



Dioxins and furans in biochars, hydrochars and torreficates produced by thermochemical conversion of biomass: a review

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Abstract

Converting raw biomass into valuable products protects the environment, improves economics, and helps tackle climate change by cutting resource demand and waste production. Thermochemical treatment is a common method for producing biochars, hydrochars and torreficates from biomass and organic wastes, which can also generate dioxins and furans and consequently limit the use of thermochemically converted chars. Here we review the presence of dioxins and furans in chars produced by hydrothermal carbonization, torrefaction, and pyrolysis processes under the influence of temperature, residence time, heating rate, pressure, and feedstock type. Dioxins and furans were mostly below 20 ng total toxic equivalence per kilogram (TEQ kg⁻¹), with the highest level of 113 ng TEQ kg⁻¹ found in over 100 samples of different char types. The most toxic products were hydrochars produced from sewage sludge. Processing temperature and feedstock type were key factors resulting in high dioxin levels in chars, and care should be taken when producing chars at temperatures up to 300 °C or using feedstocks previously contaminated with dioxins or preservatives.

Keywords Hydrothermal carbonization · Torrefaction · Pyrolysis · Thermochemical valorization · Feedstock · Sewage sludge

Abbreviations

PCDD/Fs	Polychlorinated dibenzo- <i>p</i> -dioxins and polychlorinated dibenzofurans
TEQ	Total toxic equivalence
TEF	Toxicity equivalence factor
NATO	North Atlantic Treaty Organization

Introduction

Thermochemical biomass valorization processes conducted in an inert atmosphere are technically affordable methods that transform raw biomass into high-quality chars. Thanks to this, it is attractive for use in combustion and gasification systems (Tumuluru et al. 2011), as well as for use in agricultural or environmental systems (Srivatsav et al. 2020;

Schmidt et al. 2019; Świechowski et al. 2022; Antonangelo et al. 2021; Saletnik et al. 2019). These products are also promising materials that can be implemented, among others, in the construction, chemical, pharmaceutical, and textiles industries (Ryłko-Polak et al. 2022; Gładki 2018). Depending on the technological conditions of the process, there are three basic methods of thermochemical treatment of biomass, carried out in an inert atmosphere:

- Torrefaction: process usually carried out in the temperature range of 200: 320 °C, under atmospheric pressure, in the absence of oxygen and water. The obtained solid product is most often referred to as torreficate (Zuwała et al. 2014; Whelan 2019).
- Pyrolysis: process usually carried out in the temperature range of 400: 1000 °C, under atmospheric pressure, in the absence of oxygen and water. The obtained solid product is most often referred to as biochar (Lord and Pfannkoch 2012).
- Hydrothermal Carbonization: process usually carried out in the temperature range of 150: 250 °C, under increased pressure, with the addition of water, in the absence of oxygen. The obtained solid product is most often referred

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to as hydrochar (Mohammed et al. 2020; Putra et al. 2021).

Depending on the process carried out, the obtained multifunctional carbonizate is characterized by various physical–chemical properties, which most often determine the path of its use and destination. The properties that combine chars produced in all processes are that they are materials rich in organic carbon, hydrophobic, compactable, and grindable (Tumuluru et al. 2011; Romão and Conte 2020). Although the use of chars has many positive effects and is in line with the ideas of a circular economy, adverse effects of their use have also been noted in recent years. They are related mainly to the risk of self-heating of the processed biomass and limitations associated with the high ash content in char or tar formation in biomass valorization processes (Chen et al. 2021, 2015; Cocchi et al. 2015; Wang et al. 2003; Niu et al. 2016, 2019). However, one of the most serious, recently discovered problem is that persistent organic pollutants, such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs), can be formed and transformed during the thermochemical valorization of biomass.

PCDD/Fs are stable compounds in the air and can be transported over long distances or stored in the ecosystem through the food chain (Klima et al. 2020). They are structurally and chemically similar chlorinated aromatic hydrocarbons. In overall, the term "dioxins" refers to both polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls (Srogi 2008). There are 75 dioxin compounds and 135 furan compounds, dependent on the quantity and location of chlorine atoms (Environment Agency 2009). Congeners with 4 chlorine atoms in the molecule, in positions 2, 3, 7 and 8, have the highest affinity for the aryl hydrocarbon receptor, which makes them highly harmful (Hrabák et al. 2016). According to the World Health Organization for these compounds, due to their toxicity, it is necessary to take appropriate actions in the field of public health to reduce their emission (World Health Organization 2010). The toxicity of PCDD/Fs causes heart problems, disrupts the functioning of the immune and endocrine systems, and leads to various types of cancer (Klima et al. 2020; European Environment Agency 2016).

According to Environment Australia (1999), it was found that chemical reactions responsible for the formation of PCDD/Fs never proceed with 100% yield in terms of kinetic—which means that calculation from thermodynamic considerations is problematic due to the impossibility of achieving maximum/equilibrium conversion degree. Hence, although the raw material may be rich in dioxin building blocks, such as carbon, hydrogen, oxygen and chlorine (Muñoz et al. 2006), their conversion to dioxins does not occur to a significant extent (Environment Australia

1999). Based on an experiment by Addink et al. (1998), who observed that the estimated distribution of PCDD/Fs congeners significantly differs from that obtained in the investigation, it can be concluded that thermodynamic equilibrium is never reached—thus, kinetic mechanisms are expected to dominate over thermodynamic ones in the formation of dioxins (Environment Australia 1999; Palmer et al. 2019).

The assessment of the contamination of the solid products of thermochemical valorization, such as biochars, hydrochars and torreficates with PCDD/Fs compounds is usually done by using the toxicity equivalence factors and total toxic equivalence. Toxicity equivalence factors are allocated to compounds based on experimental evidence for dioxins in comparison with the most hazardous chemical, 2,3,7,8-tetrachlorodibenzodioxin, which has a toxicity equivalence factor of 1 (van der Berg et al. 2006a, 2b; Kirkok et al. 2020). Due to the fact that the individual toxicity of dioxins is summative (van Ede et al. 2016; Kirkok et al. 2020), total toxic equivalence is calculated as the sum of individual toxicity equivalence factors, 17 toxic PCDD/Fs congeners (Table 1). Depending on the adopted method of calculating total toxic equivalency, toxicity equivalence factor values may differ slightly. As a standard, toxicity equivalence factors provided by the World Health Organization and North Atlantic Treaty Organization (NATO) are used. However, total toxic equivalence is expressed by the same formula:

$$\text{TEQ} = \sum_{n=1}^k C_n \cdot \text{TEF}_n \quad (1)$$

where TEQ is total toxic equivalence, ng TEQ·kg⁻¹; TEF: toxicity equivalence factor.

The level of contamination of chars with dioxin compounds may significantly determine the possibility of their use because there are certain limitations for some directions of chars use. The International Biochar Initiative (2015) determined that if the char is planned as a soil additive, it should not exceed the value of 17 ng TEQ kg⁻¹. The European Biochar Certificate, depending on the soil protection rules' limit values in force in two European Countries—Germany and Switzerland, determined that the biochar should not contain more than 20 ng TEQ kg⁻¹ (BBodSchV Bundes-Bodenschutz- und Altlastenverordnung (1999); Chemikalien-Risikoreduktions-Verordnung 2020; European Biochar Certificate 2022). Additionally, if the char is planned as a feed additive, it should contain less than 0.75 ng TEQ kg⁻¹ (European Union 2012). In this case, each portion of biochar dedicated for feed additive must be evaluated for the content of dioxin compounds with an accredited, specialized method, with a lower limit of detection than limit value (European Biochar Certificate 2022). Unfortunately, apart from this case, the analysis of the dioxin content in chars is often overlooked because it is commonly believed that it

Table 1 Toxicity equivalence factors provided by the World Health Organization (van der Berg et al. 2006a, b) and the North Atlantic Treaty Organization (Kutz et al. 1990)

Congener abbreviation	Congener name	World Health Organization toxicity equivalence factors	North Atlantic Treaty Organization toxicity equivalence factors
OCDD	Octachlorodibenzodioxin	0.0003	0.001
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-Heptachlorodibenzodioxin	0.01	0.01
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-Hexachlorodibenzodioxin	0.1	0.1
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-Hexachlorodibenzodioxin	0.1	0.1
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-Hexachlorodibenzodioxin	0.1	0.1
1,2,3,7,8-PeCDD	1,2,3,7,8-Pentachlorodibenzodioxin	1	0.5
2,3,7,8-TCDD	2,3,7,8-Tetrachlorodibenzodioxin	1	1
OCDF	Octachlorodibenzofuran	0.0003	0.001
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.01	0.01
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-Heptachlorodibenzofuran	0.01	0.01
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-Hexachlorodibenzofuran	0.1	0.1
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-Hexachlorodibenzofuran	0.1	0.1
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-Hexachlorodibenzofuran	0.1	0.1
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-Hexachlorodibenzofuran	0.1	0.1
2,3,4,7,8-PeCDF	2,3,4,7,8-Pentachlorodibenzofuran	0.05	0.05
1,2,3,7,8-PeCDF	1,2,3,7,8-Pentachlorodibenzofuran	0.5	0.5

is negligible in pyrolytic processes carried out in modern installations (European Biochar Certificate 2022; Bucheli et al. 2015).

A significant barrier is that the dioxin analysis, typically carried out using the gas chromatography—mass spectrometry, technique, is relatively expensive and time-consuming compared to determining other chemical pollutants (Food and Agriculture Organization 2008). Additionally, another argument aimed at omitting PCDD/Fs analysis in biomass valorization processes carried out at low temperatures, such as hydrothermal carbonization, is that the "dioxin window," occurring at 300–600 °C during which dioxin neogenesis is not achieved by the process conditions (Brookman et al. 2018; Wiedner et al. 2013a, b; Poerschmann et al. 2015). The assumptions that the dioxin content in the char will not change significantly after the thermochemical valorization process in comparison with unprocessed biomass may be wrong, because in recent years it has been shown that the composition of congeners in char can be significantly modified as a result of processes, such as hydrothermal carbonization, torrefaction or pyrolysis (Tirler and Basso 2013; Gao et al. 2017; Lyu et al. 2016; Brookman et al. 2018).

