

# Partitioning of contaminant and inorganic species during thermal devolatilization of dried sewage sludge

V.F. de Almeida<sup>1</sup>, A. Ronda<sup>1</sup>, I. Pardo<sup>1</sup>, A. Gomez-Barea<sup>1</sup>

<sup>1</sup>Chemical and Environmental Engineering Department, Universidad de Sevilla, Seville, 41092, Spain

Keywords: chlorine, nitrogen, pollutants, sewage sludge, sulfur, waste-derived fuels

Presenting author email: [aronda@us.es](mailto:aronda@us.es)

## Introduction

Nowadays, our society is shifting from a linear to a circular economy and, thus, the interest in using waste as fuels has considerably increased. Thermochemical conversion can be applied to recover the energy from several types of wastes such as demolition wood, some fuel derived from municipal solid wastes (MSW) such as refuse-derived fuel (RDF) and sewage sludge (SS). Nevertheless, a major drawback is their high load in contaminants precursors: chlorine (Cl), nitrogen (N), sulfur (S) and heavy metals (HM), which can lead to corrosion and environment pollution. For the development of this thermochemical conversion technologies such as pyrolysis, gasification and combustion, it is essential to measure the concentration of the precursor species in the fuel and the contaminants in the product streams. This work is focused on determining the partitioning of Cl, N and S during batch pyrolysis tests of dry SS in a fluidized bed (FB) reactor by measuring the concentration of these species in the feedstock, as well as in the products, i.e. in the outlet gas and the solid residue. Moreover, the effect of temperature on elements partitioning is also analyzed.

## Materials and Methods

The dried SS (DSS) investigated in this work presents the following elemental composition: C (53.6%), H (8.3%), O (28.3%), N (8.5%), S (1.3%), Cl (0.05%) in dry and ash free basis (daf), 27.8% of ash in dry basis (db) and 6.5% moisture as received (ar) with a particle size of  $500 < d < 1000 \mu\text{m}$ . The FB reactor is made of 316 stainless steel (316SS) and has an internal diameter of 51mm with a length of 250mm in the bottom and a freeboard of 81mm ID with a length of 257mm (Nilsson *et al* 2016). A batch of 700g of silica sand ( $250 < d < 500 \mu\text{m}$ ) was used as bed material. All tests were performed with  $\text{N}_2$  as a carrier gas with a gas velocity of 0.35m/s. Temperature varied from 600 to 900°C (100°C step). One test run consisted in 10 tests with the addition of 5 g of DSS. The composition of the exit gas was measured online with a gas analyzer using a non-dispersed infrared method for  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ , and with a mass spectrometer for  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and minor gases like  $\text{HCl}$ ,  $\text{H}_2\text{S}$  and  $\text{NH}_3$ . A bed sample of 100g was taken at the end of the test run, and the solid residue from the fuel was separated from the bed by sieving, and its composition was further analyzed by combustion-based techniques for C, H and N, and by Inductively Coupled Plasma (ICP) for S and inorganics.

The recovery of elements presented in dry SS was determined by the elemental mass balances, calculating the amounts of the elements entering the reactor with the fuel, and their amount in the products (gas and solid). Recovery ( $R_i$ , wt%) is defined as the mass ratio of element  $i$  in the phase and that in the fuel ( $R_i = m_i^g / m_i^f * 100$ ). Where  $m_i^g$  is the mass of the element  $i$  in the gas/solid phase and  $m_i^f$  is the mass of the element  $i$  in the fuel.

The quantities of C, H, O, N, S, Cl and inorganics that enter the reactor were calculated using the total of fuel added and its composition. The amounts of C, H, O, N, Cl and S that exit the reactor in gas form were calculated using  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  concentrations and the outlet gas stream flowrate. For the solids, using C, H, N, S concentrations in the solid residue, and the solid residue mass, the elements total exit amount in solid form was calculated. Tars and light gases were not measured in the gas product, and Cl was not analyzed in the solid residue. Due to the complexity of quantifying the solid residue mass in FB tests, it is calculated assuming that the solid residue is composed by ash and C, H, N, S. By estimating an overall ash mass loss of 20% from the initial fuel ash content, and then using the C, H, N, S content in solid residue, the solid residue mass was calculated. Results were compared with those from the key element method (KEM) in order to validate the ash mass loss assumed. In the method, the so called “key element” (KE) is assumed to remain completely in the solid residue after the thermal conversion process and then, the solid residue mass is calculated using the KE concentrations in the fuel and in the solid residue. Details on this method are out of the scope of this work and are reported elsewhere (de Almeida *et al* 2018a).

## Results and Discussion

For 5g of fuel that enters the reactor in each test run, results of the solid residue masses are presented in Table 1 below. Results of elements (C, H, Cl, N and S) recovery (wt%) for each temperature is also shown in the following Figure 1.

