Self-ignition temperatures determined in the framework of conventional thermal ignition theory does not explain why biomass is much more susceptible to spontaneous ignition in power plant mills or storages. Examining the onset of reactions at low temperatures may provide a better understanding of the process, which can then be incorporated into refined models of self-ignition for biomass and other organic solids. In the present study, the slow, transient heating of several lignocellulosic biomasses and a bituminous coal from ambient temperature to around 300°C were investigated in a lab scale tube oven, with sample sizes between 11–40 g. Tests were carried out under oxidizing (20 % O2) and inert atmospheres. Judged by off-gas measurements of CO and CO2, a reaction onset could be seen at temperatures below 100°C. Under oxidizing atmosphere, reactions were more intense and set off earlier, suggesting that a heterogeneous oxidation is the dominating mechanism in self-ignition. It could also be shown that both mechanisms compete for reactive material. While oxidation was exothermic, pyrolysis was largely thermally neutral in these experiments. Reaction behavior was seen to depend highly on the material, and the results indicate that higher ash contents may promote reaction onset. However, further work is needed to arrive at a comprehensive model of self-ignition.