Prediction of the emission of dioxins and furans during processes of thermal degradation of waste

Damià Palmer Comas

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DOCTORAL THESIS

Title	Prediction of the emission of dioxins and furans during processes of thermal degradation of waste
Presented by	Damià Palmer Comas
Centre	IQS School of Engineering
Department	Departament d'Enginyeria Industrial
Directed by	Dr. Josep Oriol Pou Ibar Dr. Jordi Díaz Ferrero

"Veles e vents han mos desigs complir

faent camins dubtosos per la mar.

Mestre i ponent contra d'ells veig armar:

xaloc, llevant los deuen subvenir

ab llurs amics lo grec e lo migjorn,

fent humils precs al vent tramuntanal

que en son bufar los sia parcial

e que tots cinc complesquen mon retorn."

Ausiàs March

Agraïments

El desenvolupament d'aquesta investigació no hauria estat possible sense la col·laboració tant de persones com d'institucions que, des d'un punt de vista personal, científic, logístic o econòmic, m'han ajudat a assolir aquesta fita. A tots i totes us voldria fer arribar el meu agraïment més sincer.

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Content

Abstract

Municipal Solid Waste (MSW) generation has been increasing in the last 20 years in most countries in the EU. Its management, under the philosophy of the Circular Economy that the EU has adopted, is an important environmental challenge that the society must solve in the years to come. Since landfilling has been clearly stated as the last option to implement, and promoted to avoid, the use of MSW incinerators with energy recovery has been continuously increasing.

The formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) has been identified as one of the environmental issues related to MSW incineration. This family of molecules, which are demonstrated to be extremely toxic, are complex to monitor in real time during the execution of the incinerating process and the flue-gas cleaning. Thus, it is difficult to establish a control philosophy on the furnace parameters and the flue-gas cleaning system that optimizes its capture and reduces its formation.

This investigation establishes a mathematical model capable to predict the atmospheric emission of PCDD/Fs of a waste incineration process, based on process variables such as temperature, oxygen content, waste composition and chlorine and metals content. This model combines a kinetic model of formation of PCDD/Fs with a process model (using ASPEN HYSYS) that is able to determine all of the heat and material balance and convert the PCDD/Fs formation (in mass production per mass of waste incinerated) to an atmospheric emission (in mass production per volume flow of flue-gas at normal conditions).

In order to optimize this model, the number of PCDD/F congeners included in the model are reduced to only those whose formation is considered as linearly independent. This study is performed with a set of industrial data. The parameters of the model obtained were reviewed and statistically validated and determined with a mixture of industrial and laboratory-scale data.

Resum

La producció de Residu Sòlid Urbà (RSU) no ha parat d'incrementar en els últims 20 anys a la major part de països de la UE. La seva gestió, adoptant la filosofia de l'Economia Circular que ha promogut la UE, és un dels reptes ambientals que la societat ha de resoldre en els propers anys. Des de la declaració de l'abocament de residus com a última opció de gestió i, en la mesura del possible, opció a evitar, l'ús d'incineradores de RSU amb recuperació d'energia ha anat agafant protagonisme com a mesura de gestió de residus.

La formació de dibenzo-p-dioxines i dibenzofurans policlorats (PCDD/Fs) es considera com un dels problemes ambientals relacionats amb la incineració de RSU. Aquesta família de molècules, que han estat identificades com extremadament tòxiques, són complexes d'analitzar en continu en temps real durant el procés d'incineració i de neteja de gasos d'escapament. És per això que les filosofies de control són difícils d'optimitzar considerant la reducció d'emissió d'aquests contaminants.

Aquesta investigació estableix un model matemàtic capaç de predir l'emissió atmosfèrica de PCDD/Fs en processos d'incineració, basada en variables de procés com la temperatura, el contingut d'oxigen, la composició del residu o el contingut en clor i metalls. Aquest model combina un model cinètic de formació de PCDD/Fs amb un model del procés d'incineració (usant ASPEN HYSYS) que determina tot el balanç de matèria i energia; convertint així la quantitat de PCDD/Fs generades (en massa per massa de residu incinerada) en un valor d'emissió atmosfèrica (en massa de contaminant per volum de gas de combustió emès en condicions normals).

Amb l'objectiu de simplificar aquest model, la quantitat de congèneres de PCDD/F inclosos al model es redueix a només aquells als que la seva formació es considera linealment independent. Aquest estudi es realitza amb un conjunt de dades d'emissions industrials, i després es revisa, i els paràmetres del model obtingut es reajusten i es validen estadísticament amb una mescla de dades d'origen industrial i d'experimentació en laboratori.

Resumen

La producción de Residuo Sólido Urbano (RSU) no ha cesado en su incremento, en los últimos 20 años, en la mayor parte de países de la UE. Su gestión, adaptada a la filosofía de la Economía Circular que ha adoptado la UE, es uno de los retos ambientales más significativos que la sociedad deberá resolver en los próximos años. Desde que el vertido de residuos ha sido claramente definido como la última opción de gestión, e incluso señalada como una opción a evitar, el uso de incineradoras de RSU con recuperación de energía han ido ganando protagonismo como medida de gestión de residuos.

La formación de dibenzo-p-dioxinas y dibenzofuranos policlorados (PCDD/Fs) se considera como uno de los problemas ambientales relacionados con la incineración de RSU. Esta familia de moléculas, que han sido identificadas como extremadamente tóxicas, son complejas de analizar en continuo durante el proceso de incineración y lavado de gases. Es por esto que las filosofías de control son difíciles de optimizar considerando la reducción de la emisión de estos contaminantes.

En esta investigación se establece un modelo matemático que estima la emisión atmosférica de PCDD/Fs en procesos de incineración, basada en variables de proceso como la temperatura, el contenido de oxígeno, la composición del residuo o el contenido en cloro y metales. Este modelo combina un modelo cinético de formación de PCDD/Fs y un modelo del proceso de incineración (usando ASPEN HYSYS) que determina todo el balance de materia y energía; convirtiendo así la cantidad de PCDD/Fs generadas (en masa de contaminante por masa de residuo incinerado) en un valor de emisión atmosférica (en masa de contaminante por volumen de gas de combustión emitido en condiciones normales).

Con el objetivo de simplificar este modelo, la cantidad de congéneres de PCDD/F incluidos en el modelo se reduce a solamente aquellos cuya formación se considera linealmente independiente. Este estudio se realiza con un conjunto de datos de emisiones industriales, y luego se revisa, y los parámetros del modelo se reajustan y validan estadísticamente, con una mezcla de datos de origen industrial y de experimentación en laboratorio.

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Nomenclature

Symbol	Description	Units
b_j	Parameters of a lineal regression for congener j	-
C_j	Amount of each congener j	log(pg/g)
C_{TOT}	Total amount of PCDD/F in the sample	log(pg/g)
E_1	Activation Energy for all $k'_{1,i}$	kJ/mol
$E_{1,i}$	Activation Energy for each $k'_{1,i}$	kJ/mol
E_2	Activation Energy for k_2	kJ/mol
f_i	Yield coefficient of PCDD/F formation	g / g of waste
$\mathbb{H}$	Hat matrix (p x p)	-
I-TEF	Toxicity Equivalency Factor of the congener i	pg of 2,3,7,8-TCDD / pg of i
K_{Cl}	Constant of saturation of the chlorine	g Cl / g waste
K_{Me}	Constant of saturation of the metal content	(g Fe + g Cu) / g waste
$k_{1,i}$	Kinetic constant of formation for the congener i	pg PCDD/F / (g · s)
k_2	Kinetic constant of combustion of PCDD/F	s^{-1}
k_{20}	Value for k_2 at a defined temperature (993K)	s^{-1}
$k'_{1,i}$	Kinetic constant of formation for the congener i	pg PCDD/F / (g · s)
$k'_{10,i}$	Value for $k'_{1,i}$ at a defined temperature (993K)	pg PCDD/F / (g · s)
L	Length of the tube occupied by the residue	m
m_i	Amount of each dioxin's congener i	pg of i / g
$\dot{m}_{air}$	Mass flow of air	kg/s
$\dot{m}_{O_2}$	Mass flow of oxygen	kg/s
m_{sample}	Mass of the sample	kg
n	Amount of observations	-
O.F.	Objective function to minimize	-

Symbol	Description	Units
p	Amount of regressors	-
R	Gas constant	J / (K · mol)
$\mathbb{R}$	Pearson correlation coefficient (r) matrix	-
T	Temperature	K
TEQ	Toxic Equivalent of the mixture	pg of 2,3,7,8-TCDD / g
T_{TOT}	Total TEQ of the sample	log(pg TEQ / g)
ν	Linear velocity of the sample in the tube	m/s
VIF_i	Variance inflation factor of the regressor i	-
$\mathbb{X}$	Dataset matrix (n x p) used to fit the models	pg / g
λ	Oxygen ratio	-
λ_C	Corrected oxygen ratio	-

1. Introduction to Municipal Solid Waste management: dealing with a growing challenge

1.1 Generation and characterization in Europe

Waste management has been identified as one of the most determinant topics to work on in order to stablish a sustainable model in the European Union (EU) in the years to come. This EU policy has been started by developing an extensive monitoring system using EUROSTAT as its main tool. It has been followed by the main Directive 2008/98/EC of the European Parliament and of the Council, where many measures to protect the environment and human health by focusing on the generation and management of waste were settled. Furthermore, the Directive also pretended to reduce the impacts of resource use by improving the efficiency, to push forward the transition to a circular economy and ensure the future competitivity of the UE member states. This Directive has been amended and actualized by Commission Decisions (European Commission, 2014) and other Directives (European Parliament and of the Council, 2018).

In order to properly identify the scope of actuation of the Directive 2008/98/EC, some operational definitions are settled. Any substance or object is defined as *Waste* when it is discarded or is pretended to be discarded. The attribution of *hazardous waste* is also given to all wastes with other special properties such as explosive, oxidizing, flammable, irritant, toxic, carcinogenic, corrosive, mutagenic and/or ecotoxic. The concept of *municipal solid waste* (MSW) is defined as waste from households, including cardboard, glass, metals, plastic, biowaste, wood, textile, packaging, electrical and electronical waste, and bulky waste such as mattresses and furniture; whatever the waste is separately collected or mixed. This definition of MSW also includes waste from other sources as long as it is similar in nature and composition to waste from households, like the waste produced in shops and stores, bars and restaurants, institutions, etc. All of the waste from production, agriculture, forestry, fishing, septic tanks and sewage sludge, vehicles and construction and demolition waste are strictly excluded from this category.

Taking all this into consideration, and with the aim of simplifying the identification of each type of waste, a wide extended list was elaborated as an Annex of the Commission Decision 2014/955/EU. This list uses a full code of six digits, which are organized as 3 pairs of digits. The first pair is used to identify the general source of the waste, and it is related to the Chapter on the list (from 1 to 20), as it is shown in Table 1. The second digits pair is used to subcategorize the source of the waste, while the third digits pair is used to add some properties of the waste that can affect to the treatment needed (such as the metal content, the chloride content, the biological origin of a tissue, etc.).

Table 1. Chapters used to define the list of wastes at Commission Decision 2014/955/EU.

Chapter	Origin of the waste
01	Wastes resulting from exploration, mining, quarrying, physical and chemical treatment of minerals
02	Wastes from agriculture, horticulture, aquaculture, forestry, hunting and fishing, food preparation and processing
03	Wastes from wood processing and the production of panels and furniture, pulp, paper and cardboard
04	Wastes from the leather, fur and textile industries
05	Wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal
06	Wastes from inorganic chemical processes
07	Wastes from organic chemical processes
08	Wastes from the manufacture, formulation, supply and use (MFSU) of coatings (paints, varnishes and vitreous enamels), adhesives, sealants and printing inks
09	Wastes from the photographic industry
10	Wastes from thermal processes
11	Wastes from chemical surface treatment and coating of metals and other materials; non-ferrous hydro-metallurgy
12	Wastes from shaping and physical and mechanical surface treatment of metals and plastics
13	Oil wastes and wastes of liquid fuels (except edible oils, 05 and 12)
14	Waste organic solvents, refrigerants and propellants (except 07 and 08)
15	Waste packaging: absorbents, wiping cloths, filter materials and protective clothing not otherwise specified
16	Wastes not otherwise specified in the list
17	Construction and demolition wastes (including excavated soil from contaminated sites)
18	Wastes from human or animal health care and/or related research (except kitchen and restaurant wastes not arising from immediate health care)
19	Wastes from waste management facilities, off-site waste water treatment plants and the preparation of water intended for human consumption and water for industrial use
20	Municipal wastes (household waste and similar commercial, industrial and institutional wastes) including separately collected fractions

To go more into detail of the use of this categorization, and as an example, municipal solid waste is included in chapter 20, without discrimination on the composition, or in the system of collection of the separated fractions, as long as the origin of the waste are households, or commercial, industrial or institutional wastes that are similar to households. The second pair of digits is used to classify the MSW into three subchapters: separately collected fractions (as 20 01), garden and park wastes (as 20 02) and other municipal wastes (as 20 03). The third pair of digits is used mainly to define the composition of the fraction (glass, textiles, paper, oil and fat, paint, metals, etc.) but also an even more concrete source of the waste (street-cleaning residue, chimney sweeping waste, sewage cleaning waste, etc.).

This Commission Decision also determines that all wastes containing polychlorinated dibenzo-p-dioxins (PCDD/Fs) exceeding a certain concentration limit are considered as hazardous. These molecules are persistent organic pollutants produced during combustion processes which toxicity is related to many diseases such as reproductive disorders, immune system disorders and cancer.

The strategy of categorizing the wastes into a list has been reproduced at all administration levels: local, regional, or national. As an example, the Decree 152/2017 from the Generalitat de Catalunya proposes a classification, codification, and waste management preferent routes for each waste in Catalonia. This regulation is constructed in base of the Commission Decision 2000/532/CE, which was approved some years before the one used for defining Table 1, but where same structure for waste categorization is used. Furthermore, this Catalan decree stablished some criteria on waste management and energetic valorisation, including also a sanctioning system in case of the infringement of the disposition (Generalitat de Catalunya, 2017).

The amount of MSW generated in the European Union increased up to 513 kg per capita in 2000, from that point it began to decrease to 480 kg per capita in 2015 (EUROSTAT, 2022). The MSW generation has been slightly increasing since then until 2020, where the average generation reached a value above 500 kg per capita again. Detailed data per country per year is shown in Table 2.

Table 2. Municipal waste generated, in the EU environment, in selected years, from 1995 to 2020. Source: Eurostat

	1995	2000	2005	2010	2015	2020	Change 2020/1995 (%)
EU	*467*	*513*	*506*	*503*	*480*	*505*	*8.1*
Belgium	455	471	482	456	412	416	-8.6
Bulgaria (2)	694	612	588	554	419	444	-36.0
Czechia	302	335	289	318	316	507	67.9
Denmark	521	664	736	758	822	845	62.2
Germany	623	642	565	602	632	632	1.4
Estonia	371	453	433	305	359	383	3.2
Ireland (1)	512	599	731	624	557	625	22.1
Greece (1)	303	412	442	532	488	525	73.3
Spain	505	653	588	510	456	455	-9.9
France	475	514	529	534	516	537	13.1
Croatia	220	262	336	379	393	418	90.0
Italy (1)	454	509	546	547	486	505	11.2
Cyprus	595	628	688	695	620	609	2.4
Latvia	264	271	320	324	404	478	81.1
Lithuania	426	365	387	404	448	483	13.4
Luxembourg	587	654	672	679	607	790	34.6
Hungary	460	446	461	403	377	364	-20.9
Malta	387	533	625	623	641	643	66.1
Netherlands	539	598	599	571	523	535	-0.7
Austria (1)	437	580	575	562	560	585	33.9
Poland	285	320	319	316	286	346	21.4
Portugal	352	457	452	516	460	513	45.7
Romania	342	355	383	313	247	287	-16.1
Slovenia	596	513	494	490	449	487	-18.3
Slovakia	295	254	273	319	329	433	46.8
Finland	413	502	478	470	500	596	44.3
Sweden	386	425	479	441	451	431	11.7
Iceland (2)	426	462	516	484	588	702	64.8
Norway	624	613	426	469	422	726	16.3
Switzerland	602	659	664	711	728	706	17.3
United Kingdom (2)	498	577	581	509	483	463	-7.0

It is difficult to determine a global pattern for the data showed. Those values of waste production per capita for 2020 vary in a wide range, from 845 kg from Denmark to 282 kg from Romania. The impact on the waste generation based on the per capita income, the style consumption of the society and the economic sector which predominates (such as tourism, industry, or primary production) is well known (EUROSTAT, 2022), but not completely reflected on the results since a combination of all of them is possible. It is also known that many countries have different solid waste collecting systems. Even into the same country, different regions may have different collecting systems. This incomplete collection of all waste production, or the fact of only collecting the fractions of MSW separately in the biggest cities, seems to be one of the factors that most affect to the data shown, since many data provided are estimations, or are only referred to the big urban centres, not taking into consideration the impact of the countryside.

When referring to the MSW composition, many similarities between its content from the areas with nonsegregated collecting systems are observed (Wikstrom and Marklund, 1998). When a developed waste management system is implemented, the social and economic use of the resources on that area have more impact on its waste composition. It is also determined that most of the MSW generated (60%) is considered to come from a biogenic origin (EUROSTAT, 2022).

With the aim of simplifying the categorization of MSW based on its composition and following a similar strategy as per the classification shown in Table 1, some wider categories considering its future treatment are commonly used. These categories are listed as follows.

- Organic matter (including food leftovers, gardening waste…).
- Paper and carboard.
- Glass (sometimes including pottery and ceramic waste).
- Plastics (whatever the polymer is used).
- Metals (such as electronical waste, cables, etc.)
- Others (basically textile, wood and small furniture)

Table 3 shows a compilation of the weight percent composition of the municipal solid waste for most of the countries of the European Union based on the categories explained before (Karak et al., 2012). Data in that table confirms that, as average for all of the countries and years studied, over the 60% of the MSW weight comes from a biogenic origin, when organic matter and paper and cardboard are considered.

Table 3. Weight percent (%) composition of MSW in most of the EU countries, in selected years, compiled by Karak et al., 2012.

Country	Year	Organic Matter	Paper	Glass	Plastics	Metals	Others
Austria	1999	30.0	27.0	11.0	13.0	7.0	12.0
	2004	35.0	22.0	8.0	11.0	5.0	19.0
Belgium	1995	41.0	16.0	6.0	5.0	3.0	29.0
	2003	39.0	17.0	7.0	5.0	3.0	29.0
Denmark	1979	34.0	34.0	6.0	7.0	5.0	14.0
	2003	29.0	27.0	5.0	0.8	6.0	32.2
Finland	1990	30.0	51.0	6.0	5.0	2.0	6.0
	2000	33.0	40.0	5.0	10.0	5.0	7.0
France	2002	32.0	20.0	10.0	9.0	3.0	26.0
Germany	1983	43.1	18.7	11.5	6.1	3.9	16.7
	2005	30.0	24.0	10.0	13.0	1.0	22.0
Greece	2001	47.0	20.0	4.5	8.5	4.5	15.5
Italy	2005	29.0	28.0	13.0	5.0	2.0	22.0
Ireland	2005	25.0	31.0	5.0	11.0	4.0	23.0
Luxembourg	1995	35.0	24.0	16.0	2.0	7.0	16.0
	2003	45.0	22.0	12.0	0.8	4.0	16.2
Netherlands	1996	30.0	32.7	3.4	4.2	5.5	24.2
Portugal	1994	34.0	23.0	5.0	12.0	3.0	23.0
	2001	35.5	25.9	5.4	11.4	2.6	19.2
Spain	2002	48.0	21.0	8.0	12.0	4.0	7.0
Sweden	2002	39.0	40.0	6.2	6.8	4.9	3.1
United Kingdom	1996	33.5	26.4	5.7	8.9	8.8	16.9
	2005	32.7	23.3	4.3	23.7	6.2	9.8
	2009	41.0	18.0	7.0	7.0	8.0	19.0

Some countries report to EUROSTAT their MSW composition, but that information is not included in their reports since not enough EU members have these data available. As an example, Spain published its last report about MSW generation and management for the year 2020. It can be concluded there that, if the undifferentiated MSW is excluded, around 60% of the MSW may be considered from a biogenic origin (Instituto Nacional de Estadística, 2020).

The elementary composition of the general MSW has been barely studied due to its variability and difficulty to achieve a homogeneous laboratory-scale sample. As a case study, a laboratory MSW was produced, which elementary content was based on the MSW composition from Sweden (Wikstrom and Marklund, 1998). For this case, organic matter represented 49%, paper represented 18%, plastic represented 8%, glass and metals represented 2% each, and others (basically textile) represented the sum to 100%. This composition was in accordance with the data shown in Table 3. The results of the elementary content of the artificial MSW in that study are shown in Table 4.

Table 4. Elementary content (in dry weight %) of an artificial MSW based on the composition of the waste from Sweden.

Element	% DW
Ash	11.0
S	0.24
C	54.2
H	7.0
N	2.0
O	25.6
Cl inorganic	0.33
Cl organic	0.37

On the other hand, the elementary content of a variety of fractions of MSW has been studied, such as electronic waste (Conesa and Soler, 2017; J Moltó et al., 2009; Moltó et al., 2011), viscoelastic polyurethane foam (Garrido et al., 2016a), PVC (Aracil et al., 2005), sewage sludge (Fullana et al., 2003), etc. Many of these publications have been used in Chapter 5 for determining a model able to predict the formation of dioxins during its combustion.

1.2 Waste Treatments – The Circular Economy Philosophy

When referring to waste management, the concepts of sustainability and sustainable development become essential and play a key role in its evolution.

The concept of sustainable development was initially overheard during the United Nations convention called Conference on the Human Environment in 1972, also known as Stockholm Conference. Back in the 60s many countries from the developed world started to protect the environment inside their countries. Governments of the developed world quickly realized that the environment impacts could not be stopped at the borders, thus a common framework and a series of coordinated actions needed to be settled. That conference agreed that the occidental developing model has indissoluble negative environmental impacts, since the economic growth is based on the use of resources and the generation of waste. Based on that, a limiting scale of time was settled, since the regeneration of resources and the absorption of the wastes are not immediate (The United Nations, 1972). After that and aggravated by the economic crisis resulting from the oil crisis in October 1973, it started to grow the idea of the limitless growing of the economy was impossible due to natural limitations. Based on that, a model of no-growth to promote a steady state economy started to be proposed (Meadows and Meadows, 1972).

The exact term of Sustainable Development was literally used as a part of a United Nations report called “Our Common Future” published in 1987. This report, also known as Brundtland Report, defines the concept of sustainable development in its Chapter II, as a process of change in which the exploitation of resources, the investments, the technological development, and the institutional change are all in harmony and enhance both current and future potential to meet human needs and aspirations (Brundtland, 1987).

The concept of sustainable development was reinforced after another United Nations conference in Rio in 1992, also known as the *Earth summit*. On that conference, the global effect of the environmental problematic was highlighted, and the need of coordinated actions made by all of the administrations and institutions was encouraged. On the socio-economical contribution to sustainable development, the interrelation between the growth of some countries and the lack of development of the major part of the remaining countries was also an agreement, as well as the global effect of the environmental degradation and the future problems to come due to the unsustainability of the actual system (The United Nations, 1992). The *Earth Summit* pretended to put the focus on the actions needed. Thus, a program to implement a sustainable development, from a local perspective, in all regions (parties), was approved. This document, known as Agenda 21, also included the necessity of making a planification of this transition integrating the participation of the common population (The United Nations, 1992).

Continuing with the idea of acting on the matter, the United Nations Framework Convention on Climate Change entered into force in 1994. This Convention identified the problematic associated to Greenhouse Gas emissions and set as a goal to stop the increase of its concentration levels in the atmosphere. The Kyoto Protocol, approved in 1997 by the United Nations (and fully valid since 2005 after a long ratification process), set de development strategy of the dispositions approved in the Framework Convention. As a main tool, the Kyoto Protocol established a significant limitation on the greenhouse gases emission for all of the developed countries (which are identified in its Annex B). The Kyoto Protocol created a trading system of emissions. Thanks to that, the developed countries were able to buy emission allowances to other countries that did not reach their limit. This emission market pretended to encourage the reduction of emissions in those countries where the economic cost of reduction was lower. This system also helped to increase the investment in countries in process of development. The Kyoto Protocol also stablished a monitoring system to ensure that the emission limits were obeyed (The United Nations, 1997). Thanks to the United Nations work related to sustainable development, most of the institutions from developed countries themselves took the lead of the regulation and legislation related to its own environment. Once this key role was taken by the European institutions, the implementation of a circular economy has become the main strategy to ensure the sustainable development.

Even though the concept called circular economy has plenty of interpretations (Kirchherr et al., 2017), there are several inputs around it that have a general agreement. As a main idea, a circular economy is one that keeps the value of a product as much as possible, by preventing the generation of waste. This strategy pretends to keep the product itself in use, before taking into consideration only the material that builds the product. Once not even its matter keeps a value, the energy within the product is still considered, just before its final disposal. As a main idea, a higher level of circularity ensures less use of natural resources and less environmental impact.

There are several strategies to increase the circularity that involve all of the stages of the production chain (Potting et al., 2017). As a general rule, an increase in the circularity supposes less environmental pressure and consumption of natural resources. Taking into consideration the innovations related to product design, first strategies pretend to develop a smarter product refusing the loss of utility of the product (R0), or even rethinking the product increasing its functions to more than one (R1). Once the idea is projected, it is desired also to increase the efficiency of the design by reducing the use of raw materials and natural resources. This strategy is commonly known as eco-design (R2).

Once the product is manufactured, strategies that pretend to extend the durability of the product or its parts are suggested. As a first try, it is proposed the reuse of a product (R3) by a second consumer that considers it still in a proper quality. If the quality is not enough, it can be repaired (R4) to reach the minimum standards needed to continue using it. If this restoration needs an important actualization it is considered as a refurbish (R5) or a remanufacture (R6) in case that only some parts of the product can be used, mixing them with new parts. If the product loses its original purpose, but it can be used with a new function, a repurpose (R7) is considered.

In any case of a product (or a part of it) that is no longer usable, the product wasted can be processed to obtain recycled (R8) raw materials. Best techniques allow to keep the original quality of the material, but other technologies need to mix the recycled matter with new raw materials.

When the excessive degradation during the process makes recycling impossible, the last strategy is the recovery of the energy within the materials by incinerating (R9) it. This last strategy should be the main substitute for landfilling or a disposal of any material which its energy is not considered.

The implementation of an appropriate waste management system has been identified as an efficient tool to reduce the greenhouse gas emission (Stanković et al., 2021). In the early 2000s, the waste management operations all over the EU countries were commonly divided in two big groups: the recovery treatments and the disposal treatments. The recovery treatments englobed all those that allowed the residue to have a secondary useful purpose, such as recycling, reusing, used for backfilling excavated areas or incinerating with energy recovering. The disposal treatments englobed landfilling, incinerating without energy recovering or other disposal methods such as secure landfill disposal. During the period 2004-2018 the amount of waste recovered in the EU increased continuously from 45.9% to 54.6%, even considering than the total amount of waste treated increased by 15% in the same period, up to a total amount of more than 2000 million tonnes. This trend can be seen in Figure 1, where the amounts of waste treated, waste recovered, and waste disposed are shown. Note that the values for year 2004 are given as a reference (index value = 100) and all of the series of data are calculated proportionally to it.