In the literature, there are currently no studies aimed at summarizing the content of PCDD/Fs in biochars, hydrochars and torreficates. Thanks to this, it may still conceal the toxic effect of their use and contribute to confirming the thesis mentioned above about the possibility of omitting to perform the analysis of the content of dioxin compounds in the chars. Several reviews mention the content of dioxins, mainly in biochar (Han et al. 2022; Huang and Gu 2019;

Steiner 2015; Qadeer et al. 2017; Zheng et al. 2019; Xiang et al. 2021; Brtnicky et al. 2021; Godlewska et al. 2021). However, they are incomplete, limited to a few sentences or paragraphs. They are not covering the complete analysis of technological processes parameters such as: temperature, residence time, heating rate, pressure and the entire spectrum of works on PCDD/Fs compounds since they were mainly focused on other toxic compounds.

It is assumed that due to several production processes of different natures and technological parameters, the final toxicity of the chars can be wildly divergent. Changing chars' production parameters may be one factor determining their final toxicity. The type of feedstock subjected to the thermochemical valorization process, which may significantly affect the final toxicity of the products, also plays an essential role (Conesa et al. 2020). Briefly summarizing, it seems necessary to outline the current knowledge on the presence of PCDD/Fs in chars produced by various thermochemical valorization processes and to specify the key aspects that may determine their final toxicity.

Therefore, this paper aims to review the literature focused on summarizing the level of contamination of chars with PCDD/Fs compounds and mechanisms responsible for their formation and transformation, depending on (i) the type of thermochemical valorization process; (ii) technological parameters of the biomass thermochemical valorization process, such as: temperature, pressure, heating rate, residence time; (iii) material/biomass subjected to thermochemical valorization processes. An additional purpose of this work is to recognize the critical research gaps in relation to the

need to identify the missing differences between some processes as elements that may determine the degree of toxicity of chars.

Total dioxins and furans contamination in solid residues from thermochemical valorization processes

Table 2 presents data related to the dioxin contamination level of solid products after the biomass and organic waste valorization processes. Based on the performed analysis, about 111 solid organic products were identified in 27 papers. Most of the resulting works are modern literature, published in 2012–2022, which seems to be a response to the voice of Verheijen et al., who wrote in 2010 that there is a need to conduct a full and comprehensive risk assessment of PCDD/Fs, in order to relate contamination toxicity to biochar type, safe application rates and conditions during pyrolysis. As a result, information on PCDD/Fs concentrations in solid residue materials was found, resulting from such processes as: pyrolysis, torrefaction, gasification, hydrothermal carbonization, hydrothermal gasification and microwave pyrolysis. Several studies also contain information on two-stage processes, such as: two-stage pyrolysis, high-temperature pyrolysis with torrefaction as part of the pre-treatment two-stage hydrothermal carbonization (Hale et al. 2012; Han et al. 2021; Wiedner et al. 2013b).

Most of the experiments focused solely on the study of processed biomass material; however, several feedstock studies used waste additives or by-products, such as: polyvinyl chloride, incineration fly ash or wood ash (Han et al. 2021; Chen et al. 2020; Grafmüller et al. 2022). It is worth noting that the table contains the names of the processes, in line with the nomenclature provided by the authors in individual papers. This is particularly visible in the case of low-temperature pyrolysis, which some authors perceive as torrefaction. Supplementary Materials provide information on bibliometric analysis strategies and the provision of information for Table 2 based on (Guo et al. 2022, Liberati et al. 2009, Khan et al. 2003). The types of pyrolysis, such as slow or conventional pyrolysis, were not distinguished.

In the vast majority of studies, the level of dioxin concentration was given in relation to a factor based on their toxicity and not the general concentration of all congeners. In general, this is a good practice, because in several studies it was observed that with an increase in total toxic equivalence, the concentration level of all congeners may decrease. Such a phenomenon was noted especially in the processes of hydrothermal carbonization of sewage sludge in the studies conducted by Tirlir and Basso (2013) and Brookman et al. (2018).

Essentially, based on the performed literature review, it can be concluded that the level of PCDD/Fs contamination of solid products resulting from thermochemical biomass valorization processing, is highly diversified. Toxicity of biochars, hydrochars and torreficates ranges from 0 ng TEQ kg⁻¹ to 113 ng TEQ kg⁻¹. It is worth emphasizing that in the vast majority of experiments, these values are close to the 0 ng TEQ kg⁻¹. Often their concentration was under the detection level. Only in four materials, the level of dioxins exceeded 20 ng TEQ kg⁻¹. In the case of PCDD/Fs concentrations, without recalculation of their toxicity equivalent, the highest concentration was noted for the torreficate, produced from the particle board. The authors observed PCDD/Fs content of 11,024.1 ng kg⁻¹ where a very high content of heptachlorodibenzodioxins and octachlorodibenzodioxin was noted (Gao et al. 2017). In opposition, in several papers the level of PCDD/Fs did not exceed 10 ng kg⁻¹.

Unfortunately, the different levels of detection of PCDD/Fs compounds caused by the use of different methods and equipment in PCDD/Fs determination may significantly reduce the possibility of understanding the influence of operating conditions on the formation and transformation of persistent organic pollutants. Admittedly, with a shallow detection level, it can be concluded that the dioxin contamination is low and will not have a significant impact on the environment, but at the detection level exceeding a few ng TEQ kg⁻¹ it cannot be determined whether char will be suitable for use as a feed additive.

Nevertheless, also an important barrier when comparing the results is the use of different total toxic equivalence coefficients, which differ in the level of individual toxicity equivalency factors. Differences between individual toxicity equivalency factors values for both indicators are small; however, assuming high contamination of the material with PCDD/Fs compounds, the differences in the final result may be significant. Hence, in the future, standardizing the reporting of the results in an appropriate unit may avoid misconduct and shed more precise light when comparing the impact of the operational conditions of the thermochemical biomass valorization processes.

During the analysis, a similar phenomenon was observed by Bucheli et al. (2015), who, reviewing the literature of a similar phenomenon—concerning the presence of polycyclic aromatic hydrocarbons and polychlorinated aromatic compounds in biochar, noted large methodological differences between individual experiments, which may to some extent limit the full understanding of later aspects of the transformation of chemical compounds. However, the authors added that when discovering a new research niche, the phenomenon of methodological discrepancy is not unusual and in previously such issues concerned soil,

Table 2 Dioxin contaminations in biochars, hydrochars and torreficates produced by thermochemical conversion of biomass

No	Feedstock type	Valorization process					Biochar/hydrochar/torreficate contamination		References
		Process	Temperature	Residence time	Heating rate	Pressure	Dioxins and furans		
			–	°C	min	°C min ⁻¹	MPa	Ng kg ⁻¹	
1	Leftover food	Hydro-thermal carbonization	I st.: 230 II st.: 180	I st.: 15 II st.: 75	–	I st.: 2.8 II st.: 1	–	<5.98*** below detection limit	Wiedner et al. (2013b)
2	Sewage sludge	Hydro-thermal carbonization	I st.: 230 II st.: 180	I st.: 15 II st.: 75	–	I st.: 2.8 II st.: 1	–	14.2***	Wiedner et al. (2013b)
3	Poplar wood	Hydro-thermal carbonization	230	480	–	30	–	<5.98**** below detection limit	Wiedner et al. (2013a)
4	Olive residues	Hydrothermal Carbonization	230	480	–	30	–	8.1****	Wiedner et al. (2013a)
5	Sewage sludge + incineration Fly Ash	Hydro-thermal carbonization	180	60	5	–	2.55	0.91***	Chen et al. (2020)
6	Sewage Sludge	Hydro-thermal carbonization	220	900	–	–	4596.1	21.4*	Tirler and Basso (2013)
7	Sewage Sludge	Hydrothermal Carbonization	235	900	–	–	4091.6	57.8*	Tirler and Basso (2013)
8	Sewage Sludge	Hydrothermal Carbonization	255	900	–	–	~2023.7	113*	Tirler and Basso (2013)
9	Sewage Sludge	Hydrothermal Carbonization	200	300	–	–	1452.2	11.08*	Brookman et al. (2018)
10	Sewage Sludge	Hydrothermal Carbonization	220	300	–	–	452.8	18.75*	Brookman et al. (2018)
11	Sewage Sludge	Hydrothermal Carbonization	240	300	–	–	129.5	45.03*	Brookman et al. (2018)
12	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	877.1	9*	Liberatori et al. (2022)
13	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	1417.6	18.7*	Liberatori et al. (2022)
14	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	950.3	13*	Liberatori et al. (2022)
15	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	1467.6	21.7*	Liberatori et al. (2022)
16	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	1179.5	12.9*	Liberatori et al. (2022)

Table 2 (continued)

No	Feedstock type	Valorization process					Biochar/hydrochar/torreficate contamination		References
		Process	Temperature	Residence time	Heating rate	Pressure	Dioxins and furans		
							–	°C	
17	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	924.6	9.1*	Liberatori et al. (2022)
18	Sewage Sludge	Hydrothermal Carbonization	210	240	~3	1.5	–	19.2***	von Eyser et al. (2014)
19	Sewage Sludge	Hydrothermal Carbonization	210	240	–	1.5	–	18.7****	von Eyser (2016)
20	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	–	13.1*	Della Torre et al. (2022)
21	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	–	9.1*	Della Torre et al. (2022)
22	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	–	14.2****	Tasca et al. (2022)
23	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	–	19.1****	Tasca et al. (2022)
24	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	–	16.1****	Tasca et al. (2022)
25	Sewage Sludge	Hydrothermal Carbonization	220	85	–	–	–	13.3****	Tasca et al. (2022)
26	Stemwood	Torrefaction	250	60	~2.5–3	–	15.8	~0.145*	Gao et al. (2017)
27	Bark	Torrefaction	250	60	~2.5–3	–	37.2	~0.194*	Gao et al. (2017)
28	Impregnated Stemwood	Torrefaction	300–345	60	~2.5–3	–	67.1	~0.033*	Gao et al. (2017)
29	Cassava Stems	Torrefaction	250	60	~2.5–3	–	37.0	~0.169*	Gao et al. (2017)
30	Particle Board	Torrefaction	250	60	~2.5–3	–	11,024.1	~38.87*	Gao et al. (2017)
31	Sewage Sludge	Microwave-Assisted Pyrolysis	300 W (power)	60	–	–	~9.9	~0.25***	Dai et al. (2018)
32	Sewage Sludge	Microwave-Assisted Pyrolysis	700 W (power)	60	–	–	~10.2	~0.26***	Dai et al. (2018)
33	Softwood	Microwave-Assisted Pyrolysis	~200	9.5–10	max. 16	up to ~0.0680	–	0.03***	Gao et al. (2016a)
34	Impregnated Wood	Microwave-Assisted Pyrolysis	~165	9.5–10	max. 16	up to ~0.0312	–	0.04***	Gao et al. (2016a)
35	Bark	Microwave-Assisted Pyrolysis	~200	9.5–10	max. 16	up to ~0.0280	–	0.29***	Gao et al. (2016a)

