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Dioxin production during the thermal treatment of meat and bone meal residues

Juan A. Conesa *, Andres Fullana, Rafael Font

Department of Chemical Engineering, University of Alicante, Ap. 99, E-03080 Alicante, Spain

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Abstract

Safe animal by-product disposal is a priority target as a result of the Bovine Spongiform Encephalopathy crisis in the European beef industry. One such disposal option is the incineration of by-product material such as meat and bone meal residues (MBM) for the purpose of energy recovery. Although currently applied, the thermal decomposition of MBM wastes has not been scientifically studied until now. A series of experiments has been performed to study the thermal behavior of MBM both in inert (N_2) and reactive atmosphere (air), both by thermogravimetry and in a horizontal laboratory furnace. As a general trend, MBM gives low PCDD/F values, compared with incineration of other wastes. Maximum yield of pollutants is observed at a nominal temperature between 700 and 800 °C.

Keywords: Pyrolysis; Combustion; Animal wastes; PCDD/F; Thermogravimetry

1. Introduction

Nowadays meat and bone meal (MBM) is being destroyed due to the possibility of being responsible for the transmission of the bovine spongiform encephalopathy (BSE), due to the presence of a protein species called 'prions', that cause Creutzfeldt-Jacob disease ('mad cows disease').

Import and export of MBM to/from/within the European Union has been banned since December 2000. Feeding MBM to cattle, sheep or goats has been banned within the European Union since July 1994.

The inactivation of the infection agent is very difficult. Only strong sodium hypochlorite treatment seems to achieve total inactivation. Germany proposed a process for the inactivation of the prions trough the use of destructive conditions (steam pressure > 3 bar; temperature > 133 °C; residence time > 20 min) and this process has been applied in many European countries, including Spain and Switzerland. The process however has many drawbacks, since these conditions destroy a major part of the infection agent, but not in totality. In many countries, brain and spinal cord (where large amounts of prions are concentrated) are removed and treated separately.

Dedicated incineration plants for MBM, as currently used in e.g., Belgium and England, only appear reasonable when sufficient quantities of MBM can be guaranteed in the long term. The most common technique is co-incineration, mainly in cement kilns. In the USA there are about 30 separate sites where cement kilns are burning hazardous waste derived fuel (US EPA, 1999).

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* Corresponding author. Tel.: +34 965 903 400x2324; fax: +34 965 903 826.

E-mail address: ja.conesa@ua.es (J.A. Conesa).

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From a thermal point of view, MBM is a good fuel (net calorific value approximately 17000 kJ kg^{-1}, similar to wood). It contains approximately 5% water, 22% ash, 40% carbon, 8% nitrogen, 6% hydrogen, 0.6% sulfur and 0.5% chloride, mainly as common salt. This composition however raises concerns about dioxin when incinerating this waste. Furthermore, MBM contains some metals (mainly copper, lead and chromine), known to act as catalysts in the PCDD/F synthesis reactions (Everaert and Baeyens, 2002).

The feeding rates in cement kilns vary from country to country. For example, in Spain the limit is 15% of the energy needed in the kilns, but there is no limit in Switzerland. Incineration of MBM and tallow is seen as useful by the cement industry, where the kiln offers good conditions for complete combustion in terms of temperature and time spent in the kiln. Substituting primary fossil fuels (coal or lignite) has moreover environmental and economic advantages (Scheuer, 2003).

Although industrially applied, the thermal decomposition of MBM wastes has not yet been scientifically studied in detail. Papers found in literature mainly deal with the reprocessing of the combustion residue. Knudsen et al. (2003) affirm that the reprocessing of the residual phosphate is difficult due to its high chloride content. Chaala and Roy (2003) suggest its use for agricultural soil enrichment in minerals and as a soil moisturizer. Deydier et al. (2003) evaluated the use of the combustion residue as a low cost substitute for materials in the process of lead sequestration from water effluents. Concerning the MBM combustion process, a paper has been found dealing with the behavior of MBM pellets in a fluidized bed combustor (McDonell et al., 2001). Beck et al. (2004) showed the effect of MBM co-combustion in a catalyzed reactor, showing an increase in catalyst activity. Other interesting effect in the co-combustion processes is the minimization of the emission of nitrogen compounds when bone meal is present (Goeran et al., 2002).

