CHARACTERIZATION OF SULFUR AND CHLORINE BEHAVIOR DURING PYROLYSIS OF BIOMASS AND WASTE

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The release of inorganic volatile S and Cl-containing species in the product gas of the gasification process poses many problems to the downstream processes, due to their corrosive nature (HCl, KCl, NaCl…) and their poisoning effect on catalysts (H_2S, COS). The objective of this study is to investigate the influence of the type and composition of feedstock, and of temperature, on the S and Cl release during pyrolysis - pyrolysis representing the first step of gasification. Particular attention is paid to the transformation of S and Cl-containing species, to the distribution of S and Cl between solid and volatile phases, and to their interaction with ash-forming elements. The selection of feedstocks was made from biomasses and wastes of biogenic and fossil origin with different initial sulfur content (0.1 - 2.6 wt. %) and chlorine content (0.1 - 50 wt. %). Two agricultural residues (colza straw and corn residues) were selected for their different ash content and composition (10 wt. % with a majority of Ca, and 3.5 wt. % with a majority of K respectively). Three waste components (wool, cardboard, and PVC) were also studied. A leaching technique was applied to the selected resources to determine the repartition of initial sulfur and chlorine into organic and inorganic forms. Organic forms of S and Cl (bound to the carbon matrix) were mainly found in wool, cardboard, and PVC, and the inorganic forms (sulfates or alkaline salts) in agricultural residues. Analytical experiments were performed in an induction heated, batch reactor operating up to 900°C, treating samples of a few grams in a fixed bed. The remaining fractions of S and Cl in the solid residue were quantified, and their chemical form was investigated by X-ray diffraction and SEM-EDX analyses. Pyrolysis tests performed at variable temperatures between 420 and 850°C show a resource-dependent retention of S and Cl in the char. For wool and cardboard, approximately 100% and 65% of S is released in the gas respectively, which corresponds to the fraction of S initially present in organic form. For PVC initially containing organically chlorinated compounds, more than 90% of the Cl is released into the gas as HCl. Thus, the organic forms of S and Cl are volatile and easily released into the gas phase even at low temperatures. For agricultural residues, Cl is mainly in the form of inorganic salts (KCl, $KClO_4$...), while about half of the S is in an organic form bound to the C matrix and the other half is in inorganic form (sulfates: K_2SO_4, $CaSO_4$...). In pyrolysis, the release of inorganic forms in the gas is partial. Different crystallized S containing forms are identified in the chars ($CaSO_4$ or CaS for colza straw, K_2SO_4 for corn residues...), which depend on the pyrolysis temperature and the ash composition. Based on these results, experiments aiming at testing in-situ cleaning methods based on chemical interactions between inorganic elements are planned. These will include either the use of additives (rich in calcium as $CaCO_3$) or the preparation of mixtures of resources selected specifically for their inorganic content, to limit the release of inorganic volatile pollutants.

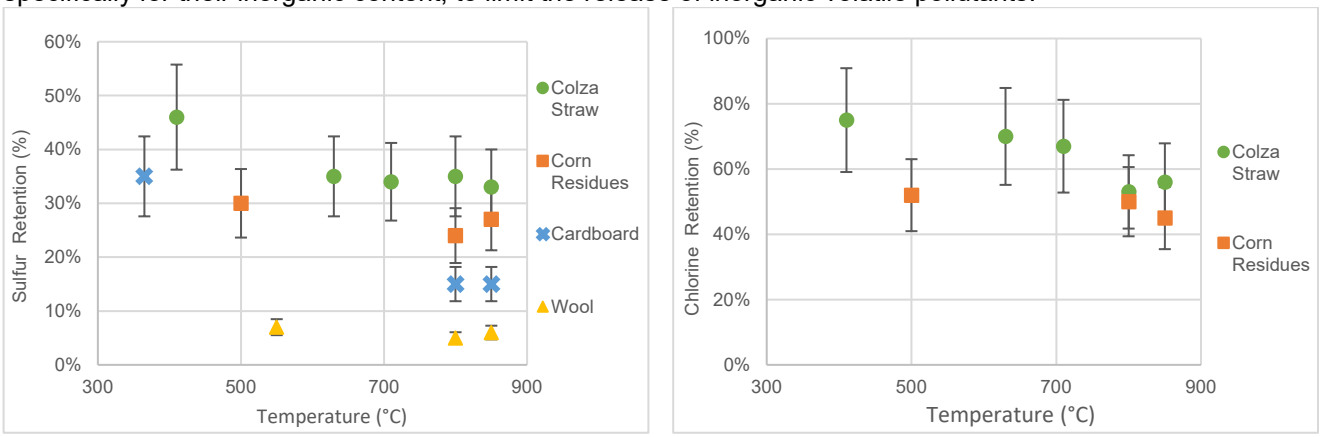

Figure 1: S and Cl retention in the char as a function of maximum pyrolysis temperature