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Evaluation of the dioxin and furan formation thermodynamics in combustion processes of urban solid wastes

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Abstract: Specific combustion programs (Gaseq, Chemical equilibria in perfect gases, Chris Morley) are used to model dioxin and formation in the incineration processes of urban solid wastes. Thanks to these programs, it is possible to establish correlations with the formation mechanisms postulated in literature on the subject. It was found that minimum oxygen quantities are required to obtain a significant formation of these compounds and that more furans than dioxins are formed. Likewise, dioxin and furan formation is related to the presence of carbon monoxide, and dioxin and furan distribution among its different compounds depends on the chlorine and hydrogen relative composition. This is due to the fact that an increased chlorine availability leads to the formation of compounds bearing a higher chlorine concentration (penta-, hexa-, hepta-, and octachlorides), whereas an increased hydrogen availability leads to the formation of compounds bearing a lower chlorine number (mono, di-, tri-, and tetrachlorides)

Keywords: dioxins; furans; formation mechanisms; combustion; urban solid wastes.

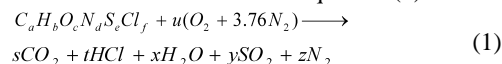
Introduction

One disadvantage of the incineration of urban solid wastes is the emission of dioxins and furans as a byproduct of the reactions of pyrolysis, gasification and combustion of the compounds present in the wastes. When the associated compounds are present, the possibility that such compounds could be formed from their constituting elements should be evaluated. These elements are Carbon (C), Chlorine (Cl₂), Hydrogen (H₂) and Oxygen (O₂). The use of combustion programs makes it possible to determine the conditions for dioxin and furan formation in combustion processes from a database that involves certain thermodynamic and physicochemical properties of dioxins

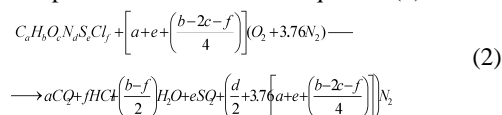
and furans [1] generated in previous works.

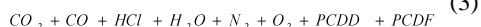
Combustion of urban solid wastes

The stoichiometric combustion of urban wastes is summarized in the equation (1).



The balanced stoichiometric reaction in function of the composition of urban solid wastes composition is shown in the equation (2).



$$C + H_2 + Cl_2 + O_2 + N_2 \longrightarrow \quad (3)$$


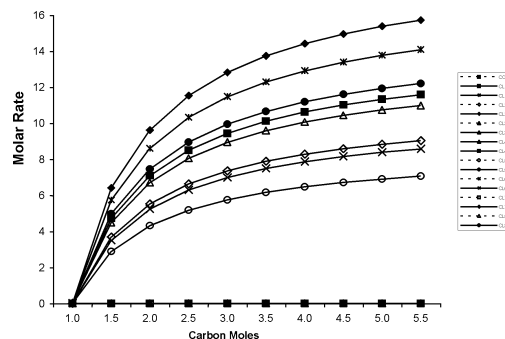
Based on the information provided in equation 3, table 1 displays the distribution of the constituting elements of dioxin and furan for each element.

ELEMENT	DISTRIBUTION IN COMBUSTION PRODUCTS
C	CO ₂ , CO, Dioxins and Furans
H ₂	HCl, H ₂ O, Dioxins and Furans (excepting octachloride compounds)
Cl ₂	HCl, Dioxins and Furans
O ₂	CO ₂ , CO, O ₂ , Dioxins and Furans

Working temperature for the modeling development is 700 K [3].

ELEMENT	MOLES	VARIATION RANGE
C	3.70	1.00 – 5.50
H ₂	1.50	0.50 – 2.60

In order to provide an improved display of the results, they are presented on graphs; for the sake of understanding and interpretation, each of them was divided in 2 parts. Figures 1a,1b, 2a, 2b, 3a, 3b, 4a and 4b shows the results obtained in the dioxin and furan formation model.



Carbon Moles	Molar Rate
1.0	100
1.5	63
2.0	45
2.5	34
3.0	27
3.5	22
4.0	18
4.5	15
5.0	12
5.5	10

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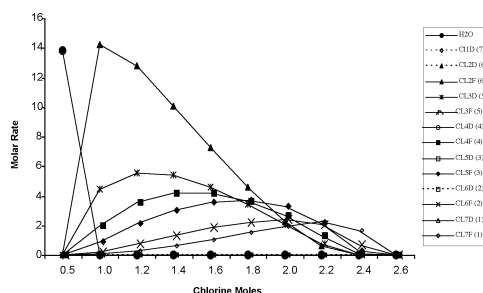


Figure 2a. PCDD/F's formation upon the variation of chlorine availability, with Hydrogen

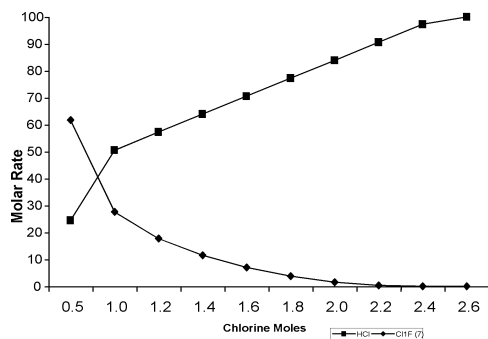


Figure 2b. PCDD/F's formation upon the variation of chlorine availability, with Hydrogen