From a thermal point of view the solid phase undergoes two important steps in a combustion process: (i) a pyrolysis stage, which devolatilizes the solid feed to yield volatiles (gases and tars) and a solid char fraction; (ii) a combustion stage, involving heterogeneous reactions of the char to yield gaseous products and an inert residue (ash). The pyrolysis and combustion stages may be sequential or simultaneous, depending on the feature of the process considered (Conesa et al., 1998; Font et al., 2001).

The present work has two different and important parts in the study of the thermal decomposition of this material: (i) the thermogravimetric behavior of the MBM both in nitrogen and air atmospheres is presented; (ii) a series of experiments in a horizontal laboratory furnace has been performed including the analysis of the pollutants produced (mainly dioxins and furans).

2. Methods and materials

The material employed (MBM) was obtained from a cement plant situated close to our working center and owned by the CEMEX group. The plant requires 15 ton h^{-1} of coke and approximately 10% is replaced by MBM materials. Table 1 presents the analysis of the MBM sample, performed in a Carlo Erba Instrument (model CHNS-O EA110), and also chloride data obtained by X-ray fluorescence. As commented before, most of the chloride in MBM is present as common salt (NaCl). The MBM was well mixed in a mortar. The amount of fatty compounds (measured by extraction in a mixture 1:1 of dichloromethane: toluene for 24 h) is approximately 12 wt%. The net calorific value (16900 kJ kg^{-1}) was measured in a calorimetric bomb (Leco Instruments) (average of two measurements).

MBM has a brownish color, a bulk weight of 680 kg m^{-3} and an intense sweet odor. It should be noted that, if stored improperly in damp conditions, MBM provides an ideal medium for a variety of bacteria, fungi or vermin. The average particle size used in this study is 0.125 mm.

The thermogravimetric experiments were carried out in a Netzsch Thermobalance, model TG209 controlled by a PC system. The atmosphere used for pyrolysis was nitrogen and for combustion was synthetic air. The mass of the samples used was 10 mg approximately. Experiments were carried out with heating rates of 10, 20 and 30 K min^{-1} over a range of temperatures that included the entire range of solid decomposition, i.e., 80–800 °C.

The experiments of the second part of the study were conducted in a horizontal furnace shown in Fig. 1. The programmed temperature of the runs was varied between 600 and 1100 °C. Fig. 1 also shows a typical temperature profile of a combustion experiment (at 850 °C). In each experiment, 0.1 g of MBM was placed in the sample holder and combusted by introducing the sample holder inside the furnace at a specific velocity (0.46 mm s^{-1}) and maintained inside the furnace for 20 min. After passing through the furnace, the reactor gas was collected in an adsorptive trap containing XAD-2 resin. After each experiment, the adsorptive trap was extracted using toluene and the extract was analyzed using a High Resolution Gas Chromatography–High

Table 1
Analysis of the raw material

C	H	S	N	O[a]	Cl[b]
40.4	6.4	0.5	7.8	11.9	0.8
Moisture 3.5%		Ash 28.7%			

[a] By difference.

[b] Measured by X-ray fluorescence.

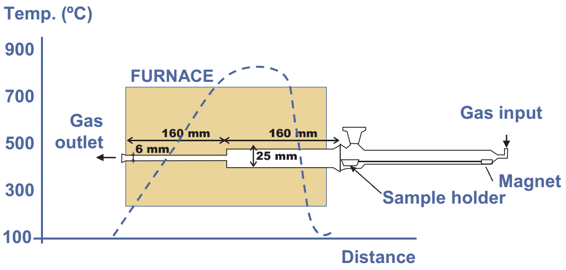

Fig. 1. Layout of the flow reactor system with associated temperature profile.

