Modeling the dehydration of t-butanol and avoidance of the formation of oligomers

The dehydration of t-butanol (TBA) in sulfuric acid is a common way for the production of very pure isobutene. The demands concerning the quality are high, in particular for the synthesis of polymers with high molecular weight. Depending on composition of the acid phase, cleavage of TBA is problematic since it leads to different yields of isobutene. Especially at temperatures above 70°C and for high acid concentrations unwanted oligomerisation of isobutene occurs.

This work investigates the optimization of the dehydration process with respect to isobutene yield under avoidance of the formation of oligomers. For this purpose a mechanistic reaction model is developed which incorporates the influence of the solvents acidity by means of the Hammett acidity function. The reaction scheme includes postulated intermediates like t-butyloxoniumion, trimethylcarboniumion, di-t-butylether (DTBE) and the protonated form of the ether.

Determination of the model parameters is based on measurements under steady state conditions in a continuous stirred tank reactor (CSTR). To study temperature dependence, liquid and gas samples are taken at 63°C, 68°C and 73°C.

Under quasi steady state assumptions (QSSA) concerning intermediates a simplified kinetic model is obtained. Coupling of the resulting kinetic equations to CSTR balance equations leads to the complete mathematical model. Fitting of the remaining model parameters to experimental data yields parameter values which allow for better understanding of the reaction mechanism. For example, formation of isobutene via decomposition of DTBE occurs and becomes more important with increasing temperature.

Combining this model with the results of Allenbach, numerical simulations can be used to compute reaction conditions, for which oligomerisation of isobutene is avoided and yield of isobutene is maximal.