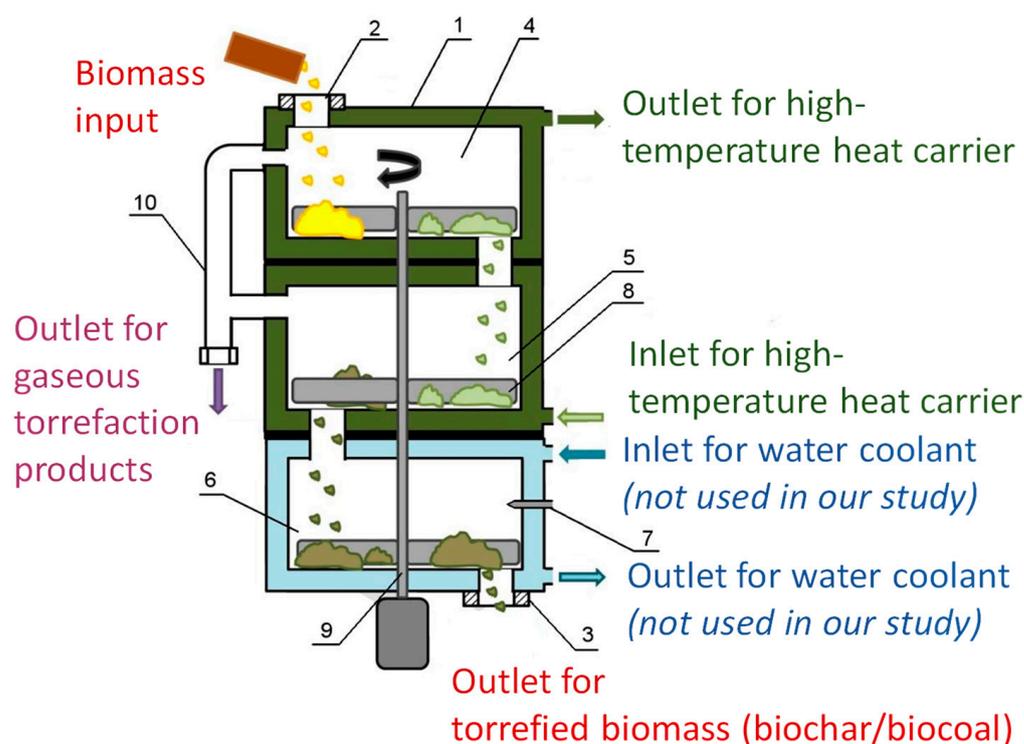
The approach provided in our study may be considered as innovative since the spraying of water downstream of the torrefaction process allows for the post-treatment of the torrefied biomass combined with biomass cooling, which can be incorporated as a single step in the lower tray within the vessel of the hearth-type torrefaction reactor, without requiring subsequent separation or drying stages to obtain the final biochar product, since water evaporated upon contact with hot biomass, and left as water vapor. For this reason, ash was not removed from the biomass as water, contrary to the conventional water washing process, and additional ash removal stages were not performed, so that the generated biochar still contained a significant share of minerals (ash). Yet, chemical analysis of the ash obtained through combustion of the treated biomass was performed in order to investigate the possibility that an improvement of ash composition, and, hence, of combustion parameters, may still occur.

This article presents the first results of the investigation and testing of the innovative two-stage biomass torrefaction technology encompassing water post-washing of torrefied

biomass, integrated within a vertical hearth reactor vessel. The innovative process was tested for the torrefaction of sunflower husk.

## 2. Materials and Methods

The process of torrefaction and water washing of biomass was carried out in a hearth-type reactor (Figure 1). The reactor consists of a vertical body (1) with a loading unit (2) in the upper part and an unloading unit for torrefied fuel (3) in the lower part. Inside the reactor vessel (1), the torrefaction process takes place on the trays (4, 5). These trays have openings for unloading the treated mixed fuel onto the bottom plate, as well as jackets into which the high-temperature heat carrier, heated in a boiler, can be supplied. The bottom of trays (4) and (5) is also heated by the high-temperature heat carrier. The lower tray (6) is intended for cooling the torrefied biomass, and fitted with nozzles (7) for supplying cooling water located in its side wall.



