THE ROLE OF POTASSIUM ON THE THERMICITY OF BIOMASS PYROLYSIS AND CHAR REACTIVITY

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The kinetics and products of biomass pyrolysis have been extensively investigated, but the aspects related to the thermicity of the conversion process are still largely unknown. Difficulties have been put into evidence to get univocal trends or figures about the pyrolysis heat or the magnitude of thermicity display. In fact, the experimental configuration and operating variables, the analysis of the data and the biomass nature are different among the various studies, all affecting the observed results. At the microscale, the exothermicity of lignocellulosic material pyrolysis appears to be mainly associated with the occurrence of secondary reactions, with an enhancement as larger initial sample mass and/or higher pressure are applied. At the macroscale, the display of exothermic effects is observed for particles and packed beds heated along the external surface. More specifically, a surprising new conversion regime, named pyrolytic runaway, has been identified for packed-bed pyrolysis of some feedstocks, subjected to mild heating temperatures typical of the torrefaction pre-treatment. The main feature is the extremely rapid and highly exothermic conversion of the entire feed under thermal conditions determined by self-heating and highly different from those externally imposed. Despite changes in the yields and quality of the products and the deterioration of the control effectiveness, the volumetric heat generation from the pyrolysis reactions could be exploited for the achievement of an autothermal process. A precise understanding of the feedstock properties that allow for this conversion regime is not yet achieved but the indigenous or added potassium content affects both the pyrolysis reaction paths and the reactivity of the resulting char.

In this study the pyrolysis of potassium impregnated wood is investigated by means of thermogravimetric analysis and a bench-scale packed-bed reactor. Also, the oxidation of char, produced from the pyrolysis process, is studied. The usual shape of the thermogravimetric curves is preserved for potassium impregnated wood though with a progressive displacement at significantly lower temperatures. The bed heating dynamics are strongly modified by the enhanced reaction exothermicity which, for high potassium contents, tend to turn the role of the external heat source simply into a starter for a self-sustaining process. The magnitude of the exothermic effect display, also including pyrolytic runaway, depends on the potassium percentage. Maximum temperature overshoots over a large part of the bed reach values up to about 150 K and correspond to minima in the char yields. For the conditions of thermal analysis, oxidative environment, and temperatures up to 750 K, chars undergo the kinetically controlled stages of oxidative devolatilization and oxidation. For the latter, as the potassium content increases, the process dynamics shift from a single to two conversion zones, corresponding to thermal and mixed catalytic-thermal activation, respectively. The ignition and burnout temperatures initially decrease, testifying an enhancement of carbon conversion. However, for potassium contents above certain threshold limits, effects appear first of saturation and then of inhibition.