Computers and Chemical Engineering 106 (2017) 385–395

Contents lists available at ScienceDirect

Computers and Chemical Engineering

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

A framework for developing a structure-based lumping kinetic model for the design and simulation of refinery reactors

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ARTICLE INFO

Article history:
Received 28 April 2017
Received in revised form 29 June 2017
Accepted 29 June 2017
Available online 1 July 2017

Keywords:
Systematic framework
Structure-based lumping kinetic model
Product yield
Product molecule-based information

ABSTRACT

This study represents a systematic framework supporting the development of a structure-based lumping kinetic model useful for designing, simulating, and optimizing refinery reactors. Utilizing the wealth of the available data and information provided by petroleomics, the framework comprises strategies for analyzing and reducing a large and complicated elementary kinetic reaction model as well as generating lumps in light of the structure and reactivity of the species included in the feedstock and product mixtures. A structure-based model developed by applying the framework cannot only predict yield but can also provide the structure-based composition of the product mixture. A case study on the hydrodesulfurization of light gas oil (LGO-HDS) was used to illustrate the applicability of the framework. The developed LGO-HDS structure-based kinetic model can describe reaction behavior and predict product distribution with high accuracy.

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1. Introduction

A reliable reaction kinetic model is an essential input for optimizing reaction operation conditions and product slates, testing and selecting optimal catalysts, synthesizing subsequent processing units, and sizing and costing necessary equipment. In refinery reactors, complex petroleum feeds comprising a large number of species are processed, resulting in a markedly large and complicated elementary reaction network. Modeling reaction kinetics of refinery reactors faces multiple challenges because characterizing molecular structures and reaction pathways of all individual species and solving their reaction kinetic equations are markedly difficult and time consuming. Conventionally, a refinery reactor's kinetic model is created using lumps of species, usually defined by physical properties such as boiling points. Thus, the reaction network can be considerably simplified and easily solved (e.g., Dave et al., 1993; Filho and Sugaya, 2001; Valavarasu et al., 2005; Singh et al., 2005; Dai et al., 2011; Wang et al., 2012; Aydın et al., 2015; Albazzaz et al., 2017). However, this type of model has multi-drawbacks: dependence on types of feedstock and lack of product's molecular composition prediction capability (Quann and Jaffe, 1992; Hu and Zhu, 2001; Froment, 2005; de Oliveira et al., 2016). These disadvantages make it unable to be applied to variety of refinery processes which are designed in the attempt of comprehensively utilizing complex and heavy feedstock fractions for producing new valuable and environmentally friendly products.

Recent advances in analytical techniques have led to the emergence of a new field: petroleomics, which attempts to characterize petroleum compositions and their products completely and correlates them with their properties and behaviors (Marshall and Rodgers, 2004, 2008; Hsu et al., 2011). It has opened new door to novel and comprehensive exploitation of both light and heavy petroleum feedstocks and the production of high-value products. In line with this concept, substantial efforts have been made to create broad databases of molecular structures and characterize the chemical and physical properties of various petroleum fractions. How to utilize the abundant available information provided by petroleomics for developing a kinetic model that can maintain fundamental chemistry information has caught increasing attention (Marshall and Rodgers 2004; Rodgers and McKenna, 2011).

In an attempt to track the fundamental chemistry transformation of the feedstock mixtures during refinery processes, Klein and Froment groups used the approach of mechanistic modeling.

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http://dx.doi.org/10.1016/j.compchemeng.2017.06.025
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They have developed detailed kinetic reaction models for different refinery processes (e.g., Stark et al., 1993; Kumar and Klein, 1999; Dewachtere et al., 1999; Froment, 2005; Campbell et al., 2009; Sotelo-Boyás and Froment, 2009). A structure-oriented lumping approach was proposed to track chemical transformation by using vectors of structural increments representing the complex feeds (Quann and Jaffe, 1992, 1996; Jaffe, 2005). A computer software, Kinetic Modeler's Toolbox (KMT) (Wei, 2004; Wei et al., 2008a; Craig, 2009; Hou et al., 2010; Hou, 2011) was created for constructing, organizing, and storing detailed kinetic models. All of these models can describe the molecular-level fundamental chemistry of refinery reactors. However, they comprise large numbers of species and reactions and require considerable computational time, thereby causing many obstacles in the design and simulation of refinery reactors that are performed primarily by using process simulators.

In our previous study (Nguyen et al., 2017), we built a new structure-based lumping kinetic model for hydrodesulfurization of light gas oil (LGO-HDS) which promises to overcome the limitations of the existing kinetic models while providing high accuracy prediction of product's structure-based composition. The current study aims to propose a systematic framework to support the development of a structure-based lumping kinetic model. Consisting of three main stages, the framework guides the users what tasks should be performed and how the abundant data created under the petroleomics concept should be allocated and utilized effectively. The application of the framework is illustrated through a case study, which aims to build a kinetic model for describing and predicting the chemistry transformations and structure-based compositions of heteroatoms containing compounds involving in LGO-HDS. Such model is essentially important for design and optimization of hydrodesulfurization reactor. Moreover, results output from the model can contribute to extend basis information on reaction behaviors of heteroatoms containing compounds, establishing foundation for creating new technologies producing more valuable and environmentally friendly petroleum products.