**Figure 1.** Scheme of the hearth-type reactor for the torrefaction of sunflower husk in an environment of gaseous torrefaction products.

The torrefaction reactor was operated in batch mode, as follows: a liquid high-temperature heat carrier (Polyalkylbenzene oil), heated in an electric boiler to a temperature of 300 °C, was fed into the reactor jacket. After the temperature recorded inside the reactor reached 250 °C, a portion of the initial biomass was loaded into the reactor. Due to the operation of the mixers installed on the shaft, the biomass moved along the trays and was torrefied in an environment of gaseous torrefaction products generated from biomass, while the reactor was heated by the high-temperature heat carrier. Hence, the torrefaction process was carried out at 250 °C. The total duration of the torrefaction process was 60 min. The biomass remained on the trays during torrefaction for 30 min. On the lower tray, torrefied biomass was cooled, and the residence time of biomass on this tray also amounted to 30 min.

In a typical reactor operation, cooling water with a temperature of 8–20 °C can be circulated along the wall of the reactor within the jacket of the lower tray; however, in such a configuration, the cooling effect may be slow and require the circulation of high amounts of water. Therefore, in our study, following an innovative approach, the cooling

effect was achieved by spraying finely sprayed water directly onto hot biomass through nozzles installed along the diameter of the lower tray. Water was supplied to the layer of hot torrefied biomass in the lower tray at such a rate that the temperature of biomass was maintained over 120 °C, so that water, upon reaching contact with the biomass, displayed a cooling effect while turning into water vapor, as the latent heat of vaporization was exceeded, following a phase change cooling effect. In order to achieve the phase change effect, water was supplied at such a rate that the temperature of the lower tray was kept higher than 120 °C. Upon following this procedure, the absence or low amounts of liquid water remaining following this cooling process eliminated the requirement for a subsequent biomass separation and drying stage, which is otherwise typically required for the removal of excess liquid water. Furthermore, additional processing stages for ash removal were not implemented. Hence, a significant mineral (ash) fraction was still included in the composition of the produced biochar.