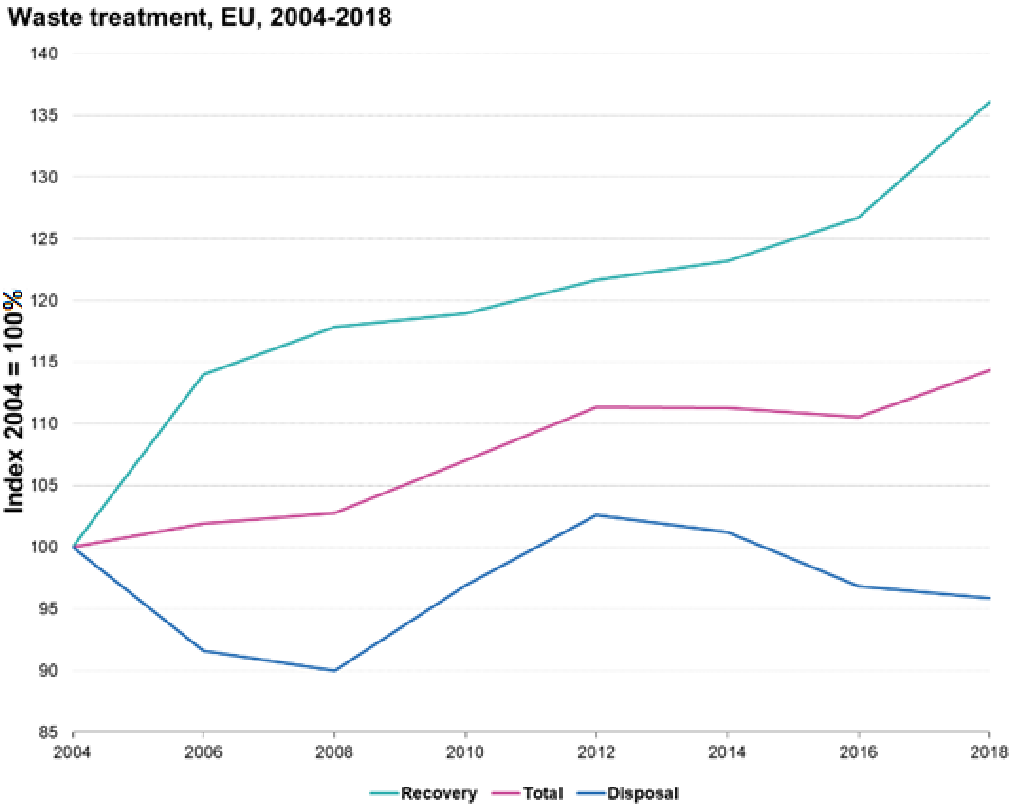


Figure 1. Total waste treated, waste recovered and waste disposed in the EU in the period 2004-2018. Note that the values for year 2004 are given as a reference (index value = 100) and all of the series of data are calculated proportionally to it. Source: EUROSTAT

To be more precise, all over the EU, in 2018, 37.9% of the waste was recycled, 10.7% was used for backfilling, and 6% was incinerated with energy recovery. The remaining waste was mainly landfilled (38.4%) and incinerated without energy recovering (0.7%) (EUROSTAT, 2022).

Directive 2008/98/EC also lays down measures to reduce the impacts of generation of waste by giving some principles of waste management. Article 4 of the document settles a waste hierarchy that should be promoted all over the EU. In few words, when prevention of waste generation is not possible, four stages are defined and only when the previous stage cannot be applied, the next stage is proposed. The aim of this strategy is to deliver the best environmental solution. From highest to lowest priority:

1. Prevention
2. Re-use
3. Recycling
4. Other recovery such as incineration with energy recovery
5. Disposal

This article has been widely extended and adapted to each national rules, taking part of most of the dissemination campaigns on proper waste management.

That directive also establishes the bases of responsibility for the producer or holder of waste. The aim of this article is not to excessively delegate it down among the treatment chain and ensure that all of the actors involved in a product (from production to distributors) share the responsibility of a correct waste management, including the collection system, the transport to the operation, and the operation itself.

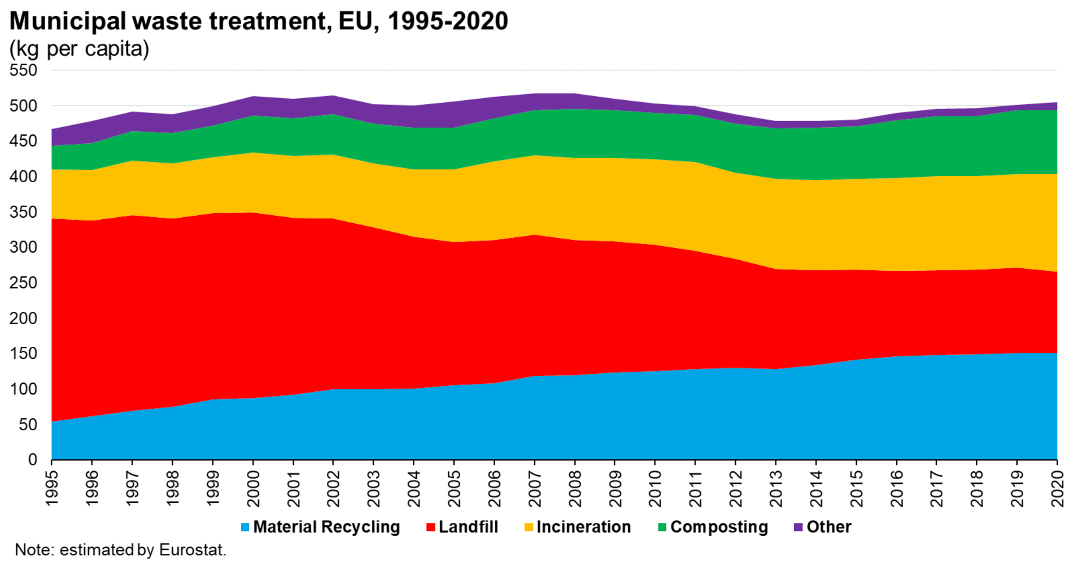
The regulation also encourages each member state to work on its self-sufficiency and proximity in terms of waste management facilities and disposal installations, considering the best available techniques, as per defined since the Council Directive 96/61/EC.

Annex I and Annex II in Directive 2008/98/EC exactly defines 15 disposal operations (D1-D15) and 13 Recovery operations (R1-R13), which include all of the accepted methods to manage waste in the EU.

Since the beginning of the 21st century, the European Union has undoubtedly supported the valorisation of municipal solid waste, encouraging the implementation of management systems where the incineration of this waste should be a priority rather than landfilling (European Parliament and of the Council, 2008). These politics address to stop the landfilling and to implement other final treatments according to the concepts of circular economy (Hogg et al., 2002). In order to fulfil this project, most countries in the European Union have promoted the construction of municipal solid waste incineration facilities (European Commission, 2016). These waste to energy strategies can be considered a powerful tool to achieve the objective of a circular economy (European Commission, 2017).

All of the energy obtained through the combustion of the biogenic content in the MSW is considered as renewable energy (Cheng and Hu, 2010; Glover and Mattingly, 2009; U.S. Department of Energy, 2007; U.S. Environmental Protection Agency, 2014).

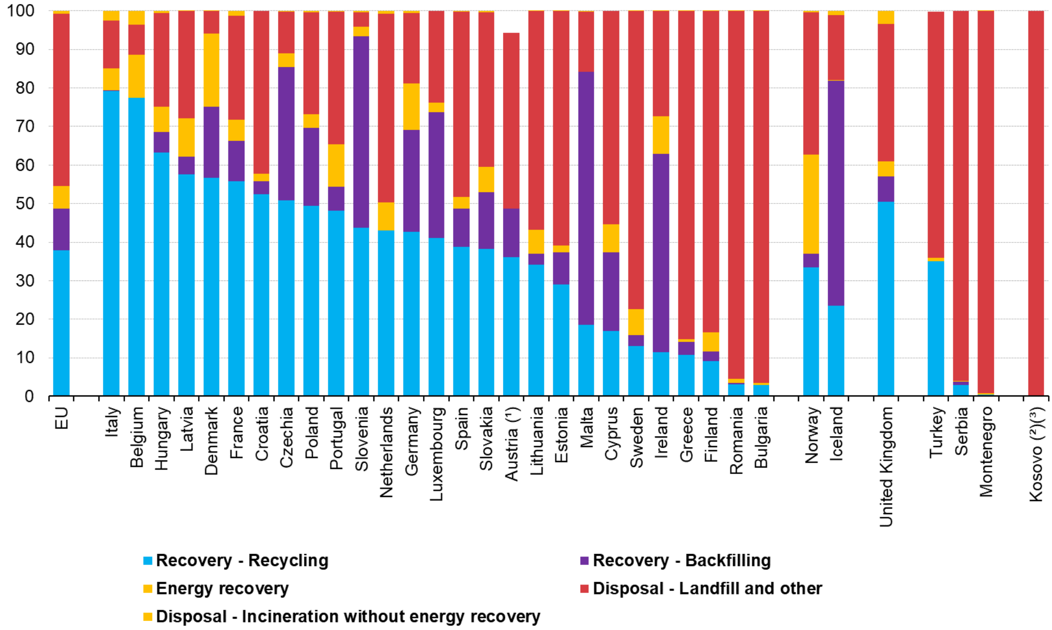
When MSW treatment is taken into consideration, it is noticeable in Eurostat publications that, landfilling is being substituted by other methods that fulfil ecological objectives: incineration with gas cleaning and energy recovery, material recycling and composting. The evolution of each treatment used is shown in Figure 2.



Note: estimated by Eurostat.

Figure 2. Municipal waste treatment used for all of the waste produced in the EU environment, per year, 1995-2020, in kg per capita. Source: EUROSTAT.

Going into the detail, published data from EUROSTAT reveals that there are several differences between countries in the EU28 when referred to general waste treatment. Germany, Sweden, and Belgium landfilled less than 10 kg per capita in 2015 while Hungary, Slovakia and Spain landfilled twice the average of the EU28, 122 kg per capita (EUROSTAT, 2022). When the percent of waste recovery and disposal (over the total treated) is observed, similar conclusions are observed, as it is shown in Figure 3.



(1) No data available for energy recovery and incineration without energy recovery.
(2) No data available for incineration without energy recovery.
(3) This designation is without prejudice to positions on status, and is in line with UNSCR 1244/1999 and the ICJ Opinion on the Kosovo Declaration of Independence.
Source: Eurostat (online data code: env_wastrt)

Figure 3. Percent of each waste treatment by type of recovery and disposal, 2018, EU environment.

All these facts suggest that incineration of MSW will prevail upon landfilling in the years to come, which may increase the total amount of atmospheric emissions derived from its combustion to the environment.

As a reference, there are up to 10 MSW incinerators in Spain, which are able to manage almost 3 million tonnes of waste per year (AEVERSU, 2016). These incinerating facilities process only 9% of the Spanish MSW while 58% is still landfilled (AEVERSU, 2016; Generalitat de Catalunya, 2016). Four of the Spanish incinerators are located in Catalonia, and another one in Mallorca. Other four are located at the northern coast of Spain, and only one more is situated in Madrid, meaning that bigger populations have started developing these facilities, but there are still important areas of the country, such as the rest of the Mediterranean coast, that have no incineration capabilities and still use landfilling as the main method. This heterogeneous distribution of the incinerators directly affects to the management systems established locally. In Catalonia 25% of the MSW is incinerated and 36% is landfilled (Generalitat de Catalunya, 2016); and in Mallorca, where the available land resources are more limited, the amount of MSW incinerated in 2013 was 55% and only 2% was landfilled (Guinea Mairlot, 2014).

Although the carbon footprint of MSW incinerators is less demanding for the environment than landfilling, other environmental issues, like polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) atmospheric emissions during waste combustion (McKay, 2002; Shaub and Tsang, 1983) and waste gasification processes (Lopes et al., 2015) should be considered. These molecules, in addition to being highly toxic, are complex to monitor in real time during the execution of the incinerating process and the flue-gas cleaning because of their low concentration in the emissions and the number of compounds to be detected (more than 200). Thus, it is difficult to establish a control philosophy on the furnace parameters and the flue-gas cleaning system that optimizes its capture and reduces its formation.

1.3 Political Achievements and Future Strategies

The legacy of the work done by the United Nations during the 90s led each of its member states to start actions in favour of sustainable development. The subsequent resolutions were focused on the implementation of the tools needed. As a first step, the UN Conference on Sustainable Development in Rio during 2012 (also known as RIO+20) released an outcome document, *The Future We Want*, where the importance of economic, social and environmental issues, at same level, were clearly settled in order to achieve a sustainable development. That document, in addition to ratifying the *Agenda 21* action plan, called for the definition of Sustainable Development Goals (SDG). The fulfilment of these objectives, quotas, targets and deadlines was measured and monitored in order to scientifically determine if each Goal was achieved or not. This strategy helped to establish a green economy based on actions that increased the sustainable development all over the world.

In September 2015 the UN General Assembly adopted the *2030 Agenda for Sustainable Development*. This Agenda followed the essentials from the *Agenda 21*, being focused into precise plans of action focused on Social, Environmental and Political strategies needed to be developed in the next 15 years. Going more into detail a total of 17 Sustainable Development Goals, with up to 169 targets, are proposed on that document:

1. End poverty in all its forms everywhere.
2. End hunger, achieve food security and improved nutrition and promote sustainable agriculture.
3. Ensure healthy lives and promote well-being for all at all ages.
4. Ensure inclusive and equitable quality education and promote lifelong learning opportunities for all.
5. Achieve gender equality and empower all women and girls.
6. Ensure availability and sustainable management of water and sanitation for all.
7. Ensure access to affordable, reliable, sustainable and modern energy for all.
8. Promote sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all.
9. Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation.

10. Reduce inequality within and among countries.
11. Make cities and human settlements inclusive, safe, resilient and sustainable.
12. Ensure sustainable consumption and production patterns.
13. Take urgent action to combat climate change and its impacts.
14. Conserve and sustainably use the oceans, seas and marine resources for sustainable development.
15. Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss.
16. Promote peaceful and inclusive societies for sustainable development, provide access to justice for all and build effective, accountable and inclusive institutions at all levels.
17. Strengthen the means of implementation and revitalize the global partnership for sustainable development.

All SDG were subdivided into more specific targets, 169 in total, which pretend to focus on the action needed to execute to fulfil the main goal. As a quick reference, goal 11.6 makes an explicit reference to reduce the environmental impact of the cities by improving the waste management, goal 12.5 also proposes to reduce substantially the waste generation based on a Circular Economy strategy. On the social and economic dimensions, there can be found explicit references to the necessity of inclusion of all the vulnerable minorities in the society, giving a special reference to gender equality as a crucial point to the development of the 2030 Agenda. Several explicit references to not leave behind to the developing countries can also be found in the text (The United Nations, 2015).

The compliance system of the SDG, which is based on indicators, plays a key role in their development all over the world. After an exhaustive study, an integrated monitoring framework was developed with the design of many indicators that could be sensitive for each goal and target. This monitoring was proposed to be done at three levels: globally, nationally, and regionally. Up to 100 Global Monitoring Indictors were reported, with several complementary national and regional sub-indicators that may help to amend them.

These indicators need to be finite, global, simple, easy to measure frequently, with a reliable origin of data, scientifically measurable and with medium term looking perspective. Also, the disaggregation of the data collected such as sex, age, income, disability, religion, economic or spatial dimensions like differentiating the metropolitan areas and the rural and urban areas is also a key point of the monitoring system (The Leadership Council of the Sustainable Development Solutions Network, 2015). The whole global indicator framework for SDG was then refined by the Statistical Commission of the UN, and a reviewing periodicity of once per year was settled. Furthermore, a robust follow-up mechanism for monitoring the progress achieved that included an inform policy and ensures the accountability of all stakeholders was adopted (General Assembly of the UN, 2017).

All of the data and other specific resources related to monitoring the SDG indicators can be easily found online (The United Nations, 2022). On that webpage, a global database is accessible to whom may be interested, where the values of all of the 231 indicators related to each target or goal are frequently updated. Also, a Progress towards the SDF report per year is published there, where every target linked to every goal is evaluated and commented. It provides a general overview of the data published (Guterres, 2022). As an example, during the period between July 2022 and July 2023, related to Goal 11 - target 112, it is published that the average municipal solid waste collection rate in cities has increased to 82%, and globally has increased to 55%.

The SDG monitoring framework also provides an SDG Country Profile, where the trends of each indicator for each country can be consulted, as long as the source and the periodicity of the data provided. As an example, the trend of the share of renewable energy in the total final energy consumption for Spain is shown in Figure 4. It is noticeable that the percent weight over the total was doubled within 20 years.

Figure 4. Renewable energy share in the total energy consumption (percent) in Spain during the period 2000-2017. Source: UN Statistics to SDG

When focusing on long-term sustainable strategy, the UN supports a Global Energy Transformation, based on The Paris Agreement. This agreement, which was adopted at the Paris climate conference (COP21) in December 2015 sets out another framework against climate change focusing on a limit for the global warming. It was adopted with the aim of increasing the global average temperature to not more than 1.5ºC by the end of the present century (The United Nations, 2015). As a part of this scenario, the net emission of CO_2 needs to drop to net zero by the end of 2050. To deal with this ambitious objective to reduce to zero the 36.5 gigatons of CO_2 emitted per year, the implementation of these six main components should be developed: renewable energies, energy conservation and efficiency, electrification in the end-use sectors, green hydrogen and its derivates, Carbon Capture Storage and Carbon Capture Utilization industry, and Bioenergy CCS (BECCS) and other carbon removal measures.

The amount of CO2 emissions that each component should reduce is estimated and shown in Figure 5.

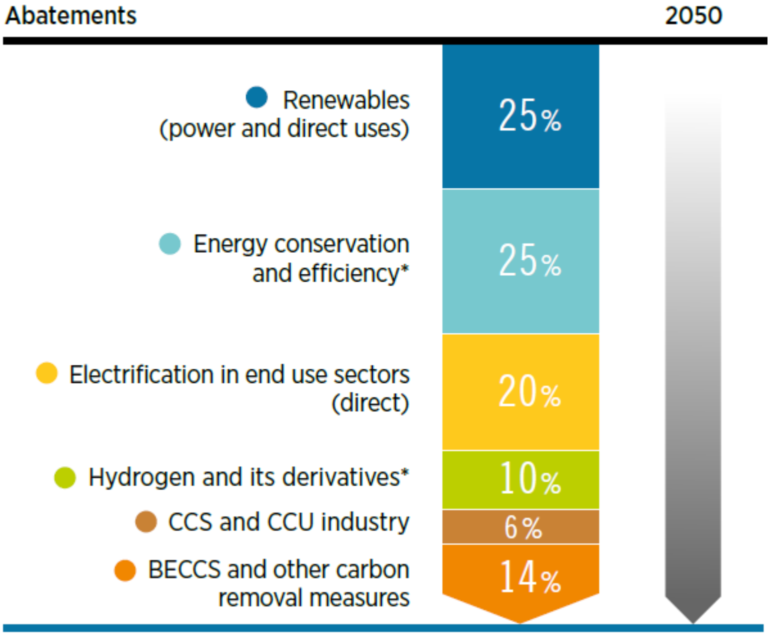


Figure 5. CO_2 emissions abatements options between the 1.5ºC Scenario. Source: IRENA in World Energy Transitions Outlook

It is noticeable there that renewable energies and energy conservation (even the energy remaining in the waste) will play a key role in the development of the long-term strategy of sustainability (IRENA, 2021).

The European Union (and its member states) has also made public its willing to be climate-neutral by 2050 as a part of the European Green Deal and with the same aim of global action against climate change of the Paris Agreement. The strategy to do so was submitted in the UN Framework Convention on Climate Change in 2020, where a call to its member states to develop long-term low greenhouse emissions strategies was done (The European Union, 2020).

Following this Framework each member state needs to develop a strategy to fulfil the Paris Agreement. In the case of Spain, its government published a report with their framework and proposals in the long-term. It is noticeable there that the governmental expectation is to exceed the limit of 1.5ºC for global warming before 2050, but despite that, the government is encouraged to fulfil the limitations of CO_2 emissions by a strategy that pretends to transform four pillars (Oficina Nacional de Prospectiva y Estrategia, 2021):

1. To change the processes that produce, storage and use energy. Basically, stopping the combustion of fossil fuels and promoting the use of electricity from renewable sources of energy. It is mentioned that the photovoltaic energy and the renewable hydrogen use will play a key role in that.
2. To change the processes of transportation of goods and people. Not only technological advances and sustainable sources of energy are discussed, but the implementation of an adapted taxation to the new reality of transportation.
3. To change the processes of obtention of goods and services. With an explicit reference to the implementation of a circular economy, it is explicitly announced that 0% of the municipal solid waste will be landfilled by 2050, thus, the use of municipal solid waste incinerator facilities in the years to come is a proven fact.
4. To change the culture of consumption of goods and services. There, an explicit mention to reduce the use of resources to not exceed the biocapacity of the planet.

2. Theoretical Foundation

2.1 Municipal Solid Waste Incineration

2.1.1 Industrial Process

Incineration is a method for waste management that drastically reduces the volume of the waste treated. It is also a secure treatment method for most of biological hazardous wastes. Basically, this method consists of the oxidation of the combustible materials which are contained in the waste whilst capturing or destroying the substances that may produce a harm to the environment. These benefits, added to the possibility of the energy recovery, converting the waste into a partially renewable fuel, supposed a rapid technological development of the industry in the last years, mostly focused on the reduction of the emissions to the atmosphere, reducing the operating costs and improving the environmental performance.

The incineration facilities can be divided into the following categories (The European Commission, 2006):

1. Municipal Solid Waste incinerators, that treat MSW and other wastes that could be similar in composition, such as commercial wastes. MSW can be pre-treated separating the recyclable fraction, just letting all the matter that is not valuable by itself, but for its combustion energy.
2. Hazardous waste incinerators, which include a wide variety of wastes.
3. Sewage sludge incinerators.
4. Clinical waste incinerators.

At the beginning of the XX century around the 20-25% of the MSW collected in the EU was incinerated, in around 400 facilities around the member states. Some countries were capable of incinerating up to 550 kg of waste per capita. With all these in mind and considering than the main alternative treatment for MSW is landfilling, the expansion of MSW incineration sector is anticipated in Europe in the years to come.

Despite all its advantages, MSW incineration supposes to deal with significant environmental challenges such as overall emissions to air and water, residue production of fly ashes and slag, odours, noise, vibrations, consumption of reactants, etc.

The linear layout of a municipal solid waste incineration facility may vary depending on the local composition of the waste treated, but mainly it may be constructed by the following modules (The European Commission, 2006):

1. **Waste reception, storage and pre-treatment.**

   Municipal solid waste is commonly collected separately by fractions. If not, it is desirable to pre-treat it by removing all of the recyclable and composable materials, which combustion may affect negatively to the efficiency, or increase the emissions derived from its combustion. As an example, peaks of organic wastes may increase the moisture and reduce the efficiency of the energy recovery; or metals and glass incineration does not apport any increase in the energy production and reduces its value as a material once incinerated. It also may affect to the parameters of the combustion and promote the formation of subproducts and pollutants.

2. **Homogenization and loading of the waste.**

   It is desirable to mix all of the wastes in the bunker just before loading the hopper that drives to the furnace. This homogenization, which is commonly done with the same waste grab used for the loading, ensures a stationary regime, a constant calorific power, and an easier control of the process.

3. **Thermal process of degradation.**

   Once the hopper is loaded, the waste is pushed through the combustion furnace using a mechanical system such as travelling grates, rollers, pushers, etc. These travelling systems allow the waste to disaggregate and react easily with the oxygen stream, to control the residence time of the waste, to allow the slag to fall off the combustion chamber and are robust enough to operate the system.

   The air used in the combustion is commonly drawn from the bunker area in order to reduce odour emissions. It is introduced in the furnace at different points to achieve a proper combustion. It is primary introduced into the furnace bottom-up to firstly dry the waste and then start the combustion process. A secondary air stream is introduced in the hottest part of the furnace to fully oxidate all the flue-gas and mix it completely, stopping the free passage of unburned gas streams, as it is shown in Figure 6.

The main parameters of the combustion, such as temperature, residence time of the gas and minimum oxygen content is strictly controlled and determined by legislation depending on the properties of the incineration facility.

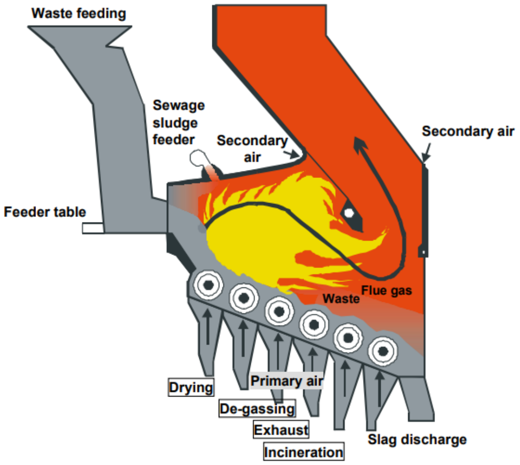


Figure 6. Primary and secondary air inlets in a MSW incinerator furnace.

4. Energy recovery

A combustion reaction is always an exothermic process. Thanks to the fast kinetics of the reaction, most of the heat of the reaction is transferred to the flue-gases, that may be cooled down before its release to the atmosphere. This necessity of cooling allows to recover the energy within the waste and also helps to clean the gases before its emission. This heat transfer is produced inside a boiler, which main characteristics will strongly depend on the flue-gas corrosion, erosion, and fouling capacity. The boiler design will also be based on the net calorific value (NCV) of the waste combusted, and the pressure and flow of steam needed in the turbine to produce electrical power (if produced). Depending on the production of the plant, the thermal efficiency of the whole process may suffer significant variations, calculated as the total heat and electricity energy per energy in the boiler, as it is shown in Table 5.

Table 5. Thermal efficiency of the plant depending on the thermal product obtained.

Plant type	Thermal efficiency
Electricity generation	17 - 30
Heat and power plants	70 - 85
Heating stations with sales of vapour/liquid streams	80 - 90
Steam Sales	90 - 100

5. Flue-gas cleaning system

The flue-gas treatment is considered as a series of unitary processes that are capable to extract the pollutants from the gas stream before its release to the atmosphere. Each of these units are designed accordingly to the substance (or similar substances) that may interact with. Commonly the stages of the gas cleaning system are:

a. Acid-gases capture by reaction with an alkaline reactant. The reaction that happens in this unitary operation may be designed as a dry, semidry, wet or a combination of them. They are commonly called scrubbers or reactive cyclones.

b. Solid-gas separation of fly ashes and other particles. The process is commonly performed using bag filters. Electrostatic precipitators may also be used, which are quite more robust against corrosion and humidity.

c. Selective reduction of NOx. This reaction process uses a reduced form of nitrogen (such as urea or ammonia) or even Natural gas or Hydrogen, to react with NOx and produce N_2. This process may be catalysed (SCR) or not catalysed (SNCR).