Resolution Mass Spectrometry AutoSpec NT apparatus for dioxin and furans production, equipped with a Hewlett-Packard GC. The spectrometer was operated in the electron impact ionization mode at a resolving power of 10000. ^{13}C-labeled PCDD/F standards (Wellington Labs, Canada) were used. A quantitative determination was performed by the isotope dilution method based on the relative response factors previously obtained from three standard solutions (EPA1613-CS1, CS2 and CS3).

A blank experiment has been done using the same experimental conditions (reactor, temperature, time, standards...) but with no sample. Assuming that 0.1 g of sample were introduced, the result of this blank run shows a total amount of 0.1 pg I-TEQ g^{-1} of sample as the lower detectable limit. This quantity is much lower than the obtained when MBM is present, as will be shown later.

Prior to the decomposition runs, the MBM material has been analyzed for dioxin and furan content by using the EPA 1613 method. The total 'background' concentration of these compounds in the raw material is 0.25 pg g^{-1} I-TEQ g^{-1} MBM, i.e., 0.25 ppt. Bearing in mind the fat content (12%) this represents 2.08 pg g^{-1} fat, similar to the content found in another MBM sample by Eljarrat et al. (2000). Other authors, nevertheless, found a much lower content of 0.09 pg g^{-1} (Guruge et al., 2003).

3. Results and discussion

3.1. Thermogravimetric study

Fig. 2 illustrates the experimental curves for ThermoGravimetry (TG) and Derivative ThermoGravimetry (DTG) (d*w*/d*T*) for pyrolysis and combustion at 10, 20 and 30 K min^{-1}. The first fact that calls our attention is that both processes coincide until a definite temperature. From this temperature onwards, the combustion process goes beyond the pyrolysis process, giving a higher weight within the temperature range of 375–545 °C at 10 K min^{-1}. This fact can only be explained by an increase of weight due to the incorporation of oxygen molecules into the structure of the MBM being decomposed (by chemical reaction or adsorption), forming an intermediate compound that is later decomposed. This behavior has been explained by using a model comprising three different processes taking place when the material decomposes (both in pyrolysis and in combustion); furthermore in the combustion, another process appears overlapping the third process observed in pyrolysis (Conesa et al., 2003).

Chaala and Roy (2003) suggested that the first process appearing in the pyrolysis is due to the dehydratation of the animal flour; the second process would be produced by the evaporation of low molecular weight

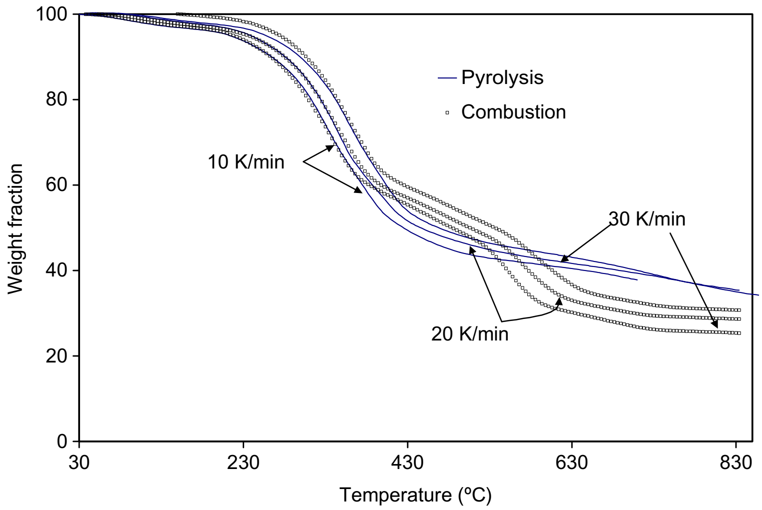

Fig. 2. Thermogravimetric behavior at the three heating rates used in the study.

compounds, whereas the third process is a consequence of the degradation of the bone portion, and the complete decomposition of the remaining intermediates.

