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RELEASE OF PCDD/Fs DURING A HYDROTHERMAL CARBONIZATION PROCESS OF ORGANIC WASTE RESIDUES

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In this paper the polychlorinated-dibenzo dioxins and furans (PCDD/Fs) release is analyzed during an hydrothermal carbonization process of the organic fraction of municipal solid waste (OFMSW). Two models to estimate the quantity of PCDD/Fs that can be released during this kind of process are presented in this paper. The first model follows a mass balance approach; the second one develops a phenomenon description based on the desorption mechanism. Finally, the effects of temperature and pressure on the whole yield of dioxins and furans are discussed.

Keywords: HTC, OFMSW, PCDD/F, modeling.

1. Introduction

Nowadays, the energy recovery of waste biomass is a more and more growing topic. Many processes to exploit these substrates have been developed, such as combustion, pyrolysis, torrefaction, gasification, biomass liquefaction, etc. Thermochemical processes, that are processes in which the inlet substrate is thermo-chemically treated without a drying pretreatment, have been studied both to stabilize the biomass to be disposed off in landfills and to obtain a carbon rich solid phase to be used in various ways: as a soil improver, as a potential way for carbon sequestration and storage, as activated carbon adsorbents, as a catalyst or for energy production and storage [1].

The hydrothermal carbonization (HTC) of the organic fraction of the municipal solid waste (OFMSW) is a quite new waste to energy pathway. The HTC thermo-chemically treats the feedstock and produces a solid phase, called hydro-char, with a carbon content higher than in the original substrate, a liquid

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phase with dissolved organic compounds and a small quantity of a gas phase mainly composed of carbon dioxide.

The HTC temperatures usually range between 180°C and 270°C. The pressure is held as high as to maintain water in its liquid phase (10 – 60 bar). This process usually is conducted at alkaline conditions (pH lower than 7). Typical residence times range between minutes to several hours. The residence time has the main effect to enhance the carbon content recovered within the hydrochar, but also to lower the total solid yield. More carbon is released into the liquid and the gaseous phase at longer residence times. Moreover, higher the temperature is, and hence higher the pressure is, higher the carbon content is in hydrochar, even though the total solid yield becomes smaller.

Lots of reactions could occur during the hydrothermal carbonization, the majority of them being the same that occur during a pyrolysis process. The HTC is mainly governed by hydrolysis, which breaks the ester and ether bonds of cellulose (at $T > 200°C$), hemicellulose (at $T > 180°C$) and lignin (at $T > 200°C$) [2, 3] by addition of water. Hydrolysis of hemicellulose produces acetic acid, D-xilose, D-manose, D-galactose and D-glucose. These last three are typically converted into 5-hydroxy-methyl-furfural (5-HMF) and then in formic or levulinic acid. The cellulose follows an analogous pathway, hydrolyzing into D-glucose, producing 5-HMF and subsequently into formic or levulinic acid. Lignin typically forms phenolic compounds. Hence, a portion of the hydrochar (the so called “coke”) is formed through the polymerization and the condensation of these water-soluble compounds. During the hydrothermal carbonization the lowering of the H/C and O/C ratios occurs, mainly because of the dehydration and the decarboxylation mechanisms. Hydroxyl groups are generally eliminated by dehydration, while carboxyl and carbonyl groups are involved during decarboxylation. Other mechanisms that may occur during the hydrothermal carbonization are demethylation, transformation reactions and pyrolytic reactions.

In HTC conditions, water changes its properties and its behavior becomes slightly similar to that of the organic solvents able to dissolve slightly polar compounds [2]. As a matter of fact, the pressurized hot water (PHW) has lower density, lower dielectric constant and near the critical point increases its capacity to solve hydrocarbons [3]. For these reasons, some hazardous compounds could dissolve in the pressurized hot water and could be removed from the biomass during the HTC process. Ones of these hazardous compounds are dioxins and furans (PCDD/F).