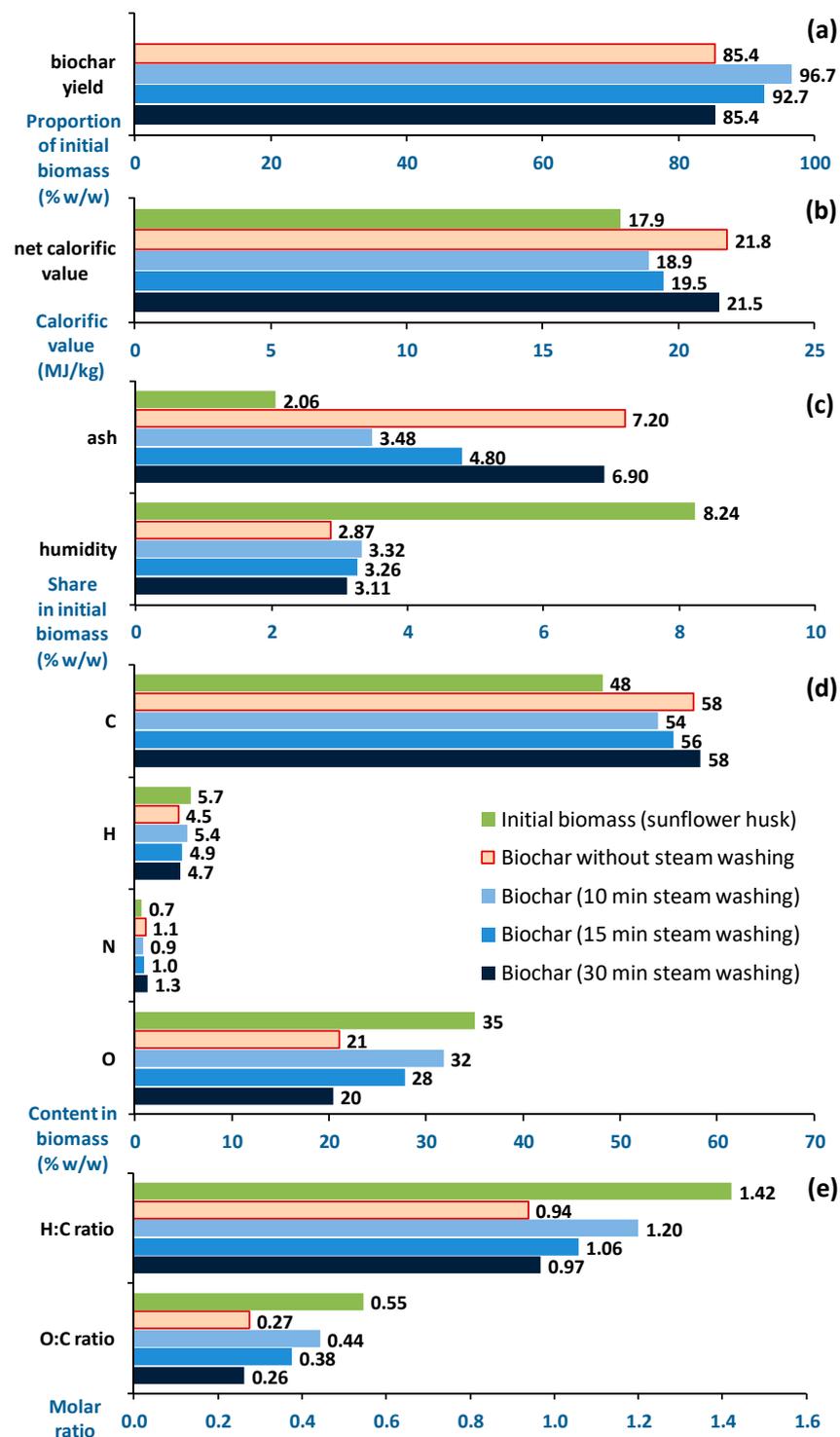
With a reactor capacity of 45 kg per batch and a total process duration of 1 h for sunflower husk biomass, the amount of water supplied for biomass cooling was kept at 15 L. Three different durations of water supply were investigated: 10, 15, and 30 min. Accordingly, water was supplied at three different flowrates amounting to 1.5 L/min, 1 L/min, and 0.5 L/min, respectively. Biomass entering the middle tray (5) had a temperature of 250 °C. Upon entering the lower tray, biomass was cooled down to 120 °C by means of the finely dispersed water. As this water evaporated, water vapor and gaseous torrefaction products were removed from the reactor through the pipeline (10). In this way, the two-stage torrefaction process was efficiently integrated into the vertical hearth reactor vessel, comprising three superimposed trays operated for biomass input and pre-heating, torrefaction, and combined water washing and biomass cooling, respectively.

Moisture content [29], ash [30], carbon, hydrogen, nitrogen [31], sulfur, and chlorine [32], calorific value [33], as well as content of volatile substances [34] in the initial biomass and resulting biochars were investigated. The contents of major elements in the ashes obtained by combustion of the initial biomass and biochar was also studied [35]. Solid fuel-Methods for determining the chemical composition of ash), along with contents of trace elements [36]. Minerals from solid fuel. Determination of trace elements in the ash by the atomic absorption method).

