Computers and Chemical Engineering 106 (2017) 512–528

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Enhancing the value of detailed kinetic models through the development of interrogative software applications

Triveni Billa [a], Scott R. Horton [a], Mayuresh Sahasrabudhe [b], Chandra Saravanan [b], Zhen Hou [a], Pratyush Agarwal [a], Juan Lucio-Vega [a], Michael T. Klein [a,c,*]

[a] University of Delaware Energy Institute, University of Delaware, Newark, DE 19808, United States
[b] Reliance Industries Limited, Ghansoli, Navi Mumbai 400701, India
[c] Center for Refining and Petrochemicals, King Fahd University of Petroleum and Minerals, Dharan, Saudi Arabia

ARTICLE INFO

Article history:
Received 21 April 2017
Received in revised form 21 July 2017
Accepted 22 July 2017
Available online 25 July 2017

Keywords:
Software applications
Detailed kinetic model
Catalytic reforming
Naphtha

ABSTRACT

A suite of user-friendly software tools was developed to help increase the accessibility of detailed kinetic models to a wide range of users from modelers to research collaborators to process engineers. The aims of these users were the basis for the software development. The tools are illustrated for development, analysis and usage of a detailed catalytic naphtha reforming model. After initial model construction, the Reaction Network Visualizer and KME (Kinetic Model Editor) Results Analyzer helped in understanding the characteristics of the reaction pathways, molecular profile and also assisted in tuning the kinetic parameters. The I/O (Input/Output) Converter permits execution of a molecular-level model in a manner which focuses on only measurable inputs and outputs. The KME Reactor Flowsheet tool increased the core kinetics model capabilities by allowing the model building to be based on data from a pilot or commercial reactor, including schemes with split feed streams and reactor bypasses.

1. Introduction

Kinetic modeling is a powerful tool that can help to improve the performance of new and existing processes. Kinetic models provide insight into the underlying process chemistry for a chemical reactor. For instance, these models can identify which reactions are kinetically relevant and which are rate limiting. This understanding can then be used in process optimization. Process optimization comes in a variety of forms ranging from short-term adjustments such as reactor temperature to long-term adjustments such as catalyst or feedstock selection. The usefulness of kinetic models is based on both the detail contained in the model and the experimental data utilized for model development.

The appropriate level of detail in the model is guided by the user's purpose. This can be limited, however, by the available experimental description of a process. Historically, experiments did not provide precise molecular differentiation of both feedstock and reactor products. The models were therefore 'lumped' in nature and lacked detail beyond observable lumps. More modern experimental techniques allow for far more molecular discrimination. For instance, advanced mass spectroscopy techniques can identify more than 50,000 unique molecular formulas (Castro-Marcano et al., 2012; Rodgers and McKenna, 2011) for heavy oil. This allows kinetic models to be built at the same level of detail if a user was so motivated.

The transition from lumped to detailed kinetic models provides some unique challenges, which is depicted in Fig. 1. One key advantage of lumped models with few equations is that the limited scope of the information allowed for the models to be easily understood. As the detail in the models increases, they become closer to representing real physical process. This detailed information makes the models much more robust and useful across a broad range of problems; however, the complexity makes the model harder to understand. This has the potential of limiting the accessibility of the model to only a small subset of potential users.

In order to discuss improvements to model accessibility, a baseline must be established on how detailed kinetic models are built and solved (Hsu et al., 2009; Ramage et al., 1980). Apart from model building, thorough understanding of the model implications, sensitivity analysis on model parameters and model reduction methodologies (Gupta et al., 2016) are crucial for real time optimization and plant monitoring. Details about many approaches like Kinetic Model Builder (Goldschen-Ohm et al., 2014), Reaction Mechanism Generator (RMG) (Gao et al., 2016; Song, 2004),

* Corresponding author at: Interdisciplinary Science and Engineering Building, 221 Academy Street, 250G, Newark, DE 19716, United States.
E-mail address: mtk@udel.edu (M.T. Klein).

http://dx.doi.org/10.1016/j.compchemeng.2017.07.009
0098-1354/

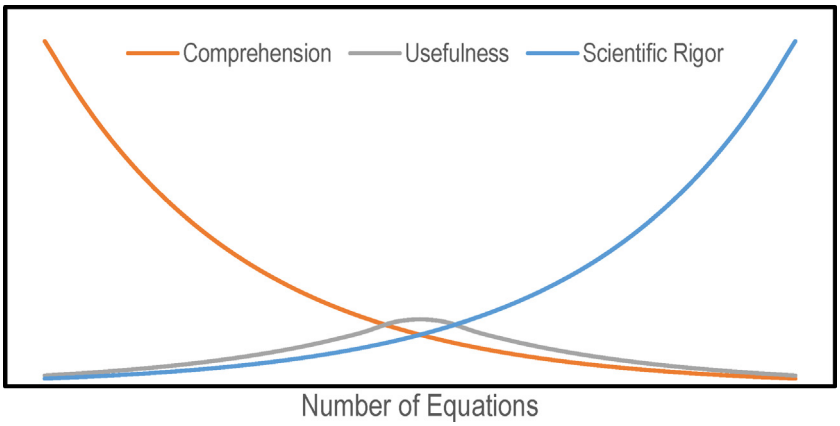

Fig. 1. Trade-offs of the comprehension and scientific rigor of models as a function of the number of equations.