The behavior of PCDD/Fs has been not completely analyzed in these conditions of temperature and pressure. Some authors, however, have already studied the PCDD/Fs release during a bio-drying process of municipal solid waste [4, 5, 6, 7], in which these compounds already present in the biomass, were freed from the volatile matter (VM) consumed during the process. Other authors have examined the behavior of the subcritical water in the extraction of dioxins from contaminated soils [8] or the dechlorination process in supercritical water [9, 10, 11].

Dioxins, furans and their congeners are commonly regarded as highly toxic compounds. For this reason, the World Health Organization (WHO) established a tolerable daily intake (TDI) of dioxin based on a linear dose-response model. WHO proposes the range 1-4 pgTEQ/kg body weight on daily basis [12].

Taking into account the toxicity of these pollutants and their effect on human health, the knowledge of the conditions whereby these compounds could be found in the products obtained after a HTC process, becomes compulsory to estimate possible relapses that could produce negative effects on the environment and humans.

The presence of PCDD/Fs in the OFMSW has been studied and measured by many authors [13, 14, 15, 16]. As a matter of fact, dioxins and furans may be formed by natural sources in many ways [17, 18, 19, 20, 21, 22, 23]. Moreover, the use of chlorinated chemicals in the industry may produce PCDD/Fs that are consequently adsorbed in the organic materials [24]. PCDD/Fs can also be produced biologically and subsequently recovered in forest soils and sediments [25, 26].

The average content of PCDD/Fs in the OFMSW was estimated to range from 1 to 5 ng_{TEQ}/kg_{TS} [4]. The typical characteristics of the OFMSW treated during an HTC process are reported in *Table 1* [27].

Table 1

Average composition of the OFMSW [wt].

Humidity	Total Solids (TS)	Volatile Matter/Total Solids (VM/TS)
70%	30%	95%

2. The PCDD/Fs release model

Approaching hydrothermal processes by means of modeling tools could be beneficial in several scientific and technical fields: for instance to predict reaction products at equilibrium resorting to thermodynamics [28], to analyze the transient state and reaction kinetics paths [29], for process simulation and optimization [30].

In this paper, an analytical model describing the mechanisms that could be involved in the release of PCDD/Fs into the pressurized hot water used in the HTC process is presented and discussed. The analytical model is composed by two models: one that follows a mass balance approach and one that develops a phenomenon description based on the desorption mechanism.

The first step of the research was the development of a simple conceptual model. This first model is used to describe the release of PCDD/Fs from the OFMSW during an HTC process. It is based on the assumption that dioxins and furans are all linked to the total solids (TS) fraction of the organic wastes. The model couple the release of PCDD/Fs to the loss in TS during the carbonization process. Using the data reported in *Table 1*, the content of PCDD/Fs referred to one kilogram of OFMSW ($C_{PCDD/F}$) can be evaluated as:

$$C_{PCDD/F} = \left(1\div5\ ng_{TEQ}/kg_{TS}\right)\cdot(30\ wt.\%\ kg_{TS}/kg_{OFMSW}) = \\ = 0.3\div1.5\ ng_{TEQ}/kg_{OFMSW} \quad (1)$$

During a hydrothermal carbonization process, some authors [1, 31, 32] found that a percentage of the initial carbon content (20÷50 wt.%, referred to the initial weight of the dry matter) is lost in the water (equation 3). This carbon is mainly the one present in the VM. For the development of the research, it has been estimated that the release of PCDD/Fs congeners from the OFMSW could be roughly represented by the amount of PCDD/Fs congeners present within the VM that is lost and carried away by the water, during the HTC. In order to quantify the amount of PCDD/Fs congeners that could be found in the liquid and gaseous products of an HTC process, the average amount of VM contained in one kilogram of organic waste (C_{VM}) has been calculated as:

$$C_{VM}\ [kg_{VM}/kg_{OFMSW}] = C_{TS}\ [kg_{TS}/kg_{OFMSW}]\cdot\frac{VM}{TS}[kg_{VM}\\ /kg_{TS}] = 30\ wt.\%\cdot 95\ wt.\% = 0.285 \quad (2)$$