The following instruments were used for the analyses: low-temperature laboratory furnace SNOL 67/350 (Umega Group, AB, Utena, Lithuania), laboratory electric furnace SNOL 10/11-V (Umega Group, AB, Utena, Lithuania), TruSpec ICP-OES analyzer for carbon, hydrogen, nitrogen, and sulfur (standard deviation is 0.01%), MGA 915-MD (Dandong Dongfang Measurement & Control Technology Co., Ltd., Yanjiang, China) atomic absorption spectrometer (standard deviation is 10%), X-Supreme8000 (EDXRF), (Oxford Instruments (Shanghai) Co Ltd., Shanghai, China) X-ray fluorescence spectrometer (standard deviation is 0.02%) MF-50 (HORIBA Advanced Techno, Co., Ltd, Osaka, Japan) moisture analyzer (standard deviation is 0.02%) (A&D Company Ltd., Tokyo, Japan), and AKB-1 bomb calorimeter (standard deviation is 0.05%) (Russian Energy Technologies LLC, Moscow, Russia). All analyzes were performed in 3 replicates.

### 3. Results and Discussion

The characteristics of sunflower husk and biochar obtained from the two-stage torrefaction process performed at different durations of combined water washing and biomass cooling are presented in Figure 2.



**Figure 2.** Characteristics of sunflower husk and resulting biochar: (a) biochar yield, (b) net calorific value, (c) ash, humidity, (d) C, H, N, O contents, (e) H:C and O:C ratios.

The analysis of data presented in Figure 2 reveals that increased durations of water washing from 10 to 30 min, corresponding to decreased rates of water spraying from 1.5 to 0.5 L/min and, hence, slower biochar cooling, resulted in changes in biochar composition, including increased ash contents, as well as carbon and nitrogen contents, along with decreased hydrogen and oxygen contents. The ash contents increased when biochar was treated with water washing because, contrary to conventional water washing, where water

remains in the liquid phase, subsequent separation steps were not implemented to enhance the removal rate of minerals, so that minerals could exit the biochar matrix only through evaporation of the supplied washing water occurring upon contact with hot biomass.

Furthermore, along with increased duration of water washing, decreased biochar yields were inversely correlated to increased net calorific values of biochar, as well as reduced H:C and O:C ratios, hinting at improved fuel properties. Yet, biochar characteristics as solid fuel appeared to be less favorable at shorter durations of water washing, but became similar to unwashed biochar at the longest duration of water washing (30 min). Hence, according to the parameters presented in Table 2, there is yet no clue that biochar quality would be improved following water washing, compared with unwashed biochar. Indeed, biochar at the longest water washing duration of 30 min held similar characteristics as unwashed biochar, whereas biochars at a shorter water washing duration of 10 and 15 min presented degraded fuel properties with regards to unwashed biochar.

**Table 2.** Microelement contents in ashes resulting from the combustion of original sunflower husk and of sunflower husk biochar.

Content of Microelements, mg/kg of ash	Biomass Used for Combustion				
	Original Sunflower Husk	Biochar without Water Washing	Biochar after Water Washing for 10 min	Biochar after Water Washing for 15 min	Biochar after Water Washing for 30 min
V	<10	<10	<10	<10	12
Mn	333	751	321	389	418
Cu	425	502	347	310	276
Ni	102	112	98	96	97
Sr	180	196	184	197	310
Cr	567	377	541	489	429
Zn	149	485	189	215	310
Pb	43	52	38	27	13
As	<10	<10	<10	<8	<5

Longer durations of water washing, and corresponding lower cooling rates of hot biomass, imply that the biomass undergoing torrefaction remained at high temperatures for a longer time, so that exothermic processes may have developed within the biomass layer [28]. On the opposite, faster rates of combined biomass cooling and water washing of hot biomass imply that the torrefaction process may have been terminated at a faster rate. Accordingly, biochar samples obtained after water washing for 10 min displayed the lowest calorific value, contained more humidity and oxygen, along with less carbon than biochar samples washed for a longer duration of 30 min.

