Converting existing coal fired power plants to biomass is a readily implemented strategy to increase the share of renewable energy. However, changing from one fuel to another is not straightforward: Experience shows that wood pellets ignite more readily than coal in power plant mills or storages. This is not very well explained by applying conventional thermal ignition theory. An experimental study at lab scale, using pine wood as an example fuel, was conducted to examine self-heating and self-ignition. Supplemental experiments were performed with bituminous coal. Instead of characterizing ignition temperature in terms of sample volume, mass-scaling seems more physically correct for the self-ignition of solids. Findings also suggest that the transition between self-heating and self-ignition is controlled both by the availability of reactive material and temperature. Comparison of experiments at 20% oxygen with those under inert atmosphere revealed two distinct pathways, pyrolysis and exothermic heterogeneous oxidation. At low temperatures and sufficient oxygen availability, heterogeneous oxidation of the solid seems to be favored over pyrolysis for wood, but not for coal. Current ignition models do not reflect the existence of these different pathways, which may be the reason behind the discrepancy between theory and observations.