Other unitary processes may be applied, like the adsorption on activated carbon of pollutants such as mercury and organic carbon compounds such as PAH, BTX and PCDD/Fs. Those are commonly ubicated just before the capture of the fly ashes, thus the used activated carbon remains with the fly ashes, and they are treated together.

6. Flying ashes treatment

It is possible the fly ashes are captured together with other solid residues from the flue-gas treatment such as the outlet solid stream from the dry scrubbers and the adsorbents that may be added just after the filtration of the fly ashes. Anyway, it is desirable not to mix these solid residues since the scrubber residue may be reused in the same stage (it is essentially calcium oxide which could work again once rehydrated). The fly ashes themselves are considered as dangerous due to their ease of being blown and dispersed. Also in their structure heavy metal oxides can be found. Thus, the main strategy to treat them is to immobilize them by solidification. This solidification reduces the release of pollutants from the block formed to water or air sources. This process is mainly done by its mixture with cement, casted into blocks and landfilled in a controlled dump. Other techniques like melting the ashes using high temperatures (>1400ºC) are also available, but the high cost of it makes it exclusive to those processes that already need those high temperatures for other purposes.

7. Slag treatment

The slag, also known as bottom ash, is the most produced (in weight) residue from municipal solid waste incineration process. The composition of this residue is controlled by the European Directive 2000/76/EC, where some requirements for its reuse as a bulk material for construction are settled. Combustion trials have demonstrated that its content in total organic carbon (TOC) is well below 1%, and it is mostly due to elementary carbon and some short-chain compounds and low volatile such as PCDD/Fs, PCB and PAH that does not cause any problems on landfills since the levels detected in the slag of modern incinerators is in the same order of magnitude of the levels found in urban soils (The European Commission, 2006).

The ferrous content is usually extracted by magnetic fields and reused in the metallurgic industry. Similar philosophy may be applied using Foucault's Current Separator devices for extracting the non-ferreous content and recycling it.

The remaining slag is commonly rehydrated and matured to stabilize the oxides which are present, and then reused.

8. Emissions monitoring

The wide variety of waste compositions is one of the main challenging issues to deal with during the incineration process, since the formation of pollutants has a strong dependence on the composition of the waste. The fluctuations in process variables such as temperature, pressure and gas flow in the furnace also strongly affect to the formation of pollutants. Thus, in order to operate the plant in a stationary regime and to fulfil the legal requirements related to emissions, a sophisticated monitoring and control system is commonly implemented in the incineration plant.

Legislation in the European Union (Directive 2000/76/EC) requires measuring continuously the emission of dust, HCl, SO_2, CO, total organic carbon, NOx and HF (in case of not adequate HCl removal facilities). With the aim of correcting the emission value and ensure that the limit of emission is never reached, some process parameters are also monitored continuously, since they are necessary to recalculate the normalized emission. These variables are the furnace temperature, the flue-gas outlet temperature, the oxygen outlet content, the pressure and the water vapor content.

Heavy metals and PCDD/F emission levels also need to be measured periodically, at least once per 3-4 months.

As a general rule, the emission of pollutants during waste incineration strongly depends on the waste composition, the furnace design and the operation of the combustion process variables. When stationary regime is maintained, those process variables can be controlled at a regime where less pollutants are produced, and also the flue-gas cleaning equipment is capable to capture those pollutants and fulfil the emission limits.

The emission of HCl, HF, metals and SO_2 normally depends on the composition of the waste and the capability of the flue-gas cleaning system to do so. Other emissions such as CO, VOC, NOx strongly depend on the furnace design and their operation conditions.

The emission of PCDD/Fs to air depend on both waste composition (since its formation is catalysed by some metals) and plant operating conditions like the temperature and the oxygen content during the flue-gas cleaning process. The methodology needed to analyse PCDD/Fs does not allow the continuous and rapid measurement of their content in the flue-gas stream. Thus, the rapid estimation of its production could help to control the process variables in a more efficient way.

Since PCDD/Fs are also contained in the municipal waste to incinerate, and a reasonable way of destroying them is by incineration at high temperatures and excess of oxygen, most of PCDD/Fs that come into the furnace are destroyed, but also a part of them is reformed and used as precursors to new PCDD/F which are produced at the flue-gas cleaning system, when temperature reaches values close to 400ºC. This material balance was performed for a waste incineration facility in Germany, where the results concluded that only 1% of the PCDD/Fs in the input was released to the gas emission (0.48 ng TEQ/kg out of 50 ng TEQ/kg in the waste). Thus, a properly controlled incineration facility acts as a net reducer of PCDD/Fs levels (The European Commission, 2006).

As an example of a modern incineration facility with energy recovery, Figure 7 shows the diagram of an MSW incinerator in Mallorca, constructed in 1997 and enlarged in 2010 that allowed all the island to establish a “zero landfilling” policy as a waste management strategy for the municipal solid waste, and resembling wastes. This facility is able to manage up to 390.000 tons of MSW in 2021 and produce a total of 290.000 MWh of energy, where 145.000 MWh should be considered as renewable energy due to the source of the carbon (TIRME SA, 2021).

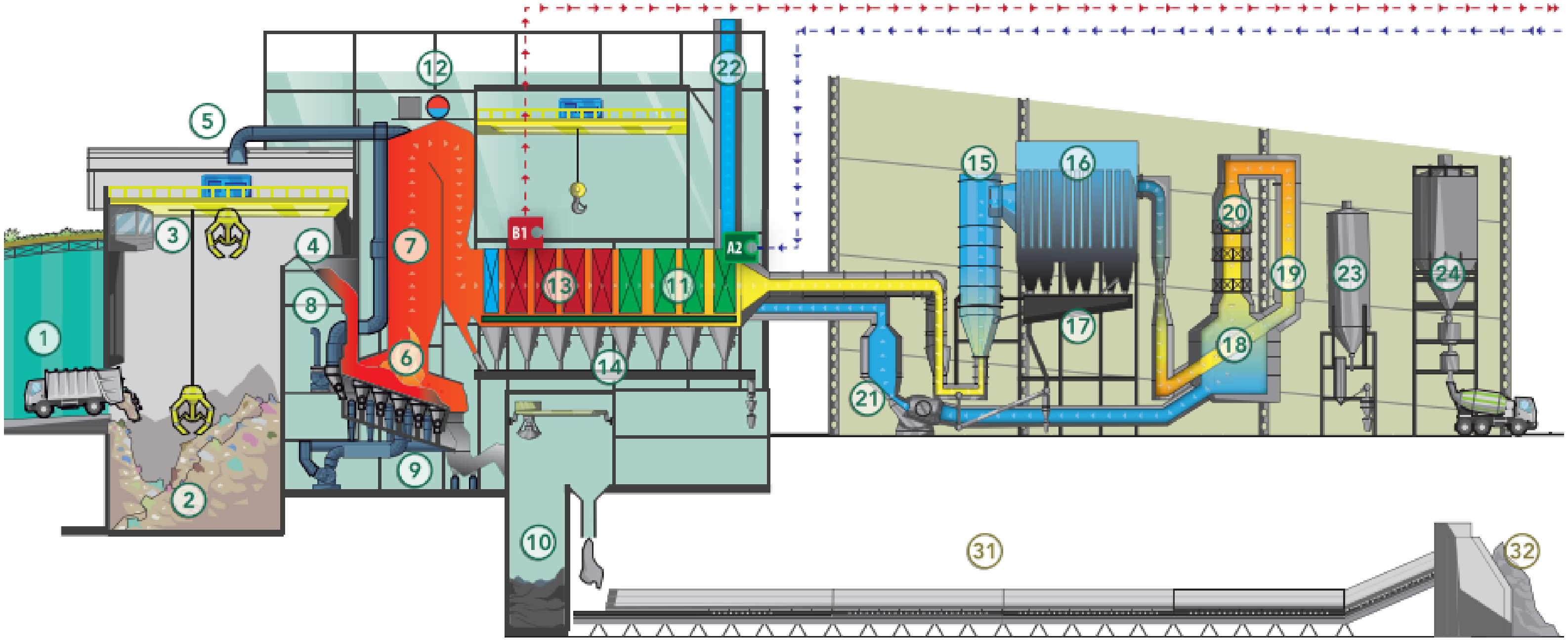


Figure 7. Diagram of a waste incineration with energy recovery facility located in Mallorca. Source: TIRME.com

1. Waste reception area
2. Waste storage bunker
3. Waste grab
4. Hopper
5. Primary air inlet
6. Rotatory grates
7. Auxiliar burners
8. Secondary air inlet
9. Slag extractors
10. Slag deposit
11. Economizer
12. Vapor generator
13. Vapor generator
14. Fly ash collector
15. Acid-gases semidry reactor
16. Bag filter for fly ashes
17. Gas recycles
18. Economizer
19. Economizer
20. SCR NOx removal
21. Draft fan
22. Chimney
23. Reactant deposits
24. Solidification of fly ashes with cement

31. Slag transportation
32. Slag maturation and hydration

2.1.2 Regulation related to emissions

As a main legal framework and based on the Directive 96/61/CE and then updated by the Directive 2008/1/CE by the European Parliament and of the Council, the Spanish government approved the *Real Decreto 815/2013* (which has been amended and updated up to December 2020). It settles the necessity of obtaining an Environmental Integrated Authorization to operate an industrial facility. This text includes the integrated point of view of the monitoring of the emissions, where a limit value of concentration for the emissions is also defined. This limit values are organized as per three categories: the daily average value, the semi-hourly limit value (A column) and the semi-hourly limit value (B column). It is defined that to fulfil the limit values, none of the daily average emission values or the semi-hourly limit value (A column) should exceed the defined limits. It is allowed that up to 3% of the measures exceed the semi-hourly limit value (B column) to still fulfil the legislation.

The text specifies the periodicity of the measures depending on the pollutant analysed, as long as the process parameters that are considered as the reference and how to recalculate the value of the emissions to correct the variability of that parameters (such as temperature, pressure, etc.). As it is shown in Annex 2 Part 2 of the Decree 815/2013, all of the emission limit values are settled in concentration units (mass weight per volume of flue-gas emitted in normal conditions). Since the volume of the gas can easily be modified by changing operational conditions, introducing excess air to the combustion or adding water vapor or nitrogen to dissolve the emission, the emission needs to be recalculated to normal conditions. These reference values are settled as a temperature of 273.15K, a pressure of 101.3 kPa, the removal of water vapor (dry gas), and an amount of excess of oxygen in the flue gas outlet that depends on the facility (11% for MSW, 6% for solid fuel, 3% for liquid fuel, 10% for cement furnaces, etc.) (Ministerio de Medio Ambiente, 2013).

The temperature and pression correction will be based on ideal gas law, and the oxygen amount will be recalculated proportionally to the difference to 21% of oxygen content, which is its content in the fresh air.

2.2 Dioxins

2.2.1 Definition

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs), also referred as PCDD/F or dioxins, are two groups of an extensive family of 210 chlorinated organic molecules. The structure of these molecules is based on two benzene rings which are bonded using oxygen forming a planar structure. When two oxygen bridges are present, a molecule of PCDD is formed; while when an oxygen bridge and a carbon bond are present, a molecule of PCDF is formed. These two main structures let 8 positions on the molecule to chlorinate. All the possible combinations, monochlorinated to octachlorinated molecules, bonded in position 1 to position 8, considering the symmetries in each structure, result in 75 possible PCDDs and 135 possible PCDFs. Their general structures are shown in Figure 8. All of the congeners can be considered as low vapour pressure solids at room temperature and atmospheric pressure. Its solubility in water is also limited.

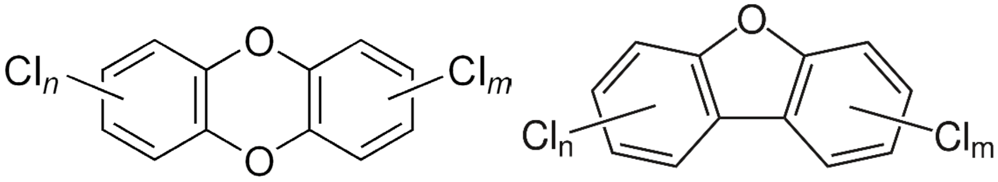


Figure 8. Polychlorinated dibenzo-p-dioxins (left) and polychlorinated dibenzofurans (right) general structure.

In terms of toxicological studies, only the congeners with four or more chlorine atoms in the 2, 3, 7, and 8 positions are considered significant (Ahlborg et al., 1992). This fact reduces the number of congeners usually studied from 210 to just 17 (10 for PCDF and 7 for PCDD). The relative proportion of these 17 congeners in a sample is called fingerprint. Since fingerprint patterns have been demonstrated to be sensitive to the kind of industrial process that produced the emission (Buekens et al., 2000; Lee et al., 2004), its analysis is considered as a powerful tool to identify the source of a PCDD/F emission. This tool has been improved using better statistical models through years, mostly based on Principal Component Analysis and Hierarchical Cluster Analysis, ensuring the homogeneity of the data used (Chen et al., 2012). The correlation between the dioxin fingerprint pattern of different samples from the emission of a similar combustion process has been analysed by some authors (Chen et al., 2012; Swerev and Ballschmiter, 1989) and used in several environmental studies in order to identify a possible Occurrence/Source relation (Cappelletti et al., 2016; Floret et al., 2007; Xu et al., 2009).

The quantity and the location of the chlorine atoms in the structure of a PCDD/F directly affects to its toxicity. In order to evaluate these toxicity differences between all congeners, some correcting factors have been developed using several databases, considering animals (Zabel et al., 1995) or humans and wildlife (van den Berg et al., 1998). The most common system is to calculate the amount of toxic equivalents (TEQ), based on NATO/CCMS criteria (Kurtz and Bottimore, 1988), using toxicity conversion factors that rescale all the amounts of each congener considering as the factor of unity the most toxic congener: 2,3,7,8-tetrachlorodibenzo-p-dioxin. Despite this toxicity conversion factors have been criticized (Gallo and Scheuplein, 1991; Nagao et al., 1993) and actualized (van den Berg et al., 2006), the International Toxicity Equivalency Factor (I-TEF) original defined values (Kutz et al., 1990) remain as the internationally adopted criteria since all legislative issues for atmospheric emissions are still referred to it (European Parliament and of the Council, 2010). All these factors are shown in Table 6 and will be commonly used in this work.

These factors allow to weigh the contribution of each congener to the total toxicity of the emission, which is calculated as described in Equation 2.1.

$$TEQ \ = \sum_{i} m_i \cdot I - TEF_i \qquad (Equation\ 2.1)$$

Where TEQ is the Toxic Equivalent of the mixture (expressed as pg of 2,3,7,8-TCDD), m is the amount of each dioxin congener (expressed as pg) and ITEF represents the Toxicity Equivalency Factor of each congener i (expressed as pg of 2,3,7,8-TCDD / pg of i).

Table 6. List of the 17 PCDD/F toxic congeners and its toxic equivalency factor, depending on the criteria used.

Congener	I-TEF NATO/CCMS	I-TEF WHO 2005
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0003
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0003

2.2.2 Impact on human and environmental health.

Persistent organic pollutants such as PCDD/F are accumulated in the adipose tissue of animals and weaken the immune system (Hsu et al., 2007). These products are wanted to be reduced or eliminated by the Stockholm Convention on Persistent Organic Pollutants because they present four main characteristics that define POPs: persistence, bioaccumulation, potential for long-range environmental transport and toxicity (The Stockholm Convention, 2001).

Toxicological effects of dioxins, which are related to their preferential binding to the aryl hydrocarbon receptor (AhR), are in a wide range of diseases such as hypertension, diabetes, weight loss (Marinković et al., 2010), reproductive disorders (Yu et al., 2000), cancer (De Roos et al., 2005) and other illness related to immune system disorders.

Several events related to PCDD/F have occurred since 1950 that have increased the concern about these compounds. During the war in Vietnam the U.S. Military sprayed, from the aircraft, an herbicide called Agent Orange over food crops and foliage with the aim of reducing the resources of the Viet Cong and improve the defensibility of the U.S. Military bases. This herbicide was a mixture of 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid. The mixture was contaminated with small amounts of 2,3,7,8-TCDD. Considering that 45000 m^3 of Agent Orange were sprayed, 150 kg of 2,3,7,8-TCDD were discharged into the Vietnamese environment (Schecter et al., 2006). There is sufficient evidence of an association between Agent Orange and Vietnamese people and U.S. Veterans suffering from soft-tissue sarcoma, Hodgkin's disease and prostate cancer (Ansbaugh et al., 2013; Institute of Medicine, 2016; Yi et al., 2014). A few years later a Swiss company was operating a chemical production plant of 2,4,5-trichlorophenol in Meda, Italy. The reactor suffered overpressure caused by excessive heating and the safety valves discharged all contents of the vessel to the atmosphere. This emission was blown south by the wind, landing in the town of Seveso. Some days after, more than 1000 rabbits and chickens had died. The soil was analysed and traces of 2,3,7,8-TCDD were found. It is believed that 2 kg of 2,3,7,8-TCCD were produced and spread in the most contaminated zone, where 730 people were evacuated. In 1984 an International Steering Committee reported that no significant human effects were found (Schecter et al., 2006). However, 20 years after the exposure it was observed that the female ratio in children whose father was exposed to Seveso disaster was significantly higher than male ratio (Mocarelli et al., 2000).

2.2.3 Dioxin formation routes and Kinetic formation models

Many questions involving PCDD/F and its formation processes remain uncertain, such as a rigorous kinetic equation that governs all of the possible formation routes. Once the thermodynamic properties of these molecules were calculated, it was found that the thermodynamic equilibrium constants of the main formation pathways for PCDD/F (and also the fluorinated compounds) strongly favour its production (Ritter and Bozzelli, 1994; Yang et al., 2010). It was also observed that the distribution of congeners obtained using the calculated equilibrium constants did not correspond to the experimental distribution published (Addink et al., 1998). This fact suggests that other routes, in addition to the gas phase reactions, should occur. The experimental distribution shows that the amount of PCDD/F obtained is noticeably lower than the predicted by the equilibrium constants; hence, the maximum thermodynamic conversion in the main formation pathways is never reached. Thus, the formation of PCDD/F is controlled by kinetic mechanisms rather than by thermodynamic mechanisms. This fact supports the idea that the formations of all PCDD/F congeners are connected to each other (Shao et al., 2012). This kinetic dependence should provoke a correlation between the amount of each congener that is produced during combustion, which is the aim of the study in Chapter 4.

Although two major dioxin formation mechanisms have been considered, de novo synthesis and precursor-based reactions, up to four different mechanistic pathways to PCDD/F formation can be differentiated with a more detailed review: gas-phase reactions, uncatalyzed surface reactions, catalytic precursors and *de novo* synthesis reactions (Environment Australia, 1999).

- Regarding gas-phase reactions, the analyses of major pathways have been studied extensively (Babushok and Tsang, 2003). These studies indicate that the formation of dioxins via the reaction of precursors occurs following hydroxy radical addition, involving unimolecular HCl elimination or chlorine losing (Ritter and Bozzelli, 1994). It is believed that these mechanisms contribute from 10% up to 50% of the total PCDD/F formation. Main precursor routes formation from chlorinated phenols, from oxidation of benzene and from other precursors like hydroquinone have also been described (Altarawneh et al., 2009). It should be noted that PCDD/F formation using gas-phase reactions only occurs at temperatures higher than 600ºC (Tuppurainen et al., 1998).

- For non-catalytic reactions on fly ash, some publications suggest the surface effect in PCDD/F formation (Konduri and Altwicker, 1994). It is accepted that surface is an adsorption place where PCDD/F precursors concentrate and favour its reaction. Differentiation between catalytic and non-catalytic surface reactions is difficult to ensure since the structure of the chemical transition state for catalytic reaction has not been clearly defined. The effect of pH of the fly ash has been studied, concluding that when pH decreases below 3.9 the total amount and toxicity values decrease (Zhan et al., 2015).
- Other authors claim that fly-ash catalysed precursor is the principal pathway for PCDD/F formation (Tuppurainen et al., 1998). The precursors are formed at high temperatures, as incomplete combustion products, and in the post-combustion zone the PCDD/F are formed by its reaction at lower temperatures (Froese and Hutzinger, 1996). Some precursors can be found as a part of the fuel. The precursor molecules react using elements in the fly ash as a catalyst to produce PCDD/F. Main processes of adsorption/desorption (Milligan and Altwicker, 1996) and global kinetics (Milligan and Altwicker, 1996) have been studied. The yield of formation of PCDD/F from dibenzofuran and benzonaphtofuran as precursors using model fly ash have been also described (Hajizadeh et al., 2011), as well as the reaction of formation of PCDD/F from polychlorinated diphenyl ethers (Altarawneh and Dlugogorski, 2014). With this pathway in mind, a pathway of PCDD/Fs formation based on the process of bleaching non-wood pulp was developed (Xia et al., 2020).
- Studying the fly-ash catalysed *de novo* synthesis pathway, it is believed that in the source of the carbon used is obtained from the solid carbon matrix of the fly ash of incinerated MSW, being able to produce complete aromatic rings in lack of oxygen (Huang and Buekens, 1996). It is also believed that chlorine is transferred from the ash surface to the carbon rings producing PCDD/F (Stieglitz and Vogg, 1987). Also, kinetic models for *de novo* synthesis in surface catalysed reactions have been

published (Huang and Buekens, 2001). The influence of catalysts and some additions on these pathways have also been studied (Wielgosiński et al., 2016). Model fly ash is used in several publications to determine the influence of catalysts (Masaki et al., 2008; Verhulst et al., 2014), oxygen concentration (Yang et al., 2015), and other process parameters like temperature.

All these publications related to PCDD/F formation support the main idea that kinetics controls the production processes over thermodynamic equilibrium. Finding this kinetic model will be the aim of the investigation in Chapter 5.

The complexity into modelling these routes into specific equations can be noticed in the most relevant publications into this topic, since most of them were published 20 years ago. The most recent studies are mostly focused on reporting the PCDD/Fs formation experienced during the combustion of specific wastes or products, with the aim of determining a specific yield of PCDD/Fs formation (in pg of TEQ per g of waste) depending on the combustion parameters or the use of catalysts, instead of finding a rule that may govern the production of these pollutants (Yasuhara et al., 2005). Some of these investigations propose the co-incineration of different mixtures of residues to promote synergistic effects and reduce the emission of pollutants. A study concludes that co-incinerating a mixture of MSW with a 20% of textile industry waste or food industry waste reduces the emission of PCDDF/s, and proposed a formation pathway (Ying et al., 2023). Other inhibition system proposed pretend to use a phosphorous source (Lu et al., 2021) and a chlorine-deactivator material (such as CaO) to affect all the *de novo* pathways. The formation of PCDD/Fs was supressed by over 95% and the chlorination of the remaining congeners formed was also decreased (Chen et al., 2023).

To model the formation of PCDD/Fs, following whatever of those routes described before, also assumes a reduction of all the variables involved in the process. Many simplifications have been considered during the attempts of modelling. One of the first model mechanisms was constructed to investigate the gas-phase formation of PCDD/Fs based on chlorophenols as precursor molecule using up to 13 reactions. The main conclusion was that the formation of PCDD/Fs was very low at temperatures above 1200ºC. Also, the effect of addition of oxygen and auxiliary fuel was studied, concluding that the increase of both also reduced the formation of PCDD/Fs (Shaub and Tsang, 1983). There have also been published models that consider four steps during the PCDD/Fs formation: reaction, desorption, dechlorination and decomposition. The model was consistent only in long timescales (Altwicker et al., 1990). Other investigation modelled the formation of PCDD/Fs, for both *de novo* synthesis and precursor-based routes, as a two-stage process. There, the formation of a graphitic initial structure was needed, which was transformed into many aromatic compounds (Huang and Buekens, 1995). Another model for *de novo* formation of PCDD/Fs in medical waste incinerators was published using data from a pilot scale incinerator, depending on the cooling regime of the incinerator from combustion temperature to ambient (Stanmore and Clunies-Ross, 2000). This model suggested that the gas-phase adsorption process was the limiting one in the formation process. Thus, the diffusion and the amount of HCl molecules adsorbed on the fly ash play a key role in the model. Other kinetic models consider three reaction steps: the global PCDD/F formation (including the carbon source gasification), the desorption of the PCDD/F formed to the gas phase, and its possible degradation to other products. This kinetic model also used as a parameter the carbon content in the fly ash, partial pressure of oxygen and temperature and it was verified using laboratory data with a good agreement (Huang and Buekens, 2001). The precursor mechanism of formation has also been developed, including within the model other parameters like chlorobenzene and chlorophenol concentration in the gas phase (Stanmore, 2002). The kinetic properties of the reactions of chlorophenols with OH radicals were also studied using molecular orbital theory calculations (Xu et al., 2010), which have been clearly identified as PCDD/Fs precursors.

The role of the chlorine during waste combustion has also been modelled depending on the chlorine species available in the combustion process, also differentiating the homogeneous and heterogeneous phase (Gullett et al., 2000).

3. Objectives

The aim of this investigation is to develop a series of mathematical models that are capable to properly estimate the atmospheric emission of polychlorinated dibenzo-p-dioxins and furans produced by the combustion of a characterized waste under a determined combustion process.

To do so, it is necessary to fit a kinetic model that is capable to determine the amount of PCDD/Fs produced that contribute to the TEQ. This result should be expressed as a yield (pg TEQ / g of waste incinerated) and it should depend on process variables such as temperature, oxygen amount in the flue-gas stream and catalyser or chlorine content. Experimental data from the study of the thermal degradation of several wastes will be used to fit the kinetic model.

In order to properly adjusting the kinetic model, it is necessary to study the interdependence between the formation of all of the 17 toxic PCDD/F congeners. With this in mind, it is proposed to establish a mathematic model that allows to reduce the congeners needed to estimate the TEQ. This reduction of the congeners to simulate will also optimize the whole process of estimation. A mixture of industrial and research data will be used to do this study. The models will also be tested and statistically bounded with other comparable data.

Once the TEQ is estimated based on process variables, it is necessary to determine the amount of flue-gas in normal conditions that vehiculates the pollutant to estimate the final value of the atmospheric emission. This final step will be developed by using a process simulation model using ASPEN HYSYS, that will be adjusted by reproducing the results obtained experimentally using a laboratory tubular furnace.