Table 2 (continued)

No	Feedstock type	Valorization process					Biochar/hydrochar/torreficate contamination		References
		Process	Temperature	Residence time	Heating rate	Pressure	Dioxins and furans		
							–	°C	
36	Food Waste	Pyrolysis	300	30	–	–	–	1.20****	Hale et al. (2012)
37	Food Waste	Pyrolysis	400	30	–	–	92.0	0.15****	Hale et al. (2012)
38	Food Waste	Pyrolysis	500	30	–	–	–	0.008****	Hale et al. (2012)
39	Food Waste	Pyrolysis	600	30	–	–	84.0	0.16****	Hale et al. (2012)
40	Digested Dairy Manure	Pyrolysis	600	30	–	–	85.8	0.13****	Hale et al. (2012)
41	Paper Mill Waste	Pyrolysis	600	30	–	–	–	0.06****	Hale et al. (2012)
42	Pine Wood	Pyrolysis	800	480	–	–	–	0.005****	Hale et al. (2012)
43	Pine Wood	Pyrolysis	900	480	–	–	91.5	0.15****	Hale et al. (2012)
44	Oak	Pyrolysis	650	180	–	–	–	0.02****	Hale et al. (2012)
45	Grass	Pyrolysis	650	180	–	–	–	0.02****	Hale et al. (2012)
46	Switchgrass	Pyrolysis	800	480	–	–	–	0.008****	Hale et al. (2012)
47	Switchgrass	Pyrolysis	900	480	–	–	–	0.22****	Hale et al. (2012)
48	Druff	Pyrolysis	850	20	–	0.1	–	< 5.95**** below detection limit	Wiedner et al. (2013b)
49	Poplar Wood + polyvinyl chloride (50/50)	Pyrolysis	900	60	20	–	27.4	–	Han et al. (2021)
50	Municipal Green-waste	Pyrolysis	–	–	–	–	–	4.2****	Downie (2011)
51	Poultry Litter	Pyrolysis	–	–	–	–	–	3.9****	Downie (2011)
52	Paper Sludge	Pyrolysis	–	–	–	–	–	2.4****	Downie (2011)
53	Sawdust (Pine Wood)	Pyrolysis	250	180	5	–	270	7.0*	Lyu et al. (2016)
54	Sawdust (Pine Wood)	Pyrolysis	300	180	5	–	610	9.6*	Lyu et al. (2016)
55	Sawdust (Pine Wood)	Pyrolysis	400	180	5	–	360	4.9*	Lyu et al. (2016)
56	Sawdust (Pine Wood)	Pyrolysis	500	180	5	–	67	2.1*	Lyu et al. (2016)
57	Sawdust (Pine Wood)	Pyrolysis	700	180	5	–	50	1.7*	Lyu et al. (2016)
58	Dry Toilet Substrate	Pyrolysis	600–650	10	~33–50	–	–	1.98*	Bleuler et al. (2021)
59	Orange and Pineapple Peels	Pyrolysis	200–250	80–90	–	–	–	4.8*	Chávez-García et al. (2020)
60	Machineel Tree and Pine	Pyrolysis	600–680	210–270	–	–	–	0.40*	Flesch et al. (2019)

Table 2 (continued)

No	Feedstock type	Valorization process					Biochar/hydrochar/torreficate contamination		References
		Process	Temperature	Residence time	Heating rate	Pressure	Dioxins and furans		
							–	°C	
61	Different Species of Wood	Pyrolysis	600–680	210–270	–	–	–	0.39*	Flesch et al. (2019)
62	Different Species of Wood	Pyrolysis	600–680	210–270	–	–	–	0.39*	Flesch et al. (2019)
63	Different Species of Wood	Pyrolysis	600–680	210–270	–	–	–	0.40*	Flesch et al. (2019)
64	Sediment	Pyrolysis	300	30	–	–	–	17.35****	Wijesekara et al. (2007)
65	Sediment	Pyrolysis	400	30	–	–	–	1.00****	Wijesekara et al. (2007)
66	Sediment	Pyrolysis	800	30	–	–	–	0.00****	Wijesekara et al. (2007)
67	Softwood	Pyrolysis	500	10	–	–	–	b.d.l.*	Grafmüller et al. (2022)
68	Softwood + Wood Ash (4.8%)	Pyrolysis	500	10	–	–	–	b.d.l.*	Grafmüller et al. (2022)
69	Softwood + Wood Ash (16.4%)	Pyrolysis	500	10	–	–	–	b.d.l.*	Grafmüller et al. (2022)
70	Softwood + Wood Ash (42.6%)	Pyrolysis	500	10	–	–	–	0.00687*	Grafmüller et al. (2022)
71	Softwood Pellet	Pyrolysis	550	10	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
72	Softwood Pellet	Pyrolysis	550	20	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
73	Softwood Pellet	Pyrolysis	550	20	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
74	Softwood Pellet	Pyrolysis	700	10	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
75	Softwood Pellet	Pyrolysis	700	20	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
76	Softwood Pellet	Pyrolysis	700	20	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
77	Wheat Straw Pellet	Pyrolysis	550	5	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
78	Wheat Straw Pellet	Pyrolysis	550	20	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
79	Wheat Straw Pellet	Pyrolysis	550	20	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
80	Wheat Straw Pellet	Pyrolysis	700	6	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)

Table 2 (continued)

No	Feedstock type	Valorization process					Biochar/hydrochar/torreficate contamination		References
		Process	Temperature	Residence time	Heating rate	Pressure	Dioxins and furans		
							–	°C	
81	Wheat Straw Pellet	Pyrolysis	700	20	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
82	Wheat Straw Pellet	Pyrolysis	700	20	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
83	Anaerobic digestate (Sewage Sludge)	Pyrolysis	550	–	–	–	–	<0.9* below detection limit	Weidemann et al. (2018)
84	Sewage Sludge	Pyrolysis	500	60	–	–	~8.8	~0.22****	Dai et al. (2018)
85	Sewage Sludge	Pyrolysis	700	60	–	–	~10.98	~0.46****	Dai et al. (2018)
86	Sewage Sludge	Pyrolysis	800	60	–	–	~9.1	~0.20****	Dai et al. (2018)
87	Waste Timber	Pyrolysis	600	20	–	–	24.90	1.33****	Sørmo et al. (2020)
88	Waste Timber	Pyrolysis	600	20	–	–	19	1.46****	Sørmo et al. (2020)
89	Waste Timber	Pyrolysis	600	20	–	–	14.44	1.62****	Sørmo et al. (2020)
90	Pure Wood	Pyrolysis	600	20	–	–	–	0.90****	Sørmo et al. (2020)
91	Sediment	Pyrolysis	800	30	10	–	–	0**	Hu et al. (2006)
92	Sediment	Pyrolysis	800	60	10	–	–	0.0005**	Hu et al. (2006)
93	Sediment	Pyrolysis	800	90	10	–	–	0**	Hu et al. (2006)
94	Softwood Bark	Pyrolysis	500	–	–	–	–	0.51**** below detection limit	Granatstein et al. (2009)
95	Wood Pellets	Pyrolysis	500	–	–	–	–	0.51**** below detection limit	Granatstein et al. (2009)
96	Digested Fiber	Pyrolysis	500	–	–	–	–	0.51**** below detection limit	Granatstein et al. (2009)
97	Switchgrass	Pyrolysis	500	–	–	–	–	0.51**** below detection limit	Granatstein et al. (2009)
98	Chicken Manure + 3 mmol Ca(OH) ₂	Hydro-thermal Gasification	200	40	0.5	26–27	–	0* below detection limit	Yildiz Bircan et al. (2011)
99	Chicken Manure	Hydro-thermal Gasification	200	40	0.5	26–27	–	0* below detection limit	Yildiz Bircan et al. (2011)

Table 2 (continued)

No	Feedstock type	Valorization process					Biochar/hydrochar/torreficate contamination		References
		Process	Temperature	Residence time	Heating rate	Pressure	Dioxins and furans		
							–	°C	
100	Chicken Manure + 3 mmol Ca(OH) ₂	Hydro-thermal Gasification	300	40	0.5	26–27	–	0* below detection limit	Yildiz Bircan et al. (2011)
101	Chicken Manure	Hydro-thermal Gasification	300	40	0.5	26–27	–	0* below detection limit	Yildiz Bircan et al. (2011)
102	Chicken Manure + 3 mmol Ca(OH) ₂	Hydro-thermal Gasification	400	40	0.5	26–27	–	0* below detection limit	Yildiz Bircan et al. (2011)
103	Chicken Manure	Hydro-thermal Gasification	400	40	0.5	26–27	–	0* below detection limit	Yildiz Bircan et al. (2011)
104	Cattle Manure	Hydro-thermal Gasification	400	40	0.5	26–27	–	0.50291*	Yildiz Bircan et al. (2011)
105	Cattle Manure + 1 mmol Cu	Hydro-thermal Gasification	400	40	0.5	26–27	–	0.1373*	Yildiz Bircan et al. (2011)
106	Olive Residues	Gasification	1200	30–45	–	0.1	–	< 5.95*** below detection limit	Wiedner et al. (2013b)
107	Poplar Wood	Gasification	1200	30–45	–	0.1	–	< 5.95*** below detection limit	Wiedner et al. (2013b)
108	Wood Chips	Gasification	550	–	–	0.1	–	< 5.95*** below detection limit	Wiedner et al. (2013b)
109	Lodge Pole Pine	Pyrolysis (2 stage)	I st.: 700–750 II st.: 300–550	I st.: < 1 II st.: 10–14	–	–	86.0	0.18****	Hale et al. (2012)
110	Poplar Wood + polyvinyl chloride (50/50)	Torrefaction (I) + Pyrolysis (II)	I st.: 300 II st.: 900	I st.: 60 II st.: 60	I st.: 10 II st.: 20	–	149.7	–	Han et al. (2021)
111	Orange and Pineapple Peels	Pyrolysis (I) + Composting (II)	200–250	I: 80–90 II: 40 days	–	–	–	3.2*	Chávez-García et al. (2020)

*World Health Organization Total Toxicity Equivalence from 2005 (WHO-TEQ 2005)

**World Health Organization Total Toxicity Equivalence from 1998 (WHO-TEQ 1998)

***North Atlantic Treaty Organization Total Toxicity Equivalence (I-TEQ)

****Unspecified TEQ

sediment and bio-waste (Bucheli et al. 2015; Lambkin et al. 2004).

