ANALYSIS OF POLLUTANTS FORMED IN THE COMBUSTION OF WOOD FURNITURE WASTES.

Moreno A.I., Font R.

Department of Chemical Engineering, University of Alicante, P.O. Box 99, E-03080 Alicante, Spain

Introduction

Residual biomass derives from activities relating to the production, processing and consumption, that in the context in which they are generated, they have no economic value. Wood is being widely used as a renewable energy, and it has several advantages over other biomass, for instance: higher energy content per volume, lower amount of ash, and very low amount of nitrogen and sulphur. Wood furniture wastes could be suitable for energy valorisation. Incomplete combustions cause environmental concerns, mainly due to particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs) and carbon monoxide (CO) emissions. Bari et al.[1] reported that the smoke formed during the combustion of wood in residential heating contains small particles, and thus representing a particular health risk because of its respirability and content of polycyclic aromatic hydrocarbons (PAHs). In addition to these pollutants, it is well known that PCDD/Fs are formed during wood combustion (even natural wood contains small quantities of chlorine). Wood furniture wastes contain non-wood materials, like adhesives, paints, preservatives and fire protection agents and these substances increase the formation of PCDD/Fs during combustion [2].

Materials and methods

A substoichiometric amount of oxygen probably promotes the formation of toxic compounds, such as: PAHs, PCBs and PCDD/Fs. Experiments under fuel-rich conditions were carried out, in order to analyse in the worse combustion conditions.

Two different experimental set-ups were performed: i) in a laboratory-scale horizontal tubular quartz reactor, ii) in a conventional residential stove.

Laboratory-scale reactor:

A scheme of the experimental set-up is show in Figure 1. This equipment has previously been described in detail by Font et al [3]. Experiments were performed with substroichiometric conditions, although in the latter part of the reactor some quartz rasching rings are placed, which promote the secondary cracking reactions.
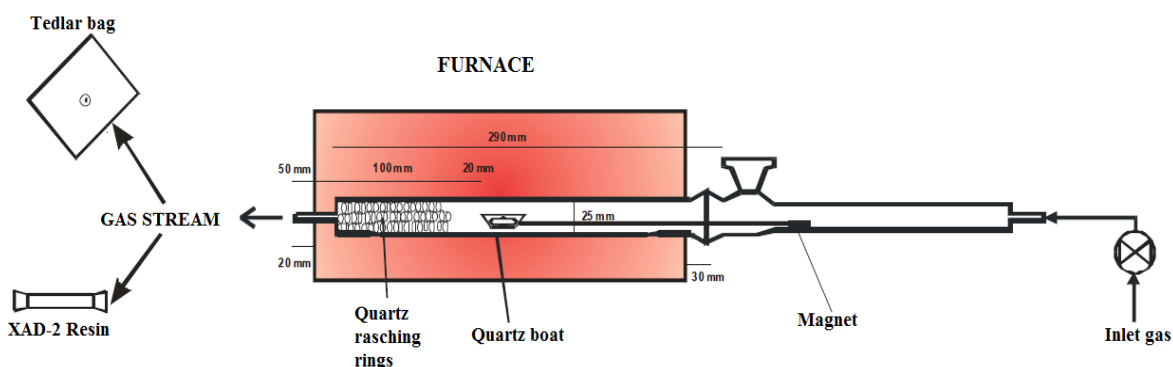

Figure 1: Scheme of laboratory-scale horizontal tubular quartz reactor.

The sampling of gases and volatile compounds was carried out with a Tedlar® bag. The gas stream passed through an adsorptive trap containing XAD-2 resin to retain the semivolatile compounds, PCBs and PCDD/Fs.

Each combustion was carried out on a milled and dry sample weighing about 0.1 g. But since PCDD/F emissions in wood are not high, 10 continuous combustions were carried out (being retained their emissions by the same XAD-2 resin), in order to amplify the signal in the analysis.

Combustion in a conventional residential stove:

In this stove, wood furniture wastes were burned under conditions of bad mixing of combustion gases with air. The set-up consists of a residential stove with a chimney, and the sampling was carried out according to U.S EPA Method 0023A (Figure 2). Sampling was initiated when the temperature of the flue gas was practically constant and was ended 90 min after. Around 2.5 kg of wood furniture wastes were burnt and a total of 1.03 Nm^3 were collected by the heated probe. The temperature inside the furnace was measured during the combustion sampling, and this varied between 420 and 780 °C.
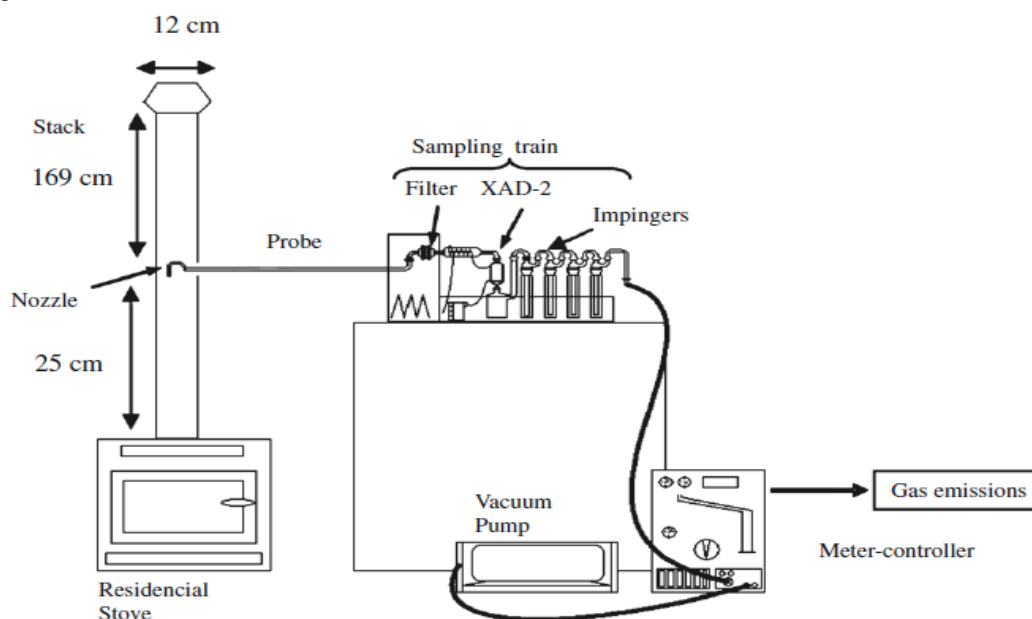

Figure 2: Scheme of the experimental set-up (residential stove and sampling train).

Methodologies of analysis:

The gases collected in the Tedlar® bags were analysed by gas chromatography: CO and CO_2 were analysed by GC-TCD and aliphatic hydrocarbons C_1-C_8 (with low boiling points) were analysed by GC-FID.

The extractions of different compounds retained in the resin were carried out with an Accelerated Solvent Extraction (ASE) according to U.S. EPA Method 3545.

The analysis of PAHs was carried out by GC-MS according to U.S. EPA 8270D method.

The simultaneous analysis of PCDD/Fs and 12 dioxin-like PCBs were performed according a method[4], which was a modification based on the U.S. EPA Method 1613.

Results and discussion

Table 1 shows the results corresponding to the formation of carbon oxides and the main light hydrocarbons. It can be observed that the $CO/(CO + CO_2)$ ratio is lower in the combustion in the residential stove than in the laboratory-scale reactor. This means that combustion was more incomplete in the laboratory-scale reactor. Noteworthy is the high value of toluene and that butanes and benzene were not detected in the residential stove combustion.

Table 1: Main volatile gases evolved in combustion experiments

COMPOUND	mg compound/kg dry sample	
	Combustion 850ºC in laboratory-scale reactor	Combustion in residential stove (420-780 ºC)
CO_2	1226448	1276842
CO	93307	30976
Ratio $CO/(CO + CO_2)$	0.07	0.02
Main light hydrocarbons:		
Methane	8329	7593
Ethene	7306	1948
Propyne	287	496
Butanes	1674	n.d.
Benzene	2399	n.d.
Toluene	84	15440
Total light hydrocarbons	20714	31633
Total gases and volatiles	1340468	1339451

Table 2: Main PAHs evolved in combustion experiments

COMPOUND	mg compound/kg dry sample	
	Combustion 850ºC in laboratory-scale reactor	Combustion in residential stove (420-780 ºC)
16 EPA priority PAHs:		
Naphthalene	2159	19.8
Acenaphthylene	1637	6.3
Fluorene	218	1.4
Phenanthrene	431	3.4
Anthracene	132	0.8
Fluoranthene	179	1.2
Pyrene	161	1.4
Benzo(a)anthracene	69	0.5
Chrysene	47	0.3
Benzo(a)pyrene	57	0.2

Table 2 shows the emission concentrations of the PAHs obtained with relative high concentration. As expected, the total emissions are higher in laboratory-scale combustion, because its combustion showed a higher $CO/(CO + CO_2)$ ratio. Khalfi et al. showed a linear correlation between CO and PAHs emissions[5].

Naphthalene, acenaphthylene, fluorene, phenanthrene and fluoranthene were the majority PAHs obtained in both cases. The most highly carcinogenic, the benzo(a)pyrene, showed a low concentration. In the laboratory-scale reactor, benzo(a)pyrene emission was 57 mg/kg dry sample, being this value similar to that obtained by other work of waste wood combustion in similar conditions[5].

Figure 3 shows the emission concentrations of PCDD/Fs. It is observed that the formation of furans was higher than that of dioxins when combustion was carried out in the laboratory-scale reactor. Instead, the octa-chlorinated dioxin (OCDD) was found as the highest of the PCDD/Fs in the residential stove combustion.