In particular, H:C and O:C molar ratios are known as the Van Krevelen parameters [37,38], which differentiate raw lignocellulosic biomass from lignite and coal-like biomass, with the latter typically displaying lower H:C and O:C ratios. According to these parameters, the characteristics of both unwashed biochar and biochar after 30 min water washing were quite similar to lignite and coal.

There are few experimental data on sunflower husk torrefaction in the literature, and the composition of sunflower husk biomass may differ from the composition investigated in our study. For instance, Bilgic et al. [28] investigated the process of sunflower husk torrefaction, and the resulting biochar contained 46.4% oxygen and 1.8% ash, whereas our sample contained 35.07% oxygen and 2.06% ash. Furthermore, the authors conducted the torrefaction process at a higher temperature of 300 °C, whereas in our study, torrefaction

was performed at 250 °C. Hence, the biochar obtained by these authors achieved higher net calorific values compared with our study.

The results of the analysis of microelements contents in the ash obtained from the combustion of original sunflower husk, as well as from biochar derived from sunflower husk, is presented in Table 2. Yrjas et al. [27] observed that, following torrefaction of winter straw, the contents of Co, Cr, Cu, and Ni in biochar ash decreased, while the content of Zn increased. Conversely, following torrefaction of spruce bark, the content of Cd, Co, Cr, Cu, Ni, Pb, and Zn in biochar ash increased, but the contents of Ti and V decreased. Following the torrefaction of winter straw, the content of Co in biochar ash remained unchanged, Ni decreased, while Cu and Zn increased. In our study, following torrefaction, Mn, Cu, and Zn contents in biomass ash increased significantly compared with initial biomass, while Cr content decreased. Following torrefaction combined with water washing for 10 min, Zn contents were lower than following torrefaction alone. However, increased durations of biochar water washing resulted in higher Zn contents. According to these analyses, torrefaction and subsequent water washing may have multidirectional effects on the contents of microelements in biochar ash (Table 2). Yet, further research is mandatory in order to confirm these findings.

Table 3 presents the results of chemical analyses of major elements in ashes resulting from the combustion of original biomass (sunflower husk), and of biochar obtained from sunflower husk, along with significant parameters for the modeling of slagging effects on boiler surfaces, together with the indices for predicted formation of ash deposits (Cl ratio and S ratio). Similar to the results obtained by Yrjas et al. [27], the contents of major elements in biomass ash did not change significantly, except for SiO<sub>2</sub>, K<sub>2</sub>O, SO<sub>3</sub>, and Cl.

After biomass torrefaction, increased durations of water washing resulted in decreased concentrations of sulfur oxide (SO<sub>3</sub>), potassium oxide (K<sub>2</sub>O), and chloride (Cl) in ash, combined with increased concentrations of silica oxide (SiO<sub>2</sub>), resulting in more favorable ash composition with regards to biomass combustion. This finding is very interesting because ash composition may have been improved through water vapor volatilization instead of leaching of the elements in liquid water, removing the requirement for subsequent biomass separation, which would require a press or filter, and drying, which would require an additional heat source.

Changes in concentrations of elements resulting from thermal treatment and combustion of biomass may be explained by the following hypotheses: (1) ash-forming elements, especially light elements, may pass into the gaseous phase due to higher temperatures achieved in the course of torrefaction and water washing, and be removed from the reactor along with water vapor, which is formed when the cooling water comes into contact with hot torrefied biomass, and (2) light elements can be volatilized as well during biomass combustion and ash formation, possibly depending on fuel structure, composition, and calorific value.

The light ions K and Cl, may have partially evaporated along the steam generated in the course of the water cooling process as dissolved acid (HCl) and alkali (KOH), respectively. HCl and KOH have lower boiling points as azeotropic mixtures in water, and the evaporation of these elements may take place until the concentration of the components in water increases up to a certain limit depending on the temperature [39–41]. At higher temperature, in combustion processes, the evaporation of the neutral salt KCl may become possible [42,43]. Furthermore, also in combustion processes taking place at high temperature, a chain of reactions can be triggered, resulting in the volatilization of silica [44]. Additionally, light ions may be evaporated in charged water droplets due to electrochemical mechanisms [45].

