

# POLLUTANT ANALYSIS DURING THE DECOMPOSITION OF COTTON FABRICS IN HELIUM AND AIR

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## *Introduction*

The growing interest in renewable energies is accompanied by intensified research and development of technical processes for the thermal conversion of biomass. Used and waste cotton fabrics (UWCF) could be used as biomass and in this way we could reduce the amount of these textile wastes in landfills. Although cotton fabrics are usually recycled by other ways, thermal decomposition of the wastes without another use is interesting to some industries, that are mainly focused in obtaining the potential energy by combustion.

Dedicated incineration plants for UWCF only appear reasonable where sufficient quantities of this waste material can be guaranteed in the long term, which is unusual. The most common option would be the co-incineration, with the advantage that the cotton fabrics are not a hazardous material. UWCF is a highly calorific, easily flammable fuel, and must therefore be mixed well and homogenized with the other waste.

In combustion processes, two important steps are present in the solid phase (i): 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 (i,ii).

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

- 1) On the one hand, the thermogravimetric behavior of the UWCF both in helium 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 a 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 (UWCF) was simulated by using a used blue T-shirt made of one hundred percent cotton. Table 1 presents the ultimate analysis of the UWCF sample, performed in a Carlo Erba Instrument model CHNS-O EA110, and also chlorine data obtained by X-ray fluorescence. The heating value has been measured in a calorimetric pump, and has a value of 17100 kJ/kg.

C	H	S	N	Cl*
45.5	6.6	<0.1	0.3	0.12
Moisture 5.0 %		Ash 0.12 %		

\*Measured by X-Ray fluorescence.

UWCF is a very low density waste, and the main problem concerning the recycling could be related to its transport. Prior to the runs, the T-shirt was cut in small pieces with an average size of 1 by 1 cm.

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 combustion process, the oxidative atmosphere used was helium:oxygen at different ratios and with the same flow rate. The sample temperature was measured with a thermocouple directly at the crucible, i.e., very close to the sample. Because a water-cooled micro-furnace was used, the temperature could be lowered rapidly.

Experiments with heating rates of 5, 10 and 20 K/min were carried out over a variety of temperatures that included the entire range of solid decomposition, 80-700 °C. The mass of the samples used was approximately 5 mg.

The runs performed in the second part of the study were conducted in a horizontal furnace. A scheme of the equipment can be found elsewhere [6]. The nominal temperature of the runs was varied between 750 and 1050 °C. In each experiment, 0.1 to 0.2 g of UWCF 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 an Autospec NT apparatus. The gas fraction was collected in a 2 L-Tedlar bag and was analyzed by gas chromatography with FID detector for hydrocarbons and with TCD detector for measuring CO, CO<sub>2</sub>, oxygen and nitrogen.

## Results and Discussion

### Thermogravimetric study

The thermal degradation of samples of cotton and cotton fabrics have been investigated using the techniques of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) between room temperature and 700 °C. Experiments were carried out with about 5 mg of sample in flowing helium and two different helium: oxygen atmospheres, using three different heating rates. A kinetic model for the decomposition of cotton fabrics has been proposed and tested.

Figure 1 shows in detail the experimental curves for cotton fabric pyrolysis at several heating rates, and also the corresponding to the combustion in air. Further you can see some results of the fits that will be presented later. Figure 1 also shows the general shape of the pyrolysis TG curves for cotton fabrics at three different heating rates (5, 10 and 20 K/min), with the general shift to higher temperatures when the heating rate increased.

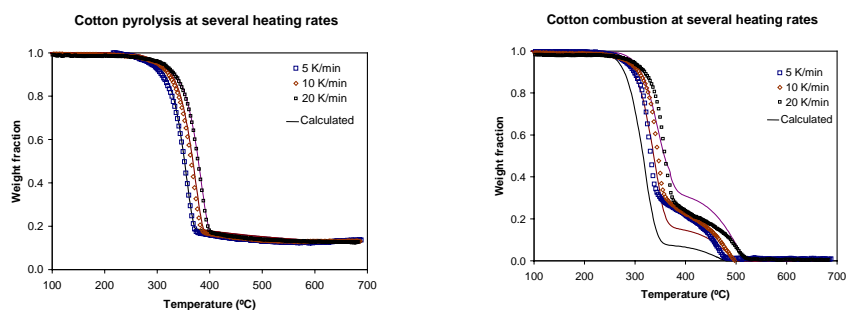


Figure 1. Experimental and calculated (model A) weight loss curves for cotton decomposition.