Influence of valorization process conditions and feedstock on the presence of dioxins in processed biomass

There are many parameters influencing the chemical composition of the processed product. The most critical ones

are: (i) process type, (ii) temperature, (iii) residence time, (iv) heating rate, (v) pressure (Garcia et al. 2022; Chatterjee et al. 2020; Conti et al. 2016; Chen et al. 2016; Rasaq et al. 2021). The type of substrate (vi) and the chemical structure of biomass also play a crucial role in shaping the final physicochemical properties of biochar (Tomczyk et al. 2020). Thus Sect. 3.1—"Feedstock" discusses the influence of the operational parameters of thermochemical valorization processes and feedstock type on the presence of dioxins in the processed solid product.

Process type

Figure 1 shows the effect of the process type on the presence of PCDD/Fs in the processed solid product. Most of the studies analyzed concerned the processes of pyrolysis and hydrothermal carbonization, while individual experiments found references to such processes as torrefaction, hydrothermal gasification and microwave pyrolysis. By far

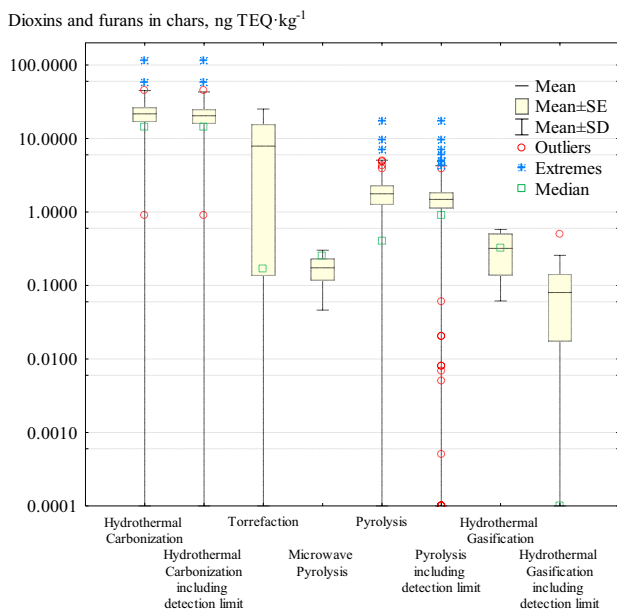


Fig. 1 Dioxin contamination of products of biomass valorization as a function of process type including solid samples from: hydrothermal carbonization ($n=23$), hydrothermal carbonization including detection limit points ($n=25$), torrefaction ($n=5$), microwave pyrolysis ($n=5$), pyrolysis ($n=40$), pyrolysis including detection limit points ($n=61$), hydrothermal gasification ($n=2$), hydrothermal gasification including detection limit points ($n=8$). TEQ denotes total toxic equivalence. SE represents standard error, and SD represents standard deviation. Solid products of hydrothermal carbonization processes are by far the most toxic among the other processes. A relatively high toxicity equivalent is also noted for pyrolysis and torrefaction products, and the lowest for microwave pyrolysis and hydrothermal gasification. However, samples with dioxin levels below the detection limit may distort some of the results. Among the processes, a different number of samples with diversified materials subjected to analysis are also noted

the highest concentrations of dioxins dominated in hydrothermal carbonization processes, where the solid residue was characterized by the concentration of PCDD/Fs in the range of $0.91 \text{ ng TEQ kg}^{-1}$ – $113 \text{ ng TEQ kg}^{-1}$, and most of the materials subjected to evaluation exceeded the value of $10 \text{ ng TEQ kg}^{-1}$.

Hydrothermal carbonization

Wiedner et al. (2013a, b), analyzing the content of dioxins in biochars, produced from various thermochemical valorization processes, showed that the sewage sludge-based hydrochar obtained from hydrothermal carbonization is characterized by the presence of dioxins at the level of $14.2 \text{ ng TEQ kg}^{-1}$. However, it should be underlined that the hydrothermal carbonization process of a different substrate—leftover food, in the same study, with similar process operating conditions, also did not allow the detection limit to be exceeded.

Tirler and Basso (2013), who obtained high toxicity of hydrochars at the level 21.4 – $113 \text{ ng TEQ kg}^{-1}$, from sludge carbonization at a temperature range of 220 – $255 \text{ }^\circ\text{C}$ in 15 h, concluded that the hydrothermal carbonization process mainly results in the dechlorination of the more chlorinated PCDD/Fs in the lateral position. The authors added that the increase in chars' toxicity is also due to the dechlorination process at the peri position up to two orders of magnitude higher. The effect of dechlorination as a possible pathway to increase toxicity in hydrothermal carbonization processes was also confirmed in the experiment conducted by Brookman et al. (2018) who obtained hydrochar toxicity at 11.03 – $45.08 \text{ ng TEQ kg}^{-1}$ during sewage sludge carbonization under similar operating conditions. It is worth noting, however, that in both works the technological parameters of the process of valorization determined the toxicity of the hydrochars. Probably, it was dictated mainly by the influence of temperature.

The phenomenon of dechlorination in hydrochar samples was also noted by Liberatori et al. (2022) investigating the change in toxicity of various sewage sludge samples before and after the hydrothermal carbonization process. The authors of the experiment also added, based on their own experiment and mainly Tirler and Basso (2013), that as a result of thermochemical valorization, there is a significant reduction in water content. They stated that due to the fact that it constitutes a significant percentage of the sample, PCDD/Fs compounds are additionally concentrated; therefore, the increase in toxicity may be the result of a combination of the dechlorination process and the accumulation of PCDD/Fs concentration in the resulting matrix (Liberatori et al. 2022; Lozano-Castell et al. 2013; Sevilla et al. 2011; Tirler and Basso 2013).

Torrefaction

In the case of another low-temperature process—torrefaction, it was concluded that the content of PCDD/Fs compounds in the processed solid product is relatively low and ranges from ~ 0.033 ng TEQ kg⁻¹ to ~ 0.194 ng TEQ kg⁻¹. The exception was impregnated stemwood, a highly contaminated substrate in which the presence of dioxins after valorization was ~ 38.87 ng TEQ kg⁻¹ in char. Gao et al. (2017) concluded based on a comparison traditional coefficient—PCDD/PCDF ratio (polychlorinated dibenzo-*p*-dioxins to polychlorinated dibenzofurans ratio), that its low value in the torrefied product may indicate de novo synthesis dominant pathways responsible of furans formation.

Comparing the PCDD/PCDF ratio is often used to identify the critical pathway of PCDD/Fs formation (Black et al. 2012; Lin et al. 2022). On the other hand, the high value of this ratio, which was obtained for the particle board torreficate, may point that, in this case, precursor pathways presided (Gao et al. 2017)—which could suggest that during torrefaction, the mechanisms responsible for PCDD/Fs formation/transformation is variable depending on the biomass type. As presented by the authors, these results are consistent with the literature in which the precursor pathway and de novo synthesis were identified as dominant mechanisms of PCDD/Fs formation, especially in this temperature zone (Gao et al. 2017; Altarawneh et al. 2009). The authors also reported that torrefaction, due to the inert nature of the process, may result in limited PCDD/Fs formation, because O₂ deficiency may inhibit the efficiency of compounds formed in the Deacon reaction (Gao et al. 2017). In addition, dechlorination/degradation of more chlorinated compounds may appear during this low-temperature process (Gao et al. 2017). This phenomenon was also noted in another biomass valorization process—hydrothermal carbonization (Tirler and Basso 2013; Brookman et al. 2018).

Pyrolysis and microwave-assisted pyrolysis

Whereas, in the pyrolysis, the presence of dioxins in the solid processed product ranged from 0 to 17.35 ng TEQ kg⁻¹, the highest value was obtained in an experiment carried out by Wijesekara et al. (2007) for contaminated sediment, which is not a typical standard biomass material. It should be added, however, that the sediment came from very polluted areas—it was contaminated with a very high amount of PCDD/Fs, polychlorinated biphenyls and heavy metals. Apart from this case, all materials found were characterized by PCDD/Fs concentrations below 10 ng TEQ kg⁻¹. Significant proportion of chars were below 1 ng TEQ kg⁻¹.

In turn, for another type of pyrolysis—microwave pyrolysis, the level of dioxins in the solid, processed product was relatively similar and ranged from 0.03 ng TEQ kg⁻¹ to

0.29 ng TEQ kg⁻¹. Nevertheless, far fewer materials were compared with each other and the dominant feedstock was different types of wood. Sørmo et al. (2020) and García-Pérez (2008) reported that the formation of dioxins by pyrolysis of biomass materials has not yet been extensively researched, especially in terms of the presence of dioxins in biochar. The authors also noted that the system's technological parameters, especially temperature, could play a vital role in the formation of dioxins in the pyrolysis process (García-Pérez 2008).