In this work, the World Heath Organization toxicity equivalence factors (WHO-TEF) were used to calculate the toxicity equivalent (TEQ) of PCDD/Fs and PCBs. Figure 4 shows the WHO-TEQ of PCDD/Fs. In the laboratory-scale, the congeners with the most important contribution to toxicity were: 12378-PeCDD, 23478-PeCDF, 2378-TCDD. In the combustion in the residential stove, the dioxins showed higher toxicity contribution than the furans, being the 12378-PeCDD, 1234678-HpCDD, 2378-TCDD the congeners with the most important contribution to toxicity. The total PCDD/FS WHO-TEQ in combustions in the laboratory-scale reactor and in the residential stove were: 292.3 and 35.0 ng TEQ/kg dry sample, respectively.

Regarding PCBs, the total WHO-TEQ in combustions in the laboratory-scale reactor and in the residential stove were: 37.3 and 0.27 ng TEQ/kg dry sample, respectively.

As expected, the total WHO-TEQ was lower in residential stove than in the laboratory-scale, due to better conditions of combustion (lower $CO/(CO+CO_2)$ ratio).
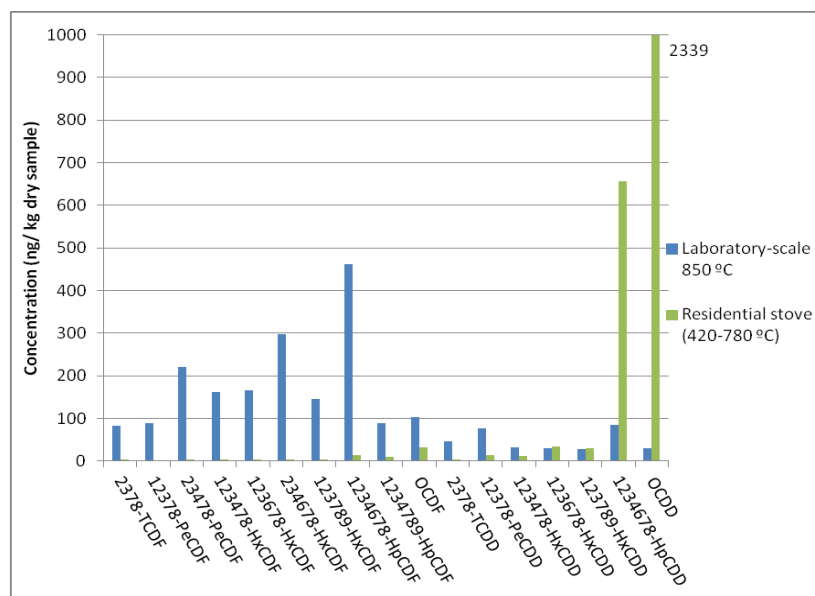
Figure 3: Concentration of 17 PCDD/Fs (ng / kg dry sample) in experimental combustions
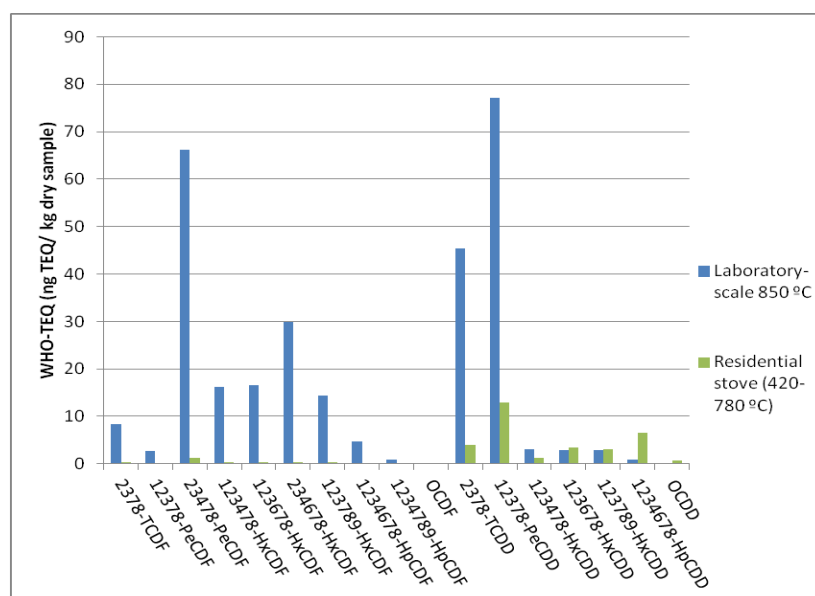

Figure 4: WHO-TEQ of 17 PCDD/Fs (ng TEQ / kg dry sample) in experimental combustions

References:

1. Bari M.A., Baumbach G., Brodbeck J., Struschka M., Kuch B., Dreher W., Scheffknecht G. (2011); *Atmospheric Environment.* 45(40): 7627-7634
2. Salthammer T., Klipp H., Peek R.D., Marutzky R. (1995); *Chemosphere.* 30(11): 2051-2060
3. Font R., Aracil I., Fullana A., Martín-Gullón I., Conesa J.A. (2003); *Journal of Analytical and Applied Pyrolysis.* 68–69(0): 599-611
4. Moltó J., Font R., Conesa J.A. (2006); *Energy and Fuels.* 20(5): 1951-1958
5. Khalfi A., Trouvé G., Delobel R., Delfosse L. (2000); *Journal of Analytical and Applied Pyrolysis.* 56(2): 243-262