Identification of the K2Ca6Si4O15 ternary phase in biomass mixtures

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Due to the growing demand for wood pellets in combustion processes, there is a need for other fuels such as agricultural residues. But their use is limited by technical issues such as fouling and ash agglomeration. Liquid appearance around 900 1150°C is known to be the main cause of ash agglomeration due to the high amount of alkali, silica and chlorine in such fuels. A promising solution is to blend different biomasses in order to appear high melting point compounds.
This study proposes a mixture formulation method based on predictions that assume thermodynamic equilibrium. For this purpose, the phase diagrams and Factsage software [1] have been used with an existing database [2]. The experimental validation of the calculations was carried out by annealing at 1000°C followed or not by air quenching at the laboratory scale - either from compressed ash chips - or from biomass pellets, which are more representative of the reality. Samples were characterized by SEM-EDX and XRD to identify the presence of liquid and crystalline phases.
One wood and four agricultural residues were selected for the study according to their ash composition (rich in Ca, K or Si), namely oak bark, rice husk, sunflower shell, grape marc and wheat straw. Several mixtures were selected with a minimum of liquid calculated by thermodynamic equilibrium.
The results on the wheat straw / oak bark ash showed that the chemical reaction was obtained after the annealing since new phases were obtained while they were absent from the ashes of single biomass. The mixture is not a simple dilution. These results are in overall agreement with the predictions except for the ternary compound $K_2Ca_6Si_4O_{15}$, clearly recognized in biomass ashes on a 50/50 mixture by XRD and SEM but which is not present in the thermodynamic databases. This ternary compound, has been recently observed in phase equilibria and crystallographic studies [3], [4]. This underlines the interest of the predictions but also the need for improvement of the existing databases especially on the CaO-K_2O-SiO_2 system.

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