Table 1. Calculated mass of the solid residue

T (°C)	600.0	700.0	800.0	900.0
Solid residue mass (mg)	1176.4	1136.6	1114.9	1107.1

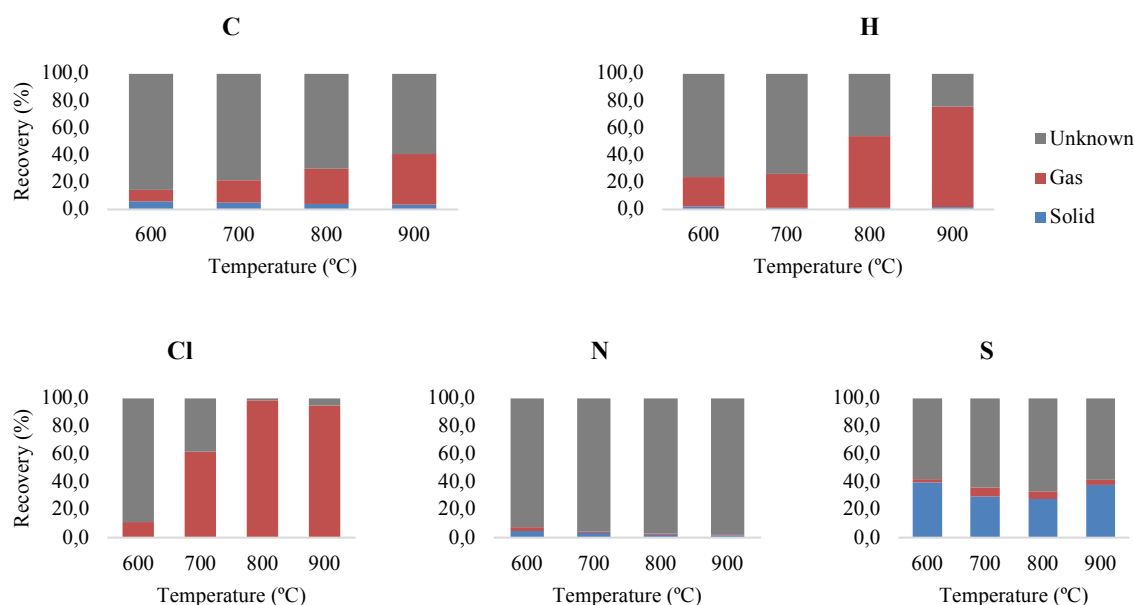


Figure 1. Recovery (%wt) of C, H, Cl, N and S between three phases: gas (red), solid (blue) and unknown (grey).

From Figure 1, it is seen that most carbon and hydrogen in the fuel are released to the gas phase and that these fractions increase with temperature. However, the fraction representing unknown C and H is high due to the non-measured light hydrocarbons and tars, which were not accounted for. The unknown fraction of these elements decreases with temperature as a result of the lower formation of tars at high temperature.

Chlorine at 800 and 900°C is totally found in the gas phase, which agrees with other literature results (Lu *et al* 2018). As Cl is not measured in the solid residue phase, the unknown Cl refers to solid Cl. Very little N-fuel is measured in the solid phase or in the gas phase as NH<sub>3</sub>, although HCN and N-tar were not analyzed. Nevertheless, it is expected to be a minor fraction compared to NH<sub>3</sub>. Probably a great deal of N is converted to N<sub>2</sub> catalyzed by the inorganic elements present in the dry SS ash like iron. Moreover, N in gas phase slightly decreases with temperature increase. Regarding S, about 40% was found in the solid phase for all temperatures. Just a low amount of S was found in the gas phase, decreasing with temperature above 700°C (evidenced when comparing results from 700 and 900°C). At 600°C all S is already released to the gas phase. It is not detected in the gas phase, though, because H<sub>2</sub>S interacts with the reactor material (de Almeida *et al* 2018b), so the unknown fraction is very high.

## Conclusions

In conclusion, the calculation of the solid residue mass enabled the calculation of elements recovery in the solid phase. Furthermore, this work explains the main trends of C, H, Cl, N and S partitioning in FB pyrolysis tests, even though for some elements the unknown fraction is elevated. Further work will be focused on the elements partitioning in other atmospheres (air and steam), different fuels (RDF and wood, the latter as reference clean biomass) and the effects of bed material on element partitioning.

## References

- de Almeida, V. F., Ronda, A., Arroyo-Caire, J., Suárez-Almeida, M., Pardo, I., Fuentes-Cano, D., Haro, P., Gómez-Barea, A. Heavy metals partitioning during thermal devolatilization of solid wastes in a fluidized bed reactor. *WasteEng Conference*. Prague - Czech Republic, July 2018a.
- de Almeida, V. F., Arroyo-Caire, J., Gómez-Barea, A. On the measurement of main inorganic contaminants derived from Cl, S and N in waste-derived syngas. Sent to *Fuel Processing Technology*, September 2018b.
- Lu, P., Huang, Q., Bourtsalas, A.T., Themelis, N.J., Chi, Y. and Yan, J., 2018. Review on fate of chlorine during thermal processing of solid wastes. *Journal of Environmental Sciences*.
- Nilsson, S.; Gómez-Barea, A.; Fuentes-Cano, D.; Haro, P.; Pinna-Hernández, G. Gasification of Olive Tree Pruning in Fluidized Bed: Experiments in a Laboratory-Scale Plant and Scale-up to Industrial Operation. *Energy & Fuels* 2016, 31, 542-554.

## Acknowledgements

This work is supported by the Spanish Ministry of Economy and Competitiveness and the European Union-FEDER (CTM2016-78089-R). The authors also acknowledge the National Council for Scientific and Technological Development of Brazil (CNPq), project 201591/2015-