Beyond the effects on ash composition, the structure and composition of biochar may also be modified by the innovative water washing process, which aims at gradually decreasing biomass temperature within 10–30 min, with an initial temperature around 250 °C, and a final temperature remaining >120 °C. Hence, potential effects on biomass

structure and composition may be similar to wet torrefaction, hydrothermal or vapothermal treatment, which are also known to improve biomass properties [46,47].

**Table 3.** Chemical composition of ash resulting from the combustion of original sunflower husk and of biochar, along with predicted indices of ash formation.

Significance for the Modeling of Slagging Effects	Parameter	Biomass Used for Combustion				
		Original Sunflower Husk	Biochar without Water Washing	Biochar after Water Washing for 10 min	Biochar after Water Washing for 15 min	Biochar after Water Washing for 30 min
Sulfur	S total in solid fuel (mg/kg)	76.6	60.9	72.0	64.5	54.7
	SO <sub>3</sub> in ash (mg/kg)	6.1	6.25	8.9	5.02	3.75
	S volatile (mg/kg)	70.5	54.7	63.1	59.5	51.0
	S volatilization rate (%)	92.0	89.7	87.6	92.2	93.1
Chloride	Cl in ash (mg/kg)	1.77	1.75	1.16	1.08	0.93
Adverse elements	K <sub>2</sub> O in ash (mg/kg)	38.99	34.05	39.16	23.03	18.14
	Na <sub>2</sub> O in ash (mg/kg)	0.93	0.63	0.35	0.43	0.75
Protective elements	SiO <sub>2</sub> in ash (mg/kg)	1.24	2.91	2.42	4.18	8.6
	Al <sub>2</sub> O <sub>3</sub> in ash (mg/kg)	0.36	0.69	0.8	0.81	0.84
Ratios	Cl ratio	26.1	10.1	12.6	4.9	2.1
	S ratio	69.0	24.8	31.9	16.6	7.4
Other elements	TiO <sub>2</sub> in ash (mg/kg)	0.02	0.17	0.03	0.02	0.07
	Fe <sub>2</sub> O <sub>3</sub> in ash (mg/kg)	0.43	7.16	1.37	1.28	1.04
	CaO in ash (mg/kg)	6.39	6.36	11.88	13.02	19.93
	MgO in ash (mg/kg)	12.05	10.79	6.35	6.89	7.62
	P <sub>2</sub> O <sub>5</sub> in ash (mg/kg)	11.72	9.24	10.13	11.6	13.93

For the purpose of calculating the indices of predicted slagging effects on boiler surfaces, sulfur (S) concentrations in solid fuel and in biomass ash were compared, and the volatilization rates of S remained similar, around 90%, for all types of solid fuel investigated.

The improvement in ash composition with regards to biomass combustion can be modeled by two criterion indicators for slagging; namely, Cl ratio and S ratio, as proposed by Niu et al. [48]. According to these authors, the criteria can be interpreted as follows: the higher the values of Cl and S ratios, the higher the probability of formation of ash deposits on convective heating surfaces of boilers, and on the opposite, ash deposits may be negligible if Cl and S ratios remain below 1.0 and 0.5, respectively.

The estimated indices of ash formation are based on the premise that changes in chemical composition of ash from biochar obtained as a result of torrefaction may reflect changes in the formation of ash deposits on heating surfaces of boilers, in which biomass is burned. Furthermore, the Cl and S ratios are based on the hypothesis that the extent of the

formation of ash deposits on boiler surfaces can be estimated according to the composition of biomass ash, since it is diminished by the presence of protective fractions as oxides (Si, Al, and S), while it is increased by the presence of risky (Cl, Na, and K), and volatile fractions (Cl, S, K and Na); the latter fractions being volatilized during biomass combustion and, hence, not found in biomass ash [48].