The volatile matter lost ($C_{VM,LOST}$) can be assessed as follows:

$$C_{VM,LOST}\ [kg_{VM}/kg_{OFMSW}] = C_{VM}\ [kg_{VM}/kg_{OFMSW}]\cdot 20\div\\ 50\ \% = 0.057\div0.1425 \quad)$$

Finally, the quantity of PCDD/Fs that could be found in the liquid and gaseous products after an HTC process has been estimated as follows:

$$Q_{PCDD/F}\left[\frac{ng_{TEQ}}{kg_{OFMSW}}\right] = \frac{C_{PCDD/F}\left[\frac{ng_{TEQ}}{kg_{OFMSW}}\right]}{C_{VM}\left[\frac{kg_{VM}}{kg_{OFMSW}}\right]}\cdot C_{VM,LOST}\left[\frac{kg_{VM}}{kg_{OFMSW}}\right] = 0.06\div\\ 0.71 \quad (4)$$

This first proposed model describes the pathways through which the molecules of PCDD/Fs adsorbed in the biomass (in this paper, the OFMSW) are released in the water during a hydrothermal carbonization process.

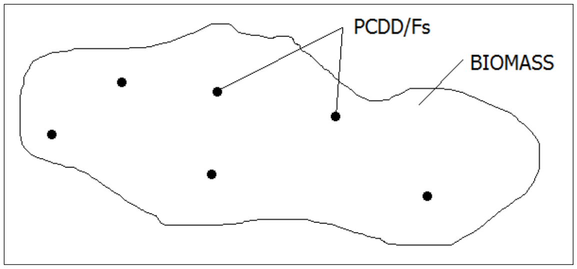

Fig. 1. The image represents the molecules of PCDD/Fs adsorbed on the surface of the biomass.

The biomass is set inside an HTC reactor and submerged in water (i.e., the solvent). A schematic representation of the process is proposed in Fig. 2. The biomass is kept inside the reactor for a preset residence time, while the hot pressurized water flows with a chosen velocity (hereinafter u_r).

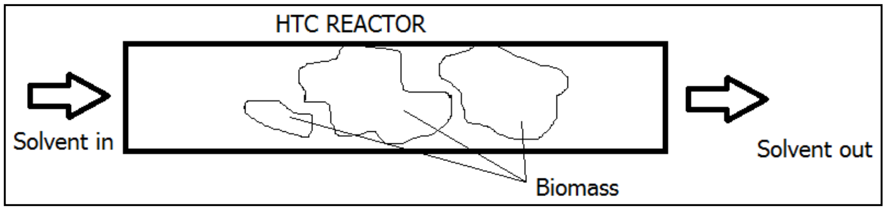

Fig. 2. Schematic representation of the process.

Taking into account that the PCDD/Fs molecules are linked to the organic carbon present within the biomass, two main pathways have been identified in order to describe how the congeners of the dioxin can leave the substrate. A general equation describing this behavior, can be written as:

$$\mathrm{M} = R + f_1(T) + f_2(P) + f_3(\tau) - f_4(ads) \tag{5}$$

where:

M	is the mass of PCDD/Fs released within the process water, $[\mathrm{ng_{TEQ}/kg_W}]$
R	is the mass of PCDD/Fs that leaves the biomass because of the loss of volatile matter
$f_1(T)$	is a functions which describes the influence of the temperature on the PCDD/Fs release
$f_2(P)$	is a functions which describes the influence of the pressure on the PCDD/Fs release
$f_3(\tau)$	is a functions which describes the influence of the residence time on the PCDD/Fs release
$f_4(ads)$	is a functions which describes the influence of the adsorption mechanism, that keeps the dioxin linked to the biomass

The effects of temperature, pressure and residence time seem to promote the release of PCDD/Fs. This is possible to the fact that the enhancement on these parameters typically contributes to enhance the amount of carbon that leaves the solid fraction of the biomass. On the contrary, the adsorption mechanism tends to keep the dioxin linked to the biomass (i.e., negative sign). Some simplifications are introduced and discussed in order to develop the research.

