# **STSM Scientific Report**

#### 1. Purpose of the STSM

The main purpose of this STSM was to analyze policyclic aromatic hydrocarbons (PAH) in the flue gas of a domestic fired-pellet boiler and a drop tube furnace (DTF) fed with various biomass fuels.

In order to collect PAH it was used a narrow tube connected to the flue gas duct of the set-ups and containing XAD-2 resin, where the lightest PAH are retained. A quartz fiber filter was placed just before it to collect the particulate matter, including soot, present in the flue gas and where presumably the heaviest PAH are adsorbed.

The analysis and quantification of the PAH is being performed in the Aragón Institute for Engineering Research and it combines Soxhlet extraction and gas chromatograph-mass spectrometer (GC-MS). The analyses are still in process and there are no final results for the moment.

# 2. Description of the work carried out during the STSM

#### 2.1 Introduction

Biomass is becoming more relevant as an energy carrier due to its high diversity and availability. In the last years, most of the efforts have been put into woody biomass as fuel; however, due to economic and environmental constrains only a part of the available forest biomass can be used. In this context, in addition to forest biomass, it is critical to use also agricultural residues for energy purposes. The extreme variability of the biomass feedstock demands for an extensive investigation on the impact of its composition in their combustion behavior, especially in their gaseous products. Combustion of biomass is associated with emission of particulate matter (PM) and soot, which have adverse health effects and have received attention in previous works [1,2]. Specifically, soot is strongly related with policyclic aromatic hydrocarbons (PAH) and these ones are considered their precursors [3]. Some of these substances have been classified by The USA Environmental Protection Agency (EPA), that completed a list with 16 priority compounds, as of greatest concern with regard to potential exposure and adverse health effects on humans. This list is often considered as a reference in environmental sample evaluation.

The use of modern pellet stoves is increasing as well as the pellet consumption, usually wood pellets, which are known to produce more PAH than any other fuel [4]. Previous works focused on this topic but evaluating PAH from biomass fuels other than wood is rare. This is the main purpose of this work. Moreover, since the conditions of combustion (combustion type, moisture content, fuel burning amount, fuel quality) play a significant role in the emissions of biomass [5], the use of a drop tube furnace under well controlled conditions could help to elucidate some light about this problem. To our knowledge, there are no previous studies related to the analysis of PAH from the combustion of biomass in a drop tube furnace.

# 2.2 Experimental investigation of the gaseous products formed during the combustion of different types of biomass

The tests have been performed in a domestic wood pellet-fired boiler shown in Figure 1, which is described in detail elsewhere [1], with the addition in this case of the PAH sampling system. Flue gas concentrations of  $O_2$ ,  $CO_2$ , hydrocarbons (HC) and  $NO_x$  were measured to gather information regarding the combustion conditions. The experimental conditions and pellet fuels are presented in Table 1.



Figure 1. Picture of the pellet boiler.

Table 1. Experimental conditions in the pellet-fired boiler.

				Emissions (dry base, at 13% O <sub>2</sub> )				
Fuel	Thermal input	Flue gas temp.	flow rate	(% vol.)		(ppm)		
Pellet	(kW)	(K)	(m3/h)	O <sub>2</sub>	CO <sub>2</sub>	СО	NO <sub>X</sub>	HC
Pine	10	381	80.88	18.41	7.08	37.1	45.6	7.8
	14	400	79.83	17.39	9.96	33.0	54.3	6.9
	17	409	92.21	17.12	10.86	66.5	55.3	3.9
Cork	10	382	86.06	18.28	6.90	661.6	142.9	6.1
	14	409	69.67	16.42	11.29	1186.1	224.2	42.6
	17	411	83.56	16.30	12.68	1269.2	228.7	70.7

The combustion in the drop tube furnace (DTF) was carried out with the following biomass fuels: grape pomace, rice husk, wheat straw and furniture residues. The DTF used is shown in Figure 2 and is described in detail elsewhere [6]. Briefly, the DTF is an electrically heated ceramic tube with an inner diameter of 38 mm and a length of 1.3 m. The furnace wall temperatures are continuously monitored by eight type-K thermocouples uniformly distributed along the combustion chamber. A water-cooled injector, placed at the top end of the DTF, was used to feed the biomass and the oxidizer to the combustion chamber. A twin screw volumetric feeder transfers the solid fuels to an ejector system from which the particles are air-transported to the water-cooled injector. In this study, measurements were carried out for all biomass fuels for DTF wall temperatures of 900 °C, 1000 °C and 1100 °C. The solid fuels feed rate was set to 23 g/h, the total air flow rate was set to 4 L/min, ensuring a second residence time in the DTF of around 2 second. The PAH collection started after the DTF reached steady-state conditions, with each measurement lasting for about 15 minutes.