CHEMKIN (Coltrin et al., 2000), Structure-oriented lumping (Quann and Jaffe, 1992, 1996), Single event kinetic modeler (Froment, 2005), ChemDoodle (Todsen, 2014), are available in the literature to build, simulate and optimize molecular level kinetic models. Rule Input Network Generator (RING), a computational tool was developed by Rangarajan et al. (Rangarajan et al., 2014, 2012a, 2012b) for building and analyzing complex thermochemical and biomass reaction networks.

In the present work, an in-house software, the Kinetic Modeler's Toolkit (KMT) (Bennett, 2009; Hou, 2011; Wei et al., 2008b), has been used to build and solve the kinetic model. There are three software packages within KMT: the Composition Model Editor (CME); the Interactive Network Generator (INGen); and the Kinetic Model Editor (KME). CME transforms experimental data on the feed into a list of molecules and mole fractions. These are the inlet conditions of the associated kinetics model. INGen utilizes this molecule list and process chemistry to build a reaction network. Finally, KME uses the reaction network and feed description to create and solve the equations that define the kinetic model. The models created by KMT are at the molecular level and provide a good basis for building robust models that accurately represent the physical process. However, the large amount of information in detailed kinetic models shifts the onus of research onto the user who must understand the model's equations and results. Unaided, the comprehension of the model can be sacrificed, reducing the accessibility of models.

In this work, we address the accessibility of models developed in KMT. First, we develop a model on naphtha reforming as an illustrative example. Next, the potential users of such a model are identified along with their goals in using the model. Finally, software tools are discussed that specifically target these different goals.

2. Development of a Naphtha Reforming Model in KMT

Catalytic reforming of naphtha is a well-known process for producing octane-rich gasoline with aromatics and byproducts of hydrogen and light gases. Traditionally, reforming was carried out in either a semi-regenerative process or a continuous catalytic reforming (CCR) unit with three or more reactors connected in series. In the CCR setup, the feed to the first reactor is a straight-run naphtha consisting of normal and branched paraffins, five- and six-ring naphthenes, and aromatics. A bi-functional catalyst is used for carrying out a wide variety of reactions such as aromatization, dehydrocyclization, isomerization and cracking. As the dehydrogenation of naphthenes is highly endothermic, the temperature drops quickly in the first reactor, and the effluent must be reheated. In later reactors, the reactions become less endothermic and the temperature drop decreases, increasing the contact time and allowing less kinetically favorable reactions to take place.

Over 50 years, reforming has been studied by many researchers and the chemistry of the process is well known. Originally, lumped models were defined to represent the kinetics of a semi-regenerative and continuous catalytic reformer. They were successful in predicting the overall composition of the product and reactor outlet temperature. These models were developed using fundamental lumps, i.e. paraffins, naphthenes and aromatics (Smith, 1959). Later models were expanded by defining more detailed lumps based on carbon number range (Kmak, 1971; Ramage et al., 1987). Further improvements came with the addition of Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics (Marin and Froment, 1982; Van Trimpont et al., 1986) to account for the presence of catalyst and the chemistry of coke formation for continuous decay of catalyst sites (Ancheyta-Juárez et al., 2001; Iranshahi et al., 2014; Padmavathi and Garimella, 1997; Rahimpour et al., 2013). Turaga and Ramanathan (Turaga and Ramanathan, 2003) reviewed developments in naphtha reforming including the details of chemistry, thermodynamics, and types of catalysts and reactors.

Lumped models are feedstock-specific and lack the isomeric detail crucial in answering many questions in reforming. In general, models must be able to accurately determine important properties like the octane number of the product reformate. However, over time, the process performance can be judged by the aromatics distribution (e.g., *ortho*-, *meta*- and *para*-xylenes and ethylbenzene), the amount of coke deposited, and the outlet temperature of each reactor. Furthermore, the outlet composition of each subsequent reactor is crucial to understanding the underlying chemistry throughout the process. These goals are better addressed by modeling at the molecular-level.

Molecular-level models have been developed using pathway level chemistries to describe a catalytic reforming process (Joshi et al., 1999; Sotelo-Boyás and Froment, 2009; Wei et al., 2008a, 2005). These studies reported how the models were developed using fundamental principles of reaction chemistry and chemical kinetics. Because reforming is a major source of octane-rich aromatics in gasoline, there is continued interest in studies on the modeling of a reformer and a better understanding of the process. While most reported models in literature are comprehensive, their practical applicability is uncertain due to the lack of thermodynamic and kinetic data. In the present work, a detailed kinetic model has been developed and evaluated against an operating, industrial reactor. The key steps in developing molecular kinetic model for a continuous catalytic reforming process have been discussed in detail in the following sections.