In a hydrothermal carbonization process, pressure is chosen so that the process water is maintained in its liquid state. As a matter of fact, it is possible to analyze the process in a “limit” condition, that is performed when choosing a couple of values of temperature and pressure referred to the saturation curve of water. In this manner, the pressure can be treated as a dependent variable. For this reason, it could be possible to consider to treat the two effects of temperature and pressure through only one function.

$$f_{SAT}(T,P) = f_1(T) + f_2(P) \tag{6}$$

Another simplification in the description of the phenomenon comes from the fact that the water solubility of apolar compounds under HTC conditions (mainly temperature) is quite low, even though it is higher if compared to the water solubility of these compounds under standard conditions. For this reason, we suppose that the effects of water on the congeners are only mechanical. This means that the hot pressurized water undermines the PCDD/Fs from the solid matrix but not dissolve them in itself.

The process can be seen also as the combination of three functions: a term describing the effects of the hydrothermal conditions ($R(\tau)$), a term related to the extraction mechanism of the PCDD/Fs from the solid matrix in which these compounds are adsorbed ($EX(\tau)$), and the adsorption term ($f(ads)$).

$$\mathrm{M} = R(\tau) + EX(\tau) - f(ads) \tag{7}$$

The first term on the right hand side of eq. (7) ($R(\tau)$), takes into account the fact that varying the hydrothermal conditions, the amount of carbon initially present in the biomass and transformed into a liquid or a gaseous phase changes. Once fixed the operational conditions in terms of process temperature and pressure, the amount of carbon that leaves the solid substrate depends only on the residence time (τ). Hence, supposing that when the carbon is transformed into liquid or gaseous compounds, the links between PCDD/Fs and that carbon are broken, it becomes possible to describe the PCDD/Fs release from the solid matrix through the same relationship which describes the carbon discharge, in terms of amount of carbon that leaves the original biomass. Thus, the mass of congeners of the dioxins and furans that leaves the solid substrate, will be strictly dependent on the kinetics of the HTC process.

The extraction term ($EX(\tau)$) takes into account the mechanical effects of the hot pressurized water on the PCDD/Fs adsorbed on the biomass. In general, in this term the convection effect of the solvent flux and the diffusion mechanism are considered. These quantities will be discussed in the following paragraph.

The third term ($f(ads)$) takes into account the mechanism of the PCDD/Fs adsorption on the biomass. This term has negative sign because it tends to keep the PCDD/Fs molecules linked to the solid substrate.

The second proposed model describes the release of PCDD/Fs from a solid substrate subjected to the thermo-physical conditions of a hydrothermal carbonization process.

$$\frac{\partial}{\partial t}\left(\varepsilon \cdot \rho_W \cdot \omega_{PCDD/F}^{W}\right) + \frac{\partial}{\partial t}\left[(1-\varepsilon) \cdot \rho_{biom} \cdot \omega_{PCDD/F}^{biom}\right] + \varepsilon \cdot \rho_W \cdot u \cdot \frac{\partial \omega_{PCDD/F}^{W}}{\partial x} - \varepsilon \cdot \rho_W \cdot D_{ax} \cdot \frac{\partial^2 \omega_{PCDD/F}^{W}}{\partial x^2} = 0 \quad (8)$$

where:

ε	is the void fraction (i.e. volume fraction not occupied by the solids), [m^3_{water}/m^3_{tot}]
ρ_W	is the water density, [kg_{water}/m^3_{water}]
$\omega_{PCDD/F}^{W}$	is the mass fraction of PCDD/Fs congeners present in the water, [ng_{TEQ}/kg_{water}]
ρ_{biom}	is the density of the biomass, [kg_{biom}/m^3_{biom}]
$\omega_{PCDD/F}^{biom}$	is the mass fraction of PCDD/Fs congeners present in the biomass, [ng_{TEQ}/kg_{biom}]
u	is the velocity of the solvent inside the plug flow reactor, [m/s]
D_{ax}	is the axial diffusion, [m^2/s]
x	is the longitudinal coordinate along the reactor

The effects of the hydrothermal process conditions, in terms of transformation of carbon into liquid or gaseous compounds, can be evaluated by imposing a mass balance on the solid fraction present within the reactor.

