Biomass is a low-carbon, resource, which is finding increasing use for heating and the generation of electricity. Biomass pyrolysis plays a central role in its combustion and is therefore receiving extensive consideration. The decomposition of biomass is also a crucial step in both fast pyrolysis and various thermal processing techniques involved in chemical manufacturing. Potassium and sodium are well-known catalysts in the thermal reactions of biomass. An expression was developed linking the rate of thermal degradation of a biomass to its potassium or sodium content. Willow samples impregnated with different potassium or sodium concentrations were studied for their pyrolysis behaviour by thermogravimetric analysis, and apparent first order kinetics derived. The developed relation yields a maximum reaction rate constant and a metal saturation constant that can predict the rate of willow pyrolysis based on temperature and concentration of potassium or sodium. Effects of sequential washing using water, ammonium acetate, and hydrochloric acid were also explored.