Validation of kinetic model based on calorimetric data

Introduction

Understanding reaction kinetic is an important step in process development and optimization.

Nowadays, different approaches are available to develop and evaluate reaction kinetic models. One of them, based on calorimetric data, is currently developed by Charles Guinand in collaboration with the EPFL, AKTS and ChemTech.
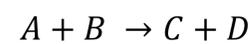
The objective of this work is to validate this approach using RC1 and DSC measurements applied to the esterification of acetic anhydride with methanol.

Reaction

The esterification of acetic anhydride with methanol has been chosen due to its well-known kinetic and autocatalytic effect (acidic environment):
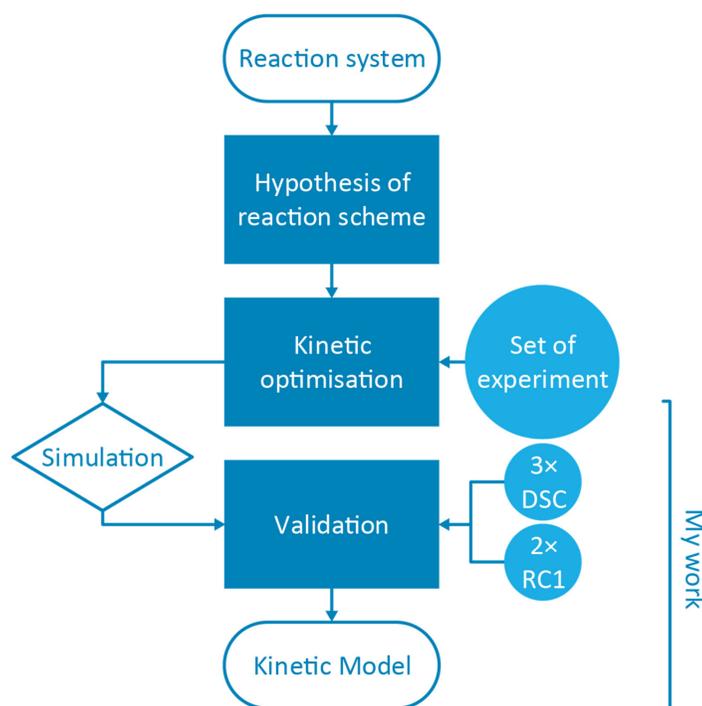

| Acetic anhydride | Methanol | Methyl acetate | Acetic acid |
| A | B | C | D |
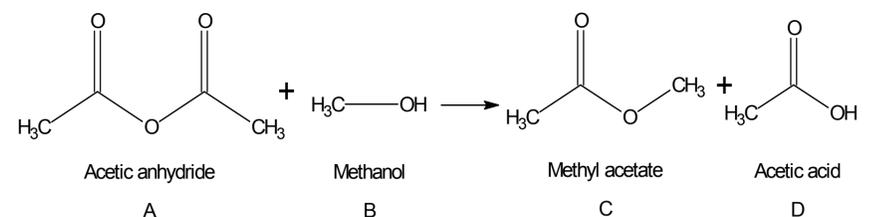
This reaction scheme can be written as:

$$A + B \rightarrow C + D$$

$$A + B + C \rightarrow 2C + D$$

Method

The approach and its application for kinetic optimization and simulation was implemented in collaboration with AKTS.

Model

The model is based on the power rate law and the rate (r) depends on temperature (T) described by the Arrhenius law:

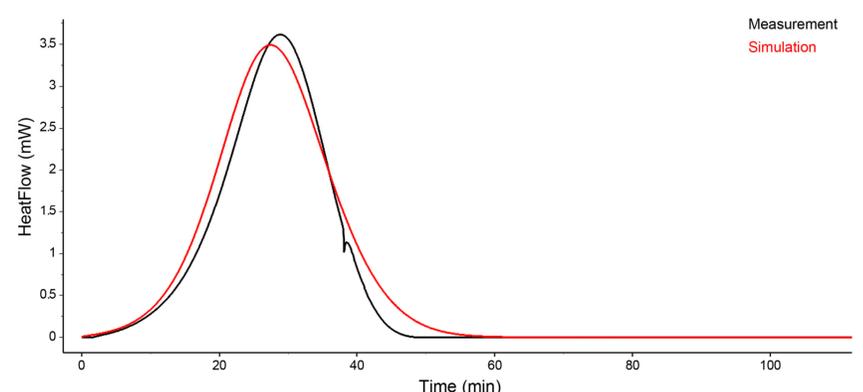$$k = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right)$$

The influence of the reagent concentrations (C_i) is expressed in the kinetic equation using exponent orders (m):

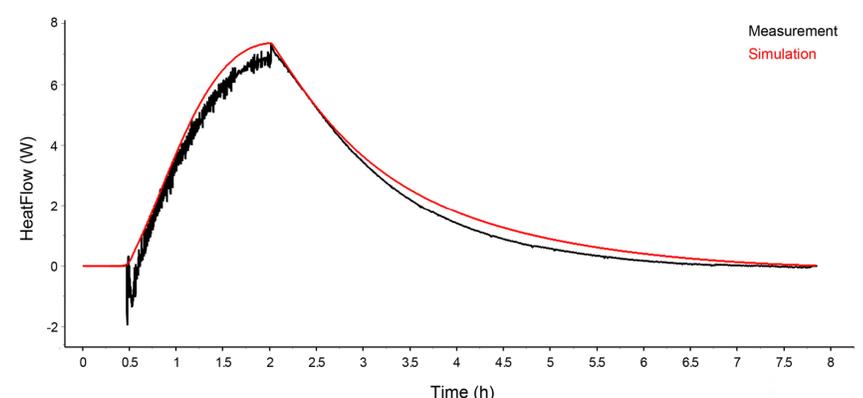$$r = k \cdot \prod_{i=1}^{I} C_i^{m_i}$$

Results

As the simulations fit well with the experimental measurements, the model can be considered as valid.

The simulation accuracy depends strongly on the experimental set used for the optimization.

Differential Scanning Calorimetry at 2K/min

Reaction Calorimeter at 50 °C

Conclusion and Outlook

Kinetic models can be developed from limited calorimetric experiments.

DSC, RC1 combined with a simulation software (AKTS-Thermokinetics) deliver quick answers regarding process optimization and thermal safety.

In order to improve this method, more complex reactions will be investigated.

Investigator

Rebetez Gonzague

Doctorant

Charles Guinand

Professor

Dr. Christophe Allemann