4. Modelling the total amount and toxicity of dioxins reducing the number of congeners needed

4.1 Introduction

Data on PCDD/F emissions analytics are available from resembling combustion processes. This information provides both concentration and TEQ for all the 17 main congeners studied. These analytics, with 17 concentration values per sample, are named as $\mathbb{X}$. The aim of this study is to determine a model that estimates the total amount and toxicity in a sample containing PCDD/F reducing the number of congeners to analyse. With this target in mind, it is proposed to determine the amount of some congeners as a lineal combination of those congeners identified as independents. Other authors have proposed some correlation between the total concentration of two groups of congeners (highly or lowly chlorinated) and the TEQ, producing an average correlation coefficient of 0.8603 for tetra- to octachlorinated (highly chlorinated) PCDD/F, depending on the selected group of congeners and the weather (summer or winter) (Song et al., 2007).

As it is explained in the Chapter 2.2.1, the Toxic Equivalents of a sample are calculated as a sum of the individual concentration of each congener multiplied by their Toxic Equivalency Factor. Since this linear combination considers all the congeners as an independent source of toxicity, it can only be used if the amount of all the congeners is known individually. This fact implies to determine the formation of all the congeners during a simulation process, which is an important amount of calculation effort. In order to minimize the number of congeners needed to determine the total amount and toxicity of a sample, some statistical studies were performed. For this purpose, many analyses were provided, from IQS-URL Environmental Laboratory, which determined the amounts and TEQ of all the main PCDD/F congeners from resembling combustion processes. The sampling, extraction and purification, and the identification and quantification of the PCDD/F were performed according to UNE EN 1948:2007 (AENOR, 2007). All the analyses were organized into separated sets, which are listed at the end of this subchapter, named as variations of $\mathbb{X}_{\mathrm{OLD}}$. From these analyses, all of the congener amounts were above the limit of quantification (LOQ) in order to reduce all possible interference caused by the uncertainty of data below the LOQ. Each analysis contained the total amount of 17 PCDD/Fs congeners.

In order to increase the source of data used, and increase the range of application, some analyses from the “Waste, Energy, Environment and Nanotechnology research group

(WEEN)" from the University of Alicante were also provided. These analyses came from their experimental research related to thermal decomposition processes of several kinds of wastes. Within these analyses, all the PCDD/F concentrations were higher than the LOQ, trying to reduce all possible interferences due to its uncertainty. These analyses were named as variations of $\mathbb{X}_{NEW}$.

All the proposed set of analyses were studied in order to evaluate if any of those analyses were considered an influential point to determine a least squares fitting between them. This was evaluated using the *Hat Matrix Criterion*, $\mathbb{H}$, according to which all influential point fulfils that:

$$\forall i / h_{ii} > 3\frac{n}{p} \qquad (Equation\ 4.1)$$

Considering n as the amount of analyses, p as the number of congeners studied and h_{ii} as the terms in the main diagonal of the *Hat Matrix* ($\mathbb{H}$), which is defined in Equation 4.2.

$$\mathbb{H} = \mathbb{X}\,(\mathbb{X}^T\mathbb{X})^{-1}\mathbb{X}^T \qquad (Equation\ 4.2)$$

Following this methodology, 5 influential points were found in the IQS-URL Environmental Laboratory dataset. These points interact excessively with the regression line. Once identified, they were checked to see if this interaction was caused by any systematic reason. Considering its origin, 4 of them were excluded from the sample because the amounts were considered extremely high. Values in the highest part of a linear regression tend to influence more in its calculation. These 4 analyses were considered far apart from the other analyses, and this was considered enough reason to exclude them. No reason was found to exclude the fifth point, so it was considered. Hence, the final $\mathbb{X}_{OLD}$ matrix was formed by a set of 133 analyses.

All the sets used, and the variations of $\mathbb{X}_{NEW,}$ are listed below. To sum up, the datasets used during the statistical studies were:

- $\mathbb{X}_{OLD}$. This set contains the first 133 analyses (133 x 17) used to study the interdependence of the data and to determine the first pair of models.
- $\mathbb{X}_{OLD,VERIFY}$. This set contains 6 analyses (6 x 17) used to verify the first pair of models.

- $\mathbb{X}_{OLD,1LOQ}$. This set contains 55 analyses (55 x 17, one zero per row) with only one congener amount below the LOQ.
- $\mathbb{X}_{OLD,2LOQ}$. This set contains 73 analyses (73 x 17, two zeros per row) with only two congener amounts below the LOQ.
- $\mathbb{X}_{NEW}$. This set contains the newest laboratory-origin 64 analyses (64 x 17) from the University of Alicante, used to increase the source of data and the range of application.
- $\mathbb{X}_{NEW,INT}$. This subset contains the 28 analyses (28 x 17) from $\mathbb{X}_{NEW}$ that are within the range of $\mathbb{X}_{OLD}$.

4.2 Correlation analysis and FIVs

Since all PCDD/Fs congeners are produced simultaneously, its reactions of formation are expected to be related. Because of this correlation, there should be a subset of k congeners, that are linearly independents of each other, which will allow to estimate the total amount and toxicity of a sample. The correlation between the amounts of all 17 congeners was studied for the dataset $\mathbb{X}_{OLD}$ using the Pearson product-moment correlation coefficient (r) between all possible pairs. Figure 9 shows all pair combination of all amounts if 17 congeners studied. The range of these amounts was between the LOQ and 10^6. In the figure it is noticeable the accumulation of data on the lower values of the scatter plot. This fact produces a false strong linear correlation, since the contribution of the highest values is considerably bigger.

Figure 9. Scatter plot for raw data.

This issue was solved using decimal logarithm of all amounts with the aim of avoiding the influence of the different orders of magnitude of the amounts. The same procedure is repeated with this transformation of the data, and the result is shown in Figure 10. In this case it is noticeable that all data is distributed along the range more homogeneously. It is noticeable that all points in most pairs in the scatter plot show a linear pattern. This fact implies that the lineal trend was strong for most pairs of congeners. Thus, all datasets were transformed using decimal logarithm of the amounts.

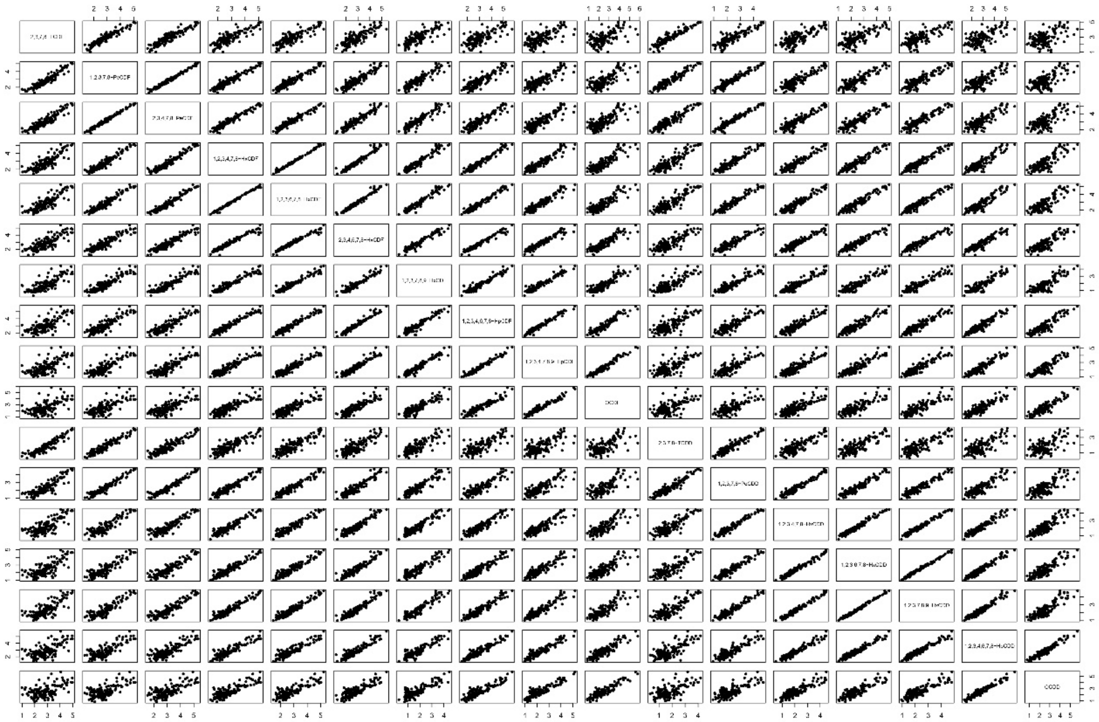


Figure 10. Scatter plot for decimal logarithm data.

Similar results were found by other authors (Head and Kennedy, 2010) between PCDD/Fs toxicity and polychlorinated biphenyl (PCB) or polychlorinated benzene (PCBz) toxicity, which are considered precursors of PCDD/F. In that investigation, decimal logarithm of the toxicity was also used.

Once this interdependence between the PCDD/Fs congeners was confirmed, a multicollinearity study on dataset $\mathbb{X}_{OLD}$ was executed in order to identify if the amount of any congener can be considered as a lineal combination of the amounts of other congeners. In this case, this congener could be discarded, conserving only the most linearly independent congeners. The selection of the most linearly dependent regressor was done using the variance inflation factors (VIFs), that considers each congener as regressor.

The correlation between the amounts of all 17 congeners was studied using the Pearson product-moment correlation coefficient (r) between all possible pairs. This was studied considering the raw data and repeated for the decimal logarithm of all amounts. These coefficients were all in a correlation matrix named as $\mathbb{R}$ matrix. These factors were calculated as the terms in the main diagonal of $\mathbb{R}$ matrix.

$$VIF_i = diag_i(\mathbb{R}^{-1}) \qquad (Equation\ 4.3)$$

It is considered that a regressor is linearly dependent as long as its VIF is above 10, which corresponds to fitting a multiple lineal regression whose coefficient of determination R^2 value is clearly below 0.90. Since the relation between VIF and R^2 is not linear, the value of R^2 was used as a definitive criterion. If this criterion was accomplished, that congener was discarded. This calculation was iterated, discarding the regressor with the highest VIF until the R^2 value was clearly below 0.90.

VIFs for all 17 congeners are shown in Table 7. It is remarkable that congeners 1, 10 and 14, corresponding to 2,3,7,8-TCDF, OCDF and 1,2,3,6,7,8-HxCDD, respectively, were considered as linearly independent since its VIF is associated to a R^2 value which is clearly below 0.90. VIF related to OCDF is also below 10 but the associated R^2 value is considered close enough to 0.90 to be discarded.

Table 7. Results for VIFs of each congener calculated iteratively. I-TEF value is extracted from (Kutz et al., 1990).

Number	Congener	I-TEF	VIF	R^2
5	1,2,3,6,7,8-HxCDF	0.1	639.3	0.9984
12	1,2,3,7,8-PeCDD	0.5	423.2	0.9976
16	1,2,3,4,6,7,8-HpCDD	0.01	315.2	0.9968
3	2,3,4,7,8-PeCDF	0.5	168.0	0.9940
4	1,2,3,4,7,8-HxCDF	0.1	141.0	0.9929
15	1,2,3,7,8,9-HxCDD	0.1	121.9	0.9918
9	1,2,3,4,7,8,9-HpCDF	0.01	99.6	0.9900
2	1,2,3,7,8-PeCDF	0.05	81.1	0.9877
8	1,2,3,4,6,7,8-HpCDF	0.01	64.5	0.9845
13	1,2,3,4,7,8-HxCDD	0.1	52.8	0.9811
6	2,3,4,6,7,8-HxCDF	0.1	31.8	0.9686
7	1,2,3,7,8,9-HxCDF	0.1	14.1	0.9289
11	2,3,7,8-TCDD	1	10.8	0.9073
17	OCDD	0.001	9.3	0.8925
14	1,2,3,6,7,8-HxCDD	0.1	5.2	0.8076
10	OCDF	0.001	3.4	0.7096
1	2,3,7,8-TCDF	0.1	2.4	0.5857

4.3 First set of models: industrial data

Once the multicollinearity was reduced, a linear regression was executed. Ordinary Least Squares (OLS) has been used as basic methodology to adjust a model to data (Kutner et al., 2005), considering the total amount of PCDD/F as a linear combination of the selected regressors.

$$C_{TOT} = b_0 + \sum_{j=1}^{k} b_j \cdot C_j \qquad (Equation\ 4.4)$$

Since the total amount of PCDD/F does not consider the TEF of each congener, one more linear regression was executed directly between the amount of each congener considered linearly independent and the total toxicity.

$$T_{TOT} = b_0 + \sum_{j=1}^{k} b_j \cdot C_j \qquad (Equation\ 4.5)$$

Where Cj was the amount of each congener j, C_{TOT} (in Equation 4.4) was the total amount of PCDD/F in the sample, T_{TOT} (In Equation 4.5) was the total TEQ of the sample and b_j were the parameters of the linear regressions of each regressor (where k was the number of selected regressors considered as linearly independent).

It was also necessary to establish an error criterion that allowed to evaluate the model obtained. It was proposed to present a graph where its dependent variable was the concentration or toxicity known from the analysis and its independent variable was the amount or the toxicity calculated via the models adjusted previously. It was expected to establish a graph with significant lineal trend, slope close to one and intercept close to zero. A linear regression was adjusted following Equation 4.4, where the total amount was calculated using the amount of the three linearly independent congeners amount (2,3,7,8-TCDF, OCDF and 1,2,3,6,7,8-HxCDD). The R^2 of this correlation was 0.9779, and the Adjusted R^2 was 0.9774. Once the linear regression was calculated, its residuals were checked in order to ensure the obtained parameters. The heteroscedasticity of residuals was checked using Breusch-Pagan test and no heteroscedasticity was found. Also, it was checked if any point can be considered atypical and diverts the correlation producing no normal distributed residuals. Following the Bonferroni test (Kutner et al., 2005), three points were considered as atypical and were excluded from the correlation. The linear regression was repeated with the remaining 130 analyses. The R^2 of this correlation was 0.9842, and the Adjusted R^2 is 0.9839. Now, residuals followed a distribution closer to normality. The adjusted parameters are shown in Table 8. This table also shows the p-value of each parameter if the null hypothesis (H_0) implies that no correlation is found between the amount of its related congener and the total amount. (H_0: Parameter = 0).

It is noticeable that none of the parameters can be considered equal to zero. This fact and the high value of R^2 are enough to validate the model 1 for Equation 4.4.

Figure 11 shows the relation between the estimated amount of PCDD/F using model 1 and the real value known by the chemical analysis provided. This model 1 was checked using $\mathbb{X}_{OLD,VERIFY}$, $\mathbb{X}_{OLD,1LOD}$ and $\mathbb{X}_{OLD,2LOD}$.

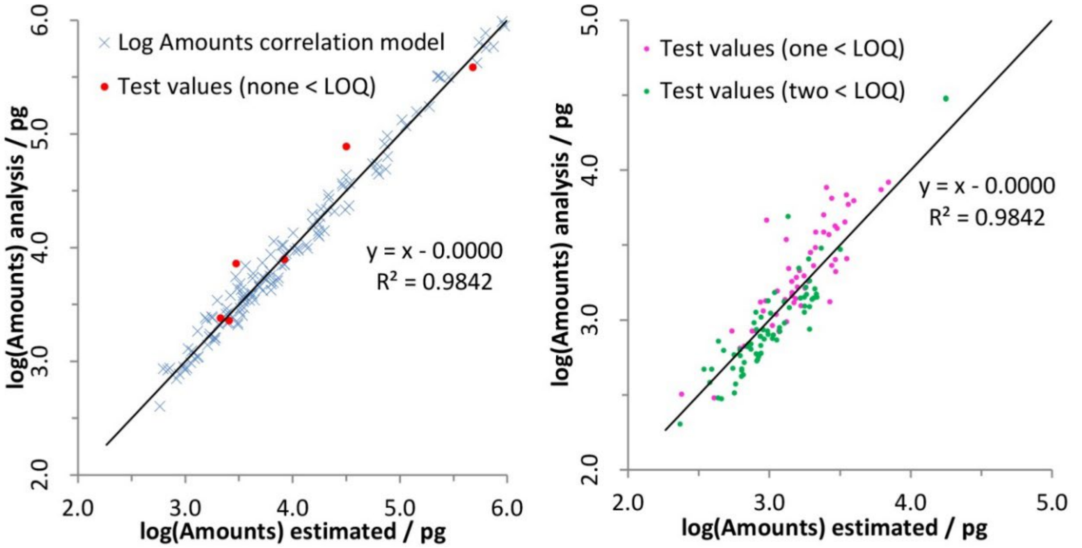


Figure 11. Total amounts estimated by model 1, considering as linearly independent the congeners 1, 10 and 14. Test values in dataset $\mathbb{X}_{OLD,VERIFY}$ are shown on the left. Test values in datasets $\mathbb{X}_{OLD,1LOQ}$ and $\mathbb{X}_{OLD,2LOQ}$, with one or two values below the LOQ on the right.

The 6 red points shown on the left graph of Figure 11 represent the dataset called $\mathbb{X}_{OLD,VERIFY}$. All of them were distributed across the entire range of the correlation and followed the model 1. For these 6 new analyses, the average relative error is 3.5% and the maximum relative error is below 9%. The graph on the right of Figure 11 represents some test values with one or two amounts of any congener below the limit of quantification. It is also noticeable that, even with these values below the limit of quantification, most of the points follow the model 1 properly. For the test values with two amounts below the LOQ, the average relative error is 4.3% and the maximum relative error is below 20%.

The correlation parameters and main statistical information of this testing linear regression for model 1 are shown in Table 9. This table also shows the p-value of each parameter considering the null hypothesis (H_0) supposes the value of the slope equal to 1 and the value of the intercept equal to 0. It should be noticed that a highly efficient correlation should present a slope close to one and an intercept close to zero.

This procedure was repeated to determine Equation 4.5, where the linear regression adjusted the total toxicity using the amount of each linearly independent congener. The results for this model 2, using the same 130 analyses that were used in model 1, are shown in Table 8. The value of R^2 for this model 2 was 0.9824.

Figure 12 shows the relation between the estimated amount of PCDD/F using model 2 and the real value known by the chemical analysis provided. Model 2 was checked using 6 new analyses with none of its amounts below the limit of quantification. In addition, model 2 was also checked using analyses where one or two congeners amounts were below the limit of quantification.

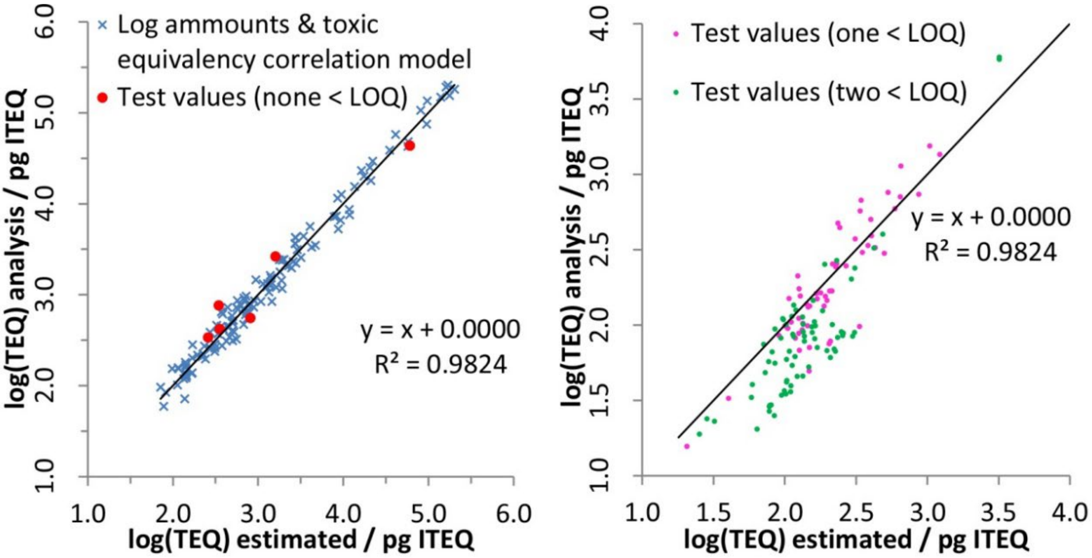


Figure 12. Total toxicity estimated by model 2, considering as linearly independent the congeners 1, 10 and 14. Test values with none amount below the LOQ on the left. Test values with one or two values below the LOQ on the right.

The 6 red points shown on the left graph of Figure 12 were 6 new analyses with none of the amounts below the limit of quantification. All of them were distributed across the entire range of the correlation and followed the model 2.

The graph on the right of Figure 12 represents some test values with one or two amounts of any congener below the limit of quantification. It is also noticeable that, even with these values below the limit of quantification, most of the points followed the model 2 properly.

The correlation parameters and main statistical information of this testing linear regression for model 2 are shown in Table 9. This table also shows the p-value of each parameter knowing that the null hypothesis (H_0) is considering that parameter equal to zero or equal to one. The same conclusion can be extracted for model 2, since the p-value for slope determines that is equal to one, and the value for the intercept is equal to zero.

Table 8. Parameters and statistic data for models 1 and 2.

Model		Variable	Parameters			
			b_{14}	b_{10}	b_1	b_0
1	n=130	Value	0.507	0.256	0.248	1.403
	$R^2 = 0.9842$	Std. error	0.0244	0.0195	0.0180	0.0333
		p-value for $H_0 : b_j = 0$	<0.0000	<0.0000	<0.0000	<0.0000
2	n=130	Value	0.483	0.089	0.454	0.409
	$R^2 = 0.9824$	Std. error	0.0260	0.0208	0.0191	0.0355
		p-value for $H_0 : b_j = 0$	<0.0000	<0.0000	<0.0000	<0.0000

Table 9. Parameters for the testing of model 1 and 2 linear regression

Model	1		2	
Regression parameters	slope	intercept	slope	intercept
Value	1.000	0.000	1.000	0.000
Std. Error	0.0112	0.0457	0.0118	0.0381
p-value for H_0 : Intercept = 0		1.0000		1.0000
p-value for H_0 : Slope = 1	1.0000		1.0000	

These two models can be used to estimate the total amount and TEQ using only three congeners. Other models have been published using the correlation between TEQ or total amount and mono- to tri-chlorinated dibenzodioxin (Gullett and Wikström, 2000) producing similar adjusted values. The results of other models using the correlation between PAHs and PCDD/Fs showed a coefficient of determination of 0.62, while the multiple regression analysis with naphthalene, fluorene and phenanthrene showed that the coefficient of determination was 0.85 (Yan et al., 2010). The models presented in this work are more accurate than other correlations used on on-line dioxin detection based on the amount of trichlorobenzene, tetrachlorobenzene and dioxins, whose coefficients of determination (R^2) were around 0.89 (Guo et al., 2014).

4.4 Testing the first set of models with new data

The two previous models defined in Chapter 4.3 capable to determine the dioxins total amount and toxicity (TEQ) of an atmospheric emission based on the concentration of 1,2,3,6,7,8-HxCDD, OCDF and 2,3,7,8-TCDF have been tested with the dataset $\mathbb{X}_{\mathrm{NEW,INT}}$. As explained above, this dataset comprises a number of 28 new PCDD/F analyses from laboratory experiments whose total amount and TEQ fall within the range of the $\mathbb{X}_{\mathrm{OLD}}$ set. Figure 13 shows the interrelationship between the calculated dioxins total amount and TEQ using previous models 1 and 2, and the values from dataset $\mathbb{X}_{\mathrm{NEW,INT}}$. In these graphs, it is worth mentioning that the linear trend is still strong, even acknowledging that the slope is not close to 1 and the intercept is not close to zero. This fact suggests that a new adjustment of the model may be needed.

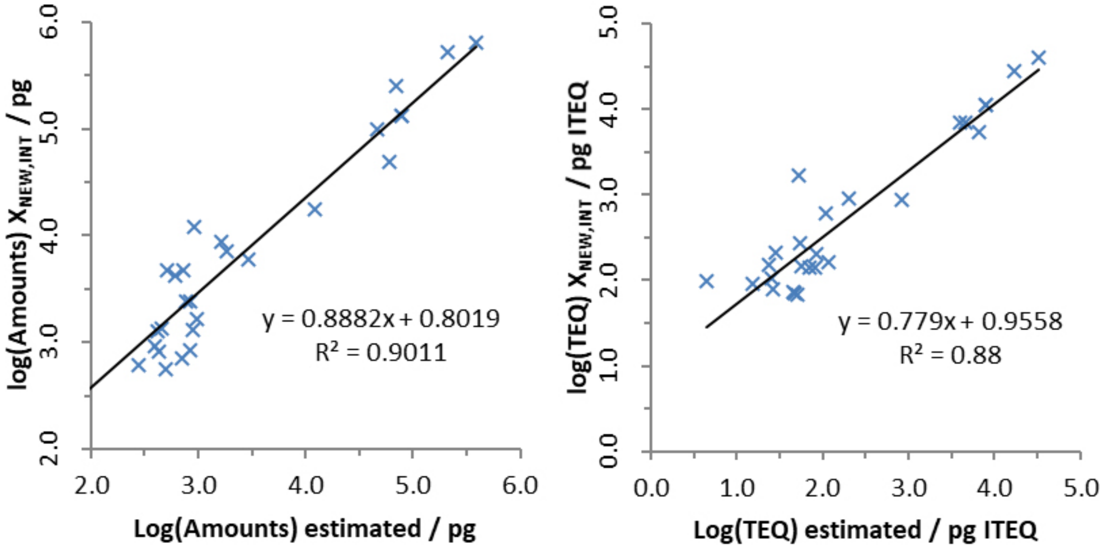


Figure 13. Total amounts estimated from previous model 1 (left) and total toxicity estimated from previous model 2 (right) using $\mathbb{X}_{\mathrm{NEW,INT}}$ dataset.

4.5 Second set of models: industrial and research data

In order to increase the source of data used, and increase the range of application, it is proposed to update the first pair of models combining $\mathbb{X}_{OLD}$ with $\mathbb{X}_{NEW}$. Thus, multicollinearity study is repeated combining both datasets (194 x 17) and comparing it to the results of the previous study using $\mathbb{X}_{OLD}$, which is shown in Table 10.

Table 10. Results for VIFs of each congener calculated sequentially, discarding the most linearly dependent congener after each iteration. The left half shows the results for both datasets mixed together (XOLD + XNEW) and the right half shows the results from XOLD as a comparison (Palmer et al., 2018).

