Sulfation of Condensed Potassium Chloride by SO2 has important implications for deposition and corrosion in combustion of biomass. In the present study, the sulfation of particulate KCl (90–125 μm) by SO2 was studied in a fixed bed reactor in the temperature range 673–1023 K and with reactant concentrations of 500–3000 ppm SO2, 1–20% O2, and 4–15% H2O. The degree of sulfation was monitored by measuring the formation of HCl. Analysis of the solid residue confirmed that the reaction proceeds according to a shrinking core model and showed the formation of an eutectic at higher temperatures. On the basis of the experimental results, a rate expression for the sulfation reaction was derived. The model compared well with literature data for sulfation of KCl and NaCl, and the results indicate that it may be applied at even higher SO2 concentrations and temperatures than those of the present study. Simulations of sulfation of KCl particles with different size indicate that only for very small KCl particles, below 1 μm, a considerable in-flight sulfation is achievable at the short gas residence times typical of combustion systems.