Cotton is mainly composed by cellulose. For the kinetic model, the first attempt was to only include one species (i.e. cellulose), but the results were not satisfactory. For the pyrolysis process two different fractions should be included to explain all the runs performed at the different heating rates. Some authors [iii, iv] included two series reactions in the combustion process for cellulose decomposition, but two parallel reactions are also possible:

A) Series reaction:



where Volatiles(1) and (2) would represent different gas or volatile compounds and S refers to a solid material formed by decomposition.

B) Parallel reactions:



where  $C_1$  and  $C_2$  refer to different parts of the solid material to be decomposed (cotton in this case).

The kinetic equations associated with the schemes have been many times presented (see for example [v]).

The results of the fit considering model (A) are shown in Figure 1. As it can be seen, the model satisfactorily fits the pyrolysis runs, but not the combustion ones, because the second part of the curves is not explained. The model should be improved. Pyrolysis runs using model (B) are satisfactorily fitted using the following kinetic constants:

Fraction 1:	$k_0 = 3.36 \cdot 10^{11} \text{ seg}^{-1}$	E/R= 20094 K	n= 0.65
Fraction 2:	$k_0 = 3.64 \cdot 10^{14} \text{ seg}^{-1}$	E/R= 22933 K	n=2.8
Contribution of fraction 2: 0.08			

The quality of the fit is similar to that shown in Figure 1. The combustion runs are also satisfactorily explained using the following kinetic constants:

Fraction 1:	$k_0 = 1.24 \cdot 10^{11} \text{ seg}^{-1}$	E/R= 18371 K	n= 1.26
Fraction 2:	$k_0 = 8.08 \cdot 10^{10} \text{ seg}^{-1}$	E/R= 20820 K	n=1.77
Contribution of fraction 2: 0.24			

The fit is a lot better than the one obtained with model (A), and is shown in Figure 2. The parameters obtained are quite similar both for pyrolysis and combustion, with the exception of those corresponding to Fraction 2. This is foreseeable, because pyrolysis and combustion weight losses are similar in the first stages (compare both graphs in Figure 1).

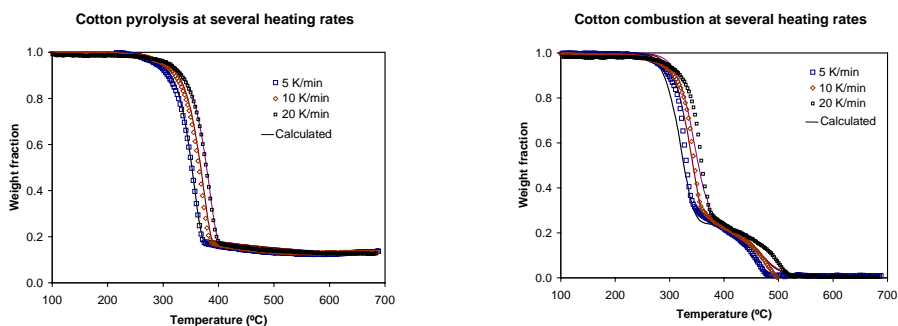


Figure 2. Fit obtained with model B.

### Pollutant production

Cotton fabric has been analyzed for PCDD/F content (see Figure 3), in order to establish the level of pollutant in the sample itself. The analytical procedure comprises the extraction with toluene, change of solvent to hexane, acid treatment with conc. sulphuric acid and cleanup using the FMS equipment with three different columns (silica, alumina and activated carbon).  $^{13}\text{C}$  labeled compounds included in EPA 1613 method were used. Values of total PCDD/F content between 0.1 and 360 pg I-TEQ/g were found for different textile materials [vi].

Runs were performed in the horizontal laboratory reactor to analyze gases and semivolatile species (including dioxins). Several temperatures were tested, and the mass of sample was maintained nearly 150 mg. Runs were performed both in nitrogen (pyrolysis) and air (combustion) atmosphere.