3.2. Pollutant production

Fig. 3 shows the dioxin and furan production at several temperatures, expressed in terms of (sum of all congeners from tetra to octachlorinated species) produced per gram of MBM decomposed ($pg\,g^{-1}$). Table 2 presents the yields obtained for each chlorination degree, from tetra to octachlorinated. From these data, I-TEQ values could be calculated and are also presented in Table 2. As it is known, only 2,3,7,8 congeners contribute in the calculation of the I-TEQ value. Although it is not shown in the tables, in almost all the experiments sum of PCDD, PeCDF and HxCDD represents almost an 80% of the I-TEQ value obtained. There is a very low yield of octachlorinated species, i.e., lower chlorinated homologues are mainly formed. Although biological matrices like meat contain traces of copper containing enzymes as essential elements, the major part of the chloride present in the MBM sample is in the form of NaCl, as commented above. Addink et al. (1998) already showed the limited chlorinating ability of NaCl for PCDD/F formation, i.e., the increase in the amount of NaCl does not vary the yields of PCDD/F.

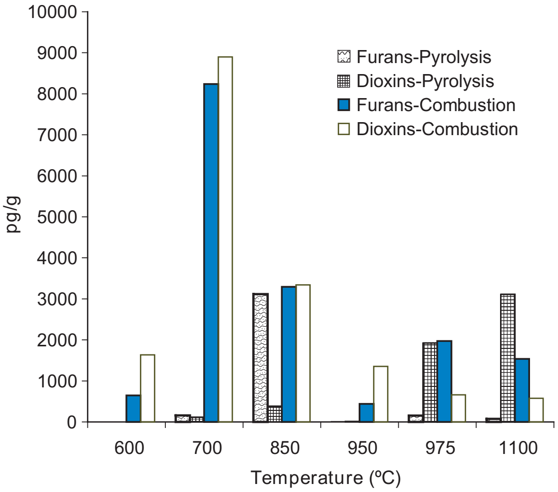

Fig. 3. Sum of all congeners of dioxins and furans from MBM in the horizontal reactor at several temperatures.

Yields of PCDD/F found in this work ranged between 3000 $pg\,g^{-1}$ and 9000 $pg\,g^{-1}$. In terms of total I-TEQ the values ranged approximately between 5 and 45 $pg\,I\text{-}TEQ\,g^{-1}$ (compared to the 0.25 $pg\,I\text{-}TEQ\,g^{-1}$ of the raw material). There is hence a significant formation of PCDD/F both in pyrolysis and combustion. The values obtained are apparently high in comparison with source concentrations (US EPA, 2001) in industrial incinerators for sewage sludge (270 $pg\,g^{-1}$) and municipal waste incineration (20–1000 $pg\,g^{-1}$). The comparison of data among raw materials is difficult, since the results could strongly be a function of the specific conditions of the system used. Using the experimental method of this paper, Fullana et al. (2002) found concentrations of 25000 $pg\,g^{-1}$ using sewage sludge as material, whereas Samaras et al. (2000, 2001) found 10 times higher yields of PCDD/F for refused derived fuel (RDF) using a horizontal reactor similar to the one used in the present work and working at very high temperatures (≅1000 °C). Apparently, MBM gives low PCDD/F values, approximately 10% compared with incineration of other materials. A likely explanation can be found in the work of Samaras et al. (2000) and the following papers of this group. Meat contains large amounts of peptides, which undergo formation of urea and ammonium salts under incineration, which have been shown to be good inhibitors for PCDD/F.

