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Slagging and Fouling during Coal and Biomass Cofiring: Chemical Equilibrium Model Applied to FBC

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Supporting Information

ABSTRACT: A thermodynamic model was applied to foresee the occurrence of fouling, slagging, and bed agglomeration phenomena during fluidized bed monocombustion of three different types of biomass, namely straw pellets, olive cake, and wood pellets. The cocombustion effect in reducing the occurrence of deposits and agglomerates of blends of 5, 15, and 25% (wt.) biomass with coal was also assessed. Chemical fractionation was applied to evaluate the reactive and nonreactive fraction of elements in the fuels, which was used to estimate their partition between the freeboard and bottom zone of the boiler. Qualitative and semiquantitative analytical techniques, namely, X-ray diffraction and scanning electronic microscopy – energy dispersive spectroscopy were used to compare the results from the simulation with the mineralogical and morphological composition of ash and deposits formed during combustion. The thermodynamic modeling revealed to be a powerful tool in foreseeing the formation of melt and liquids salts, depending on the temperature and chemical composition of fuels. The main discrepancies observed between the experimental and simulated data were due to particularities of the combustion process, which are not incorporated in the software, namely, kinetic limitations of the reactions, possible occurrence of secondary reactions in the ashes, and elutriation effects of ash and silica sand particles.

1. INTRODUCTION

Biomass thermochemical conversion through combustion (and cocombustion) has socioeconomic and environmental benefits; however, problems associated with its use are also documented.[1] Ash related problems like deposit formation in the convective heat transfer zones (fouling) and refractory zones of the boiler (slagging), agglomeration (in case of the fluidized bed combustion), and corrosion are usually the principal causes for the malfunctioning of the combustion systems.

According to the actual knowledge, the ash problems associated with biomass combustion are mainly related to the quantity, reactivity, and interaction of Si, K, Ca, Cl, and S. Na and Mg have similar behavior to K and Ca, respectively. Nevertheless these elements exist usually in minor quantities in biomass. K in the presence of Cl, S, and Si undergoes many undesirable reactions during combustion, e.g. alkali reactions with Si forming alkali silicates (which melt or soften at low temperatures), and reactions of alkali with S and Cl forming alkali sulfates and chlorides, which deposit inside the combustor and heat exchanger surfaces.[2] Ca may affect the equilibrium reactions binding to Si as calcium silicates, decreasing potassium silicates formation and increasing potassium salts.[3,4] The physical properties and the inorganic composition of the different types of biomass could vary significantly, turning difficult the prevision of biomass ash behavior during combustion. Usually, herbaceous biomass ash has high Si and K content and woody biomass ash has high Ca content, which may justify the different behavior of the ashes formed during combustion. Soil contamination is another problem[5] contributing to the ash formation.

Possible operational measures to decrease problems related to biomass ashes produced in fluidized beds combustors (FBC) are as follows: 1) decrease process temperatures and avoid hot spots; 2) fuel refinement (e.g., through leaching, thus extracting Na and K); 3) cofiring with fuels having less problematic ashes; 4) modify the composition of bed material and their size distribution and 5) use of additives to modify ash behavior.[3]

The cofiring of biomass with coals allows diluting problematic elements and modifies ash composition. Besides dilution effect, the reactivity of inorganic elements has also an important role in the compounds formation. Some reactions are favored relatively to others, influencing the mineralogical composition of ashes and the salts formation and consequently the ash melting temperatures. The interactions between Al, Si, and S from coal and the alkali elements from biomass may interfere with the properties of fly ash and ash deposits.[6,7] During cofiring of coal with biomass the formation of alkali-alumina-silicates is thermodynamically favored, which promotes the alkali sequestration in bottom ashes and its decrease in the gaseous stream. The alkali-alumina-silicates remaining on the bottom ashes have relatively high melting temperatures, decreasing slag, and sintering of the ash and bed material. The ash deposition in the convective zones of the boilers and surface corrosion may also be reduced because less alkali chlorides are volatized.[8] The reaction of S from coals with alkali species from biomass may also have an important role in preventing fouling and corrosion, because K_2SO_4 is less corrosive than KCl.[6]

Most of the interactions between the elements during coal and biomass cofiring have been identified. Nevertheless, the

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