Thermodynamics in Dioxins Formation

Dirk Verhulst[1], Jie Yang[2], Xiaodong Li[2], Alfons Buekens[2]*

[1] Extractive Metallurgy and Energy Efficiency, Reno, Nevada, USA

[2]State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China.

* Corresponding author: abuekens@vub.ac.be

Introduction

Formation. Dioxins arise by several sequences of chemical reactions starting either from *precursor* compounds, such as chlorophenols (cf. the Seveso accident[1]) or from metal-catalysed low temperature oxidation of carbonaceous substrates, such as char, soot, activated carbon, polycyclic aromatic hydro-carbons, etc. The latter is often denoted as *de novo* synthesis[2,3,4,5,6] and was studied extensively in a context of waste incineration[7,8]. This scope was later extended successfully to applications in thermal metallurgical processes[9,10]. This synthesis has several distinctive features, such as (a) the concurrent generation of a wide array of chlorinated aromatic compounds with as building blocks benzene (PCBz), naphthalene (PCN), biphenyl (PCB), etc., and also oxygenated compounds, such as phenol (PCPh), furan, benzofuran, dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD), as well as sulphur- and nitrogen-compounds; (b) a ratio of PCDF to PCDD larger than one. The wide range of compounds formed in *de novo* synthesis (cf. a) was shown in its evolving products[11] and demonstrated on fly ash from various dioxin-generating processes[12,13]. Starting as an empirical observation the rationale for (b) is to be found in the propensity of the carbon being oxidised to generate much more PCDF than PCDD, yet this tendency is attenuated by some precursor route formation of PCDD by PCDF. Hell et al.[14] demonstrated a large absence of scrambling in the *de novo* formation of PCDF.

Important Parameters. The formation of dioxins, i.e. PCDF + PCDD (+ PCB) following the *de novo* route depends on a number of factors, in particular temperature (preferably 300-350 °C), an adequate availability of oxygen, required to break down carbon structures, and of chlorine, necessary to convert those into the chlorinated form. Since both these elements (O, Cl) are ubiquitous in numerous sur-roundings the rate-controlling factor in dioxins formation is generally the availability of suitable cata-lysts to accelerate both oxidation and chlorination at low temperature.

Chlorine (Cl_2) is a much more powerful chlorinating agent than is hydrogen chloride (HCl). Moreover, in an oxidising atmosphere it is thermodynamically favoured over HCl throughout the temperature range of maximum dioxin forming activity (250-400 °C). The presence of reducing agents, such as SO_2, H_2 or CO would, however, limit the chlorine equilibrium concentration as well its actual concen-tration, restricting the chlorinating capability of the reactive medium and hence the formation of diox-ins. In the case of the model fly ash (MFA) considered further the chlorine required for chlorination of aromatic structures can be provided by either of two ways: a heavy metal chloride, or else sodium chloride. Since the latter is a most stable compound it will be necessary to convert it into other com-pounds of adequate stability to make it act as a Cl-donor. In this work the MFA is composed of: acti-vated carbon (AC; 2.5 wt. %) as a source of carbon, sodium chloride (NaCl; 10 wt. % Cl) as largest source of chlorides, a metal compound (0.1 wt. % metal) as catalyst and possibly as supplemental source of (reactive) chlorides, and the balance as silicon dioxide (SiO_2).

Catalytic metals are essential not only in catalysing the chlorination of the carbonaceous substrates (AC) that are parents to dioxins, but also in oxidising these carbonaceous materials at temperatures well below 500 °C. Prior to this thermodynamic study the capabilities of a series of oxides and chlo-

rides to form dioxins were examined: a Model Fly Ash was constituted with copper (CuO, CuCl$_2$), cadmium (CdO, CdCl$_2$), Cr (Cr$_2$O$_3$, CrCl$_3$), Ni (NiO, NiCl$_2$) and Zn (ZnO, ZnCl$_2$) as catalytic compound. Operating conditions were: 350 °C, 1 h reaction time, and 21, 10, 6, and 0 vol. % of oxygen. Moreover, some experiments featured a reducing atmosphere composed of hydrogen and nitrogen.

Thermodynamics. Thermodynamics could affect the ease of formation, the distribution, and destruction of dioxins; this may happen at several levels, such as:

- Gas/solid partition, i.e., the partition between the gas and the particulate phase, and gas/liquid equilibrium and distribution data.
- The relative stability, concentration and level of chlorination of various chloroaromatic congeners and isomer groups.
- Providing gaseous chlorine, a highly potent chlorinating agent to the system.
- Providing volatile heavy metal chlorides that eventually act as dioxins' formation catalyst[15].