It is important to remark that the yields obtained in pyrolysis runs are unexpectedly high. From data in

Table 2
Yield of each species as a function of temperature and pyrolysis/combustion condition, expressed as $pg\,g^{-1}$

	T (°C)	TCDF	PeCDF	HxCDF	HpCDF	OCDF	TCDD	PeCDD	HxCDD	HpCDD	OCDD	Total I-TEQ
Pyrolysis	700	87.5	71.6	65.7	11.3	0.294	44.8	72.1	45.1	1.95	0.319	7.7
Pyrolysis	850	1.9	60.9	189.9	2863	1.65	69.1	60.2	234.8	17.1	0.840	20.2
Pyrolysis	950	8.2	3.7	45.5	17.2	0.052	6.9	7.9	28.8	18.1	0.098	6.62
Pyrolysis	975	6.38	102.9	40.4	3.48	0.029	1613	132.5	107.6	70.5	0.079	0.796
Pyrolysis	1100	10.6	31.9	22.6	6.8	0.058	16.1	6.9	3076	11.6	0.199	1.74
Combustion	600	28.4	286.9	225.4	105.4	0.489	131.2	311.9	1101.5	92.2	0.299	5.62
Combustion	700	1434	5840	644.0	311.2	6.8	476.4	6025	2107	282.3	3.1	25.7
Combustion	850	294.4	2995	308.4	101.4	0.591	2213	1126	172.5	52.3	1.7	43.0
Combustion	950	29.9	410.2	76.2	16.2	1.2	403.5	948.5	2.6	20.5	2.6	1.31
Combustion	975	2.4	52.1	1855	65.9	0.611	59.9	271.1	297.2	33.7	0.129	1.40
Combustion	1100	41.7	534.1	625.5	333.1	3.3	102.5	62.9	325.3	82.2	1.4	5.01

Table 2, the I-TEQ value obtained in the present work in the absence of oxygen (pyrolysis) represents 50% of the value obtained in combustion runs. This is surely related to the amount of oxygen present in the MBM itself. As presented in Table 1, tested MBM contains a 11.9% of oxygen, i.e., a total of 1.19×10^{11} pg of oxygen/gram of sample, that is an amount obviously very much higher than the amount needed to form thousands of pg of dioxins/furans: part of these oxygenated organic compounds could form precursors like phenols and esters that could produce dioxins and furans in the absence of oxygen. The amount of oxygen needed to dioxin formation is very low.

In relation to the temperature behavior, we found the maximum production of PCDD/F between 700 and 800 °C. Bearing in mind that the reactor is non-isothermal, there is no proof that the PCDD/F formation occurs at this temperature. Note that the maximum total yield is obtained at 700 °C, but the maximum in terms of I-TEQ is produced in the runs performed at 850 °C, due to the dominant presence of HxCDF, HxCDD and TCDD. It is know that the production of products of incomplete combustion is higher at 700–900 °C (Fullana et al., 2000). These compounds react in the post-combustion cooling zone to form PCDD/F. At temperatures higher than 950 °C the I-TEQ decreases drastically to less than 10 pg I-TEQ g^{-1}. It has been reported that under less-than-optimum conditions (such as insufficient oxygen), PCDD/Fs may be formed at temperatures that normally would exceed the threshold temperature of 800 °C for PCDD/F formation (Gullett et al., 1990; Walker and Huntley, 1997). Insufficient oxygen within the furnace frequently leads to the formation of various PAH-type compounds, especially during the phases of devolatilization.

Fig. 3 also illustrates that the ratio PCDD/PCDDF is close to one, whereas the typical concentration of PCDF in combustion of wastes is several times higher that the concentration of PCDD. Data show that there is a slight variation of the ratio PCDD/PCDF with temperature, but it is too small to discuss it from a mechanistic point of view. The ratio *D*/*F* is found to be higher than one, only in the case precursor-synthesis (chlorobenzenes or chlorophenols). A high value of the *D*/*F* ratio is an indicator that a precursor of PCDD is present in the original sample (Altwicker, 1996; Everaert and Baeyens, 2002). Some chlorobenzenes and chlorophenols are used as bactericide in waste disposal to prevent decomposition of organic material. In this sense, Ghorishi and Altwicker (1996) found a similar PCDD/F distribution during combustion of dichlorobenzene, which is sound with presence of a precursor in the MBM. The analysis of these compounds was unfortunately not performed in the raw MBM, but a reference to a similar material containing 0.55 mg kg^{-1} of organic chlorine has been found (German Federal Environmental Agency, http://www.umweltbundesamt.de/).

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