$$\frac{\partial}{\partial t}\left[(1-\varepsilon) \cdot \rho_{biom} \cdot \omega_{PCDD/F}^{biom}\right] = -K_R \cdot \left(\rho_{biom} \cdot \omega_{PCDD/F}^{biom}\right)^n + F(ads) \quad (9)$$

where:

K_R	is the rate of the carbon released in the liquid or gaseous phases with respect to the carbon initially present in the biomass, during an HTC process, [s^{-1}]
n	is the order of the reaction ($n \sim 1$), [-]
$F(ads)$	is the function which describes the adsorption mechanism that links the PCDD/Fs to the solid matrix, [$ng_{TEQ} \cdot m^{-3} \cdot s^{-1}$]

The term K_R can be evaluated considering the kinetic relationship that governs the hydrothermal carbonization process. A literature review [33] has highlighted that some authors evaluated this kinetics both through linear interpolations or through Arrhenius-type relations. Because linear interpolations usually suffer from the fact that they are built on experimental data, in this discussion an Arrhenius-type relationship has been used. Typical Arrhenius relationship has the form

$$K_R = A_R \cdot e^{-\left(E_{a,R}/_{RT}\right)} \tag{10}$$

where:

A_R is the pre-exponential factor
$E_{a,R}$ is the activation energy, [kJ/kg]
R is the gas constant, (8.3143 $\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
T is the temperature, [K]

If the chemical reaction has order 1, the rate constant (K_R) and the pre-exponential factor (or frequency factor, A_R) assume the measurement unit [s^{-1}]. The terms A_R and $E_{a,R}$ have to be evaluated experimentally, fitting eq. (10) to experimental measurements.

To obtain the whole physical description of the process, the adsorption term $F(ads)$, which takes into account the mechanism of PCDD/Fs adsorption on the organic carbon of the biomass (i.e., on the fraction of the total solids) must be determined. In literature there are many expressions for the evaluation of the adsorption mechanism:

$$A_D = C_{ads} \cdot e^{-(B_{ads} \cdot T)} \tag{11}$$

where:

A_D is the adsorption rate of PCDD/Fs on the biomass, [s^{-1}]
C_{ads} is a constant to be experimentally evaluated, [s^{-1}]
B_{ads} is a constant to be experimentally evaluated, [K^{-1}]
T is the temperature, [K]

Considering this expression, it is possible to determine the adsorption term as:

$$F(ads) = A_D \cdot \rho_W \cdot \omega^W_{PCDD/F} \tag{12}$$

Hence, the general equation of the model becomes:

$$\frac{\partial}{\partial t}\left(\varepsilon \cdot \rho_W \cdot \omega^W_{PCDD/F}\right) + \varepsilon \cdot \rho_W \cdot u \cdot \frac{\partial \omega^W_{PCDD/F}}{\partial x} - \varepsilon \cdot \rho_W \cdot D_{ax} \cdot \frac{\partial^2 \omega^W_{PCDD/F}}{\partial x^2} = \\ = K_R \cdot \left(\rho_{biom} \cdot \omega^{biom}_{PCDD/F}\right)^n - A_D \cdot \rho_W \cdot \omega^W_{PCDD/F} \tag{13}$$

3. Discussion

Eq. (13) has the following unknowns: $\omega^W_{PCDD/F}$, D_{ax}, A_R, $E_{a,R}$, $\omega^{biom}_{PCDD/F}$, C_{ads} and B_{ads}. The other parameters are all known and listed in *Table 2*.