For the PCDD/F analysis, a temperature of 850 °C was selected. Figure 3 presents the yield of each isomer considered, both in pyrolysis and combustion, considering their contribution to the I-TEQ value. A total of 14.8, 9.3 and 15.4 pg I-TEQ/g were found in the T-shirt, pyrolysis and combustion runs, respectively. For the PCDD/F analysis of the T-shirt, a blank was done obtaining a null value. As we can see, there is not a global generation or destruction of dioxins. This fact calls our attention, because runs in similar conditions carried out with other materials (sludges, meat and bone meal), gave much more dioxins when decomposed than the original sample. Yields of PCDD/F found in the decomposition of meat and bone meal ranged between 3000 pg/g and 9000 pg/g. In industrial incinerators we found higher emission factors [vii] for sewage sludge (270 pg/g) and municipal waste incineration (20-1000 pg/g). The comparison of our data with the data of other materials is a complex task because emissions factors are strongly dependent of the system used. With the same system Conesa et al. [viii] found concentrations of 25 000 ng/kg using sewage sludge as material. In contrast, Samaras et al.[ix] found yields of PCDD/F 10 times higher for refused derived fuel (RFD) using a horizontal reactor similar to the one used in the present work.

Respect to the yields of the different PCDD/F, both octa-furans and octa-dioxins show a high decrease when the T-shirt is decomposed in nitrogen and air. In all the samples analyzed 2347-PeCDF is the congener that mostly contributes to the total I-TEQ. The typical concentration of PCDF in combustion of wastes is several times higher than the concentration of PCDD, as obtained in the present runs.

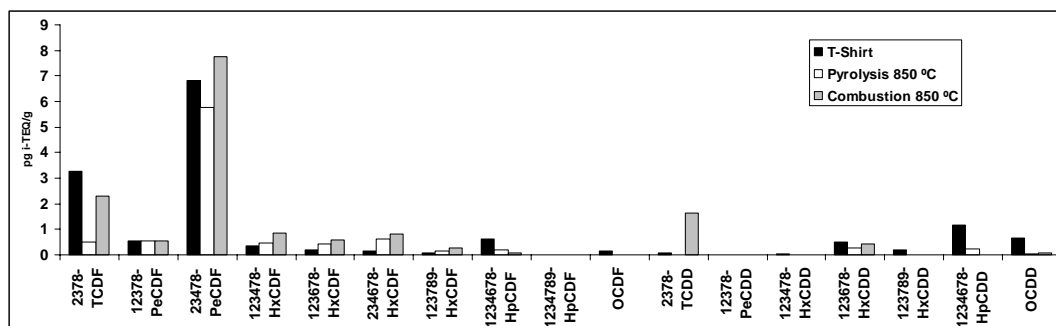


Figure 3. Dioxin and furan analysis.

The gases were also analyzed. Some results are presented in Figure 4, corresponding to the compounds obtained in major yields.

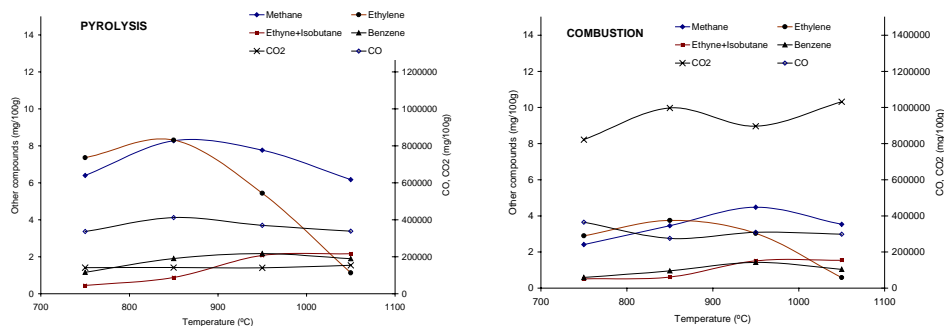


Figure 4. Gas analysis of the main compounds obtained from runs.

The following general trends, could be remarked:

- The yields of different hydrocarbons are higher in pyrolysis than in combustion, whereas the yields of carbon oxides (CO and CO<sub>2</sub>) are higher in combustion.
- Aromatic compounds present an increase in the yield as the temperature is increased.
- Ethylene yield decreases at high temperature.

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