Gao et al. (2016a), investigating the mechanism of dioxin formation in the microwave-assisted process, suggested that the two main pathways responsible for PCDD/Fs formation during other thermochemical treatments—de novo synthesis and dechlorination—are of minor importance during the microwave-assisted process. The authors of the experiment concluded that in this valorization process, precursor-based reactions, including (chloro)phenol and reactive intermediate phenoxy radicals, may play a crucial role in the formation of PCDD/Fs in this process. Also, in the discussion, it was emphasized that the model microwave-assisted pyrolysis conditions such as low operating temperature, lack of oxygen and fast heating rate might be vital parameters in governing the path of formation/transformation PCDD/Fs or other chlorinated compounds (Gao et al. 2016b).

Makles et al. (2001) stated that during the pyrolysis of wastes contaminated with organochlorine compounds, including dioxins, furans and polychlorinated biphenyls, without getting into the complexity of pyrolytic processes, divided into temperature, pressure or type, it should be stated that these wastes can be disposed of in environmentally friendly products. Referring these words to biomass, the progress made in the last two decades in the field of thermochemical valorization of this material, mechanistic aspects of PCDD/Fs formation/transformation and methods of their determination made the type of process to be considered as one of the critical factors determining the possibility and direction of use the processed solid product. This information seems particularly important in optimizing the selection of the process type to meet the required standards and keep the environmental footprint as low as possible. During pyrolysis and similar processes, dioxins and furans can be produced, so choosing the appropriate technology involved in biochar production is essential (Osman et al. 2022).

Hydrothermal gasification

Compared to other processes, the thermochemically processed solid product from hydrothermal gasification processes was characterized by the lowest toxicity due to the fact that in products, Yildiz Bircan et al. (2011) obtained results in the range of 0–0.50291 ng TEQ kg⁻¹. It should be

summarized, however, that this process is the least known process in terms of the presence of dioxins in the solid product after thermochemical processing; therefore, more experiments in this area are needed to draw further conclusions.

Temperature

Figure 2 shows the effect of the process temperature on the presence of PCDD/Fs in the solid product after valorization. In general, in the case of pyrolysis, it should be noted that the peak concentration of dioxins in biochar observed occurred in the range of temperatures up to 300 °C, after which a clear downward trend was observed.

Hale et al. (2012) found that producing biochar at higher temperatures—between 500 and 600 °C—may lead to obtaining biochar with a lower concentration of PCDD/Fs. Lyu et al. (2016), by evaluating the effect of temperature on biochar toxicity, confirmed that biochars produced at higher pyrolysis temperatures—greater than 400 °C, are safer in terms of PCDD/Fs and polycyclic aromatic hydrocarbons concentration. The authors added that the high-temperature biochars due to their less toxicity character, seem to be more adapted to be implemented as a soil additive, because their toxicity was in the range of 1.7–2.1 ng TEQ kg⁻¹. Biochars produced up to 400 °C were in range of 4.9–9.6 ng TEQ kg⁻¹. These results may be because the

running temperature used in the low-temperature valorization processes may not be sufficient for the PCDD/Fs compounds to evaporate from the carbonized surface to the gas phase (Gao et al. 2017).

Chávez-García et al. (2020) reported a similar concentration of dioxins—4.8 ng TEQ kg⁻¹ in biochar during orange and pineapple peels pyrolysis in the temperature range of 200–250 °C. However, in the experiment of sediment pyrolysis, Wijesekara et al. (2007) obtained in the low-temperature range significantly lower toxicity of the thermochemically valorized product compared to the raw material. The authors noted almost 7 times fewer PCDD/Fs—it changed from 117.82 ng TEQ kg⁻¹ to 17.35 ng TEQ kg⁻¹. The main compounds that remained in the solid were dioxins, mainly 2,3,7,8-tetrachlorodibenzodioxin, and 1,2,3,7,8-pentachlorodibenzodioxin congeners. It is also worth emphasizing that in the same work, the authors also pyrolyzed the sediment at 400 °C and 800 °C—and a similar tendency was observed as in the works described above—in the char produced at 400 °C, the level of toxicity was 1 ng TEQ kg⁻¹, and in that produced at 800 °C no PCDD/Fs were found (Wijesekara et al. 2007).

In another pyrolytic process—microwave-assisted pyrolysis—Gao et al. (2016a) confirmed that the formation of chlorinated organic compounds and persistent organic pollutants can occur at low-temperature valorization up to 200 °C, which formally should be a constraint for the de novo synthesis. The authors also indicated that the low temperature, typical for the microwave-assisted pyrolysis process, is one of the main aspects determining the governing of the PCDD/Fs formation path (Gao et al. 2016a). The remaining research works on the presence of dioxins in biochar after biomass processing during different pyrolysis temperatures did not cover the area of low temperatures.

Weidemann et al. (2018), when examining the effect of temperature between 550 and 700 °C, observed that all evaluated biochars were characterized by the content of PCDD/Fs below the detection limit, which was in the range of 0.6–0.9 ng TEQ kg⁻¹. Even biochar produced from digestate, which can contain high amounts of contaminants including dioxins, furans and polycyclic aromatic hydrocarbons (Farghali et al. 2022), did not exceed the detection limit. Based on this information, the authors concluded that, regardless of the temperature and the pyrolysis unit, biochar may have an insignificant influence on the environment in relation to dioxins, furans and polycyclic aromatic hydrocarbons, when it is used as an additive to soil. It also needs to underline that it was observed that the formation of monochlorinated dibenzofuran took place more easily in specific pyrolytic conditions than in other types of specification (Weidemann et al. 2018). The authors stated that this compound was an exception, whose concentration was higher than the blank sample concentration and its formation was more visible in

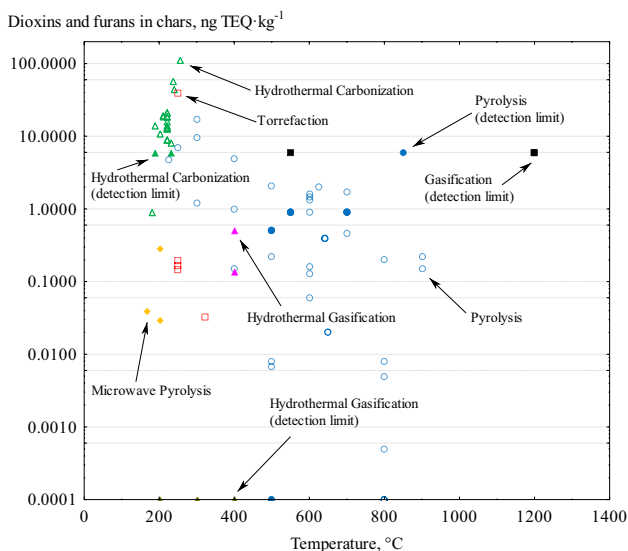


Fig. 2 Dioxin contamination of solid products of biomass valorization as a function of temperature. TEQ denotes total toxic equivalence. The temperature of the process determines the toxicity of the final products. The highest toxicity is observed in samples processed in the temperature range of 200–350 °C, characteristic of hydrothermal carbonization and torrefaction processes. Increasing the process temperature to typically pyrolytic, exceeding 400 °C, reduces the toxicity of the products. Samples produced at very high temperatures, close to 800 °C, are characterized by low toxicity

larger pyrolytic unit with lower temperatures in comparison with the smaller unit with higher temperature.

Slightly different results were observed by Dai et al. (2018), when examining the presence of dioxins in three phases for different temperatures of conventional pyrolysis—500 °C, 700 °C and 800 °C, obtained toxicity in the range of ~0.20 to ~0.46 ng TEQ kg⁻¹. The authors observed that the highest concentration of dioxins in biochar was observed for the material produced at 700 °C, mainly due to the high amount of 2,3,7,8-tetrachlorodibenzodioxin and 2,3,4,7,8-pentachlorodibenzodioxin, and the lowest for this produced in 800 °C. They suggested that these phenomena could be explained by the decomposition of PCDD/Fs molecules. However, due to the fact that a large amount of PCDD/Fs compounds shifted to the gas phase at 400 °C (Shiomitsu et al. 2002; Dai et al. 2018), no significant differences in the concentration of PCDD/Fs were observed between the biochars, and their characteristics was very similar (Dai et al. 2018). In short, it seems that a possible measure to mitigate the negative effects of biochar toxicity in terms of PCDD/Fs formation is production at temperatures higher than 500 °C (Mohamed et al. 2023; Brtnicky et al. 2021), but then the emission of these compounds in the gas phase should be controlled.

In the case of hydrothermal carbonization, an upward trend was observed in the presence of dioxins in the hydrochar along with the increase in the temperature of the process. From research by Brookman et al. (2018) it should be concluded that the temperature of the hydrothermal carbonization process can significantly determine the toxicological properties of the processed product. By increasing the process temperature from 200 to 240 °C, the authors obtained a gradual increase in the toxicity of hydrochar with the interval 20 °C, and the product produced in 240 °C was characterized by 9 times greater toxicity compared to the sewage sludge, which was input in the process. An important observation made in this experiment was the fact that the dechlorination of highly chlorinated compounds—mainly octachlorodibenzodioxin, octachlorodibenzofuran and 1,2,3,4,6,7,8-heptachlorodibenzodioxin, which in the hydrochar produced in 240 °C, constituted 1%, 15% and 5% of the concentration that was in the input (Brookman et al. 2018).

Tirler and Basso (2013), conducting hydrothermal carbonization of the same substrate at 220 °C, 235 °C and 255 °C, observed similar phenomena. The authors observed when increasing the operating temperature of the process to 235 °C that there is a high reduction in octachlorodibenzodioxin concentration, and the new pattern of homology profile change of the chlorinated compounds in the valorized product is similar to the "natural pattern" previously discovered in ball clay (Tirler and Basso 2013; Ferrario et al. 1999). Overall, it has been concluded that the high-pressure

valorization process is significantly similar to the geochemical "natural formation" of PCDD/Fs, while further increasing the operating temperature of the process causes the PCDD/Fs profiles to have similar properties in terms of higher dechlorination rate of dioxins, to the older sediments pattern (Tirler and Basso 2013; Gaus et al. 2001, 2002).

