THE PRODUCTION OF POLLUTANTS DURING THE DECOMPOSITION OF MEAT AND BONE MEAL

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Introduction

Nowadays meat and bone meal (MBM) is being destroyed due to the possibility of being the responsible for the transmission of the bovine spongiform encephalopathy (BSE). From December 2000 importing these feeds to European Union (EU) countries and their export outside the EU were banned. Feeding MBM to cattle, sheep or goats has been banned within the EU since July 1994. The government currently sees the only possible alternative in thermal treatment, as incineration or gasification destroys potential BSE pathogens in high temperature processes where the material remains in sufficiently hot incinerators for long enough, with an adequate oxygen supply, and thereby rules out the risk of subsequent infection as far as possible.

Dedicated incineration plants for MBM, as they are currently being set up in England, only appear reasonable where sufficient quantities of MBM can be guaranteed in the long term (1). The most common is the co-incineration, mainly in cement kilns. In the USA there are about 30 separate sites where cement kilns are burning hazardous waste derived fuel (2).

MBM is a highly calorific (ca. 17000 kJ/kg), easily flammable fuel, and must therefore be mixed well and homogeneised with the other waste. Incineration of MBM and tallow is seen as useful by the cement industry, because the thermal process where cement clinker is burnt has good conditions for complete combustion in terms of temperature and time spent in the oven. At the same time, substituting primary fossil fuels (coal and lignite) has environmental and economic advantages.

In combustion processes, two important steps are present in the solid phase (3): i) a pyrolysis stage, in which the solid feed undergoes devolatilization reactions to yield volatiles (gases and tars) and a solid char fraction; ii) a combustion stage, in which the char undergoes heterogeneous reactions to yield gaseous products and an inert residue (ash). Pyrolysis and combustion stages may be sequential or contemporary, depending on the feature of the process considered (3,4).

The present work has two different and important parts in the study of thermal decomposition of this material:

1) On the one hand, the thermogravimetric behavior of the MBM both in nitrogen and air atmospheres is presented and discussed. A kinetic scheme able to correlate simultaneously (with no variation of the kinetic constants) the runs performed at different heating rates and different reaction atmospheres is presented.

2) Furthermore, a series of runs in an horizontal laboratory furnace have been performed, and the analysis of the pollutants produced (mainly dioxins and furans) are presented in this contribution.

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 t/h of coke approx. 10 % replaced by MBM materials. Table 1 presents the ultimate analysis of the MBM sample, performed in a Carlo Erba Instrument model CHNS-O EA110, and also chlorine data obtained by X-ray fluorescence. It should be noted that most of the chlorine in MBM is present as common salt

(NaCl). The amount of fatty compounds (measured by extraction in a mixture 1:1 of dichloromethane:toluene for 24 h.) is approximately 12 % wt. The heating value has been measured in a calorimetric pump, and gives a value of 16900 kJ/kg.

C	H	S	N	Cl*
40.4	6.4	0.5	7.8	0.8

Moisture 3.5 %   Ash 28.7 %

*Measured by X-Ray fluorescence.

MBM has a brownie color and a bulk weight of c. 680 kg/m3, as well as an intense sweet odor. It should be noted that, if stored improperly in damp conditions, MBM provides an ideal medium for every kind of bacterium, fungus 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 with a flow rate of 20 ml/min (STP), according to the specifications of the equipment. In the case of combustion, the oxidative atmosphere used was synthetic air with the same flow rate. The sample temperature is measured with a thermocouple directly at the crucible, i.e., very close to the sample. Because a water-cooled microfurnace is used, the temperature can be lowered rapidly.

Experiments with heating rates of 10, 20 and 30 K/min were carried out over a range of temperatures that included the entire range of solid decomposition, 80-800 °C. The mass of the samples used was 10 mg approximately.

The runs performed in the second part of the study were conducted in a horizontal furnace. An scheme of the equipment can be found elsewhere [6]. The nominal temperature of the runs was varied between 600 and 1000°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). After passing through the furnace, the reactor gas was collected in an adsorptive trap. After each experiment, the adsorptive trap was extracted and the extract was analyzed using different GC-MS techniques, as this study involves analysis of several different classes of compounds. The HRGC-HRMS analyses were performed on a Autospec NT apparatus.

Results and Discussion
Thermogravimetric study
Figure 1 shows in detail the experimental curves for TG and DTG (dw/dT) for pyrolysis and combustion at 10 K/min. The first fact that calls our attention is that both processes coincide until 375 °C. From this temperature, the combustion process goes beyond the pyrolysis process, giving a higher weight at some temperature range (375 to 545 °C at 10 K/min approx.). This fact could only be explained assuming an increase of weight due to the incorporation of oxygen molecules (mainly by chemical reaction) into the structure of the MBM being decomposed, forming an intermediate compound that later is decomposed. Bearing in mind the form of the DTG curve (see Figure 1), it can be observed that at least three different processes take place when the materials decompose (both in pyrolysis and in combustion). In the combustion, another process appears overlapping the third process observed in pyrolysis.
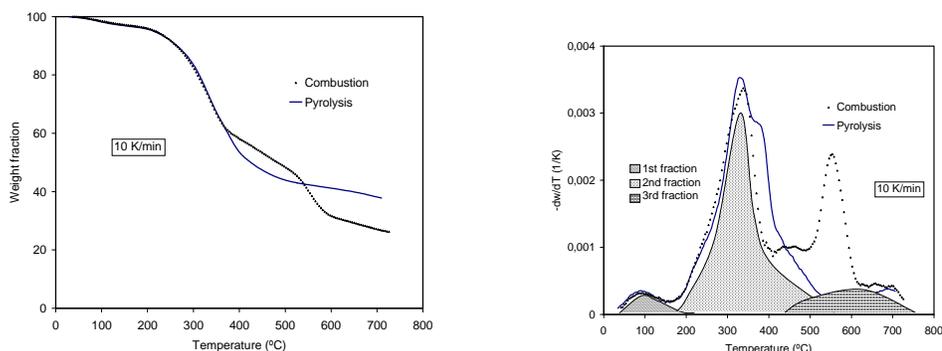
Figure 1. Thermogravimetric behavior at one of the three heating rates used in the study.