Table 2

Known parameters of the model

Parameter	Description	Unit of measurement
u	Fixed *a priori*	$m \cdot s^{-1}$
ε	Fixed *a priori* on the basis of the charge of the reactor	$m^3_{water} \cdot m^{-3}_{tot}$
ρ_W	Evaluated in function of the temperature and pressure of the HTC process	$kg_{water} \cdot m^{-3}_{water}$
R	Gas constant	$kJ \cdot kg^{-1} \cdot K^{-1}$
ρ_{biom}	Average density of the biomass. Experimentally measured	$kg_{biom} \cdot m^{-3}_{biom}$
n	Reaction order (set to be a first order reaction)	--

The pre-exponential factor (A_R) and the activation energy ($E_{a,R}$), related to the hydrothermal conditions term, are linked to the carbon recovery mechanism which occurs during the hydrothermal carbonization. Therefore, having at disposal experimental data of carbon yield during an HTC process, it is possible to evaluate the two parameters, by applying the following procedure:

1. rewrite the Arrhenius relation present in eq. (10), taking the natural logarithm of all the terms:

$$\ln(K_R) = -\frac{E_{a,R}}{R \cdot T} + \ln(A_R) \tag{14}$$

2. plot $\ln(K_R)$ versus ${}^{1}/_{T}$, obtaining a straight line, whose gradient and intercept can be used to determine the two parameters (A_R) and ($E_{a,R}$).
3. the activation energy is defined to be $(-R)$ times the slope of a plot of $\ln(K_R)$ vs. ${}^{1}/_{T}$, hence:

$$E_{a,R} = -R\left[\frac{\partial \ln(K_R)}{\partial({}^{1}/_{T})}\right] \tag{15}$$

The moles of PCDD/Fs adsorbed in a kilogram of biomass (A_D) and the parameters C_{ads} and B_{ads}, can be evaluated experimentally following a procedure similar to that previously proposed for the Arrhenius relationship. Briefly, the equation to plot is:

$$\ln(A_D) = -(B_{ads} \cdot T) + \ln(C_{ads}) \tag{16}$$

The plot of $\ln(A_D)$ versus (T), will assess the values of C_{ads} and B_{ads}.

Therefore, to solve eq. (13), three other equations are needed, because of the number of the remaining variables ($\omega^{W}_{PCDD/F}$, D_{ax} and $\omega^{biom}_{PCDD/F}$).

A linearly independent equation useful to solve the system is obtained imposing an initial condition. At t = 0 it is supposed that no molecule of PCDD/Fs congeners are present within the water, so

$$\omega_{PCDD/F}^{W}\Big|_{t=0} = 0 \text{ ng}_{\text{TEQ}}/\text{kg}_{\text{W}} \tag{17}$$

This initial condition implies also the fact that the amount of PCDD/Fs present within the biomass can be evaluated as

$$\omega_{PCDD/F}^{biom}\Big|_{t=0} = \hat{q} \cdot \gamma_{TS} \text{ ng}_{\text{TEQ}}/\text{kg}_{\text{biom}} \tag{18}$$

where:

$\hat{q}$ is the average amount of PCDD/Fs present within the biomass before being processed (i.e., 1–5), [$\text{ng}_{\text{TEQ}}/\text{kg}_{\text{TS}}$]

γ_{TS} is the amount of total solids present inside the biomass, [$\text{kg}_{\text{TS}}/\text{kg}_{\text{biom}}$]

Another linear independent equation to exploit for the solution of the model can be evaluated by imposing a boundary condition. This condition describes the behaviour of the flux of solvent and of the axial diffusion near the inner surfaces of the HTC reactor. Under this condition

$$u|_{BC} = 0 \text{ m/s} \tag{19}$$

$$D_{ax}|_{BC} = 0 \text{ m}^2/\text{s} \tag{20}$$

and eq. (13) becomes

$$\frac{\partial}{\partial t}\left(\varepsilon \cdot \rho_W \cdot \omega_{PCDD/F}^{W}\right) = K_R \cdot \left(\rho_{biom} \cdot \omega_{PCDD/F}^{biom}\right)^n - A_D \cdot \rho_W \cdot \omega_{PCDD/F}^{W} \tag{21}$$

Eq. (21) has to be verified at every time at the boundaries.

The batch reactor solution is reported in this paragraph. In this case the HTC process is performed discontinuously and during the process the flux of solvent has no velocity ($u = 0$). An approximation has been introduced: considering that the system reaches the temperature and pressure typical of an HTC process (T = 180 – 250°C and P = 10 – 50 bar) very quickly, the release of PCDD/Fs during this transitory is considered to be negligible.

