How beneficial could be the use of reaction calorimeter in chemical reaction engineering?

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Highlights
- Use of adiabatic calorimeters for the characterization of thermal runaway.
- Use of non-isothermal conditions for kinetic constant estimation.
- Influence of kinetic and thermodynamic constants via global sensitivity analysis.

1. Introduction

The origin of reaction calorimeters is traced back to the calorimetry technique development [1]. It is a power tool essentially used to assess and/or characterize the risk of thermal runaway of a chemical system [2][3][4]. Calorimetry is also an appealing method using temperature or heat-flow rate as a signal [5][6]. Nevertheless, using the calorimetric method requires perfectly characterizing the reactor environment from a thermal viewpoint. For instance, one must verify that the heat loss is negligible, characterize the value of the global heat transfer coefficient, measure the heat capacity, etc. Except for a single reaction step, it is challenging to determine the kinetics of several consecutive or parallel reactions based on temperature or heat-flow rate.

Salcedo et al. [7] showed the possibility and the benefits of developing kinetic models in different thermal modes (isothermal adiabatic and isoperibolic). This approach to developing kinetic models in different thermal modes is rare in the literature. Using only reaction calorimeter to develop a kinetic model for a complex model could be a priori non-sufficient. By complex model, we mean a system with multiphasic and several reactions. To develop kinetic models for such a system, one needs to know the concentration evolution of different species [7,8]. Using adiabatic conditions in reaction calorimeters requires not to withdraw samples to avoid interference with temperature, limiting the kinetic description of all reaction steps. On the other hand, one could imagine combining some experiments in isothermal conditions, including offline analysis, and some in adiabatic conditions. The benefit of adiabatic conditions is that we do not have to analyze several samples during the experiments.

We studied the hydrogenation of 5-HMF, a multiphasic system with several exothermic reaction steps. Hydrogenation of 5-HMF, issued from the hydrolysis of cellulose, can lead to several interesting molecules used as biofuels or as intermediates [9]. We aimed to determine the impact of the number of adiabatic and isothermal runs on the kinetic modeling. In the first step, we produced synthetic data with different noise levels in isothermal and adiabatic conditions. In the second step, by using different sets of synthetic runs with noise, we carried out kinetic modeling to determine the kinetic constants and the sum of squared residuals. It is essential to stress that the true kinetic constants used to create synthetic data were not obtained experimentally, but we created virtual true kinetic constants.

2. Methods

Figure 1 shows the reaction steps for the hydrogenation of 5-HMF over a virtual catalyst. We imagined that the true mechanism follows a Langmuir-Hinshelwood with the dissociation of hydrogen. Synthetic data in isothermal and adiabatic conditions were obtained from the resolution of ordinary differential equations using the true kinetic and thermodynamic data. These ODEs were solved by DDAPLUS solver using a modified Newton algorithm, and installed in the software Athena Visual Studio. Two types of synthetic data were produced, one at low error and the other at high error.
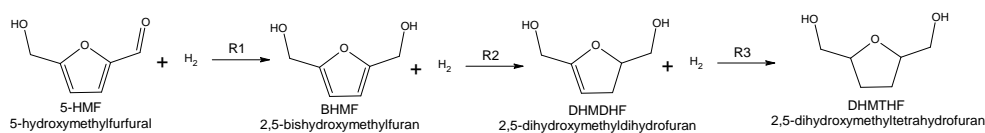
Figure 1. Reaction steps for the hydrogenation of 5-HMF to DHMTHF.

3. Results and discussion

The impact of the number of adiabatic runs on kinetic model results was evaluated by using different approaches: A1: all isothermal and adiabatic runs were used in the modeling stage; A2: all isothermal runs were used in the modeling stage; A3: all adiabatic runs were used in the modeling stage; A4: 15 runs were used in the modeling stage, including 14 isothermal runs and 1 adiabatic run; A5: 15 runs were used in the modeling stage, including 13 isothermal runs and 2 adiabatic runs; A6: 15 runs were used in the modeling stage, including 10 isothermal runs and 5 adiabatic runs; A7: 15 runs were used in the modeling stage, including 9 isothermal runs and 6 adiabatic runs and A8: 15 runs were used in the modeling stage, including 7 isothermal runs and 8 adiabatic runs. Figure 2 shows that the fit of the model to experimental data (mean value) is good.
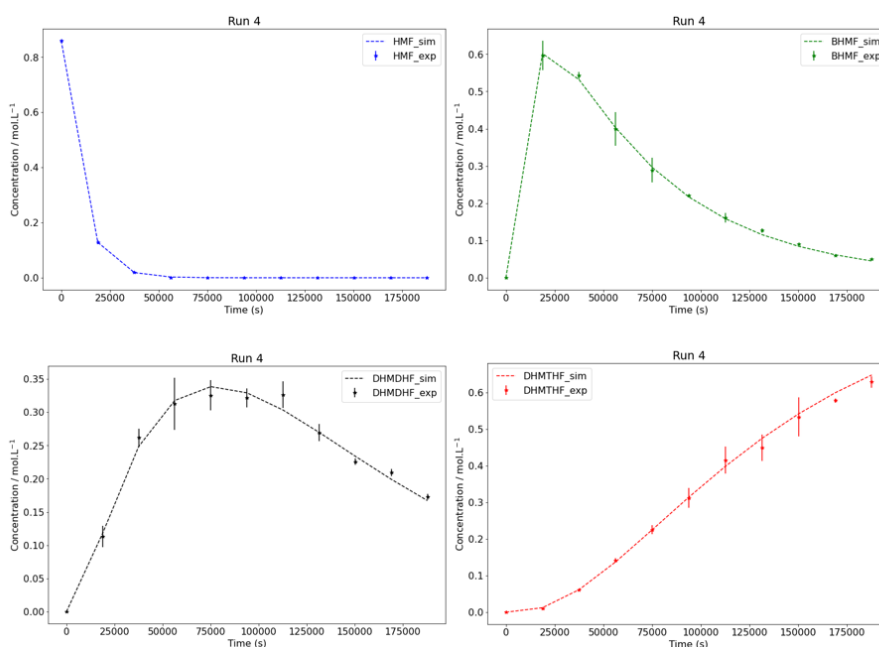
Figure 2. Fit of the model to experiment concentration with low error for Run 4 for Approach1.

4. Conclusions

Mixing adiabatic runs and isothermal runs for parameter estimation has two benefits. Firstly, it allows to decrease the analytical stage, and secondly it allows to get some models for product optimization, pinch analysis and thermal runaway assessment.

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