Figure 2. Picture of the drop tube furnance

The PAH collection system, which is shown in Figure 3, consisted of a quartz microfiber filter (pore diameter lower than 1  $\mu$ m) connected to the outlet gas stream, and just after it, where the particulate matter are collected, it was placed a XAD-2 resin packaged in a thin quartz tube (300 mm length, 8 mm internal diameter). This tube was divided in two parts by quartz wool, the first one (3 g of resin) with the purpose of retaining PAH in the gas-phase and the other one (2 g of resin) in order to check that all the PAH where retained in the first part. The distance between the filter and the resin was minimized in order to avoid losses of PAH by condensation (the temperature was measured in this location to be above 120 °C).



Figure 3. Picture of the collection system: the particle filter and the quartz tube

The sample extraction and analysis, to be carried out at the Aragón Institute for Engineering Research, is summarized in Figure 4. Few tests are also being carried out at Instituto Superior Técnico. XAD-2 resin and material collected in the filters will be analyzed.

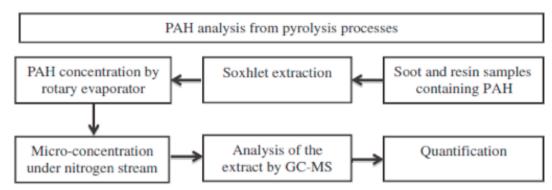


Figure 4. Procedure of the sample analysis developed to determine PAH concentration

This procedure consists of a first Shoxlet extraction, which lasts 24 hours, using a total amount of 200 mL of DCM (dicloromethane) and 4 extraction cycles per hour. Followed by PAH concentration by rota-evaporation, managing 5 mL of sample extract and then they undergo micro-concentration using a gentle nitrogen stream to give a final volume of 1.5 mL. The analysis is carried out with a GC-MS system for PAH separation, identification and quantification.

## 3. Description of the main results obtained

The analysis and quantification of the PAH is currently taking place in the Aragón Institute for Engineering Research. There are no final results for the moment.

#### 4. Future collaboration with host institution

Taking into account the fruitful cooperation established between the two research institutions, the Aragón Institute of Engineering Research and Instituto Superior Técnico will continue to collaborate in the area of the formation and emission of PAH from biomass combustion.

## 5. Foreseen publications/articles resulting or to result from the STSM

Authors are preparing two manuscripts for submission to international scientific journals, one reporting the experiments undertaken in the domestic pellet-fired boiler and other reporting the experiments in the DTF as follows:

- 1. Colom, J. M., Fernandes, U., Alzueta, M. A. and Costa, M. (2016). Characterization of polycyclic aromatic hydrocarbons in the flue gas and particulate matter of a domestic biomass-fired boiler. In preparation.
- 2. Colom, J. M., Fernandes, U., Alzueta, M. A. and Costa, M. (2016). Emissions of polycyclic aromatic hydrocarbons during biomass combustion in a drop tube furnace. In preparation.

In addition, a summary of the results will be presented at the  $2^{nd}$  General Meeting of the COST Action CM1404 that will take place in Lisboa from 14 to 16 of November 2016.

#### 6. Acknowledgements

The authors express their gratitude to the COST Action CM1404 (EU) for financial support.

#### 7. References

- [1] Fernandes, U., and M. Costa. "Particle Emissions from a Domestic Pellets-Fired Boiler." Fuel Processing Technology 103 (2012): 51–56.
- [2] Fitzpatrick, E.M. et al. "Emission of Oxygenated Species from the Combustion of Pine Wood and Its Relation to Soot Formation." Process Safety and Environmental Protection 85.5 (2007): 430–440.
- [3] Richter, H, and JB Howard. "Formation of Polycyclic Aromatic Hydrocarbons and Their Growth to Soot a Review of Chemical Reaction Pathways." Progress in Energy and Combustion Science 26.4-6 (2000): 565–608.
- [4] Oanh, NTK, LB Reutergardh, and NT Dung. "Emission of Polycyclic Aromatic Hydrocarbons and Particulate Matter from Domestic Combustion of Selected Fuels." Environmental Science and Technology 33.16 (1999): 2703–2709.
- [5] Zhang, Hefeng et al. "Particle Size Distribution and Polycyclic Aromatic Hydrocarbons Emissions from Agricultural Crop Residue Burning." Environmental Science and Technology 45.13 (2011): 5477–5482.
- [6] Wang, Gongliang, Rene Zander, and Mario Costa. "Oxy-Fuel Combustion Characteristics of Pulverized-Coal in a Drop Tube Furnace." Fuel 115 (2014): 452–460.