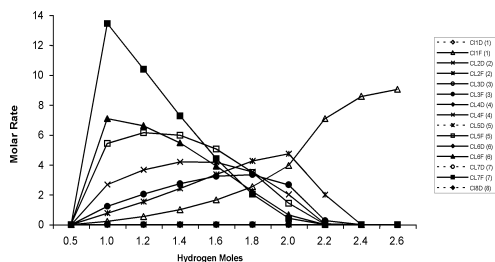


Figure 3a. Production of PCDD/F's upon the variation of hydrogen availability with chlorine

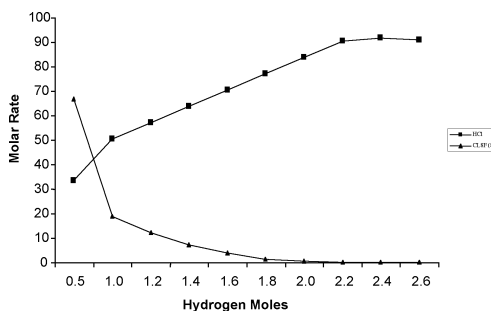


Figure 3b. Production of PCDD/F's upon the variation of hydrogen availability with chlorine

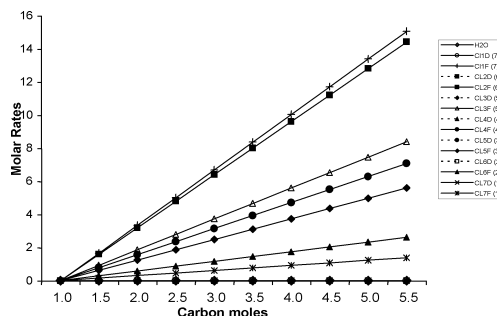


Figure 4a. Production of PCDD/F's upon the variation of carbon availability with chlorine and hydrogen

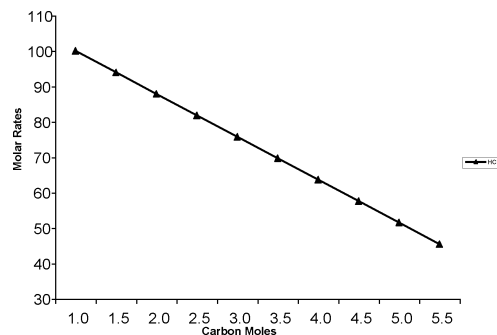


Figure 4b. Production of PCDD/F's upon the variation of carbon availability with chlorine and hydrogen

As can be seen in figure 1a and b, carbon in low quantities is more likely to form carbon monoxide. In proportion to the increase of carbon availability, the onset of dioxin and furan formation occurs, and the quantity of carbon monoxide decreases asymptotically. The formation of PCDD/F's begins in a relatively similar manner in all the families, with the significant increase of carbon availability. We noted that the families with lower chlorine proportions are more likely to be formed, even if the other families are also formed.

Figures 2a and 2b show that the presence of hydrogen with low chlorine availability leads to the formation of compounds with low chlorine content and high hydrogen requirements (mono, di and trichloride, because chlorine behaves as a limit reactive substance). With the increase of chlorine availability, hydrogen is consumed as HCl and dioxin and furan formation is increased (hydrogen, in this case, behaves as a limit reac-

tive substance). In other words, dioxin and furan production decreases with the increase of chlorine availability.

Figures 3a and 3b show that the presence of chlorine with low hydrogen availability leads to the formation of compounds with high chlorine requirements (hexa, hepta and octachlorides, hydrogen behaves as limit reactive substances). The increase of hydrogen availability makes chlorine to be consumed as HCl and decreases furan and dioxin formation (chlorine in this case acts as a limit reactive substance).

Figures 4 shows that hydrogen and chlorine in small carbon quantities are likely to form chlorhydric acid. With the increase of carbon availability, dioxin and furan formation is increased, and in turn, the chlorhydric acid formation is decreased. Carbon availability favors dioxin and furan formation.

Conclusions

According to the results obtained, low oxygen quantities are required to favor dioxin and furan formation. When the oxygen excess or a content close to the required one for a stechiometric reaction are evidenced, combustion conditions favor carbon dioxide formation, which leads to the absence of oxygen and carbon availability to form carbon monoxide, dioxins and furans.

Hydrogen and chlorine are likely to form chlorhydric acid, when they are found in similar molar quantities. When there is a low availability or deficit of such compounds, they behave as sites in which chlorine behaves as a limit reactive substance. Then the greatest part of the element forms chlorhydric acid, but the hydrogen-related deficiency leads to the formation of dioxins and furans with high chlorine requirement and low hydrogen requirement. When the hydrogen is

present as a limit reactive substance, the greatest part of the element forms chlorhydric acid, but the chlorine-related deficiency leads to the formation of dioxins and furans with high chlorine requirement and low hydrogen requirement.

Carbon is likely to form carbon monoxide in low oxygen quantities. Decreased carbon availability is known to hinder the formation of dioxins and furans, because the formation leads to monoxide. In the presence of an increased availability of this element, all the dioxin and furan families present a high requirement of the same (12 carbons per molecule), regardless of the specific family of this type of compounds.

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