Simulate chemical reactions and derive kinetics from milli-scale flow calorimetry

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Introduction

Continuous reaction technology has many advantages over traditional batch reactors including higher productivity, stable product quality and increased process safety. In particular, the determination of the enthalpy and kinetics of the reaction is a fundamental part of the safety assessment of a process. The closer this determination is to the industrial process, the more robust the safety data will be. It is well known that significant deviations occur for non-selective reactions[1]. Recently, we have shown that the enthalpy of reaction can be measured in the continuous flow calorimeter without extensive calibration and that the accuracy of the measurements is highly dependent on the process parameters applied, in particular the flow rate[2,3]. In fact, the resolution of the sensors can be increased as desired with different flow rates and the obtained data becomes highly reliable.

In contrast to the well-established calorimetry, obtaining kinetic data directly from a polytropic temperature profile is a relatively new discipline. To our knowledge, this could be addressed by two means; segment wise analysis as reported by Frede *et al.*[4], and a temperature profile fitting approach reported by Imamura *et al.*[5].

In this work, we present a third approach by combining the temperature profile fitting approach with various reaction temperatures to improve the data quality and reduce uncertainty. The oxidation of sodium thiosulfate with hydrogen peroxide (Eq 1) served as model reaction and was carried out in a milli-scale continuous flow calorimeter (Contiplant, Fluitec, Switzerland), that is scalable to production scale[2].

$$2\ Na_2S_2O_3 + 4\ H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4\ H_2O \qquad 1$$

Results and Discussion

The quality of the determination could be improved by adapting the modelling described by Stegehake[6]. Therefore, the oxidation reaction was performed at 20 and 60 °C and different flow rates. For each temperature profile, several pairs of E_a and k_0 were evaluated that best fit with the measured temperature profile (Fig. 1). The here presented software allows to freely choose reaction kinetics model. For this evaluation, a second order reaction model was assumed (Eq 2).

$$-r_{Na2S2O3} = k \cdot c^1_{Na2S2O3} \cdot c^1_{H2O2} \qquad 2$$

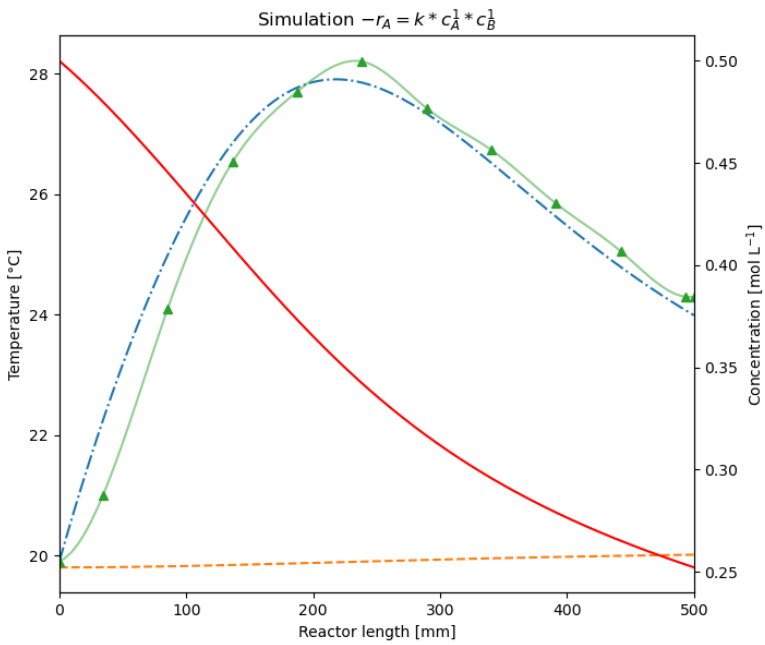

Fig. 1 Simulation of the product temperature (blue dash-dotted), heat transfer medium temperature (orange dashed) and Na_2S2O_3 concentration (red line) of the progress of the chemical reaction (1) and comparison with measured data (green triangles). Heat of reaction, kinetics model and kinetics parameters could be freely selected.

According to Stegehake, there are many pairs that fit well, so different E_a have been fixed and k_0 fitted. These pairs correlate in a linear regression but with different slopes for each temperature. The intersection of all correlations represents the true kinetic parameters (Fig. 2).

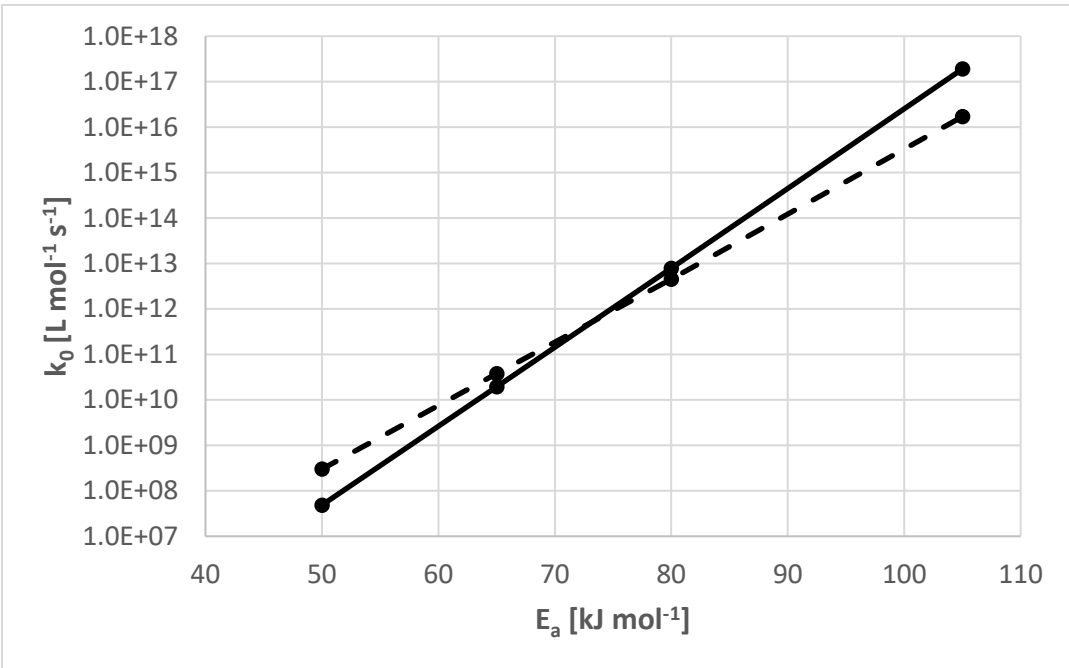

Fig. 2 Determination of activation energy E_a and initial reaction rate constant k_0. Flow rate was 40 ml min^{-1}. 20°C (solid line); 60°C (dashed line).

The obtained value of E_a and k_0 are therefore 73.1 kJ mol^{-1} and 5.1×10^{11} L mol^{-1} s^{-1}, respectively. These values fit well with literature references[4,7–9].

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