In addition, the values found in the literature, which included the hydrothermal carbonization process carried out at temperatures of 210–230 °C (von Eyser et al. 2014, von Eyser 2016; Liberatori et al. 2022; Wiedner et al. 2013b; Della Torre et al. 2022; Tasca et al. 2022), had significantly lower total toxic equivalence coefficients—up to 21.7 ng TEQ kg⁻¹, than those accomplished at temperatures of 235–255 °C, which were in the range of 45.03–113 ng TEQ kg⁻¹ (Brookman et al. 2018; Tirler and Basso 2013). Hence, it can be expected that the process temperature, both in the hydrothermal carbonization process and in other thermochemical biomass valorization processes, is one of the main factors determining the choice of PCDD/Fs formation and transformation path and, consequently, the toxicity of the carbonized solid product.

Residence time

Figure 3 shows the effect of the residence time of the process on the presence of PCDD/Fs in the solid product after valorization. In general, it is well known that during combustion, reaction time is one of the relevant factors affecting PCDD/Fs formation (Stieglitz et al. 1989; von Eyser et al. 2014).

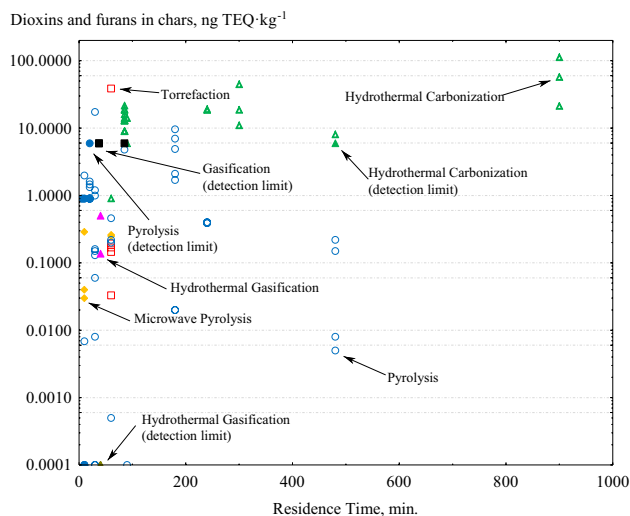


Fig. 3 Dioxin contamination of products of biomass valorization as a function of residence time. TEQ denotes total toxic equivalence. In the case of hydrothermal carbonization, a slight linear increase in toxicity is observed with increasing residence time of the substrate in the heating chamber. For other process types, linear trends are not clearly noticeable. Most of the products were made in a processing time of up to 200 min

In the case of pyrolysis processes, no clear linear trend was found related to the increase or decrease of biochar toxicity due to the residence time modification. Very few works have focused on evaluating residence time as a variable that can determine the toxicity of a solid product after biomass valorization.

Hale et al. (2012) found that a lower concentration of toxic compounds characterizes biochars produced in the conditions of longer keeping in the working chamber. The substrates, which were kept in the working chamber for 480 min at different pyrolysis temperatures, were characterized by the content of dioxins at the level of 0.005 ng TEQ kg⁻¹–0.22 ng TEQ kg⁻¹. Most of the pyrolysis processes shown in Fig. 1 were carried out in times of up to 100 min, which is the typical range for conventional pyrolysis processes (Zhao et al. 2018).

In addition to the studies mentioned earlier by Hale et al. (2012), experiments above 100 min were conducted by Lyu et al. (2016), who for pyrolysis sawdust in 180 min. obtained the dioxin content at the level of 1.7–9.6 ng TEQ kg⁻¹. In opposition, for a slightly longer residence time, Flesch et al. (2019) obtained low dioxin content at level 0.39–0.40 ng TEQ kg⁻¹ during pyrolysis different species of wood in 210–270 min. Hu et al. (2006) also evaluated the dioxin content, who, during pyrolysis at 800 °C, modified the residence time in the range of 30 min., 60 min. and 90 min. The increase in residence time from 30 to 60 min resulted in an increase in the content of dioxins from 0 ng TEQ kg⁻¹ to 0.0005 ng TEQ kg⁻¹, during the modification from 60 min. to 90 min. allowed to reduce the content of dioxins again to 0 ng TEQ kg⁻¹. It is also necessary to underline that Weidemann et al. (2018) did not observe a change in biochar toxicity due to a change in the substrate residence time in the range of 5–20 min, but PCDD/Fs in all cases were below the detection limit.

Slightly different results were observed in the case of the hydrothermal carbonization process, where a slight upward trend of increasing PCDD/Fs concentration is noticeable, along with increasing the residence time of the substrate in the working chamber. However, the value of 113 ng TEQ kg⁻¹ obtained by Tirlir and Bosso (2013) during hydrothermal carbonization of sewage sludge at 255 °C for 900 min was responsible for this phenomenon vastly. It was the highest hydrothermal carbonization temperature for which the presence of PCDD/Fs compounds in the solid product was checked, which caused an increase in the linear function's angle of inclination.

Nevertheless, when comparing different residence times for the same substrate and at the same temperature, the presence of PCDD/Fs compounds in the solid product after processing was relatively similar. Such a comparison can be observed for sewage sludge processed at 220 °C. For the shortest residence time of 85 min, the dioxin range

concentration was 9.1–21.7 ng TEQ kg⁻¹, depending on the substrate's origin, and for the 300 min, it was 18.75 ng TEQ kg⁻¹ (Brookman et al. 2018; Liberatori et al. 2022; Della Torre et al. 2022). Extending the residence time to 900 min resulted in a dioxin concentration of 21.4 ng TEQ kg⁻¹ (Tirlir and Basso 2013). Von Eyser (2016) and Von Eyser et al. (2014), conducting the process at a temperature lower by 10 °C for 240 min, also obtained a similar range of dioxin concentrations at 18.7–19.2 ng TEQ kg⁻¹.

Hence, it can be assumed that the residence time, as a variable of technological parameters of the hydrothermal carbonization process, may have a much lower impact on the content of PCDD/Fs in a solid product than, for example, temperature. Anyhow, Brookman et al. (2018) reported that further research, especially regarding the reaction time effect, is vital to emphasizing or refuting the results related to the impact of process conditions and the pre-contamination of input material subjected to the valorization process.

Heating rate

Figure 4 shows the effect of the heating rate of the process on the presence of PCDD/Fs in the solid product after valorization. In conclusion, no apparent effect of this factor on the increase or decrease of the dioxin content in the final product was found. None of the 27 reviewed articles focused on determining the role of the heating rate as a factor that could determine the final toxicity of solid residue. Unfortunately, most of the works did not decide to describe the

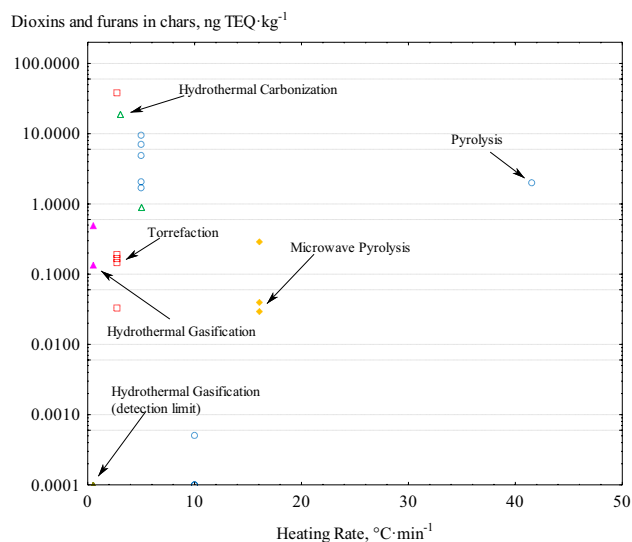


Fig. 4 Dioxin contamination of products of biomass valorization as a function of heating rate. TEQ denotes total toxic equivalence. No significant influence of the heating rate parameter on the toxicity of solid products of thermochemical processing was observed. Compared to the temperature and processing time, few authors choose to provide information on the heating rate

conditions of heating the working chamber in the methodical section. It can be assumed that in conventional pyrolytic processes, the effect of a slower heating rate may be similar to a slight extension of the residence time because the substrate stays longer in the working chamber around the target temperature.

Only an interesting observation in the context of heating rate was noticed during the microwave pyrolysis process. Gao et al. (2016b) noted that in microwave-assisted pyrolysis, the pathways of PCDD/Fs formation might also be determined by kinetic factors as well as the reactivity of precursors of intermediates, as evidenced by the presence of dioxin and furan compounds, such as 1-monochlorinated dibenzodioxin, 4-monochlorinated dibenzofuran. In addition, the authors, based on other studies (Dong and Xiong 2014), provide information that in the microwave pyrolysis process, which is characterized by a high heating rate, kinetic processes are crucial, which is explained by the effective energy transfer (Gao et al. 2016b; Dong and Xiong 2014). Briefly summarizing, in this experiment, it was recognized that a high heating rate, as a typical process condition for microwave-assisted pyrolysis, may be one of the key elements determining the choice of dioxins, furans and polychlorinated naphthalenes formation path (Gao et al. 2016b).

Pressure of the process

The effect of increased pressure in the thermochemical valorization of biomass is highly noticeable when comparing the concentration of PCDD/Fs in hydrothermal carbonization processes with traditional pyrolysis processes. Most products resulting from high-pressure techniques are more toxic concerning PCDD/Fs compounds than processes carried out under normal conditions (Table 2). However, the differences due to the nature of these processes are presented in Sect. 3.1.1. Nevertheless, little information has been found in the literature, allowing us to define the role of pressure and its modification to the presence of dioxins in the final product after valorization. As in the case of heating rate, most research works did not include information on the pressure in the process in the methodological section. While in the case of pyrolysis processes, it is understood that most of the processes are characterized by atmospheric pressure, in the case of hydrothermal carbonization and hydrothermal gasification, the pressure range is much greater. It is worth mentioning, however, that during the hydrothermal carbonization process, the pressure is self-generated and increases automatically (Türçan et al. 2022), depending on the process temperature.