For the kinetic model, the following was considered:

      - Both in pyrolysis and combustion: thermal decomposition of three fractions:

$$\text{Fi} \xrightarrow{\ Pyrolysis\ } \text{Si + Vi} \qquad\qquad\qquad i = 1, 2, 3$$

      - Only when oxygen is present: reaction with the oxygen of a fourth fraction, represented by 'R', with incorporation of oxygen to the structure of the pyrolytic solid being produced, producing the formation of an intermediate compound that later is decomposed:

$$R + O_2 \xrightarrow{\ k_a\ } R{\cdot}O \xrightarrow{\ k_d\ } CO_2 + H_2O + ...$$
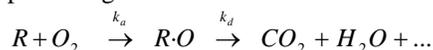
At any time:

R = S1 + S2 + S3 (solid formed by the pyrolytic decomposition)

Note that there is no further evidence of the incorporation of oxygen to the structure of MBM. It is supposed that the incorporation is produced by the partial degradation of the carbonaceous material, that produced a more 'opened' structure, giving some sites to bond oxygen molecules.

Pollutant production

Figure 2 shows the dioxin and furan production at several temperatures. Both total and I-TEQ yields are presented.
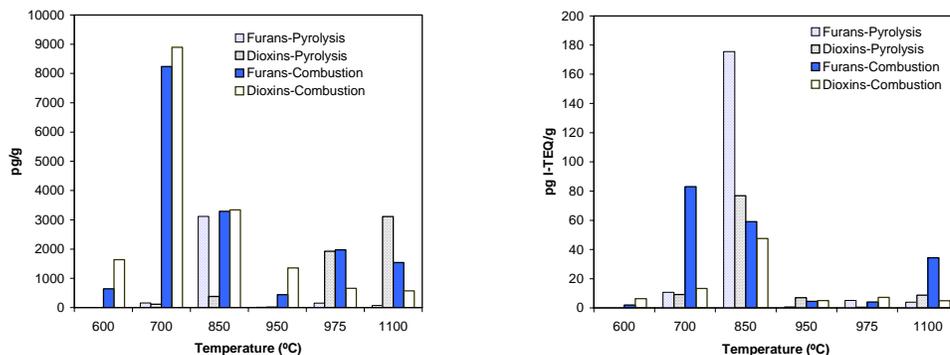

Figure 2. Dioxins and furan production from MBM in the horizontal reactor.

Yields of PCDD/F found in this work ranged between 3000 pg/g and 9000 pg/g. This results are apparently high in comparison with emission factors [5] in industrial incinerators for sewage sludge (270 ng/kg) and municipal waste incineration (20-1000 ng/kg). The comparison of data

whit the other materials is a complex task because emissions factors are strongly dependent of the system used. Using same system Conesa et al. [6] found concentrations of 25 000 ng/kg using sewage sludge as material. On the other hand, Samaras et al.[7] found yields of PCDD/F 10 times higher for refused derived fuel (RFD) using a horizontal reactor similar to used in the present work. According whit this results combustion of MBM does not present a special tendency to formation of PCDD/F.

In relation to temperature behavior the maximum production of PCDD/F is between 700-900 ºC. It is know that this rage of temperature is where the production of PICs (products of incomplete combustion) is higher. These compounds react in the post combustion cold zone to form PCDD/F. At temperatures higher than 950 ºC the I-TEQ decreases drastically to less than 40 ng I-TEQ/kg.

From Figure 2 it is also interesting to remark that the ratio between PCDD/PCDDF is close one. Nevertheless, the typical concentration of PCDF in combustion of wastes is several times higher that concentration of PCDD (i.e. dioxin to furans ratio higher than unity). Only in the case that a reaction between dioxins precursors (as chlorobenzenes or chlorophenols) is present, the ratio D/F is found to be higher than one. The high value of ratio is an indicator that a precursor of PCDD is present in the original sample. Some chlorobenzenes and chlorophenols are used as bactericide in waste disposal to prevent decomposition of organic material, unfortunately analysis of this compounds was not performed in the original MBM, but a reference to a similar material containing 0.55 mg/kg of organic chlorine has been found.

Conclusions

A kinetic model for the decomposition of MBM has been proposed and tested. Incorporation of oxygen into the structure has been proposed to explain weight increases during combustion.

In relation to pollutants generation it can be concluded that combustion of MBM does not generate a yield of PCDD/F that makes a difference from other biological organic wastes as sewage sludge or RFD. The yield of PCDD/F decreases drastically when the combustion is performed at temperature higher than 950 ºC and consequently it is desirable that the incineration of MBM will be performed at less at this temperature.

References

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