$X_{OLD} + X_{NEW}$				X_{OLD}			
R^2	VIF	Congener	Number	Number	Congener	VIF	R^2
0.9875	80.2	1,2,3,6,7,8-HxCDF	5	5	1,2,3,6,7,8-HxCDF	639.3	0.9984
0.9850	66.9	1,2,3,7,8-PeCDF	2	12	1,2,3,7,8-PeCDD	423.2	0.9976
0.9745	39.2	1,2,3,4,7,8-HxCDD	13	16	1,2,3,4,6,7,8-HpCDD	315.2	0.9968
0.9720	35.7	1,2,3,4,7,8-HxCDF	4	3	2,3,4,7,8-PeCDF	168.0	0.9940
0.9682	31.5	1,2,3,4,6,7,8-HpCDD	16	4	1,2,3,4,7,8-HxCDF	141.0	0.9929
0.9636	27.5	1,2,3,4,6,7,8-HpCDF	8	15	1,2,3,7,8,9-HxCDD	121.9	0.9918
0.9625	26.7	2,3,4,7,8-PeCDF	3	9	1,2,3,4,7,8,9-HpCDF	99.6	0.9900
0.9584	24.0	1,2,3,4,7,8,9-HpCDF	9	2	1,2,3,7,8-PeCDF	81.1	0.9877
0.9564	22.9	1,2,3,7,8-PeCDD	12	8	1,2,3,4,6,7,8-HpCDF	64.5	0.9845
0.9477	19.1	1,2,3,7,8,9-HxCDD	15	13	1,2,3,4,7,8-HxCDD	52.8	0.9811
0.9364	15.7	2,3,4,6,7,8-HxCDF	6	6	2,3,4,6,7,8-HxCDF	31.8	0.9686
0.9111	11.2	OCDF	10	7	1,2,3,7,8,9-HxCDF	14.1	0.9289
0.8839	8.6	1,2,3,6,7,8-HxCDD	14	11	2,3,7,8-TCDD	10.8	0.9073
0.8039	5.1	1,2,3,7,8,9-HxCDF	7	17	OCDD	9.3	0.8925
0.7823	4.6	2,3,7,8-TCDF	1	14	1,2,3,6,7,8-HxCDD	5.2	0.8076
0.7834	4.6	2,3,7,8-TCDD	11	10	OCDF	3.4	0.7096
0.5503	2.2	OCDD	17	1	2,3,7,8-TCDF	2.4	0.5857

Considering $\mathbb{X}_{OLD}$ + $\mathbb{X}_{NEW}$ dataset, it can be observed that all VIFs are lower. This may be caused by the fact that the $\mathbb{X}_{OLD}$ dataset comes from industrial processes and $\mathbb{X}_{NEW}$ dataset comes from laboratory scale and experimental research. Despite these lower values, it is noticeably that the seven more independent congeners are the same in both datasets, although in a different order, as shown in Table 10. This fact reflects that the correlation between the formation of all 17 congeners is similar enough in both datasets, even considering the differences that may occur between industrial processes and laboratory scale processes.

Since this similar behaviour has been demonstrated comparing the values in Table 10, combining both datasets cannot be considered as arbitrary. Thus, congeners 2,3,7,8-TCDF, OCDF and 1,2,3,6,7,8-HxCDD are still considered as the ones linearly independent.

A new model 1’ was adjusted based on Equation 4.4, where the total dioxins amount was a linear combination of the amount of 2,3,7,8-TCDF, OCDF and 1,2,3,6,7,8-HxCDD. The datasets used were $\mathbb{X}_{\mathrm{OLD}}$ and $\mathbb{X}_{\mathrm{NEW}}$. The R^2 of model 1’ was 0.9705, and the Adjusted R^2 was 0.9702. The Adjusted R^2 takes into consideration the amount of regressors used in the model in order to avoid overfitting. Since both R^2 and Adjusted R^2 are almost equal, the possibility of overfitting is discarded. The parameters of the model are shown in Table 11. The same table includes the p-value assigned to each parameter when the null hypothesis (H_0) supposes that the tested congener and the total PCDD/F amount are not interdependent at all (H_0: Parameter $b'_j = 0$). Since the evaluation of p-values gave extremely low quantities, all of the parameters of model 1’ can be considered as significantly different to zero. This fact and the high value of R^2 are enough to validate model 1’ for Equation 4.4.

The same method was replicated to adjust model 2’ based on Equation 4.5, where the TEQ was a linear combination of the amount of 2,3,7,8-TCDF, OCDF and 1,2,3,6,7,8-HxCDD. The results for this model 2’, using datasets $\mathbb{X}_{\mathrm{OLD}}$ and $\mathbb{X}_{\mathrm{NEW}}$, are shown in Table 11. The value of R^2 for model 2’ was 0.9575, and the Adjusted R^2 was 0.9570. Following the same criteria as for model 1’, the possibility of overfitting is discarded since both R^2 and Adjusted R^2 are almost equal.

Table 11. Parameters and statistic data for the readjusted models: model 1’ for predicting PCDD/F amounts (pg) and model 2’ for TEQ values (pg I-TEQ).

Model		Variable	Parameters			
			b_{14}	b_{10}	b_1	b_0
	n=194	Value	0.351	0.389	0.225	1.560
1’	$R^2 = 0.9705$	Std. error	0.0258	0.0207	0.0216	0.0309
		p-value for $H_0 : b_j = 0$	<0.0000	<0.0000	<0.0000	<0.0000
	n=194	Value	0.349	0.182	0.378	0.762
2’	$R^2 = 0.9575$	Std. error	0.0295	0.0237	0.0247	0.0354
		p-value for $H_0 : b_j = 0$	<0.0000	<0.0000	<0.0000	<0.0000

Figure 14 shows the relationship between the dioxins amount or TEQ, determined with models 1’ and 2’ respectively; and the results from the chemical analysis provided by the laboratory.

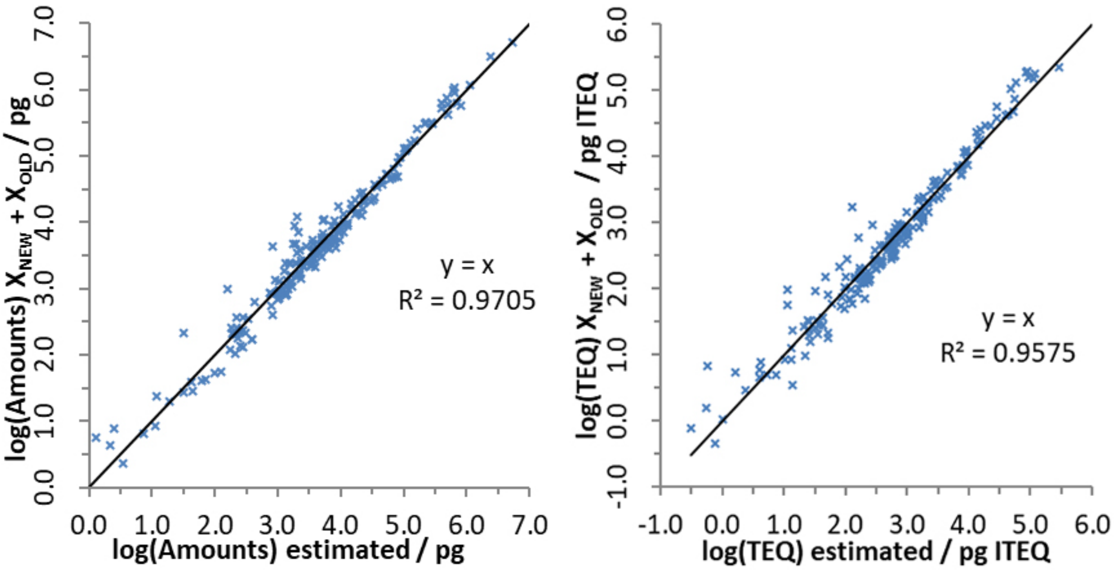


Figure 14. Total amount determined by model 1’ (left) and total toxicity determined by model 2’ (right), both calculated considering congeners 1, 10 and 14 as linearly independent.

The correlation parameters and main statistical information of the testing of the linear regressions for models 1’ and 2’ are shown in Table 12 and Table 9. Same table includes the p-value assigned to the slope when the null hypothesis (H_0) supposes that the calculated total PCDD/F amount or TEQ and the results from the chemical analysis are equal (H_0: slope = 1). The p-value assigned to the intercept when the null hypothesis supposes this parameter equal to zero is also included. These values confirm that model 1' and model 2' are highly efficient correlations since their slope is significantly equal to one and their intercept is significantly equal to zero.

Table 12. Parameters for the testing of the readjusted model linear regressions.

Model	1'		2'	
Regression parameters	slope	intercept	slope	intercept
Value	1.000	0.000	1.000	0.000
Std. Error	0.0126	0.0482	0.0152	0.0448
p-value for H_0 : Intercept = 0		1.0000		1.0000
p-value for H_0 : Slope = 1	1.0000		1.0000	

4.6 Improvement of the models presented with Bootstrap method.

Model 1' and model 2' are directly conditioned by the datasets used in their adjustment. Thus, the resampling Bootstrapping method was used in order to quantify the ability of the models to predict the variability of the total amount or the equivalent toxicity with the dataset used. For the resampling process, both sets $\mathbb{X}_{\mathrm{NEW}}$ and $\mathbb{X}_{\mathrm{OLD}}$ are used to adjust the new version of the models. Since the total amount of analyses will remain constant, some analyses may be used more than once in each adjustment. This process is iterated a large number of times (3000 iterations in this case) and all the parameters of each fit are collected in order to determine the confidence interval of the regression parameters. The value of the parameter of the model is equalled to the average of that parameter through all the iterations, and the standard error of that parameter is associated to its standard deviation. The confidence intervals are determined using the percentiles related to the selected statistical significance (95% in this case).

Once the models 1' and 2' are adjusted, the confidence intervals of their parameters are determined by an iterative resampling method with replacement. The resulting values obtained using the bootstrap method follow a normal (Gaussian) distribution. Hence, the value of each parameter used to define model 1' and model 2' will be equalled to the average of the values collected through 3000 iterations. The values of the percentile 2.5 and 97.5 represent the limits of the interval of confidence of 95%. The results of the bootstrapping are shown in Table 13.

Comparing the values of the parameters determined in Table 11 with the interval of confidence determined in Table 13, it is noticeable that all of them are in the interval of confidence and also close to the average value.

Regarding the values of R^2 and its low standard error it can be concluded that the percent of variability expressed through model 1' and model 2' is very stable to changes in the used dataset.

The results shown for model 1' and model 2' were also published (Palmer et al., 2019).

Table 13. Bootstrapping method results.

Model	Variable		Parameters			
		R^2	b_{14}	b_{10}	b_1	b_0
1'	Average	0.9711	0.354	0.386	0.225	1.560
	Std. Error	0.0056	0.0387	0.0285	0.0316	0.0423
	Percentile 2.5	0.9587	0.274	0.327	0.166	1.480
	Percentile 97.5	0.9812	0.429	0.439	0.290	1.640
2'	Average	0.9583	0.350	0.180	0.379	0.759
	Std. Error	0.0085	0.0364	0.0286	0.0356	0.0518
	Percentile 2.5	0.9400	0.277	0.124	0.307	0.656
	Percentile 97.5	0.9734	0.421	0.237	0.447	0.862

4.7 Discussion of the statistical models presented.

As shown in the previous sections, models 1' and 2' proposed in the section 4.5 can satisfactorily determine the total PCCD/F amount and TEQ from thermal processes based on the amount of only three congeners as an input. Compared to models 1 and 2 (Palmer et al., 2018), shown in sections 4.3 and 4.4, the current ones have a wider range of application, with increased number and sources of data. The dataset used to adjust the new models comprised 194 analyses ($\mathbb{X}_{\mathrm{OLD}} + \mathbb{X}_{\mathrm{NEW}}$), as opposed to the 133 ($\mathbb{X}_{\mathrm{OLD}}$) used in models 1 and 2, which represents an increase of almost 50% in the number of considered samples. In addition, the new dataset included data not only from industrial processes, but also from laboratory thermal decomposition experiments, broadening the scope of application of the models.

Considering that all 194 analyses come from thermal decompositions from both industrial and laboratory-scale processes, models 1’ and 2’ can be considered suitable for combustion processes in general. In the same way as in the first set of models, the values of the amount of the three congeners used to calculate the total PCDD/F amount or TEQ must be above the limit of quantification.

As it was discussed previously, many other models have been proposed, based on the interdependence between the concentration of mono- to tri-chlorinated dibenzo-*p*-dioxins and TEQ or the total concentration (Gullett and Wikström, 2000), with lower values for the coefficient of determination. The low P-values of many of these models that use low chlorinated PCDD/Fs as regressors also reflect that the correlations may be determined by chance. Furthermore, the use of monochlorinated to trichlorinated dibenzo-*p*-dioxins as a regressor is not as favourable as the use of some of the 17 toxic congeners, since the low chlorinated PCDD/F congeners frequently are not analysed nor controlled by the legislation.

The presented models 1’ and 2’ are still more accurate than those discussed during chapter 4.3. The resampling method allow us to statistically validate the parameters, determine their confidence intervals and the accuracy of the models by determining their root mean square errors (RMSE) and mean absolute errors (MAE). Considering those accuracy values for model 1’ and 2’, MAE values were 0.1541 and 0.1733 and RMSE values were 0.2115 and 0.2424.

5. Modelling the formation of dioxins in thermal decompositions of different types of residues

5.1 Introduction

The aim of the present chapter is to propose a kinetic model for the formation and destruction of different PCDD/Fs congeners, and to determine the kinetics parameters involved. The experimental data to fit the parameters will be data obtained from the decomposition of different wastes from previously published articles. The kinetic study proposed pretends to be simple enough to be used in a HYSYS simulation model, where the operational parameters needed to estimate the total PCDD/Fs emissions will be determined using the process model. In order to simplify the kinetics, a correlation between the formation of the PCDDF/s congeners previously explained in chapter 4 will also be taken into consideration (Palmer et al., 2019, 2018). The results were finally published (Palmer et al., 2021).

5.2 Experimental procedure

5.2.1 Origin of the thermal decomposition data

Thermal decomposition of several wastes was studied, in different but comparable conditions, by other authors from the University of Alicante laboratory, which have been published during more than 15 years. The experimental equipment used in their studies consisted of an oven with controlled temperature where the sample was introduced at a controlled speed. Thorough these years, different systems for the introduction of wastes were used, but following a general scheme, shown in Figure 15. In such systems, the waste sample was introduced at a controlled speed into an oven with a programmed temperature. The nominal temperature of the runs was varied between 500 and 1000 ºC. The residence time of the volatiles evolved was determined, and the pollutants evolved were sampled in a XAD-2 resin, that later was extracted with solvents for analysis of different species. In the present work, only PCDD/Fs will be considered. The analytical procedure comprises the extraction with toluene, change of solvent to hexane, acid treatment with sulphuric acid (when needed) and clean-up using the Power PrepTM system (FMS Inc., MA, USA) with three different columns: silica, alumina and activated carbon (FMS Inc., MA, USA). 13C labelled compounds included in the EPA 1613 method (U.S. Environmental Protection Agency, 1994) were used. The PCDD/Fs analysis was carried out by high resolution gas chromatography coupled to a high-resolution mass spectrometer (HRGC/HRMS). For HRGC, an Agilent HP5890 gas chromatograph equipped with a PTV inlet with septumless head was used. For HRMS, a Micromass Autospec Ultima NT mass spectrometer (Micromass, Waters, UK) with a positive electron impact (EI+) source was employed. A blank without sample, using the laboratory scale reactor in the same conditions as the runs, was done before the combustion experiments.

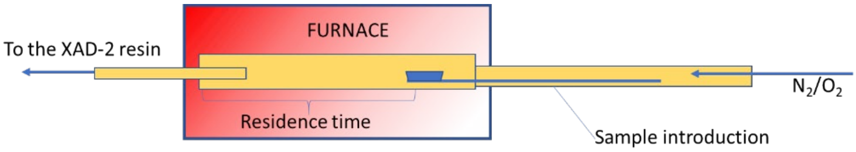


Figure 15. Schematic figure of the batch laboratory scale tubular reactor.

As a result of this work, a complete set of data was collected, combining different wastes and conditions of thermal decomposition (temperature, residence time, oxygen presence). Specifically, data from the following previously published investigations were used in the present work (classified by the waste used in the study):

- Meat and bone meal (MBM) (Conesa et al., 2005)
- Poly vinyl chloride (PVC) (Aracil et al., 2005)
- Cotton and polyester fabrics (Molto et al., 2006, 2005)
- Sewage sludges (Conesa et al., 2007; J A Conesa et al., 2011a; Galvez et al., 2007)
- Paper wastes (Conesa et al., 2008)
- Electronic waste (including materials from mobile phones and electric wires) (Conesa et al., 2013; J Moltó et al., 2009; Moltó et al., 2011)
- Polychloroprene (PCP) (Aracil et al., 2010)
- Solid Recovered Fuel (SRF) (J A Conesa et al., 2011)
- Viscoelastic memory foam (VMF) and flexible polyurethane foam (FPUF) (Garrido et al., 2017; Garrido and Font, 2015)
- Furniture wood waste (Moreno et al., 2017)
- Automotive Shredder Residue (ASR) (Rey et al., 2016)
- Pine cones and needles (Moltó et al., 2010)

Using all data on the list, a study of the evolution of the emissions of PCDD/Fs was done, as a function of the conditions in the decomposition zone. Apart from temperature and residence time of the gas in the hot zone, the presence of oxygen was controlled by using a constant flow of air and modulating the rate of introduction of the waste. In order to quantify the air excess (or defect), an oxygen ratio was used in all those publications, which was defined as:

$$\lambda = \frac{(\dot{m}_{O_2})_{actual}}{(\dot{m}_{O_2})_{stoic}} = \frac{\dot{m}_{air} \cdot 2\,3}{\frac{m_{sample} v}{L}\left(\frac{\%C}{12} + \frac{\%H}{4} + \frac{\%S}{32} - \frac{\%O}{32}\right) \cdot 3\,2} \qquad (Equation\ 5.1)$$

Where:

%O, %H, %S, %C = weight percentage of oxygen, hydrogen, sulphur and carbon in the waste sample, $\dot{m}_{air}$= air flow rate (kg/s), m_{sample}= weight of the waste (kg), L= length of tube occupied by the residue (m), ν= linear velocity of introduction of the tube (m/s).

Using this definition, a value of λ lower than one involves combustion in sub-stoichiometric conditions while values of λ higher than unity represent excess air.

Previous work shows that the presence of small amounts oxygen in the gas can promote the formation of PCDD/Fs, and that the emission in the pyrolysis conditions is not zero (Conesa et al., 2007; Rey et al., 2016). The oxygen needed for that formation is obviously present in the waste. With the aim to introduce the oxygen ratio data in a kinetic model, a change in the definition of the oxygen ratio is needed, bearing in mind the presence of oxygen in the waste samples themselves. In this sense, the following corrected oxygen ratio (λ_C) is defined:

$$\lambda_C = \frac{(\dot{m}_{O_2})_{actual}}{(\dot{m}_{O_2})_{stoic}} = \frac{\dot{m}_{air} \cdot 23 + \frac{(\%O) m_{sample} \cdot v}{L}}{\frac{m_{sample} v}{L}\left(\frac{\%C}{12} + \frac{\%H}{4} + \frac{\%S}{32}\right) \cdot 3\,2} \qquad (Equation\ 5.2)$$

Note that all published data was based in the definition given in Equation 5.1 and the corrected oxygen ratio has been recalculated for all runs before using them for kinetic modelling. Table 14 shows all data used in the work in this chapter, with mention to the specific conditions and PCDD/Fs emission.

Table 14. Dataset used to fit the kinetic model. λ_C is calculated following Equation 5.2. As it is explained in Chapter 4, only 3 PCDD/F congeners are needed to express most of the variability of all of the 17 congeners.

Waste	**Chlorine content % (g/g waste)**	**Metal content % (g/g waste)**	**λ_C**	**Temp. (ºC)**	**Residence time (s)**	**Yield of congener 1 (pg/g)**	**Yield of congener 10 (pg/g)**	**Yield of congener 14 (pg/g)**
MBM	0.8	0.001	0.07	700	2.36	60.64	6.54	0.62
MBM	0.8	0.001	0.07	700	1.97	1.86	0.29	0.41
MBM	0.8	0.001	0.07	850	1.9	1.92	1.66	67.71
MBM	0.8	0.001	0.07	950	4.11	0.2	0.05	0.04
MBM	0.8	0.001	0.07	975	3.7	0.1	0.03	0.02
MBM	0.8	0.001	0.07	1100	1.62	0.25	0.07	0.05
MBM	0.8	0.001	0.07	1100	1.62	0.07	0.04	7.78
MBM	0.8	0.001	0.65	600	3.2	0.18	0.49	0.24
MBM	0.8	0.001	0.67	700	2.7	8.13	27.03	5.68
MBM	0.8	0.001	0.82	700	2.1	78.87	0.52	0.08
MBM	0.8	0.001	0.84	850	1.73	0.12	0.02	0.08
MBM	0.8	0.001	0.72	950	1.94	0.11	0.42	0.12
MBM	0.8	0.001	0.71	975	1.92	0.3	3.06	4.1
MBM	0.8	0.001	0.78	1100	1.78	1.19	3.31	0.37
MBM	0.8	0.001	0.47	1000	1.59	26.93	3639.63	1.2
MBM	0.8	0.001	0.07	600	2.46	0.27	7.04	0.5
MBM	0.8	0.001	0.07	850	1.73	10.24	6.69	3.9
MBM	0.8	0.001	0.07	1000	1.59	2.4	35.1	3.7
MBM	0.8	0.001	1.55	600	2.46	1.62	0.97	3.31
MBM	0.8	0.001	1.51	850	1.73	10.41	20.76	0.69
MBM	0.8	0.001	1.73	1000	1.59	52.82	12.49	1.56
PVC	55.2	0.001	0.0006	850	3.54	4.1	1171	10.5
Cotton Fabrics	0	0.001	0.7	850	3.54	3.56	6.01	1.06
Polyester	0.01	0.45	0.71	850	3.54	3.31	9.89	6.99
Sewage sludge	0.18	0.02	0.57	850	1.77	19	797	9.4
Sewage sludge	0.18	0.02	0.57	850	1.77	6	517	4.5
Sewage sludge	0.18	0.02	0.57	850	1.77	2.8	3.4	13
Sewage sludge	0.18	0.02	0.57	850	1.77	12	4.8	9.4
Sewage sludge	0.18	0.02	0.57	850	1.77	1.2	17	13

Waste	Chlorine content % (g/g waste)	Metal content % (g/g waste)	λ_C	Temp. (ºC)	Residence time (s)	Yield of congener 1 (pg/g)	Yield of congener 10 (pg/g)	Yield of congener 14 (pg/g)
Sewage sludge	0.18	0.03	0.44	850	1.07	8.06	5.91	6.45
Sewage sludge	0.18	0.03	0.57	850	1.07	2.05	27.93	3.92
Sewage sludge	0.18	0.03	0.73	850	1.07	7.24	100.71	25.63
Sewage sludge	0.18	0.03	0.88	850	1.07	1.22	64.01	0.99
Sewage sludge	0.18	0.03	1.2	850	1.07	0.22	0.93	1.94
Electronic circuit	0.06	15.42	0.39	500	5.72	8.39	18.67	4.52
PVC	55.2	0.001	1	850	3.54	88670	803000	110510
PVC	30.58	44.59	0.46	375	7.24	232440	372904000	987300
PCP	36	0.001	0.71	850	3.54	4589.55	12867.59	1055.27
PCP	36	0.001	0.0365	850	3.54	1.22	53.25	1.17
PCP	36	0.001	0.71	850	3.54	4589.55	12869.33	1055.35
Sewage sludge	0.18	0.02	0.38	850	0.36	133.6	209.79	5.18
Sewage sludge	0.18	0.02	0.38	850	0.36	20.87	192.57	20.97
Sewage sludge	0.18	0.02	0.38	850	0.36	12.66	22.97	6.61
Sewage sludge	0.18	0.02	0.38	850	0.36	40.98	102.85	17.16
Sewage sludge	0.18	0.02	0.38	850	0.36	10.56	149.38	25.19
Halogen free wire	0.06	0	0.5	700	0.43	193.2	248.07	1.07
Halogen free wire	0.06	44	0.5	700	0.43	141.72	162.89	1.83
PVC wire	23.9	0	0.5	700	0.43	1851.12	154172.4	373.52
PVC wire	12	50	0.5	700	0.43	25813.05	276994.75	2250
Furniture wood	0.06	0.03	0.39	850	3.54	14.3	18.81	6.54
ASR	0.03	6.56	0.39	600	0.5	6200	23800	232
ASR	0.03	6.56	0.96	600	0.5	12800	192300	1160
ASR	0.03	6.56	1.54	600	0.5	5010	7360	767
VMF	0.01	0	0.82	750	3.34	2.2	10.3	1.5

Waste	Chlorine content % (g/g waste)	Metal content % (g/g waste)	λ_C	Temp. (ºC)	Residence time (s)	Yield of congener 1 (pg/g)	Yield of congener 10 (pg/g)	Yield of congener 14 (pg/g)
Electronic circuit	0.06	15.42	0.54	850	3.54	7.67	1868	99
Electronic circuit	0.06	15.42	0.39	850	3.54	0.81	31.4	14.49
Mobile case	0.07	1.22	0.18	500	5.72	25.6	164	2945.6
Mobile case	0.07	1.22	0.18	850	3.54	2.4	228	12.8
Pine Needles	0.22	0.4	0.36	500	5.72	10.11	44.59	25
Pine Needles	0.17	0.27	0.35	500	5.72	7.42	79.95	154.47
Pine Cones	0.22	0.4	0.36	850	3.54	38.21	46.5	8.76
Pine Cones	0.17	0.27	0.35	850	3.54	0.09	38.44	14.78
Tomato plant	2.13	0.28	0.46	500	5.72	75.87	67.02	65.68
Tomato plant	2.13	1.14	0.46	850	3.54	7.39	77.23	42.31

5.2.2 Mathematical assumptions and data treatment.

As it is demonstrated in Chapter 4, there is a dependence between the emissions of all PCDD/F congeners, since the models explained there were able to estimate the total amount and toxicity using only the amount of 1,2,3,6,7,8-HxCDD, OCDF and 2,3,7,8-TCDF in the sample. The kinetic model of formation explained in this chapter will only consider these three congeners since knowing those three amounts is enough to estimate the total amount and toxicity of an atmospheric emission.

For fitting the kinetic model to the experimental data, an optimization of the kinetic constants has been performed using MATLAB software. The experimental data on the emission of the three considered congeners were transformed by using decimal logarithm, as the emission factors at the different runs were clearly of many different orders of magnitude. In that situation, the logarithm of the experimental data and those calculated by the model were compared using the following Objective Function (O.F.):

$$O.F. = \sum_{\substack{three\ cong.\\ i=1,2,3}} \left(\log(PCDD/F)_{i,\ expe.} - \log(PCDD/F)_{i,\ calc.}\right)^2 \qquad (Equation\ 5.3)$$

In the previous equation, $(PCDD/F)_i$ represents the measured amount of all three congeners in the emission of the dioxins and furans considered (in pg/g).

5.2.3 Kinetic model proposed

A mechanistic scheme for the synthesis and elimination of the three considered congeners should be proposed and tested. For that purpose, the following reaction steps are considered:

$$C + aO_2 \overset{\boldsymbol{k_{1i}}}{\rightarrow} bCO + cCO_2 + \ d\ (Aromatics) + f_i\ (PCDD/F)_i \qquad (Reaction\ 5.1)$$

$$(PCDD/F)_i + O_2 \overset{\boldsymbol{k_2}}{\rightarrow} other\ products \qquad (Reaction\ 5.2)$$

In the scheme, 'C' represents a carbonaceous part of the wastes to be decomposed, and the subindex 'i' refers to each one of the congeners considered (i=1, 2, 3). The values of 'a', 'b', 'c', 'd' and 'f' represents the yield coefficient of each species, in (g of species/g of waste decomposed). Parameter 'f_i' would represent the PCDD/F yield from the carbonaceous material and should be different for each congener. Once the different species are formed, they can react with the oxygen present in the surrounding atmosphere, following the second reaction shown in the previous scheme.