Thus, the model can be represented through the following equation:

$$\frac{\partial}{\partial t}\left(\varepsilon \cdot \rho_W \cdot \omega_{\frac{PCDD}{F}}^{W}\right) - \varepsilon \cdot \rho_W \cdot D_{ax} \cdot \frac{\partial^2 \omega_{\frac{PCDD}{F}}^{W}}{\partial x^2} = K_R \cdot \left(\rho_{biom} \cdot \omega_{\frac{PCDD}{F}}^{biom}\right)^n - A_D \cdot \rho_W \cdot \omega_{\frac{PCDD}{F}}^{W} \tag{22}$$

To evaluate the amount of organic carbon transformed into liquid or gaseous compounds (K_R) an Arrhenius-type relation has been chosen. Treating with experimental data, it might be useful to evaluate the kinetic of the HTC process through a modified Arrhenius' equation:

$$K_R = A_R \cdot \left(\frac{T}{T_0}\right)^n \cdot e^{-\left(E_{a,R}/RT\right)} \tag{23}$$

where:

T_0 is a reference temperature, [K]

n	is a unit less power ($-1 < n < 1$)

Another form that can be used to better fit the data is the so called stretched exponential form, reported in eq. (24).

$$K_R = A_R \cdot exp\left[-\left(\frac{E_{a,R}}{R \cdot T}\right)^{\gamma}\right] \tag{24}$$

where:

γ	is a dimensionless number of the order of 1

It could be of interest to evaluate the K_R term through linear relationships, which take into account the effects of some main parameters governing the HTC process. Hereinafter two relations are suggested.

$$K_R = \alpha_0 + \alpha_1 \cdot T + \alpha_2 \cdot \tau + \alpha_3 \cdot S \tag{25}$$

where:

α_i	are dimension less tuneable parameters, evaluated fitting experimental data
T	is the temperature, [K]
τ	is the residence time, [h^{-1}]
S	is the percentage of solids in the inlet, [-]

Eq. (25) can be written also in the following form

$$K_R = \alpha_0 + \alpha_1 \cdot \theta + \alpha_2 \cdot \vartheta + \alpha_3 \cdot \sigma \tag{26}$$

In this case, θ, ϑ and σ are the dimensionless temperature, the dimensionless residence time and the dimensionless percentage of solids in the inlet, respectively. These three dimensionless values can be evaluated choosing appropriate reference values of temperature, residence time and concentration.

If the pH has to be considered as influencing parameter, the following formulation can be proposed.

$$K_R = x_0 + x_1 \cdot T + x_2 \cdot \tau + x_3 \cdot pH \tag{27}$$

where:

x_i	are dimension less tuneable parameters, to be evaluated fitting experimental data
T	is the temperature, [K]
τ	is the residence time, [h^{-1}]
pH	is the pH of the reaction, [-]

The use of more than one relationship for the evaluation of the K_R term might be of interest in the study of the robustness of the model or when studying specific conditions of the process. The relationships can also emphasize the influence of particular parameters (for example, the pH).

4. Conclusions and developments

A novel approach on the description of the PCDD/Fs release during a hydrothermal carbonization process has been presented in this paper (no modeling of this phenomenon has been previously proposed in the HTC literature). This mathematical model predicts the amount of PCDD/Fs congeners that can be found within the liquid phase downstream of an HTC process. This amount is described through two pathways: the transformation of the carbon initially present within the inlet biomass into liquid and gaseous compounds (with the consequent release of the PCDD/Fs congeners into the liquid phase) and the effects of the solvent flux on the surface of the biomass. The model considers also the possibility for the PCDD/Fs congeners to be adsorbed on the surface of the biomass during the process.

Future work will be the validation of the model through experimental data and the improvement of the relationships which describe the kinetics of the HTC process and the adsorption mechanisms at the HTC process conditions. Moreover, it must be verified if the PCDD/Fs saturation conditions are reached in the liquid phase with the consequent release of these pollutants into the atmosphere. If these phenomena were dominant, according to eq. (4) the emission factor into the atmosphere could be higher than the one of a modern incinerator.

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