The Cl and S ratios were calculated according to the following equations, with all parameters being expressed in a weight basis (as %  $w/w$ , or here as mg/kg), and presented in Table 3. All weight concentrations were measured in biomass ash, except for S total in Equation (3), which was measured in biomass (solid fuel).

$$\text{Cl ratio} = \frac{[\text{Cl}] + [\text{K}_2\text{O}] + [\text{Na}_2\text{O}]}{[\text{SiO}_2] + [\text{Al}_2\text{O}_3]} \quad (1)$$

$$\text{S ratio} = \frac{[\text{S volatile}] + [\text{K}_2\text{O}] + [\text{Na}_2\text{O}]}{[\text{SiO}_2] + [\text{Al}_2\text{O}_3]} \quad (2)$$

$$\text{S volatile} = [\text{S total in solid fuel}] - [\text{SO}_3 \text{ in ash}] \quad (3)$$

As a result of the two-stage torrefaction process with water washing compared with original biomass, the composition of biomass ash evolved as follows:  $\text{SiO}_2$  increased sharply, CaO increased up to 3.1-fold,  $\text{K}_2\text{O}$  decreased up to 2.1-fold,  $\text{SO}_3$  decreased up to 1.6-fold, and Cl decreased up to 1.9-fold. Lower Cl,  $\text{K}_2\text{O}$  and  $\text{SO}_3$  contents may imply reduced corrosion rates of convective boiler heating surfaces under ash deposits, as corroborated by lower Cl and S ratios.

According to Cl and S ratios of biomass ash, the occurrence of ash deposits should be lower following the combustion of torrefied sunflower husk. Indeed, torrefaction is commonly applied in order to improve biomass properties as a solid fuel for subsequent combustion. Additionally, the current study reveals that the innovative two-stage torrefaction process combining water washing and biomass cooling may result in a further decrease in the Cl and S ratios, especially at longer durations of water washing. Therefore, the combustion of biomass generated from the innovative two-stage torrefaction process may result in lower ash deposit formation on the surfaces of biomass boilers. However, this hypothesis based on current knowledge of combustion processes may still require further testing and validation in future research involving combustion experiments.

It is technically possible to further increase the duration of cooling of torrefied biomass. However, increased cooling times will reduce the efficiency of the torrefaction reactor. Furthermore, increased cooling times may also result in self-heating taking place in the layer of torrefied biomass and the risk of self-ignition of the biomass. Therefore, further studies are required to optimize the duration of the water washing stage and to validate our results.

Compared with other experiments performed for the purpose of improving biomass composition through pre-washing or post-washing of biomass (Table 1), our study reveals that the quality of torrefied biomass may be improved within a minimal number of additional steps and additional equipment, since: (1) the post-treatment by water washing is integrated into the lower tray of the reactor; and (2) additional steps of separation and drying for water removal are not required, as the supplied water evaporates upon contact with hot torrefied biomass.

The suggested process configuration is in line with the recently published techno-economic analysis by Abelha and Kiel (2020) [49], which suggest that post-washing of torrefied biomass may be more economically feasible compared with pre-washing of biomass prior to torrefaction. Additionally, compared with other approaches for water washing of biomass (Table 1), the proposed process integrating torrefaction and water washing may result in energy savings. According to data from Meesters et al. [50], during water washing, 1 kg of biomass can capture up to 2 kg of water, which would typically require significant energy for drying, amounting to approximately 8200 kJ/kg of biomass.

However, in our case, these additional energy costs can be avoided, since the supplied water already evaporates in contact with hot torrefied biomass.