It is important to note that the proposed model considers the decomposition of each congener by reaction with oxygen. As a first approach, the kinetic constant for this reaction of decomposition is considered the same for the three congeners.

Formation of the chlorinated dioxins and furans (Reaction 5.1) is clearly influenced by the presence of metals and chlorine (Verhulst et al., 2014). Literature shows that the presence of a small amount of both metals or chlorine increases dramatically the formation of PCDD/Fs species. On the other hand, a clear excess of these species would not increase the

PCDD/F production rate anymore. For modelling such behaviour, it is proposed to use a parameter in the kinetic equation that accounts for the 'saturation' of the chlorine and metal effects, being The Chlorine Effect (Chl.E) and the Metal effect (Me.E) as explained in Equation 5.4 and Equation 5.5 respectively.

$$(\mathrm{Chl.E.}) = \frac{[\mathrm{Cl}]_{\text{in the sample}}}{\left([\mathrm{Cl}]_{\text{in the sample}} + \mathrm{K}_{\mathrm{Cl}}\right)} \qquad (Equation\ 5.4)$$

$$(\mathrm{Me.E}) = \frac{[\mathrm{Fe}+\mathrm{Cu}]_{\text{in the sample}}}{\left([\mathrm{Fe}+\mathrm{Cu}]_{\text{in the sample}} + \mathrm{K}_{\mathrm{Me}}\right)} \qquad (Equation\ 5.5)$$

The values of K_{Cl} and K_{Me} are constants to be optimized, and they represent half of the concentration that would saturate the corresponding effect of its presence. This means that a waste containing an amount of chlorine higher than two times the K_{Cl} value would present the maximum effect of this reactant in the reaction rate, but a higher amount would present the same effect. The same mathematic structure is proposed for the metal presence, with its corresponding value of K_{Me}.

A dependence of the kinetics on the presence of oxygen is necessary to account for the experimental evidences, for both reactions. As a first approximation it is considered a first-order dependence on the λ_C (corrected value of the oxygen ratio).

With these considerations, the differential rate equations for the above set of reactions are:

$$-\frac{dC}{dt} = k_{1,i} \cdot C \cdot \lambda_c \cdot (Chl.E.) \cdot (Me.E.) \qquad (Equation\ 5.6)$$

$$\frac{d(PCDD/F)_i}{dt} = f_i \cdot k_{1,i} \cdot C \cdot \lambda_c \cdot (Chl.E.) \cdot (Me.E.) - k_2 \cdot (PCDD/F)_i \cdot \lambda_c \ (Equation\ 5.7)$$

In this sense, a high presence of oxygen (high value λ_C) would produce a high amount of dioxins through Reaction 5.1 (in Equation 5.6) but also an important amount of these product would react following Reaction 5.2 (in Equation 5.7). Note that in pyrolysis conditions the amount of oxygen within the sample it is enough to produce a certain amount of PCDD/Fs. On the other hand, if λ_C is high, the Reaction 5.2 would be predominant and the amount of PCDD/Fs that survive would be nil.

The initial condition of Equation 5.7 is $(PCDD/F)_I = 0$ at the initial position of the sample (residence time t=0). Equation 5.7 will be integrated by numerical methods (Euler method) until the corresponding residence time of the experiment, assuming that the reactor is isotherm at the temperature of the run. During the integration, it is not possible to distinguish between f_i and k_{1i}, so a value of $k''_{1,i}=(f_i \cdot k_{1,i})$ would be considered. Also, the variation of 'C' species is negligible (much minor than variation of dioxins and furans yields), and a constant value is expected. In this way, so a value of $k'_{1,i}=(f_i \cdot k_{1,i} \cdot C)$ will be considered. Note that the presence of chlorine and metals does not affect the rate of the second reaction, as it would be produced in the gas phase, reacting the different volatile species with the oxygen present.

The variation of the kinetic constants with temperature follows the Arrhenius equation:

$$k'_{1,i} = k'_{10,i} \cdot \exp\left(-\frac{E_{1,i}}{RT}\right) \qquad (Equation\ 5.8)$$

$$k_2 = k_{20} \cdot \exp\left(-\frac{E_2}{RT}\right) \qquad (Equation\ 5.9)$$

For the sake of simplicity, and as a first approach, the activation energies for the formation of all three congeners will be considered equal ($E_{1,1}=E_{1,2}=E_{1,3}=E_1$).

The parameters of the model are then: $k'_{10,1}$, $k'_{10,2}$, $k'_{10,3}$, E_1, k_{20}, E_2, K_{Cl} and K_{Me} (8 parameters for a total of 64 runs). It is known that a great interrelation exists between the pre-exponential factor, activation energy and reaction order (Schwaab and Pinto, 2007), so with the aim of reducing it, the constants at a defined temperature (k_{993K}) was optimized instead of the pre-exponential factor, that is easily calculated from the following equations:

$$k_{0i} = k_{993K} \cdot exp\left(\frac{E_i}{R \cdot 993}\right) \qquad (Equation\ 5.10)$$

$$k_i = k_{993K} \cdot exp\left(\frac{E_i}{R \cdot 993} - \frac{E_i}{R \cdot T}\right) \qquad (Equation\ 5.11)$$

Other more complicated models have been tested for the fitting of the experimental data, but not significant improvement was found. The modifications considered include the variation of the reaction order for the effect of oxygen in both reactions, and the consideration of three different activation energies for Reaction 5.1.

Other authors have already used same equations for describing the formation and destruction of dioxins shown in Reaction 5.1, as long as the use of the Arrhenius equation to describe the effect of temperature on the kinetic constants of each reaction. As a main difference, other authors did not take into account the oxygen content in Reaction 5.2 (Lin et al., 2023).

5.3 Results and discussion

The complete dataset used to fit this model is shown in Table 14. (Congener 1= 2,3,7,8-TCDF, Congener 2 = OCDF, Congener 3 = 1,2,3,6,7,8-HxCDD).

The integration of the equations used to determine the amount of the 3 selected congers was performed following Euler's method (First Order Runge-Kutta Method). The optimization of the Objective Function (O.F.) defined in the Equation 5.3 was done by using a multidimensional unconstrained nonlinear minimization (Nelder-Mead) by using the function 'fminsearch' of the Matlab language. Considering that the results of this optimization method depend on the starting point, for the optimization of the kinetic constants, data from wastes where chlorine and metal content is not too high were considered to start with this optimization. Once a better starting point was determined, all of the observations were introduced in the system (Chapra and Canale, 2009).

Table 15 (third column) shows the values of the optimized parameters. Figure 16 shows the fitting of these 46 runs, presenting the calculated vs. experimental values of the yields of each congener. A satisfactory correlation has been obtained (O.F.=180.1), with a good ordering of the runs in all three cases. It can be checked that the activation energies obtained in the fitting are quite low, in the order of 15-45 kJ/mol. Similar values were obtained for a unique reaction that modelled the formation of all dioxins as a single congener, with an activation energy of 71 kJ/mol as a result (Huang and Buekens, 2001).

The values of the preexponential factors calculated (Table 1), indicate that congener 2 is favoured vs. the other two congeners, as the value of $k'_{10,2}$ is one order of magnitude higher than the other two.

Respect to the value optimized for K_{Cl}, as commented before, it would indicate that a concentration of chlorine higher than twice 0.0509 g/g, i.e., 10.18 wt. % of chlorine, would not produce an increase in the formation rate. In the same sense, K_{Me} is ca. 0.25 wt. %, i.e., a very small amount of metals is needed to get the maximum formation rate.

Table 15. Parameters of the kinetic model and optimized values.

Parameter	Units	Optimized value (n=46)	Optimized value (n=64)
		O.F.=180.1	O.F.=338.0
$k'_{10,1}$	pg PCDD/Fs / (g waste·s)	$5.73\cdot10^5$	$2.10\cdot10^4$
$k'_{10,2}$	pg PCDD/Fs / (g waste·s)	$1.73\cdot10^6$	$8.47\cdot10^4$
$k'_{10,3}$	pg PCDD/Fs / (g waste·s)	$5.03\cdot10^5$	$6.18\cdot10^4$
E_1	kJ/mol	16.79	12.16
k_{20}	s^{-1}	$2.23\cdot10^2$	$2.15\cdot10^4$
E_2	kJ/mol	44.56	54.36
K_{Cl}	g Cl/g waste	0.0509	0.0450
K_{Me}	g (Fe+Cu)/g waste	0.00259	0.0175

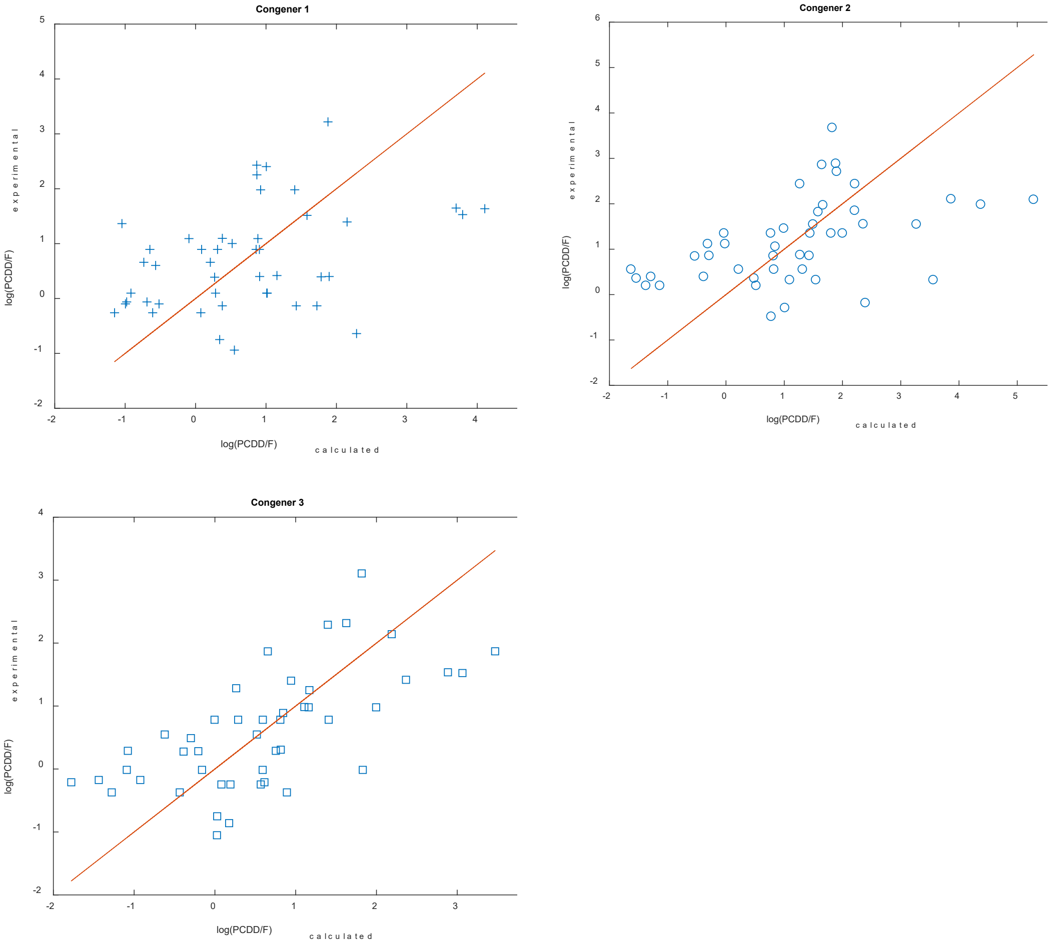


Figure 16. Results of the fitting using optimized values of the model adjusted using 46 runs for 2,3,7,8-TCDF (Cong. 1), OCDF (Cong. 2) and 1,2,3,6,7,8-HxCDD (Cong. 3).

Using the optimized values of the kinetic constants, it is possible to predict the emission of the rest of experiments carried out. In this way, a simulation of all other runs, without regarding the content of chlorine or metal in the waste, has been done using the kinetic constants optimized with n=46 runs, shown in Table 15. Figure 17 shows the results of the fitting/simulation of n=64 runs. As it can be seen, the simulated values of the emissions are satisfactory.

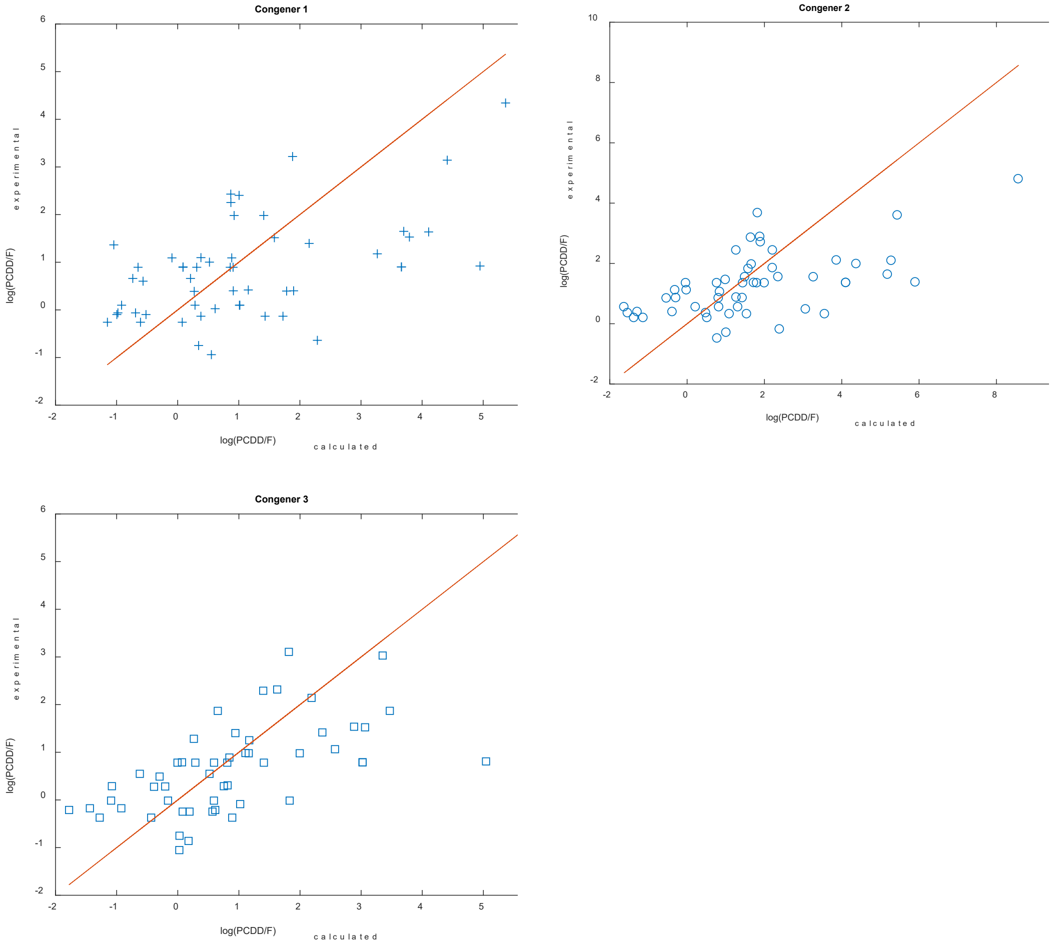


Figure 17. Results of the fitting using optimized values of the model adjusted using 64 runs for 2,3,7,8-TCDF (Cong. 1), OCDF (Cong. 2) and 1,2,3,6,7,8-HxCDD (Cong. 3).

Also, an optimization of the kinetic constants was done using all 64 runs presented in Table 14. The optimized values are also shown in Table 15 (last column). As it is noticeable, the values of the activation energies found considering all runs are a little bit higher but very low, now in the range 10-55 kJ/mol. The value of $k'_{10,2}$ is the highest one, compared to the values for the other two congeners, as was obtained considering less runs.

The proposed model with the optimized kinetic constants has been used for the simulation of the formation and destruction of the selected PCDD/Fs congeners in different situations. For doing this, values of temperature, ratio of oxygen, chlorine and metals content in the sample were selected, and the model was used to calculate the variation of the concentration of the dioxin congeners with residence time.

In a first simulation, the following values were used: $\lambda_c = 0.57$; metal content=0.0003182 g metal/g waste; chlorine content = 0.001804 g chlorine/g waste. Figure 18 shows the evolution of the concentration of Congener 1 with the residence time at different temperatures (500, 850 and 1000 ºC). As it is shown, a low temperature increased the amount of dioxin produced, mainly because Reaction 5.2 does produce a consumption of this species. In this way, at 1000 ºC the destruction of such pollutants is much higher than at lower temperatures.

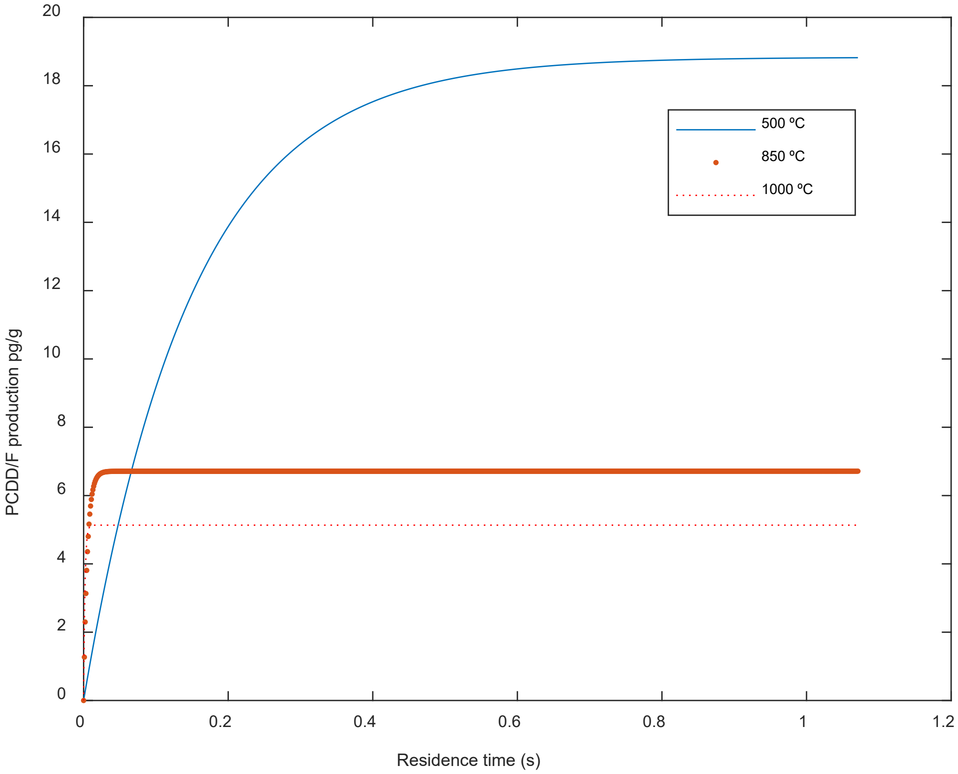


Figure 18. Evolution of the production of PCDD/Fs (Congener 1) with residence time at different temperatures.

A second simulation has been done, in this case maintaining temperature at 850 ºC and varying the value of λ_c. Figure 19 shows the results using the same values of the rest of variables presented before and using three different values of λ_c. As it can be seen, a higher destruction of PCDD/Fs is logically found at the higher value of λ_c, related to the presence of oxygen.

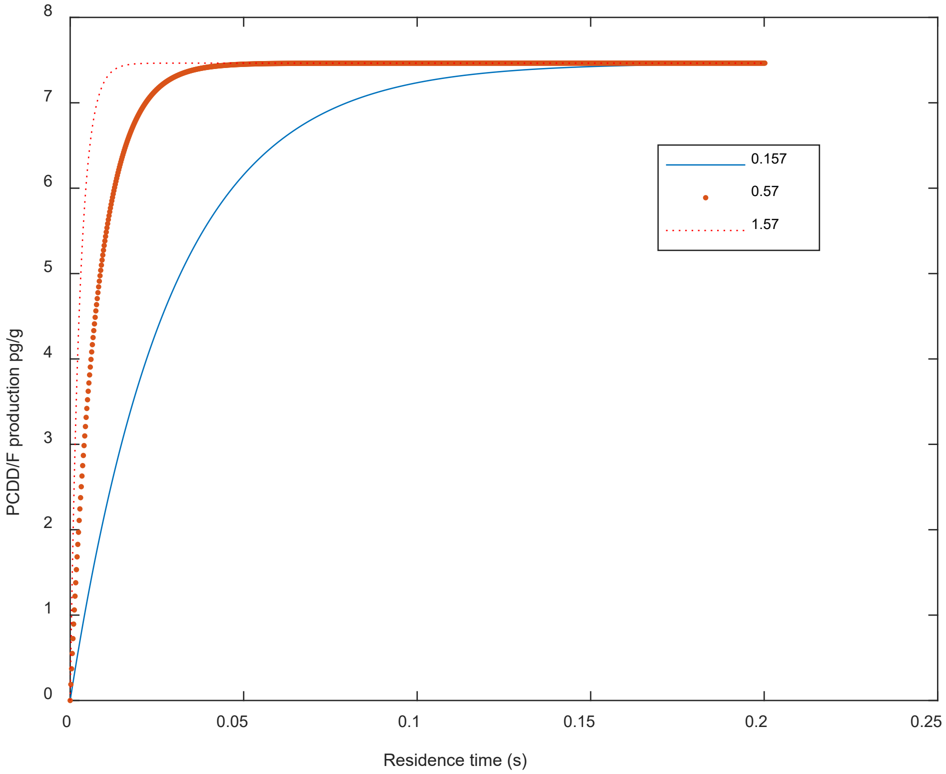


Figure 19. Evolution of the production of PCDD/Fs (Congener 1) with the amount of oxygen in the atmosphere (λ_c.values of 0.157, 0.57 and 1.57).

A third simulation was done, this time to see the effect of the metals in the waste (mathematically equivalent to the presence of chlorine in the presented model). Figure 20 shows the results for this simulation, where temperature and other variables are maintained invariants for all three values of metal content used. As expected, a high increase of PCDD/F production is observed when increasing the metal content from 0.3 % to 3 %, but the increase is not so important if the metal content is increased to 30 %.

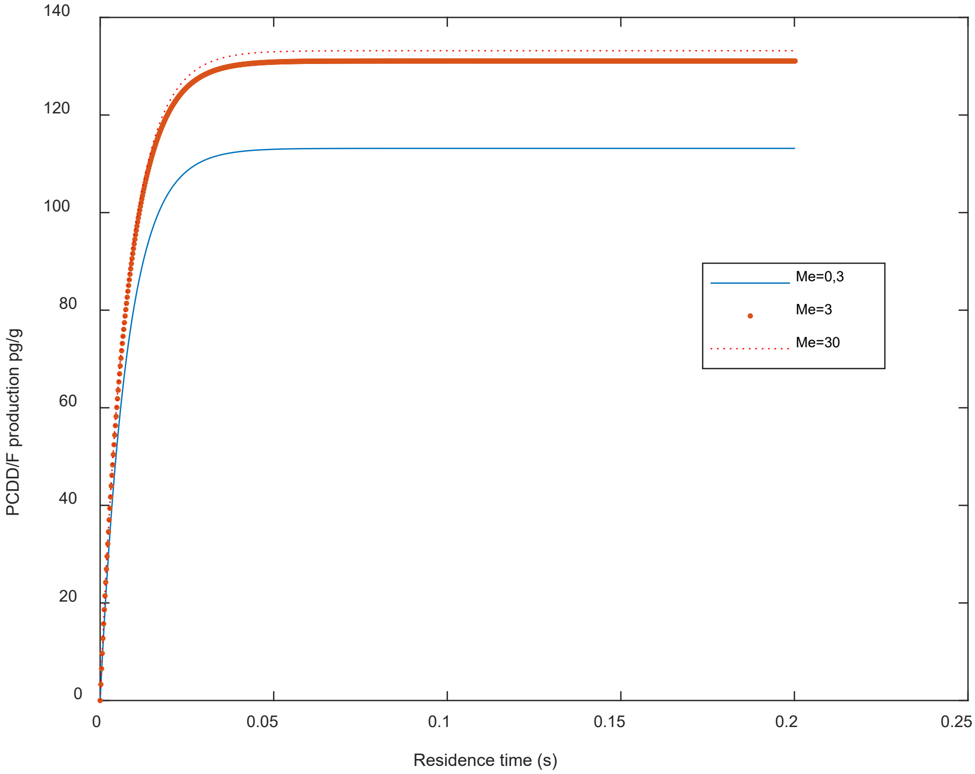


Figure 20. Evolution of the production of PCDD/Fs (Congener 1) with the amount of metals in the waste (values metal content of 0.3, 3 and 30 %).

One last simulation was done to show the effect of chlorine content in the waste in PCDD/F production. Figure 21 shows the result for this simulation where temperature, oxygen ratio and metal content are maintained invariants for all three values of chlorine content used (1, 15 and 20 %). As it was expected, a similar behaviour with metal content is produced, since both saturation effects have been simulated using mathematically equivalent expressions. As it can be seen, another sharp increase in PCDD/F production is observed when increasing the chlorine content from 1 % to 15 %, but the increase is not so important when the metal content is increased up to 20 %.

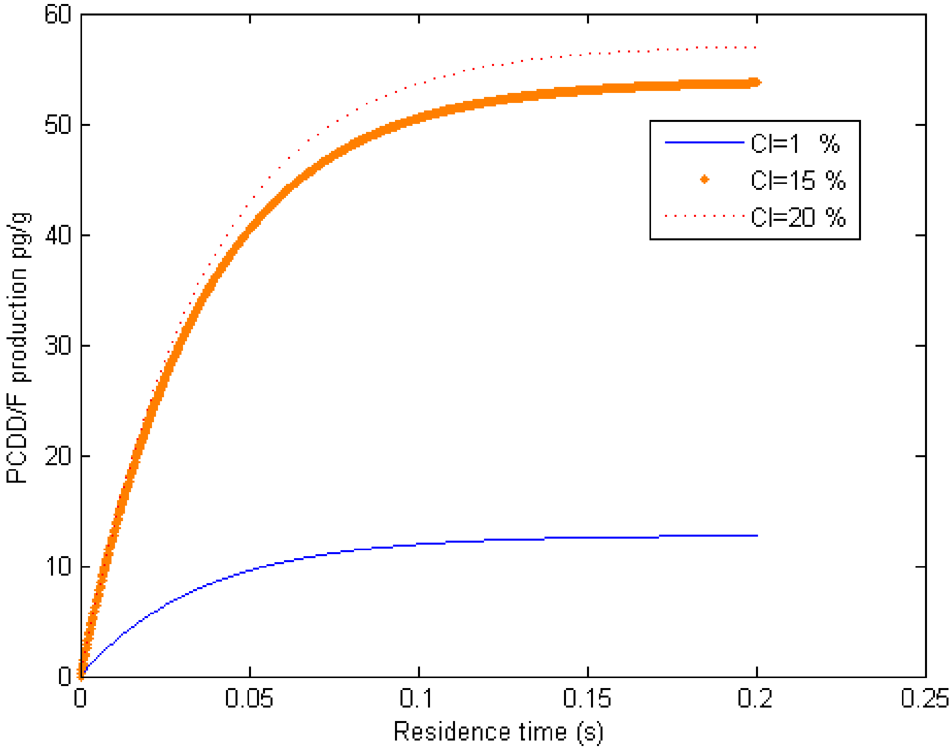


Figure 21. Evolution of the production of PCDD/Fs (Congener 1) with the amount of chlorine in the waste (chlorine, Cl = 1, 15 and 20 %).

