

SYSTEMATIC APPROACH TO REACTION ANALYSIS: FROM MECHANISM DISCOVERY TO REACTION OPTIMIZATION

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Summary

This paper focuses on improving productivity and effectiveness in the tasks of mechanism analysis, kinetic estimation and reaction optimization by developing a systematic software framework called the REX Suite. The software guides researchers towards maximum reaction performance and is designed to be chemist-friendly, thereby allowing researchers to focus on their goal without having to build and solve the complex differential algebraic equation systems that govern reactor behavior. This framework has been applied successfully in applications ranging the spectrum from petrochemicals, polymers to pharmaceuticals. The software also includes infrastructure to store and access reaction libraries.

Keywords

Deployable software and databases for reaction engineering, Reaction Path Analysis, Dynamics and control of chemical reacting systems.

Introduction

The first step after the chemist conceptualizes a new reaction route is experimentation. Following the first seed experiments, in the process of reducing byproducts and improving reaction performance, the questions that arise are:

- What is the most probable reaction mechanism?
- How should the next experiments be designed?
- What is the best performance that can be achieved for this reaction route?

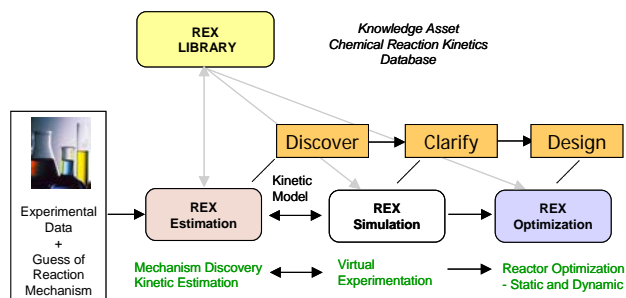
The objective of our work is to develop a systematic approach to answer the questions posed above. The major tasks involved in answering the questions above are:

- Mechanism and Kinetic Model Discovery
- Experiment Design
- Reactor Performance Optimization

Through our engagement in numerous projects in reaction performance maximization in the chemical industry, we have developed a comprehensive software REX for accomplishing these tasks productively. In designing the software, we paid special attention to the research

workflow. Our goal is to have the researcher use the software as a thinking partner in his workflow.

In the first stage of process development, the researcher may search the reaction library in REX for reactions of interest. The library also stores chemical kinetic models for each reaction set, so one may extract a reaction set for simulation studies before starting experimentation. Following experimentation, we enter the *mechanism discovery* stage. Here, the experimental reactor data and hypothesis of the reaction mechanism may be entered into the software. REX auto-generates the mathematical models for the reaction system and reconciles the mechanism hypothesis with the observed experimental data to generate kinetic parameter estimates. Subsequently, one may move to the *optimization* mode in REX, where the kinetic model is used to find the maximum performance for this reaction system. The *next experiment* could then be conducted at this point to verify the model. A schematic of the different aspects of the REX software is shown below.



The estimation and optimization modules in REX allow analysis of a wide range of reaction systems and models. Kinetic estimation studies can be performed with microkinetic models that consider detailed reactions, for example, the surface transformations in solid-gas catalysis directly, or with macrokinetic models such as the Langmuir-Hinshelwood models. Microkinetic models may be entered in natural mechanism form, and the model generator automatically generates the surface reaction constraints. REX supports a wide range of reactor configurations for experimental data, including multiphase operation. In the estimation process, a variety of weighting methods for reconciling measurements is supported, with flexible options to manually override auto-generated weights. For example, situations where species cannot be distinguished but are measured together as a group are handled with ease in the model construction phase. Algorithms for the parameter estimation employ techniques to increase parameter uniqueness.

Similarly, the reactor optimization module features a rich set of options for maximizing reaction performance. One may consider several reactor alternatives ranging from plug flow/fixed bed reactor, recycle reactors to CSTR trains. Integrated reaction-separation optimization studies can also be performed. For batch reactors, one may

perform dynamic profile optimization of operating variables such as temperature, pressure, feedbatch flow and/or outflows, along with evaluation of control strategies.

These reactor models often tend to be nonlinear differential algebraic systems. However, due to automated model generation and advanced optimization algorithms in REX, the researcher is spared the tedious tasks of building, debugging and constructing solvers for the mathematical models. We use orthogonal collocation on finite elements to discretize the reactor differential equations to a set of algebraic equations[1]. With this, the differential algebraic optimization problem is now converted and solved as a nonlinear optimization model. Efficient profile initialization techniques are also employed to ensure robustness and efficiency in performance. Higher index systems that commonly arise in batch reactors with pressure control are also handled effectively. We have leveraged the years of experience in industrial applications to ensure high computational reliability in REX. Therefore, the chemist can focus on reaction performance effectively.

Besides the software, we have developed a systematic workflow procedure for analyzing chemical kinetic systems. In this paper, we illustrate our systematic approach for reaction analysis and performance improvement with examples ranging from petrochemicals, polymers and fine chemicals. These examples, which mirror our experience in industrial settings, will illustrate the efficiency gains that REX delivers in the steps of

mechanism discovery, efficient experiment design and reactor performance maximization.

1. Cuthrell, J.E. and L.T. Biegler, "On the Optimization of Differential-Algebraic Process Systems," *AIChE J.* 33(8), 257 (1987).