Still, a question arises regarding water consumption for the process. There is a possibility that condensable gases exiting the torrefaction reactor may be recovered and converted into a liquid phase in a condenser, while also allowing additional energy recovery from the condenser by means of a heat exchanger. The obtained torrefaction liquor may then be recycled and applied for the cooling of torrefied biomass in place of raw water. The moderate level of water addition amounting to 15 L for 45 kg of initial biomass, or 0.3 L/kg of biomass, may provide for the technical feasibility of such an approach for water recycling. Furthermore, further systems can be developed for the extraction of valuable products from the recovered liquid phase, as well as the use of non-condensable gases for energy recovery or as catalyst. For example, a share of the produced biochar may be used as an adsorbent for the capture of valuable organic compounds or minerals from the recovered liquid phase.

Hence, further research focused into the development and integration of technically simple, low-cost processes may contribute to future designs for efficient and sustainable biomass torrefaction systems.

#### 4. Conclusions

Torrefaction is usually viewed as a suitable technology for biomass pretreatment prior to biomass combustion, resulting in improved biomass characteristics as a solid fuel. In our study, we proposed an innovative two-stage torrefaction process in order to further improve biomass characteristics with regards to subsequent biomass combustion. The two-stage torrefaction process associates biomass torrefaction, water washing and cooling within a hearth reactor vessel, with biomass drying and torrefaction taking place on the upper trays, and combined water washing and biomass cooling taking place on the lower tray, as an efficient process design.

Biomass temperature was maintained above 120 °C by supplying low amounts of finely sprayed water to torrefied biomass, so that the supplied water turned back into water vapor, and biomass cooling could be achieved efficiently without requiring a subsequent biomass drying stage. Hence, the proposed biomass torrefaction technology may allow fast and reliable cooling of torrefied biomass, while suppressing exothermic processes that may otherwise develop in hot torrefied biomass in the absence of cooling, improving the reliability and fire safety of the torrefaction process.

The proposed process of torrefaction and subsequent water washing of the obtained biochar is innovative for the following reasons: (1) the process combines the stages of water washing and cooling of biochar into a single operation, streamlining the process and reducing the number of steps required, (2) biochar after water washing does not require separation and drying, because the treated biomass remains dry as the water used for cooling and washing evaporates upon contact with hot biochar, eliminating the need for additional cost-intensive and energy-intensive stages for biomass treatment, (3) the process requires moderate amounts of water (0.3 L/kg of treated biomass) compared with other biomass washing processes described in the literature, hence, the recycling of water-rich condensed gaseous torrefaction products for the purpose of water washing may come into consideration.

While the biochar generated following the innovative combined biomass water washing and biomass cooling process still contained high shares of minerals (ash), the composition of these ashes may have been improved. Improved ash composition resulted in significant reductions in Cl and S ratios, indicating improved characteristics of combusted biomass following torrefaction of sunflower husk. Further reduction in Cl and S ratios was achieved following post-washing of torrefied biomass with finely sprayed water according to the innovative two-stage torrefaction process, and the effect was increased at higher duration of water washing. This suggests that ash deposits on boiler surfaces resulting from the combustion of the improved biochar may decrease further upon application of the

innovative post-washing treatment. Overall, Cl and S ratios in biomass ash were reduced more than 2-fold between initial biomass and torrefied biomass obtained after 1 h of torrefaction at 250 °C and water washing in the innovative two-stage process. The improved Cl and S ratio were linked to improved ash composition, including lower levels of sulfur oxide (SO<sub>3</sub>), potassium oxide (K<sub>2</sub>O) and chloride (Cl) in ash, combined with higher levels of silica oxide (SiO<sub>2</sub>).

Nevertheless, the obtained results relate only to a specific laboratory experiment conducted on the processing of sunflower husks, so that all the above conclusions are preliminary and may require further research on various biomass types and torrefaction technologies at laboratory and pilot scales. In particular, a review of previous studies, provided in Table 1, suggests interesting avenues of research for process optimization, such as the recycling of condensable torrefaction products as a water source for biomass cooling, along with the valorization of biochar and liquid products for the production of high-value biomaterials following a biorefinery approach.

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