6. Modelling an MSW incineration process to estimate the atmospheric emission

6.1 Introduction

Up to now, the total amount (or TEQ) emission models (explained in chapter 4) and the kinetic model of PCDD/F formation (explained in chapter 5), once combined, are able to estimate properly the TEQ emission, in picogram TEQ per gram of waste, considering only operational parameters of the combustion process such as temperature, oxygen content, and chlorine or metal content. Those emission values, which are in relation to the amount of waste consumed, cannot be considered as an atmospheric emission value, since there is a lack of information related to the gas flow that vehiculates the PCDD/Fs; therefore, its concentration is also unknown.

In order to estimate the atmospheric emission, all of the experiments taken into consideration to determine the kinetic model of formation of PCDD/Fs have been simulated using an ASPEN HYSYS Model. Once the atmospheric emission values are obtained, a better estimation of compliance with the standard legislation can be done. As it is explained in chapter 2.1.2, volumetric gas flow, water vapour content, temperature, pressure and oxygen amount at the emission point are needed.

The simulation of processes has become a powerful tool to design, assess and optimize engineering processes. One of the most used simulators for Chemical Engineering projects is ASPEN HYSYS. As a resume, this tool allows the users to easily construct a mathematical model that represents the complete heat and material balance of an industrial process. At a first stage, the simulator basically describes a series of equations which are connected to an interface architecture that easily combines the equations. Once this heat and material balance equations are defined, the user needs to introduce some constrains and parameters to solve those equations and completely fulfil the heat and material balance. Thanks to the Object-Oriented Design of the program, there is a rapid connection between parameters introduced and solving equation. This separation between the interface elements and the solving algorithm reduces the possibility of introducing incoherent information, since all of those parameters that can be obtained by calculation, are rapidly solved and showed in the mathematical model. The solving algorithm follows a non-sequential strategy, that allows to both use the parameters that are settled upstream and downstream to solve the system.

At first stage, a fluid package needs to be settled. This information includes the property package, the components used in the heat and material balance, the reactions needed, and the basic parameters needed to represent the interaction between components, the vapor-liquid equilibrium, the relation between temperature, pressure and composition, etc.

When a simulation model is started, it is mandatory to define the simulation basis environment. There, a fluid package and a library of components need to be defined. The fluid package includes the information needed to calculate the physical properties of the components included, as long as the thermodynamical equilibrium results. The matter transformation details (and the energy needed for that) also need to be included, defining the chemical reactions that may occur during the process.

Once these rules are introduced in the model, the simulation environment of the process needs to be developed in a space called flowsheet. When adding objects to the flowsheet, such as streams, vessels, heat transfer equipment, reactors, pipes, etc. a series of equations are added to the balance, and a series of parameters are required to solve the system. Once solved, all of the heat and material balance streams and process parameters are well known and available to be used, instead of needing to measure them experimentally.

6.2 Basis of Design

The aim of the HYSYS Simulation model was to reproduce all the data available from each experimental thermal decomposition in the real furnace to fulfil the heat and material balance and use the resulting calculations to calculate the atmospheric emission value. With this in mind, some assumptions and simplifications were considered, which are explained in the chapters to come.

6.2.1 Origin of the thermal decomposition data

During the same experimental procedures of thermal decomposition of wastes, which are explained in chapter 5.2.1, all the evolved pollutants from each run were sampled and analysed, beyond PCDD/Fs. These evolved pollutants content was expressed in the references used as a mass yield, related to the mass of waste introduced in the furnace (mg of pollutant per kg of waste).

Gases and volatile compounds were analysed by gas chromatography coupled to different detectors: CO_2 and CO were quantified using a thermal conductivity detector (GC-TCD, model Shimadzu GC-14A, fitted with an Alltech CTR I column) while light hydrocarbons (C1–C6) together with benzene, toluene and xylenes were analysed using a flame ionization detector (GC-FID, model Shimadzu GC-17A, fitted with an Alumina KCl Plot capillary column). Six different gas standard mixes containing known amounts of hydrocarbons C1–C6, CO_2 and CO, with the balance completed with N_2, were used to calibrate the gas chromatographs.

To analyse the organic semivolatile compounds, the sampling resin was Soxhlet extracted with dichloromethane in accordance with the US EPA method 3540C35 or by means of accelerated solvent extraction (Dionex ASE 100) with dichloromethane/acetone (1:1 vol.) according to U.S. EPA method 3545A36. The extracts were concentrated to approximately 1 ml and a recovery standard was added. For the 16 priority PAH analysis37, deuterated internal standards were added to the resin at the beginning of the process and the extracts were analysed by HRGC-MS (Agilent 6890N GC coupled to an Agilent 5973N MS) with an Agilent HP5-MS capillary column (30 m × 0,25 mm i.d. × 0.25 μm) in accordance with the U.S. EPA method 8270D38. These compounds were analysed in the SCAN mode (35–550 amu) with native standards used to identify and quantify them, whereas other semivolatile compounds were identified by comparison with the NIST mass spectral library, interpolating between the response factors from the two nearest deuterated standards for semi-quantification.

The elemental analyses of the wastes were also studied on these previous publications. The final CHNS analysis was carried out in a Perking Elmer 2400 (Perking Elmer, UK). The ash content was obtained by calcination at 850ºC. Oxygen content was estimated by difference. Chlorine content was analysed using the EPA Method 5050 by ionic chromatography using DIONEX DX500.

A complete dataset was collected from 98 experimental runs, that combined 20 different wastes and conditions of thermal decomposition: temperature, residence time, and oxygen ratio. Specifically, data from the following previous studies were used in the present work (classified according to the waste used in the simulation study):

- Meat and bone meal (Conesa et al., 2005)
- Poly vinyl chloride (PVC) (Aracil et al., 2005)
- Cotton and polyester fabrics (Molto et al., 2006, 2005)

- Sewage sludges (Conesa et al., 2007; J A Conesa et al., 2011a; Galvez et al., 2007)
- Tomato Plant (Molto et al., 2010)
- Electronic waste (including materials from mobile phones and electric wires) (Conesa et al., 2013; J. Moltó et al., 2009; Moltó et al., 2011)
- Polychloroprene (Aracil et al., 2010)
- Solid Recovered Fuel (SRF) (J A Conesa et al., 2011)
- Mattresses wastes (viscoelastic and polyurethane foams) (Garrido et al., 2017; Garrido and Font, 2015)
- Furniture wood waste (Moreno et al., 2017)
- Automotive Shredder Residue (ASR) (Rey et al., 2016)
- Pine cones and needles (Moltó et al., 2010)

In a previous publication (Garrido et al., 2016b) it was checked the reproducibility of the procedure performed during all these runs, considering the variety of wastes used, where it was noticeable that it was good enough for all the pollutants analysed in the effluent gases from pyrolysis of polyurethane. In the same way, the new data used to improve the model that was able to estimate the total PCDD/Fs amount and TEQ, explained in chapter 4.4, also came from these runs. In that chapter it is explained how the combination of both datasets could not be considered as arbitrary. Thus, all the runs that formed those two datasets can be considered as an entire one.

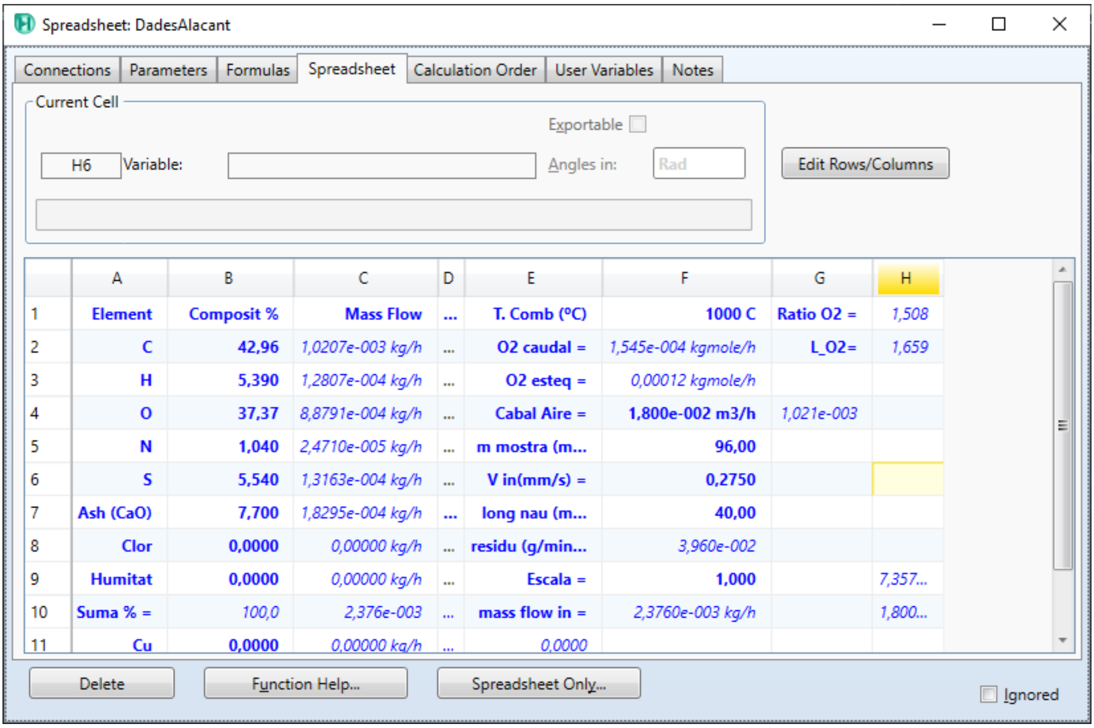
6.2.2 Simulation of the waste introduced in the furnace

Since the elemental composition of the wastes and the moisture content were already known, it was decided to add one material stream per element into the Aspen HYSYS model, representing all those elements (C, H, O, N, S, and Cl), where each element was considered as pure. Its mass flow was calculated in a Spreadsheet block as it is explained in Equation 6.1.

$$\dot{m}_\iota = \frac{m_{sample} \cdot v}{L} \cdot \%Element_i \qquad (Equation\ 6.1)$$

Where %Element$_i$ = weight percentage of the represented element i in the waste sample (such as nitrogen, oxygen, hydrogen, sulphur and carbon), m$_{sample}$= weight of the waste (kg), L= length of tube occupied by the residue (m), ν= linear velocity of introduction of the tube (m/s).

Once all mass flows were calculated, the value of the oxygen ratio (λ_C) was recalculated according to Equation 5.2 for double-checking the values introduced. After that validation, the calculated mass flow of each element was exported from that spreadsheet to its corresponding pure material stream. For all those material streams, pressure and temperature were also set as 25ºC and 1 atm. All those streams were combined into a single one as a summation of all the elements. Then, another current containing only pure water was added, which represent the moisture of the waste. This resulting stream simulates the waste introduced in the horizontal furnace. Later, one current with air (21% Oxygen and 79% Nitrogen, as molar percent) at 1 atm and 25ºC was also added. Both material streams were driven into a Conversion Reactor block, which parameters were adjusted for every run, in order to fulfil the heat and material balance. The spreadsheet block used is shown in Figure 22.



Current Cell: H6

	A	B	C	D	E	F	G	H
1	Element	Composit %	Mass Flow	...	T. Comb (ºC)	1000 C	Ratio O2 =	1,508
2	C	42,96	1,0207e-003 kg/h	...	O2 caudal =	1,545e-004 kgmole/h	L_O2=	1,659
3	H	5,390	1,2807e-004 kg/h	...	O2 esteq =	0,00012 kgmole/h		
4	O	37,37	8,8791e-004 kg/h	...	Cabal Aire =	1,800e-002 m3/h	1,021e-003	
5	N	1,040	2,4710e-005 kg/h	...	m mostra (m...	96,00		
6	S	5,540	1,3163e-004 kg/h	...	V in(mm/s) =	0,2750		
7	Ash (CaO)	7,700	1,8295e-004 kg/h	...	long nau (m...	40,00		
8	Clor	0,0000	0,00000 kg/h	...	residu (g/min...	3,960e-002		
9	Humitat	0,0000	0,00000 kg/h	...	Escala =	1,000		7,357...
10	Suma % =	100,0	2,376e-003	...	mass flow in =	2,3760e-003 kg/h		1,800...
11	Cu	0,0000	0,00000 kg/h	...	0,0000			

Figure 22. Spreadsheet block used to introduce the data needed to simulate the mass streams introduced in the furnace. Dark blue figures are the values taken from the dataset. Light blue figures are calculated and used to model the waste stream.

6.2.3 Simulation of the formation of pollutants in the furnace.

As it is explained in Chapter 6.2.1, the emission of CO, CO_2, light hydrocarbons and semivolatile organic compounds during the combustion runs are known values. In order to reproduce the emission of these pollutants in the HYSYS model, some reaction equations were defined to be used in the HYSYS Conversion Reactor block. Prior to that definition, the chemical components involved in the reactions must be specified. In addition to the components explained in chapter 6.2.2 to represent the waste stream, carbon monoxide (CO), carbon dioxide (CO_2), sulphur dioxide (SO_2) and hydrochloric acid (HCl) are added.

With these components, the HYSYS model is able to simulate all the compound emissions on a weight/weight basis for each run, with the exception of all of the emitted hydrocarbons. In order to simplify the HYSYS model, it is decided to represent all of them as a total organic content (TOC) using a single component, which should be the most representative from all of the hydrocarbon emissions in the heat and material balance.

With the aim of selecting a representative compound of total hydrocarbon emissions, the average H/C ratio of the emission was calculated for each run, based on the relationship explained in Equation 6.2.

$$Average\ {}^{H}\!/_{C} = \frac{\sum_{i}^{all\ analysed\ HCs}\left[\frac{mg\ of\ compound\ i}{g\ of\ waste}\cdot\left({}^{H}\!/_{C}\right)_{i}\right]}{\sum_{i}^{all\ analysed\ HCs}\left[\frac{mg\ of\ compound\ i}{g\ of\ waste}\right]} \qquad (Equation\ 6.2)$$

Results of the Average H/C calculation of the total hydrocarbon emissions during the combustion and pyrolysis of Viscoelastic Memory Foam at a range of temperatures (550ºC, 650ºC, 750ºC and 850ºC) are shown in Table 16. The table shows the contribution to the average of each hydrocarbon based on the emission values published (Garrido et al., 2017). The last row shows the final Average H/C value for each run. It is noticeable that the results vary from 0.95 to 2.62. Same analysis was performed for all the dataset used and explained in chapter 6.2.1, where the average H/C ratio underwent a drop between 0.80 and 3.90. With these results, a single compound representing the total hydrocarbon emissions was propylene, since its average H/C ratio was 2 and it was a very common hydrocarbon formed in most of the runs studied. Thus, propylene (C_3H_6) was also added as a component in the HYSYS simulation model.

Table 16. Results for Average H/C calculation for the hydrocarbon formation during pyrolysis and combustions of Viscoelastic Memory Foam at different temperatures (550ºC to 850ºC).

Hydrocarbon	$(H/C)_i$	Pyrolysis				Combustion			
		550ºC	650ºC	750ºC	850ºC	550ºC	650ºC	750ºC	850ºC
Methane	4.00	0.27	0.57	1.27	1.50	0.33	0.42	0.35	0.89
Ethane	3.00	0.10	0.16	0.16	0.08	0.05	0.07	0.04	0.04
Ethylene	2.00	0.29	0.30	0.68	0.90	0.37	0.39	0.28	0.59
Propane	2.67	0.03	0.02	0.01	0.00	0.01	0.01	0.00	0.00
Propylene	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isobutane	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08
Acetylene	1.00	0.00	0.00	0.00	0.02	0.01	0.01	0.01	0.00
n-Butane	2.50	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
1-Butene	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trans-2-Butene	2.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Isobutene	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cis-2-Butene	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopentane	2.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Pentane	2.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Propyne	1.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,3-Butadiene	1.50	0.00	0.01	0.03	0.02	0.00	0.00	0.00	0.00
2-Butyne	1.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Butyne	1.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Hexane	2.33	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01
cis-2-Hexene	2.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzene	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Toluene	1.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Xylenes	1.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Propene	2.00	0.05	0.09	0.04	0.04	0.03	0.02	0.00	0.00
Acetaldehyde	2.00	0.98	0.71	0.15	0.00	0.58	0.38	0.19	0.00
1-Buten-3-yne	1.00	0.00	0.00	0.01	0.02	0.00	0.00	0.02	0.04
2-Pentene	2.00	0.00	0.05	0.04	0.02	0.11	0.08	0.04	0.00
Ethanol	3.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
1,3-Butadiene	1.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Propanal	2.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetone	2.00	0.00	0.03	0.00	0.00	0.00	0.01	0.00	0.00
1,3-Cyclopentadiene	1.20	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.02
Acrylonitrile	1.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Acetamide	2.50	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.12
Total HC =		**1.83**	**2.00**	**2.42**	**2.62**	**1.49**	**1.40**	**0.95**	**1.81**

Once all the components were added, the reactions of formation of each component were defined in the HYSYS model as a reaction set. These reactions considered to happen inside the furnace were:

$$C + {}^{1}/_{2}\, O_2 \rightarrow CO \qquad (Reaction\ 6.1)$$

$$C + O_2 \rightarrow CO_2 \qquad (Reaction\ 6.2)$$

$$3\, C + 3\, H_2 \rightarrow C_3H_6 \qquad (Reaction\ 6.3)$$

$$Cl + {}^{1}/_{2}\, H_2 \rightarrow HCl \qquad (Reaction\ 6.4)$$

$$S + O_2 \rightarrow SO_2 \qquad (Reaction\ 6.5)$$

$$H_2 + {}^{1}/_{2}\, O_2 \rightarrow H_2O \qquad (Reaction\ 6.6)$$

These reactions were introduced in HYSYS as a unique reaction set and defined as conversion reactions, and then assigned to a conversion reactor block. This kind of reaction calculates the composition of the outlet stream based on the conversion value (in %) of the limiting reagent selected. In each run, the conversion value of each reaction was selected manually in order to exactly fit the results of the simulation with the results of the analysed pollutants from the thermal decomposition runs explained in chapter 6.2.1.

Since there is a competence between carbon and chlorine to react with the amount of hydrogen in the sample, the definition of the oxygen ratio was slightly modified in order to take it into account. This modification is shown in Equation 6.3.

$$\lambda_C = \frac{(m_{O_2})_{actual}}{(m_{O_2})_{stoic}} = \frac{\dot{m}_{air} \cdot 23 + \frac{(\%O) m_{sample} \cdot \nu}{L}}{\frac{m_{sample}\nu}{L}\left(\frac{\%C}{12} + \frac{1}{4}\left(\%H - \frac{\%Cl}{35.5}\right) + \frac{\%S}{32}\right) \cdot 32} \qquad (Equation\ 6.3)$$

Where:

%O, %H, %S, %C = weight percentage of oxygen, hydrogen, sulphur and carbon in the waste sample, m_{air}= air flow rate (kg/s), m_{sample}= weight of the waste (kg), L= length of tube occupied by the residue (m), ν= linear velocity of introduction of the tube (m/s).

Using this definition, a λ_C value below one still implies combustion under sub-stoichiometric conditions, while λ_C values above one represent excess air. Under pyrolytic conditions, the λ_C value can be different from zero if the sample waste contains oxygen. In this case, a limited amount of oxygen can be a source of production of oxygenated compounds, particularly PCDD/Fs and related compounds.

6.2.4 Run simulation in HYSYS and calculation of the atmospheric emission

The experimental runs were simulated using Aspen HYSYS V10 setting a Fluid Package based on the Peng-Robinson Equation of State. A representation of the model is shown in Figure 23. The waste introduced in the furnace was simulated using a stream per each component (C, H, O, N, S, Cl and moisture), as it is explained in chapter 6.2.2. Later, another current with air at 1 atm was added. The simulated currents entered a conversion reactor (set at each run's combustion temperature) where the reaction operates on a stoichiometric basis and will run until either the limiting reagent is exhausted, or the specified conversion has been achieved. In this conversion reactor, the Reaction 6.1 to Reaction 6.6 took place. Note that mass balances were solved and forced to fulfil the analytical results, and the conditions of P, V and T were calculated following the Peng Robinson equation of state, being all calculations integrated in the HYSYS tool. The mass balance was fitted to the experimental data manually, so that to the gas stream the consumed O_2 was eliminated and the generated CO_2, CO, COT (represented as propylene) and all the products of those reactions were added to the stream.

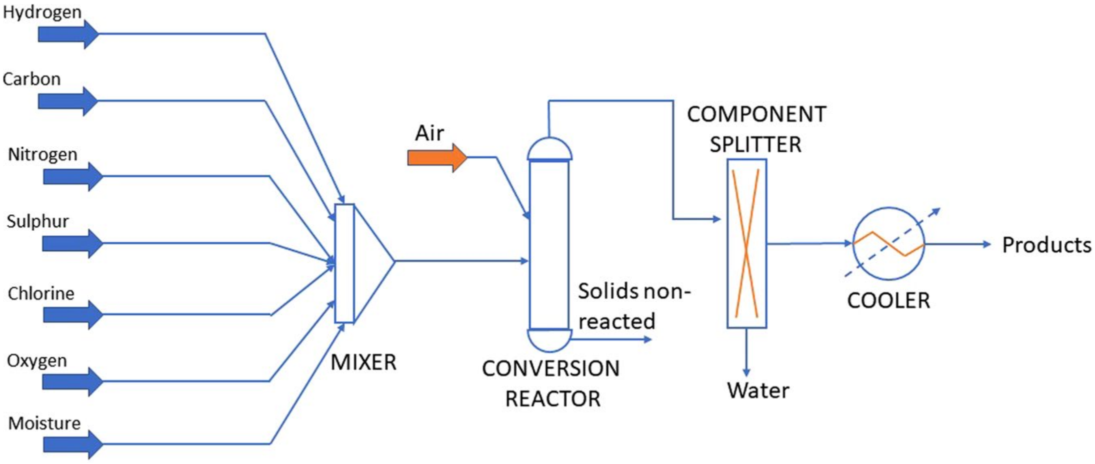


Figure 23. Schematic diagram of the units and streams used to simulate the thermal decomposition runs in the Aspen HYSYS model.

The reactor's bottom stream contains all the solid products that can be produced, such as Sulphur or Carbon excess that does not react during pyrolysis or combustions with a low O_2 ratio. The model includes a component splitter, coming after the reactor, that eliminates water vapour without producing any changes to other properties. The final current is then cooled at 25 °C (normal conditions). The oxygen's molar fraction is then obtained, and the normalised flowrate can be calculated based on this last current, by using a relationship that normalizes the effect of the oxygen content at the output gas flow, which is defined in Equation 6.4:

$$Normalized\ gas\ flow \left(\frac{Nm^3}{h}\right) = Output\ gas\ flow \left(\frac{Nm^3}{h}\right) \cdot \cdot \frac{21-11}{21-\%O_2\ in\ the\ output\ gas} \qquad (Equation\ 6.4)$$

In the previous equation, the oxygen percentage under normal conditions was established at 11% since it is the reference that the legislation determines for waste incineration facilities. Following this procedure, the different simulation runs performed in the laboratory allowed calculating the emissions on a normalised standard basis and then estimating the emissions of industrial-scale equipment.

This HYSYS model allows us to estimate the total gas flow rate of the exhausted gas as well as its oxygen content. Following this procedure, it was possible to calculate the normalised flow rate (25 °C, 1 atm, 11% O_2) and then to estimate the corresponding atmospheric emissions based on industrial equipment.

The calculation of the atmospheric emission is described as follows in Equation 6.5. Obtaining the TEQ required in the equation could also be the result of using the kinetic model of PCDD/Fs formation described in chapter 5:

$$
\begin{aligned}
PCDD/Fs_{Emission}\left(\frac{pg\ I-TEQ}{Nm^3}\right) = PCDD/Fs_{Yield}\left(\frac{pg\ I-TEQ}{g\ sample}\right)\cdot \\
\cdot\, Sample\ flow\left(\frac{g_{sample}}{h}\right)\cdot \\
\cdot\left[Normalized\ gas\ flow\left(\frac{Nm^3}{h}\right)\right]^{-1} \qquad (Equation\ 6.5)
\end{aligned}
$$

The result of this equation could be used to check whether the legal limit of 0.1 ng ITEQ/Nm^3 of the EU (European Parliament and of the Council, 2010) and the 0.5 ng TEQ/Nm^3 of the Chinese emissions standards (Environmental Protection Administration (China), 2006) is exceeded or not.

6.3 Results and discussion

The HYSYS simulation models were able to provide the output gas flow (Nm^3/h) and the oxygen content (v/v %) of the exhausted gas for each run. The results are shown in Table 17. This table also shows the value of the oxygen ratio of each run and also the relation Nm^3 per kg of sample introduced in the furnace, since a strong correlation between both variables was noticed.

Table 17. Values for the exhausted gas flow emission at the exit of the furnace and its content in oxygen, provided by the HYSYS simulation models. Wastes codification: ASR for automotive shredder residue, VMF for viscoelastic memory foam, FPUF for flexible polyurethane foam.

Waste	Temperature / ºC	Oxygen ratio / λ_C	STD Gas flow emission / Nm^3/h	O_2 in flue gas / (v/v%)	STD gas flow per waste mass / Nm^3/kg waste
Tomato Plant	500	0.46	0.0300	0.0	2.265
Tomato Plant	850	0.46	0.0300	0.0	2.265
ASR	600	1.54	0.0293	17.2	10.910
ASR	600	0.96	0.0289	12.8	6.620
ASR	600	0.59	0.0290	7.6	3.854
ASR	600	0.39	0.0309	0.0	2.565
ASR	600	0.0642	0.0066	0.0	0.506
ASR	850	1.25	0.0292	16.5	10.879
ASR	850	0.98	0.0288	11.3	6.664
ASR	850	0.58	0.0280	5.0	3.682
ASR	850	0.36	0.0308	0.0	2.413
ASR	850	0.0642	0.0102	0.0	0.787
VMF	850	0.84	0.0215	0.0	5.995
VMF	750	0.84	0.0215	5.1	5.990
VMF	650	0.84	0.0212	4.1	5.923
FPUF	550	0.11	0.0011	0.0	0.342
FPUF	850	0.11	0.0010	0.0	0.315
FPUF	550	0.85	0.0171	6.8	5.345
FPUF	850	0.85	0.0171	1.5	5.340
Pine Needles	500	0.36	0.0184	0.0	3.358
Pine Cones	500	0.35	0.0189	0.0	3.451
Pine Needles	850	0.36	0.0183	0.0	3.344
Pine Cones	850	0.35	0.0211	0.0	3.844

Though one may consider it a very rough rule, a correlation exists between the values of the total calculated amount of gas and the introduced oxygen ratio (Conesa et al., 2020). This dependence is shown in Figure 24.