Since for a large part of the results, which may be of crucial importance for the conclusions, no precise and detailed quantitative information was provided on pressure, it was

decided not to discuss the effect of pressure on the presence of PCDD/Fs compounds in biochar/hydrochar. In individual articles, information was also not found in which pressure was proposed as a driving/limiting factor for various pathways of formation or transformation of PCDD/Fs in the biomass valorization process.

The only report found in the literature was the statement of von Eyser et al. (2014) who, noting high total toxicity equivalent, after hydrothermal carbonization of sewage sludge at a temperature of 210 °C and a pressure of 15 bar, found that higher pressure during the hydrothermal carbonization might shift the temperature range required for PCDD/Fs formation. Hence, potential mechanisms of the hydrothermal carbonization process, in which pressure is perhaps one of the components determining the formation/transformation of PCDD/Fs, responsible for the increase in toxicity of valorized products, are described in Sect. 3.1.1.

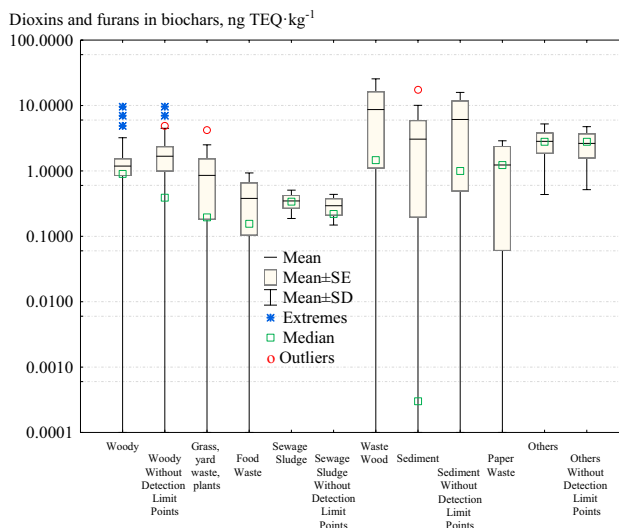


Fig. 5 Dioxin contamination of solid products of pyrolysis and torrefaction depending on substrate type including: woody ($n=34$), woody without detection limit points ($n=17$), grass, yard waste, plant biomass ($n=6$), food waste ($n=4$), sewage sludge ($n=4$), sewage sludge without detection limit points ($n=3$), waste wood ($n=5$), sediment ($n=6$), sediment without detection limit points ($n=3$), paper waste ($n=2$), others ($n=6$), others without detection limit points ($n=4$). TEQ denotes total toxic equivalence. SE represents standard error and SD represents standard deviation. The most toxic biochars and torreficates are those produced from waste wood, sludge and waste from the paper industry, i.e., substrates that may be initially contaminated with dioxins. Most biochars do not exceed a dioxin content of level 1 ng total toxic equivalence per kilogram (TEQ·kg⁻¹). A high variability in the toxicity of the samples can be observed between different types of substrates

Feedstock

Biomass type

Figure 5 shows the effect of the type of biomass on the toxicity of the valorized products in the torrefaction and pyrolysis processes. In general, a high diversification of the toxicity equivalent of the torreficates and biochars can be seen, depending on their source of origin. Compared to other types of biomass, very high total toxicity equivalent values were observed, especially in the case of thermochemical wood processing. However, it should be noted that an essential barrier in comparing biomass types is the different number of samples subjected to different types of biomass. Exceptionally high dioxin contamination, about ~ 38.87 ng TEQ kg^{-1} , was obtained in the case of the impregnated stem-wood torrefaction process (Gao et al. 2017), which can be classified as waste wood. Such phenomena may be because the presence of organic preservatives and other contaminants in the wood/biomass can contribute to the enhanced formation of PCDD/Fs during the thermal treatment of wood/biomass (Gao et al. 2017; Bhargava et al. 2002; Lundin et al. 2013; Lundin and Jansson 2014).

In the case of traditional wood substrates, some of the highest literature values were found in the case of sawdust from pine wood, which contained 1.7 ng TEQ kg^{-1} –9.6 ng TEQ kg^{-1} , depending on the process temperature (Lyu et al. 2016). In general, the initial presence of dioxins, organic compounds and the chemical composition of biomass can significantly affect the final toxicity of the processed solid product (Liberatori et al. 2022).

It has been showed that PCDD/Fs are present in a wide range environmental matrices related to atmospheric exposure (Hermanson and Johnson 2015; Wagrowski and Hites 2000; Clarkson et al. 2002; Guéguen et al. 2011; Wen et al. 2009). In the case of wood, it is especially noticeable because as suggested by Hermanson and Johnson (2015) based on their own and other observations (Catinon et al. 2009; Hermanson and Johnson 2007; Hermanson and Hites 1990; Salamova and Hites 2010; Zhao et al. 2008; Qiu and Hites 2008; Zhu and Hites 2006), trees in their lifetime are passive collectors of dioxins and other organic pollutants. It results mainly from soil contamination, which may be caused by such phenomena's as: atmospheric deposition, fluvial erosion or dumping (Hermanson and Johnson 2015; Wagrowski and Hites 2000).

Another example of biomass typical containing PCDD/Fs is rice as well as wheat straw. This is due to the presence of impurities of herbicides, such as pentachlorophenol or chlornitrofen, that have been widely used in paddy fields (Minomo et al. 2011). The resulting emissions from 6 TEQ· kg^{-1} to 22 ng TEQ· kg^{-1} of raw biomass were found by Muto et al. (1993).

One of the higher mean values of toxicity equivalents was also obtained in the solid residue after the thermochemical treatment of the sediment. However, this was because one of the samples processed at low temperatures had a dioxin content of 17.35 ng TEQ kg^{-1} . The remaining samples of the processed sediment were characterized by relatively low toxicity, indicated by the obtained median. Nevertheless, it needs to be marked that the sediment considered in this work came from a polluted area (Wijesekara et al. 2007). The conducted studies indicate that the sediment toxicity equivalent is different in different river basins, mainly due to various factors, i.e., land use, river slope, rainfall amount, dam construction and surface soil pollution (Kanematsu et al. 2006).

In addition, compared to the hydrothermal carbonization process, very low toxicity equivalent values were obtained for sewage sludge, which administration is a significant threat to the ecosystem's functioning and human well-being (Urbaniak and Wyrwicka 2017). However, they were processed in pyrolytic temperatures, allowing some of the dioxins to evaporate into the gas phase (Gao et al. 2017; Shiomitsu et al. 2002; Dai et al. 2018). High differences in the concentration of PCDD/Fs were also obtained by Downie (2011), examining the contamination of biochars produced from paper sludge, poultry letters and municipal green waste.

Overall, based on the review of the above works, the role of biomass type seems to be significant in shaping the final toxicity of biochar produced from torrefaction and pyrolysis. However, to a large extent, the type of biomass is determined by its place of origin, which may be characterized by variable exposure to dioxin contamination. According to the Government of Japan (2012), these compounds can pollute soil and water because they bind to particulate matter and fall to the ground in the atmospheric pathway. Hence, the pollution of different types of biomass can be differentiated due to the fact that their emission has both a natural background—e.g. volcanic eruptions, forest fires and natural combustion (Nhung et al. 2022; Feshin et al. 2006; Salamanca et al. 2016; Reiner et al. 2006) and anthropogenic background—e.g. incineration, combustion, industrial processes (Nhung et al. 2022; Mudhoo et al. 2013; Rathna et al. 2018; Holtzer et al. 2007). The variability of the exposure potential of different types of biomass by PCDD/Fs, resulting from the origin of biomass from other locations/environments or the distance from large emitters of these compounds, may cause significant differences in the initial concentration of dioxins in biomass (Haddad and Moqbel 2018).

In addition, on the example of plant biomass, which is characterized by a heterogeneous anatomical structure within the same species and varieties (Waliszewska et al. 2021; Sobol et al. 2022), due to the importance of many factors such as location of biomass growth, age and part of plants (Waliszewska et al. 2021), significant differences

are observed in their chemical composition. As reported by Zhang et al. (2017), biomass fuels are characterized by a variable composition in terms of cellulose, lignin, proteins as well as organic and inorganic compounds, which significantly affects the generation of PCDD/Fs.

Hence, both the chemical composition and the initial concentration of dioxins in biomass can significantly determine the toxicity of solid products of thermochemical valorization of biomass. A crucial observation was also noted in the experiment concerning the distribution of dioxins, furans and polychlorinated naphthalenes isomers from the products of microwave-assisted woody biomass, where the authors reported that the dioxin and furan congeners profile after the process is not significantly changed (Gao et al. 2016b). Hence it is expected that the biomass's chemical composition may not have as much impact on the congeners' profile as actual concentrations (Gao et al. 2016b).

In the case of hydrothermal carbonization processes, a slightly different situation was noted since most of the substrates processed were sewage sludges (Fig. 6). In various articles, valorized products' toxicity was highly diversified, but most of the products were processed in different

technological parameters of hydrothermal carbonization. Liberatori et al. (2022) observed that the sludge hydrochar from 6 sources has significantly other toxicity equivalents in the range of 9.1 ng TEQ kg⁻¹–21.7 ng TEQ kg⁻¹. Based on this observation, the authors concluded that the final concentration and toxicity of the hydrochars were mainly due to the concentration of organic compounds in the unprocessed substrate. Similar results were observed by Tasca et al. (2022) investigating the toxicity of hydrochars produced from four different sewage sludge samples. Wiedner et al. (2013a, b) also pointed out that the selection of raw materials for the hydrothermal carbonization process should be preceded by essential care, significantly if they are contaminated with dioxins. In the case of sewage sludge, this is of particular importance as chlorinated organic compounds are absorbed into them since they will not permanently be removed entirely during various treatments in sewage treatment plants (Liberatori et al. 2022; Dai et al. 2007; Wu et al. 2009).

Besides this, three other substrates that underwent the hydrothermal carbonization process were found in the literature—leftover food, poplar wood and olive residues. Only the latter was characterized by the toxicity equivalent exceeding the limit detection, achieving a concentration of 8.1 ng TEQ kg⁻¹ (Wiedner et al. 2013a, b). Nevertheless, the detection limit for poplar wood and leftover food, which was 5.98 ng TEQ kg⁻¹, was relatively high compared to other materials.