Thermodynamics may teach lessons regarding the potential of various metals to transfer oxygen and oxidise carbonaceous matter, c. q. transfer chlorine and chlorinate carbon. Both should proceed at rather low temperature, of say 200 to 500 °C, since high temperatures would lead to complete dioxins' destruction. These fundamental considerations are later confronted with experiments showing the relative capability of such compounds to generate dioxins and – to some extent – actual reaction intermediates were identified by appropriate techniques.

Finally, there is the fingerprint of 210 polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). Their relative stability is highest at ca. 450 °C, yet it remains precarious in any oxidising surroundings, whereas hydrogenating or plainly inert conditions will favour stepwise dehydrochlorination. There has also been an argument whether, or not, the fingerprint of dioxins is thermodynamically determined. The positive and negative opinions are roughly in balance.

Materials and methods

The Model Fly Ash used to generate dioxins has been described above: apart from a constant source of carbon (AC) and chloride (NaCl) a variety of substrates is introduced in order to check their dioxin forming capabilities and compare these with a blank MFA. The XANES spectrum was established for identifying the speciation occurring during the testing of NiO and NiCl$_2$ samples.

Thermodynamic methods of study depend on the use of well-known fundamental principles, on software to optimise thermodynamic functions and on a data bank with chemical compounds and their thermodynamic properties at different temperatures. It is important to delineate carefully the system under scrutiny, to decide on the compounds and on their reactions to be included in the thermodynamic computations, or not. For this reason, a critical assessment of the tendencies derived, on the basis of thermodynamic considerations and data, is essential.

Thermodynamic data on dioxins can be derived from experimental data, such as chromatographic retention times[16] or from group contribution methods and from molecular modelling methods[17]. Li et al.[18] determined numerous experimental data using a Knudsen cell and (in his Ph. D.) suggested that unstable dioxins exhibit their highest stability at ca. 450 °C. Tan et al. [19] (2002) confirmed that - thermodynamically - PCDD/Fs cannot exist to any significant extent in whichever oxidising processes, but they may still be formed as unstable intermediates in trace concentrations. Such intermediate products could become permanent if the reaction conditions do not sustain subsequent complete oxidation.

Another area of thermodynamic considerations has been the Deacon equilibrium and the ways in which it is influenced by the presence of sulphur and its oxides. Some interesting observations were made in the Canadian pulp & paper sector regarding the ways in which the sulphur/chlorine ratio influences upon dioxins' formation while burning hog fuel in boilers. Duo and Leclerc[20] even developed a semi-empirical model based upon both thermodynamic analysis and kinetic considerations.

Results and discussion

The experimental results on the formation of dioxins in *de novo* tests performed on Model Fly Ash (MFA) doped with the aforementioned compounds copper (CuO, $CuCl_2$), cadmium (CdO, $CdCl_2$), Cr (Cr_2O_3, $CrCl_3$), Ni (NiO, $NiCl_2$) and Zn (ZnO, $ZnCl_2$) are shown in table 1.

Table 1. Dioxin concentrations generated under different atmosphere

		$CuCl_2$	CuO	$CrCl_3$	Cr_2O_3	$NiCl_2$	NiO	$ZnCl_2$	ZnO	$CdCl_2$	CdO
N_2	ng/g	590	7.4	23.5	0.264	5.98	0.077	3.1	0.39	0.87	0.186
	ng I-TEQ/g	9.31	0.196	0.129	0.006	0.184	0.002	0.037	0.007	0.015	0.004
6% O_2	ng/g	9400	37.21	460	7.41	185	2.39	87.9	0.76	2.7	0.158
	ng I-TEQ/g	52.5	1.02	1.92	0.098	5.36	0.049	1.20	0.021	0.052	0.004
10% O_2	ng/g	10100	47.45	754	9.98	221	5.41	118	2.44	6.63	2.297
	ng I-TEQ/g	54.6	1.09	3.74	0.165	5.34	0.092	2.49	0.044	0.179	0.057
21% O_2	ng/g	11200	88.6	1030	17.6	1010	9.21	342	2.78	16.3	5.88
	ng I-TEQ/g	54.2	1.76	5.16	0.138	26	0.076	5.36	0.069	0.320	0.059

In all cases the *de novo*-formed dioxin concentrations obviously increase with the oxygen content of the carrier gas, with a highest and lowest total PCDD/F-output of 11200 ng/g ($CuCl_2$ in 21% O_2) and 0.077 ng/g (NiO, in N_2) respectively. The order with respect generative capacity of each metal additive was found to be :

$$CuCl_2 > CrCl_3 > NiCl_2 > ZnCl_2 > CuO > Cr_2O_3 > CdCl_2 > NiO > ZnO > CdO$$
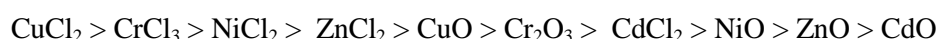
The thermodynamic analysis is on-going and various first results will be presented during the Madrid Conference.

Acknowledgement

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