2. A framework for the development of structure-based kinetic lumping model

As discussed above, the principal aim of this study is to propose a systematic framework supporting the development of a structure-based kinetic lumping model by utilizing the available information created under the concept of petroleomics. The KMT has been proven to be a powerful tool that can provide intensive information regarding to molecular compositions and detailed kinetic reaction networks of different petroleum fractions (Wei, 2004; Wei et al., 2008b; Craig, 2009; Hou et al., 2010; Hou, 2011). Thus, it can be used as the primary means of supplying data necessary for developing a structure-based kinetic model.

Simulations are run in the KMT to obtain the required data. The physical properties and distillation characteristics of input and output mixtures as well as the types of molecular structures are input to the KMT, in addition to the reaction conditions. The former can be easily obtained through the typical experiments that are performed for analyzing petroleum fractions, while the latter are analyzed by using FT-ICR MS (Fourier Transform Ion Cyclotron Resonance Mass Spectrometry). A discussion regarding how KMT operates and outputs the required data is beyond the scope of this paper. Detailed information can be found in the literature (Wei, 2004; Wei et al., 2008a; Craig, 2009; Hou et al., 2010; Hou, 2011). After simulation, the KMT outputs the molar flow rates of species included in the input and output mixtures at different reaction time intervals and the types and reaction kinetic parameters of elementary reactions caused by individual species. The detailed reaction kinetic model output from KMT is markedly complicated, consisting of large numbers of species and elementary reactions. It must be simplified before it can be used for developing a structure-based lumping kinetic model.

In this study, a systematic framework is developed based on the availability and types of data provided by the KMT. As shown in Fig. 1, the framework includes three main stages:

- Reducing detailed elementary reaction network
- Building structure-based lumps of species and a lump-based reaction network
- Estimating lump-based reaction rate constants

2.1. Stage 1: reducing detailed elementary reaction network

The simplification of the elementary reaction output from the KMT can be performed by removing the unimportant species and elementary reactions while maintaining important fundamental chemistry information on the elementary reaction network. Many methods have been proposed in the literature for reducing the complexity of detailed kinetic models. They are primarily used for reducing mechanisms of the thermal cracking or combustion of hydrocarbons. These include, for example, analysis of reaction rates (Turányi and Bérces, 1989; Turányi, 1990), genetic algorithms (Edwards et al., 1998), an adaptive discretization procedure (Briesen and Marquart, 2000), impulse parametric dynamic sensitivities (Perumala et al., 2013), flux flow projection trees (Liu et al., 2014), and a combination of lumping and reduction processes (Stagni et al., 2014). Detail discussion on advantages and disadvantages of these methods can be found somewhere in literature.

As the above mentioned, output from the KMT the detailed kinetic reaction models are markedly complicated, consisting of a large number of species and reactions having dynamic changes of flowrates and reaction rates respectively. To reduce these models, the reduction method should be able to evaluate the importance of each reaction or species on the basis of its contribution to the entire system while capturing its dynamic transition during the process. Moreover, it should provide a quick analysis of large detailed models and a flexible control of errors. Thus, it can be applied to on-the-fly simulation and adapt to different requirements of model adequacy.

In this study, the importance of an elementary reaction is judged by its contribution to the total rate of production or consumption of the output product. This concept is similar to that of Turányi and Bérces (1989), Turányi (1990). However, in this proposed method the dynamic changes with time of all reactions and species are accounted. Each reaction and species are evaluated on the basis of their contribution to the whole system, not to a number of reactions or species initially defined through a bias selection. On the other hand, the error caused by the reduction can be defined and controlled by users to prevent the loss of important information and adapt to different simulation purposes.

As shown in Fig. 1a, the necessary data for the reduction stage include the molar flow rates of species involved in the input material flow and the reaction rate constants of elementary reactions. These data are provided by the KMT simulation.

- Calculate the contribution coefficient $S_{ij,t}$

$$s_{ij,t} = \frac{\upsilon_{ij} R_j\left(k_j, c_{i,t}\right)}{\sum_{j=1}^{p} \upsilon_{ij} R_j\left(k_j, c_{i,t}\right)} \tag{1}$$

υ_{ij} is the stoichiometric coefficient of species i in reaction j, R_j is the rate of reaction j, k_j is the kinetic parameter of reaction j, $c_{i,t}$ is the concentration of species i at reaction time interval t, and p is

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