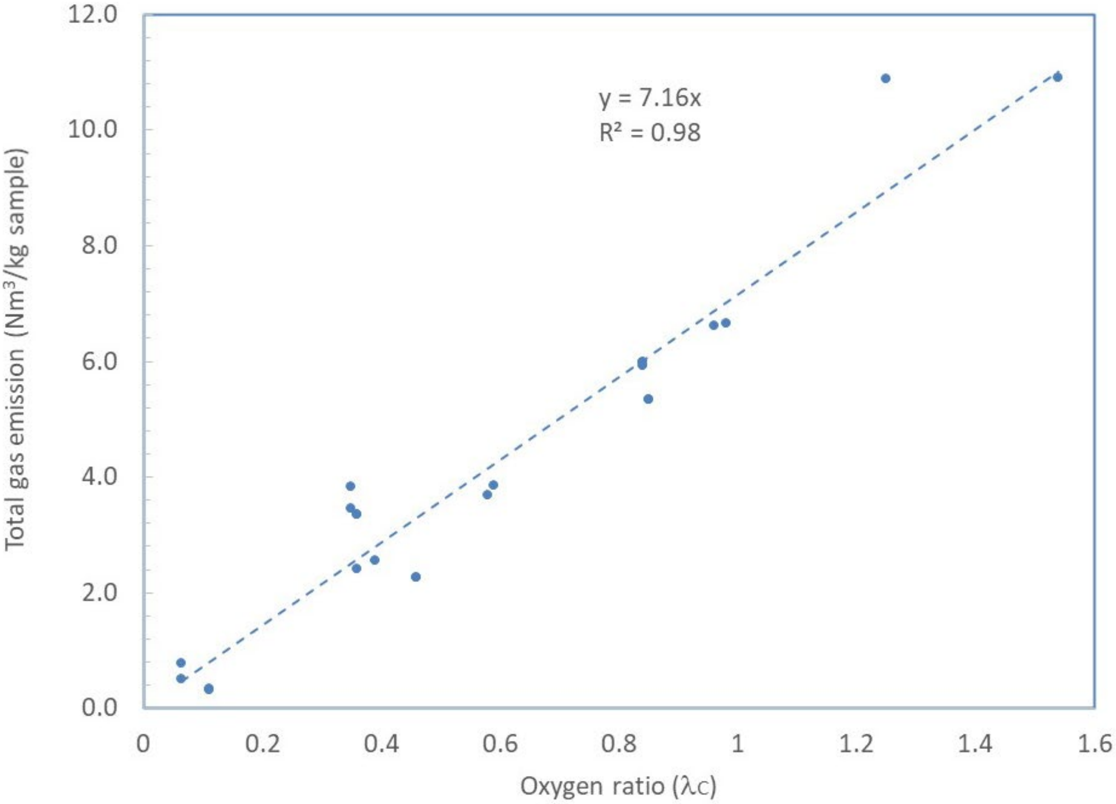


Figure 24. Correlation between the total gas emission of the exhausted gas and the oxygen ratio of the thermal decomposition process.

This correlation can be modelled following the Equation 6.6.

$$\frac{Nm^3 gas}{kg\ sample} = 7.1566 \cdot \lambda_c \qquad (Equation\ 6.6)$$

Adding this new correlation to Equation 6.5 simplifies the estimation of the PCDD/Fs atmospheric emission, which could be estimated as it is described in Equation 6.7.

$$PCDD/Fs_{Emission}\left(\frac{pg\ I-TEQ}{Nm^3}\right)=\frac{PCDD/Fs_{Yield}\left(\frac{pg\ I-TEQ}{g\ sample}\right)}{7.1566\cdot 10^{-3}\cdot\lambda_c\left(\frac{Nm^3}{g\ sample}\right)}\qquad (Equation\ 6.7)$$

This Equation 6.7 was applied to all of the runs explained in chapter 6.2.1, considering that the total PCDD/Fs toxicity was calculated as the summation of all of the amounts of each congener multiplied for its Toxicity Equivalent Factor. These results are shown in Table 18.

Table 18. Results for the PCDD/Fs atmospheric emission estimation for each residue studied applying Equation 6.7. Wastes codification: MBM for meat and bone meal, PVC for poly vinyl chloride, SRF for solid recovered fuel, ASR for automotive shredder residue, VMF for viscoelastic memory foam, FPUF for flexible polyurethane foam.

Waste	Temperature / ºC	Oxygen ratio / λ_C	Total PCDD/Fs / pg I-TEQ/g	Emission / ng I-TEQ/Nm^3
MBM	700	0.07	90.40	180.00
MBM	700	0.07	7.65	15.30
MBM	850	0.07	20.10	40.00
MBM	950	0.07	6.61	13.20
MBM	975	0.07	0.77	1.54
MBM	1100	0.07	0.45	0.90
MBM	1100	0.07	2.94	5.86
MBM	600	0.65	5.52	1.19
MBM	700	0.67	27.80	5.80
MBM	700	0.82	57.40	9.76
MBM	850	0.84	1.59	0.30
MBM	950	0.72	1.05	0.20
MBM	975	0.71	4.97	1.00
MBM	1100	0.78	4.95	0.90
MBM	1000	0.47	106.00	31.40
MBM	600	0.07	5.89	11.70
MBM	850	0.07	25.10	50.00
MBM	1000	0.07	32.70	65.20
MBM	600	1.55	8.58	0.80
MBM	850	1.51	26.60	2.46
MBM	1000	1.73	151.00	12.20
PVC	850	0.00	215.00	50020.00
PVC	850	0.09	4580.00	7180.00
PVC	375	0.46	183.00	55.50

Waste	Temperature / ºC	Oxygen ratio / λ_C	Total PCDD/Fs / pg I-TEQ/g	Emission / ng I-TEQ/Nm^3
PVC	850	1.00	224000.00	31300.00
Polychloroprene	850	0.71	11400.00	2240.00
Polychloroprene	850	0.04	22.20	84.90
Polychloroprene	850	0.04	23.40	89.30
Polychloroprene	850	0.71	11400.00	2240.00
Cotton Fabrics	850	0.70	8.36	1.67
Polyester fabrics	850	0.71	15.70	3.09
Sewage Sludge	850	0.57	1720.00	421.00
Sewage Sludge	850	0.57	58.50	14.30
Sewage Sludge	850	0.57	31.70	7.77
Sewage Sludge	850	0.57	35.70	8.74
Sewage Sludge	850	0.57	19.80	4.84
Sewage Sludge	850	0.44	33.50	10.60
Sewage Sludge	850	0.57	9.55	2.34
Sewage Sludge	850	0.73	73.00	14.00
Sewage Sludge	850	0.88	12.30	1.96
Sewage Sludge	850	1.20	4.59	0.50
Electronic waste	500	0.23	7.33	4.45
Electronic circuits	500	0.58	3.41	0.80
Electronic waste	500	0.05	29.10	90.20
Electronic circuits	500	0.39	28.20	10.10
Electronic Waste	850	0.23	76.40	46.40
Electronic Circuit	850	0.54	165.00	42.60
Electronic Waste	850	0.05	76.40	237.00
Electronic Circuit	850	0.39	23.50	8.42
Mobile Case	500	0.18	867.00	672.00
Mobile Case	850	0.18	17.70	13.70
Mobile Case	500	0.02	6.11	42.70
Mobile Case	850	0.02	6.11	42.70
Halogen free wire	700	0.50	71.00	19.80
Halogen free wire	700	0.50	66.90	18.70
PVC wire	700	0.50	6940.00	1940.00
PVC wire	700	0.50	41300.00	11500.00
SRF	850	1.45	777.00	74.80
SRF	850	1.00	2790.00	390.00
SRF	850	0.66	301.00	63.60
SRF	850	0.49	117.00	33.30
ASR	600	0.06	309.00	673.00

Waste	Temperature / ºC	Oxygen ratio / λ_C	Total PCDD/Fs / pg I-TEQ/g	Emission / ng I-TEQ/Nm^3
ASR	600	0.39	7110.00	2540.00
ASR	600	0.59	7720.00	1830.00
ASR	600	0.96	28500.00	4150.00
ASR	600	1.54	5440.00	493.00
ASR	850	0.06	22.50	48.90
ASR	850	0.36	76.90	29.80
ASR	850	0.58	29.70	7.14
ASR	850	0.98	50.40	7.17
ASR	850	1.52	81.00	7.44
FPUF	550	0.11	6.80	8.60
FPUF	550	0.11	30.70	38.80
FPUF	850	0.11	18.50	23.50
FPUF	850	0.11	28.60	36.10
FPUF	550	0.85	65.10	10.70
FPUF	550	0.85	60.70	10.00
FPUF	850	0.85	62.90	10.30
FPUF	850	0.85	96.60	15.90
VMF	550	0.12	2.86	3.45
VMF	650	0.12	3.78	4.55
VMF	750	0.12	5.39	6.50
VMF	850	0.12	0.20	0.20
VMF	550	0.82	0.55	0.00
VMF	650	0.82	3.41	0.60
VMF	750	0.82	3.48	0.60
VMF	850	0.82	20.30	3.45
VMF	850	0.82	17.70	3.01
Furniture Wood Waste	850	0.39	21.00	7.50
Furniture Wood Waste	850	0.39	15.20	5.45
Furniture Wood Waste	850	0.39	20.10	7.20
Solid Wood	850	0.39	1.79	0.60
Pine Needles & Cones	850	0.36	54.50	21.10
Pine Needles & Cones	850	0.35	601.00	240.00
Pine Needles & Cones	850	0.36	50.40	19.60
Pine Needles & Cones	850	0.35	98.20	39.10
Tomato Plant	500	0.46	923.00	280.00
Tomato Plant	850	0.46	147.00	44.60

The emission levels calculated using Equation 6.7 (shown in Table 18) were, in most cases, above the legal limit. This means that thermal decomposition under experimental conditions would (sometimes) produce a very high level of pollutants, in some cases exceeding 2500 ng I-TEQ/Nm^3. This result was expected, as the decomposition processes were carried out under conditions of poor oxygen presence (fuel-rich combustions), that maximise the formation of incomplete combustion products. Also the effect of the chlorine and metals is noticeable in wastes such as PVC, polychloroprene and the electronic wastes. Nevertheless, the model allows calculating the emissions of industrial thermal decomposition equipment under optimised operating conditions.

A study presenting actual emission of PCCD/Fs in municipal solid waste (MSW) incinerators (Everaert and Baeyens, 2002) showed that the emissions were usually in the range 0.5–31.8 ng ITEQ/Nm^3. MSW used in that investigation is similar to the SRF used in our study, both coming from household waste. Table 18 shows that the emission for SRF decomposition in oxygen-rich conditions ($\lambda_C = 1.45$) is 74.8 ng ITEQ/Nm^3.

However, emissions under pyrolytic conditions should not be compared with proposals within legal limits, since these limits refer mainly to combustion conditions with excess air and the aim of a pyrolytic process is keeping the evolved gas for a future use. During pyrolytic runs the amount of oxygen in the reaction atmosphere is almost zero (as it only comes from the oxygen in the waste itself). For this reason, the extrapolation of the composition of the gases obtained in pyrolytic runs to the standard 11% O_2 can be difficult.

In previous studies (Juan A. Conesa et al., 2011), the upper limit of industrial equipment emissions was estimated based on an average volume of evolved gases and a particular waste feed rate. In the present study, the emitted pollutants under the different oven conditions could be easily extrapolated to larger equipment, maintaining the decomposition conditions.

Using the results in Table 18 it was calculated the average PCDD/Fs emissions during the thermal decomposition of all wastes used, without distinguishing decomposition conditions (presence of air, temperature). The aim was to estimate which wastes tended to produce more dioxins and furans during their primary decomposition. The results are shown in Figure 25 on a logarithmic scale, as the values were quite different across the wide range of wastes tested.

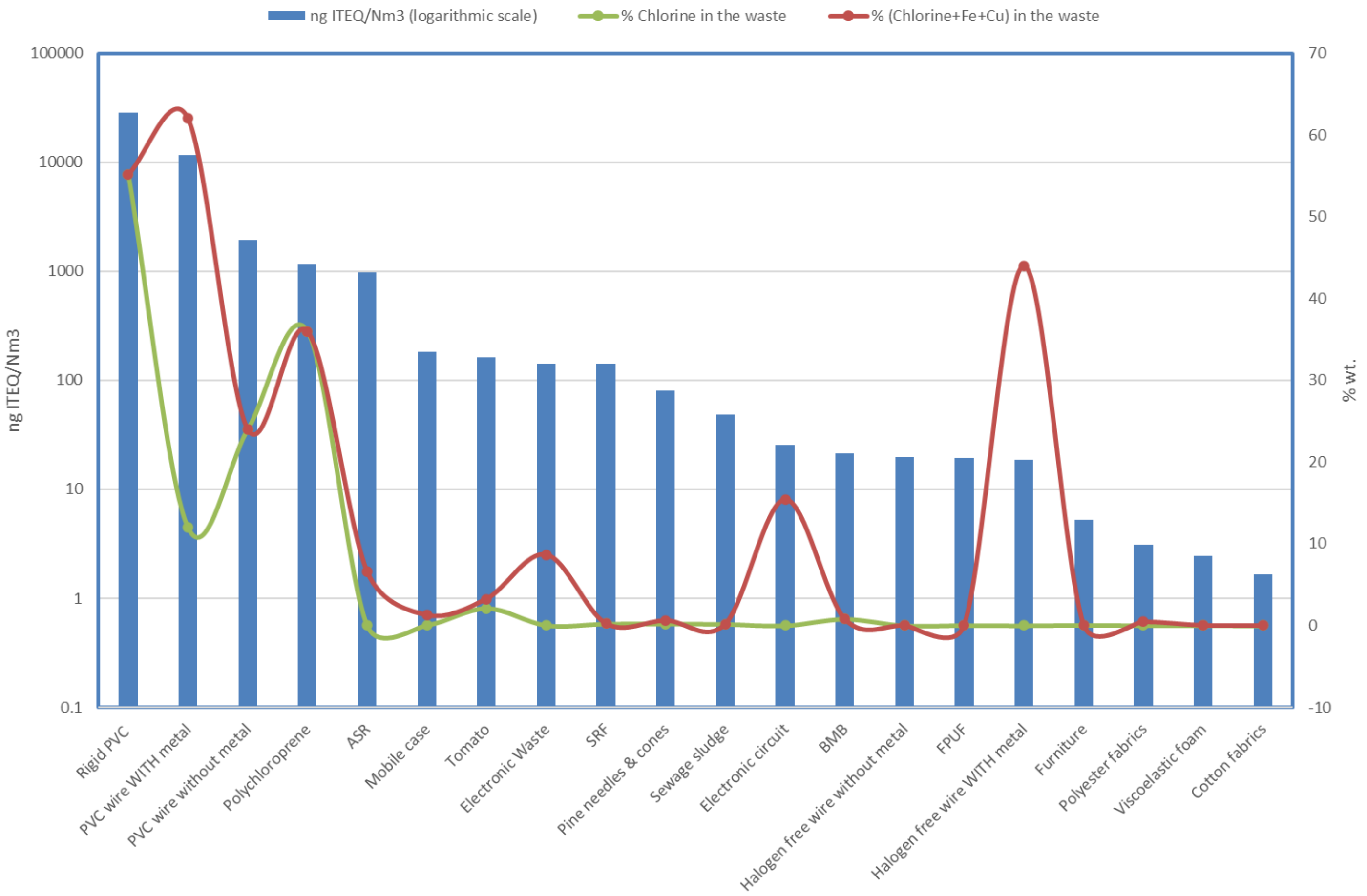


Figure 25. Average of the atmospheric emissions of PCDD/Fs from the thermal decomposition of each waste shown in Table 18. The chlorine and metal content in the waste is also shown to help with its interpretation.

Figure 25 also shows the percentage of chlorine present in the waste, and the percentage of the sum of chlorine and some of the major catalysts of PCDD/Fs formation such as iron and copper (Cl + Fe + Cu). The amount of emitted PCDD/Fs can be seen to closely correlate with the presence of chlorine. A few notable exceptions, however, are worth mentioning. The decomposition of PVC wire in the presence of metals (mainly Cu) produced a substantial amount of dioxins, which was much higher compared to when no metal was present. This points to the fact that the presence of metal catalyses the formation of these pollutants. The presence of metal was also high in the "Electronic circuit" and "Halogen free wire with metal" samples. Low emissions in both cases indicated that the presence of metal alone was insufficient to produce high amounts of dioxins: a certain percentage of chlorine in the waste is also needed. This result is compatible with previous literature that examined the role of the presence of metals and chlorine in the production of PCDD/Fs (Conesa et al., 2009; Dong et al., 2013; McKay, 2002; Stanmore, 2004, 2002; Tuppurainen et al., 1998).

It is worth noting that the data in Figure 25 represent the dioxin and furan content in the gas emitted during the primary decomposition, with no influence of the post-combustion process usually present in the incinerators, and obviously with no presence of air pollution control devices. Emissions from a real incineration plant would be affected by both processes, greatly diminishing the pollutants emitted. All of these results were also published (Conesa et al., 2020).

Furthermore, in recent years, abundant research has been conducted on the ability of certain N and S containing compounds to prevent the formation of PCDD/Fs during the thermal destruction of wastes. Thiourea, ammonia thiosulphate and sulfamic acid have been extensively studied. Different authors (Soler et al., 2018; Wang et al., 2016) describe a drop of over 95% in emissions of chlorinated compounds when these compounds are present.

7. Conclusions

A global mathematical model that is capable to properly estimate the atmospheric emission of polychlorinated dibenzo-p-dioxins and furans produced by the combustion of a characterized waste under a determined combustion process has been developed. This model has been constructed as a combination of two models: a kinetic model of PCDD/F formation and a process simulation model that calculates the combustion parameters and the flue gas flow data by simulation.

For a proper ratio of observations per parameter needed in the model, a reduction of the amount of PCDD/F congeners simulated is achieved. An exhaustive study to determine which congeners best represent the total PCDD/F emission has been performed.

Once studied the interdependence between the formation of all of the 17 toxic PCDD/F congeners using industrial data, a similar pattern in their formation was found, proving that only the formation of 2,3,6,7,8-HxCDD, OCDF and 2,3,7,8-TCDF can be considered as linearly independent.

Two models (model 1 and model 2) have been adjusted using multiple linear regression based on this pattern found. Those models properly estimate the total amount and the total toxicity of a sample knowing the amount of the congeners highlighted before.

Both models have been validated studying the residual analysis of the regression and determining the p-value associated to each parameter. The p-values of all of the parameters needed for each model were determined as significant, since none of them could be statistically considered close enough to zero.

The slope and the intercept of the testing of models 1 and 2 were also checked. The p-values ensured that the parameters of the slope and the intercept were statistically equal to 1 and 0, respectively. The coefficient of determination for models 1 and 2 were 0.9842 and 0.9824. Both models were also tested using 6 new analyses, where the average relative error is 3.5% and the maximum relative error is below 9%. Thus, it can be ensured that both models properly estimate the total amount and the total toxicity.

These 2 correlations are limited to all samples with the amount of 1,2,3,6,7,8-HxCDD, OCDF and 2,3,7,8-TCDF above the LOQ.

The behaviour of the two models using analyses that contain one or two congener amounts below the LOQ have been tested too. In this case, the average relative error is 4.3% and the maximum relative error is below 20%.

These two models have been tested and readjusted (model 1' and model 2') with new data provided from research laboratory runs, increasing its scope of application. The multicollinearity of the 130 analyses used for model 1 and model 2 were compared to the multicollinearity found after adding 64 new analyses. As a result, same congeners can be considered as linearly independents.

Same validation process was repeated for the new models, studying the residual analysis of the regression, and determining the p-value associated to each parameter. Same conclusions were found since none of the parameters of both models could be statistically considered close enough to zero.

The slope and the intercept of the testing of models 1' and 2' were also studied in the same way. The p-values ensured that the parameters of the slope and the intercept were statistically equal to 1 and 0, respectively.

The intervals of confidence of the parameters of the models were obtained using Bootstrapping method. As a result, it has been demonstrated that the percent of variability expressed through model 1' and model 2' is very stable to changes in the used dataset.

The accuracy of the new models has also been evaluated by calculating the mean absolute error and the root mean squared error. MAE values were 0.1541 and 0.1733 and RMSE values were 0.2115 and 0.2424 for model 1' and model 2'. Thus, it can be ensured that both models properly estimate the total amount and the total toxicity and increase the source of data used to both industrial and laboratory-scale samples.

This reduction of congeners to estimate the total amount of PCDD/Fs produced was used for fitting a model that represents the kinetics of the formation and destruction of PCDD/Fs that only depends on process variables. This model represents the formation of PCDD/Fs using a *de novo* synthesis route from the carbonaceous part of the waste, and its destruction by its combustion with oxygen. For this purpose, the main variables needed are the temperature, which effect on the kinetics is governed by the Arrhenius equation, and the oxygen ratio. The model also considers a saturation effect for the presence of chlorine and metals, where the saturation constants result to be around 10% for chlorine and 3.5% for metals. Thus, the content of metals and chlorine in the waste is also demonstrated to be a sensitive variable.

Since the number of congeners needed to estimate the PCDD/Fs production was reduced to only 3, the parameters needed for fitting the kinetic model of production were reduced to only 8. Thanks to that reduction, the 64 laboratory runs that were used for fitting the kinetic model were enough to ensure a proper calculation.

The kinetic model was tested simulating variations on its main parameters to estimate the effects of the oxygen ratio, the temperature, and the chlorine and metal content, showing the utility of the model, with results in concordance with the experiences and feedback received from the industry sector.

As a main singularity, this kinetic model represents the formation of PCDD/Fs considering only process parameters such as temperature, oxygen ratio and chlorine/metal presence, regardless of the nature of the combusted waste.

A process simulation model that is able to calculate the flue-gas volume flow, the amount of oxygen and moisture in it, and its thermodynamical properties was adjusted. It was used to reproduce the experimental conditions used during the combustion of several wastes and determine its flue-gas production and conditions.

The results of the process simulation model were used to determine a correlation capable to calculate the flue-gas flow at normal conditions based on the oxygen ratio of the combustion process.

This correlation, once combined with the kinetic model of PCDD/Fs production, is able to properly estimate the atmospheric emission of polychlorinated dibenzo-p-dioxins and furans produced by the combustion of a characterized waste under a determined combustion process.

This final global correlation was used to estimate the PCDD/F atmospheric emission during the primary decomposition of several wastes, with no influence of the post-combustion process usually present in the MSW facilities, to show how the combination of all process variables studied may affect to an atmospheric emission.

8. Thesis Contributions

During the development of this investigation, various contributions to scientific knowledge have been made. All those participations are listed below these lines.

Scientific Publications:

Palmer, D., Pou, J.O., Gonzalez-Sabaté, L., Díaz-Ferrero, J., 2018. Multiple linear regression based congener profile correlation to estimate the toxicity (TEQ) and dioxin concentration in atmospheric emissions. Science of the Total Environment 622–623, 510–516. https://doi.org/10.1016/j.scitotenv.2017.11.344

Palmer, D., Pou, J.O., Díaz-Ferrero, J., Conesa, J.A., Ortuño, N., 2019. New Models Used to Determine the Dioxins Total Amount and Toxicity (TEQ) in Atmospheric Emissions from Thermal Processes. Energies (Basel) 12, 1–11. https://doi.org/10.3390/en12234434

Conesa, J.A., Ortuño, N., Palmer, D., 2020. Estimation of Industrial Emissions during Pyrolysis and Combustion of Different Wastes Using Laboratory Data. Sci Rep 10, 1–11. https://doi.org/10.1038/s41598-020-63807-w

Palmer, D., Pou, J.O., Díaz-Ferrero, J., Conesa, J.A., Ortuño, N., 2021. Kinetics of the formation and destruction of PCDD/Fs in a laboratory tubular furnace. Chemosphere 276. https://doi.org/10.1016/j.chemosphere.2021.130175

Contributions to scientific congresses:

A research poster was presented during the 5th Reunión Nacional de PCDD/F y COP in June 2017 in Barcelona, where the initial study on estimation of Dioxins concentration in atmospheric emission based on congener profile correlation was explained. This investigation was then presented to Science of the Total Environment, which resulted in the first publication of the list.

Internships at other universities:

During June and July 2018, a stage internship was performed at REMAN Investigation Group from University of Alicante. There, with Dr. Juan A. Conesa and Dr. Núria Ortuño, the research of all of the data needed to determine the kinetic model of Dioxins formation was done. This internship resulted in a collaboration that allowed us to publish the three remaining articles listed.

9. Future Work

Once after the conclusion of this scientific work, several investigation lines to follow have been identified.

At first stage, an improvement of the accuracy of the kinetic model of dioxins formation explained in chapter 5 could be achieved by using a single waste which is more representative of the MSW composition, instead of using a wide variety of specific wastes. This laboratory-produced MSW could be decomposed at different conditions of temperature, oxygen ratio, residence time and chlorine and metals content, following a design of experiments methodology to improve the accuracy of the results.

Secondly, the thermal decomposition of this new waste could be performed not in a tubular furnace, but in a combustion chamber that better represents the industrial conditions of a MSW Incinerator facility, such as a fluidized bed reactor with suspended sand and post-combustion zone. This kind of reactor would ensure a turbulent flow regime and the suspended sand would provide a surface on which to react and produce dioxins in a way more similar to a real MSW incinerator.

After that, the model that simulates the behaviour of a MSW incinerator facility could be improved by adding the precise information of a real process, as long as the information needed to convert it to a dynamic model, such pipe information, complete control loops and actuators, etc. This new model would allow us to perform multiple scenarios, such as the development of a new control philosophy that minimizes the PCDD/F emission, or the quantification of the PCDD/F emission due to security scenarios like emergency shut-downs or full-plant restarts.

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"I què hauria de fer?

Trobar un protector ric, servir-lo amb disciplina,

i com una heura fosca que circumda una alzina

i l'usa de puntal mentre llepa l'escorça,

pujar amb astúcia en comptes d'elevar-me per força?

No, gràcies.

Voler sempre que el peix acabi al cove,

mentre que en tot moment nado i guardo la roba?

No, gràcies!"

Cyrano de Bergerac d'Edmond Rostand