Chlorine content

When chlorine is present, dioxins, furans and polychlorinated naphthalenes are known to form as trace elements in thermal processes (Gao et al. 2016a, b). Hale et al. (2012) observed that the produced biochar from food waste was characterized by significantly higher toxicity in terms of PCDD/Fs concentration than other substrates, which was related to the high presence of chlorine in the product. The importance of crucial role of chlorine was also observed during the microwave-assisted pyrolysis of woody biomass, where high concentrations of PCDD/Fs during the thermochemical treatment of tree bark proved the impact of the chemical composition of the raw material on the formation of these compounds (Gao et al. 2016a, b). Wiedner et al. (2013b), while producing biochars with dioxin contamination not exceeding the detection level, found that biomass raw materials were characterized by a shallow content of chlorine, which could prevent the formation of these compounds. However, the authors stated that when planning biochar production, it needs to avoid raw materials contaminated with chlorinated adhesives and use chlorine-free biomass feedstock.

An interesting phenomenon was also observed by Grafmüller et al. (2022), who, observing the increase in

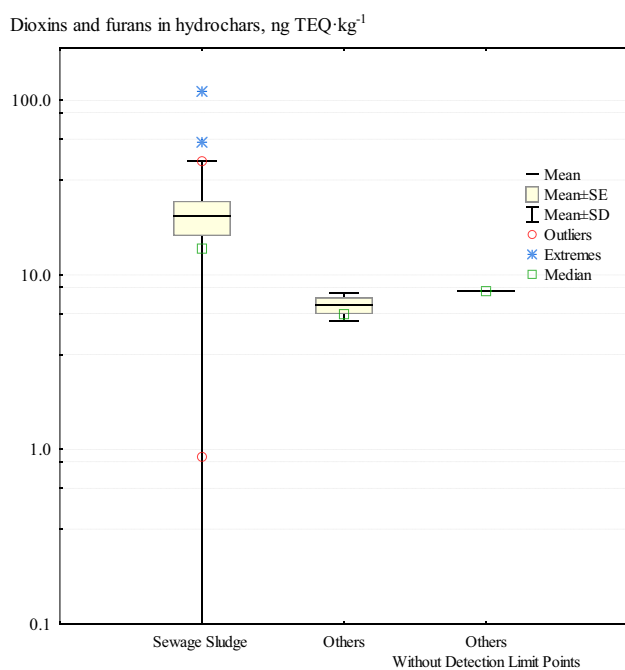


Fig. 6 Dioxin contamination of products of hydrothermal carbonization depending on substrate type including solid samples of sewage sludge ($n=22$), others ($n=3$) and others without detection limit points ($n=1$). TEQ denotes total toxic equivalence. SE represents standard error and SD represents standard deviation. Most of the materials tested during hydrothermal carbonization are sewage sludge, the average and median toxicity of which exceeds 10 ng TEQ·kg⁻¹, which is a relatively high result compared to other samples. In the future, other materials should be tested to better compare the results of sewage sludge with other types of materials

PCDD/Fs concentration after adding a high amount of ash to softwood, found that chlorine is a component of PCDD/Fs, therefore increasing the amount of it in the feedstock after adding wood ash, probably made polychlorinated contaminants more likely to form. It is widely recognized that the formation of dioxins in pyrolysis processes in the presence of chlorine is still a developing scientific topic but feasible (García-Pérez 2008; Sørmo et al. 2020), especially in the presence of such forms of chlorine as NaCl or MgCl₂, which may have different origins (Sørmo et al. 2020; García-Pérez 2008).

On the other hand, there are also different opinions, as Tirlir and Basso (2013) found that inorganic chlorine sources are insufficient to form PCDD/Fs compounds in hydrothermal carbonization conditions—based on a test experiment, where 1 g of sodium chloride was added to clay matrix. An interesting summary of the significance of the role of chlorine seems to be the statement of Gao (2016) Gao et al. (2017), who, in their works, did not always observe the upward trend of PCDD/Fs compounds with an increase in chlorine content. Hence they reported that the presence of chlorine in the biomass might be essential. However, it is not the only factor contributing to chlorinated compounds' formation (Gao et al. 2017; Gao 2016; Gullett et al. 2000).

Metal catalysts

There are also reports in the literature showing metals' catalyzing role in forming PCDD/Fs in the products of thermochemical biomass valorization. In general, it is well known that the presence of contaminants in the form of metal catalysts in biomass can stimulate the formation of PCDD/Fs in thermal processes (Zhang et al. 2017). In particular, metal oxides and chlorides are classified as highly catalytic compounds for the generation of PCDD/Fs (Cagnetta et al. 2016; Hagenmaier et al. 1987; Liao et al. 2016). Cagnetta et al. (2016) based on own and other works (Addink and Olie 1995; Weber et al. 2001; Hagenmaier et al. 1987; Lomnicki and Dellinger 2002) stated that the importance of the catalytic pathway is more substantial than homogeneous reactions and transition metals, both in the precursor pathway and de novo synthesis, significantly affect the intensification PCDD/Fs formation efficiency.

In a study on biomass torrefaction, Gao et al. (2017) found that the high presence of metals such as Cu and Fe in impregnated wood can act as a catalyst to enhance dioxin formation. Earlier, the same research team observed a similar phenomenon during microwave-assisted pyrolysis, whereby it was found that metal-based preservatives can affect the thermal degradation of biomass—and such action may support the generation of polychlorinated

compounds (Gao et al. 2016a; Tame et al. 2007). It is also worth mentioning an interesting observation related to the potential use of biochar, discovered by Edo et al. (2017), who found that after the thermochemical valorization process, the elements catalytically active, mainly Cu and Fe, remain in the biochar; therefore, when using this product for energy by combustion, these metals can support the formation of dioxins.

Perspective

Although the problem of the presence of PCDD/Fs in biochar and other products of thermochemical biomass valorization is relatively new, significant progress has been made in recent years to explain the determinants and mechanisms of the formation and transformation of PCDD/Fs compounds in these processes. However, there is still a substantial research niche in this field which is necessary to complete as it can be an essential step in clean biomass utilization and valorization processes. First of all, it is recommended to continue research in the field of low temperatures, especially the torrefaction process, with a correspondingly lower temperature interval than before to precisely determine the temperature at which a downward trend in the toxicity equivalent of PCDD/Fs will be observed. It is essential for the low-energy acquisition of materials that can be added to the soil or a dietary supplement for animal nutrition.

In addition, a necessary need for pyrolysis processes is to clarify to a greater extent the importance of the role of residence time for the presence of toxic PCDD/Fs congeners in the solid residue after the valorization process. Although it is generally known that process time is an essential factor determining the presence of dioxins in combustion processes (Stieglitz et al. 1989; von Eysler et al. 2014), there is a need for a more significant expansion of research on this topic in valorization processes. Hence, experiments conducted at a constant temperature but with a variable residence time may be helpful.

In the case of hydrothermal carbonization processes, there seems to be a high need to test more materials for the presence of toxic PCDD/Fs congeners, which will be differentiated in terms of chemical composition because sewage sludge was the most frequently evaluated substrate so far. It is also necessary to define the role of pressure to a greater extent by constant parameter monitoring during the process, which may help determine the range of pressures followed by a dramatic increase in PCDD/Fs concentration in the final product of processing. In addition, it may also be a vital step for all processes to determine the effect of the heating rate as a factor that could potentially affect PCDD/Fs formation. Further work on the content of

dioxins in biochars and hydrochars produced from biomass and organic waste from heavily polluted areas may also be a source of valuable scientific information.

From a technical point of view, it also seems crucial in the future to standardize the reporting of experimental results in terms of either one of the accepted toxic equivalents or both. Currently, reporting the results as a sum of 17 toxic congeners can significantly hinder the understanding of the mechanistic aspects of dioxin formation and transformation. Additionally, if the result is given only for one of the equivalents mentioned above, it may be a significant barrier when comparing the results with the research of other authors.

Conclusion

Biochars, hydrochars and torreficates are promising technologies that effectively use biomass and organic waste, which are by-products of other processes. The resulting high-quality products in thermochemical valorization processes, characterized by the possibility of multi-directional development, make them an ideal tool for implementing a circular economy. However, persistent organic pollutants present in chars, such as toxic PCDD/Fs, can significantly reduce the effectiveness of chars, questioning their safety and environmental neutrality.

The literature published so far shows that the content of dioxins in chars is highly diversified and depends on the valorization process. The highest risk of increased dioxin content is associated with chars produced in the low-temperature range between 200 and 300 °C, in processes such as torrefaction and hydrothermal carbonization. This is mainly because these processes may involve the dechlorination of more chlorinated congeners, mainly octachlorodibenzodioxin and heptachlorodibenzodioxin to less chlorinated congeners, which are characterized by higher toxicity factors. Additionally, the temperature in these processes is too low for the dioxins to be shifted into the gas phase. Modifying technological parameters of thermochemical valorization processes, particularly temperature, also significantly influences the char's quantitative and qualitative characteristics of dioxins.

It is also worth emphasizing that the conducted analysis showed high differences between the type of feedstock, its chemical composition and the final toxicity of the product after processing. First, to obtain dioxin-free char, it is necessary to avoid biomass and organic waste contaminated with chlorinated compounds or preservatives. In addition, an unprocessed feedstock that may be contaminated

with dioxins can also be risky in the chars production processes due to the potential transformation of PCDD/Fs to more toxic congeners. One should be aware, however, that dioxins will probably always be present in char matrixes in trace amounts, but their detection will be impossible due to detection limits. Nevertheless, we demonstrated that the vast majority of chars found in the literature were characterized by a dioxin content below 20 ng TEQ kg⁻¹, which is safe regarding the law regulations threshold as a soil additive.

The progress made in recent years in studying the content and main mechanisms of the formation and transformation of PCDD/Fs in chars has significantly contributed to the development of clean biomass valorization processes. Nevertheless, an extensive research niche and gaps still need to be completed, especially in low-temperature areas.

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Declarations

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Consent for publication Not applicable.

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