



Generalized model of n-heptane pyrolysis and steam cracking kinetics based on automated reaction network generation



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ABSTRACT

Mathematical model of n-heptane pyrolysis under thermal cracking and steam cracking conditions was developed. The objective was achieving good generalization by combining two different data sources for model identification. The data sources included experimental pyrolysis data for many structurally different hydrocarbons measured at reference conditions as well as the data for n-heptane measured in different reactors at different reaction conditions. The model was developed using the automated reaction network generation. The generated network included hydrogen abstraction, β -scission, radical isomerization and recombination reactions, the kinetic parameters of which were expressed as functions of 26 group contribution factors. Molecular reactions and radical additions were substituted by 12 formal shortcut molecular reactions. The initial values of kinetic parameters and group contribution factors were adopted from previous study, where they were obtained by regression based on the experimental data involving wide range of linear, branched and/or cyclic hydrocarbons. More experimental data on n-heptane pyrolysis measured under different conditions, including the use of two different reactors, were added to the data set used for the parameter optimization. The model simulations showed good agreement with the experimental data even for the validation samples. Thus, the proposed approach proved the ability to produce models achieving good generalization.

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1. Introduction

Steam-cracking is one of the fundamental and the most important processes in the petroleum processing industry, aimed at producing light olefins, such as ethylene, propylene, butenes and aromatics. The process is based on the thermal non-catalyzed decomposition of various hydrocarbon feedstocks by pyrolysis reactions. The feedstock quality and the processing parameters have a great potential impact on the economy of the process. Previously, we developed a mathematical model of steam-cracking process [1], which has been successfully used in the industrial practice [2–6]. In order to further improve the model capabilities, there is a long-term objective of replacing the included semi-mechanistic kinetic model by a one based on mechanistic approach.

Mathematical models of steam-cracking can be divided between empirical and mechanistic ones. Empirical models [7,8] often rely on simplifying the complex network of radical reactions by substitute molecular reactions. They can describe the experimental data very well within the experimental region, but due to the substitute nature of the kinetic parameters used, they generalize not as well as the more mechanistic approaches. Thus, the possibility of extrapolating results to the different piece of equipment is very limited. Mechanistic models based on the kinetic description of the radical mechanism do not have this kind of disadvantage, as they are usually much more complex, even for very simple feedstocks.

Mechanistic models were initially designed specifically for a single feedstock molecule (or a single type of molecule), such as the one developed by Sundaram and Froment [9,10], who were interested in the development of the mechanistic model describing the thermal cracking of butanes. A fully integrated mechanistic model was firstly published later by Allara and Shaw [11]. They published the complete system of free-radical chemical reactions (elementary

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steps) together with recommended values of kinetic parameters supplemented by values obtained by other authors. Mechanistic modeling continued by careful investigation of assumptions that were initially made without positive prove such as the differences between 1D and 2D model of steam-cracking tubular reactor [12]. Other authors created models for more complex feedstock molecules [13,14], tested significance of several reactions pathways and compared their results with previously known literature data.

As increasingly more variable feedstocks started being processed by the industry, it requires steam-cracking models to become more flexible. Designing the mechanistic model “manually” becomes very time-consuming process, prone to many errors and inconsistencies, hence more complex approaches were employed. Primary pyrolysis reactions can be described by relatively simple set of general kinetic rules and the automated reactions network generation (RNG) became a new standard practice. One of the first tools that could be used for this purpose was published by Di and Lignola [15] under the name KING (Kinetic Network Generator). Other authors [16,17] were interested in developing similar tools for mechanism generation and its application for steam-cracking of ethane.

There are several papers aimed at using RNG for modeling of steam-cracking of more complex individual components as feedstock. Van Geem et al. [18,19] utilized this approach for modeling of *n*-hexane. Using this kind of model, it was possible to investigate in details original assumptions such as QSSA (Quasi steady state species) or μ -hypothesis [20,21] or significance of pressure-dependent kinetic parameters [22,23].

Another task in steam-cracking modeling is to find a reliable source of kinetic parameter values. An interesting approach shared by several groups of authors [8,22,24,25] involves determining the kinetic parameters by ab initio calculations or similar tools of computational chemistry. In order to reduce number of necessary parameters, some authors follow the path of reducing the reaction mechanism. Permual et al. [26] developed a method allowing the simplification of reaction mechanism based on dynamic sensitivities analysis and used it in their pyrolysis and combustion model. Huang [27] presented a reduction method based on sensitivity and principal component analysis and demonstrated its properties on example of its application to a methane-rich fuel consumption model. Edwards, Androulakis, and Mitsos [28–30] used reduction methods based on linear or non-linear programming, solving the model reduction as a constrained optimization problem, the elimination of species and/or reactions being done, so as to produce the simplest model with an acceptable model reduction error.

Another approach is calculating the parameters using the group-contribution and bond additivity methods, like the one developed by Benson [31]. The exact implementation may focus either on greater detail of the specific type of radical reactions description [32], or the substantial reduction of the number of kinetic parameters [33].

The comparison provided above shows the automated RNG approach is superior, but the authors focus more on the aspect of developing extremely detailed models of single compound cracking, rather than universal model modeling the cracking of arbitrary hydrocarbon, which would be more suitable for development of industrial steam-cracking models. Most authors also find necessary to adjust the kinetic parameters to fit the experimental data, because the kinetic parameters of the complex reaction networks are inter-correlated and it is hard to combine parameters obtained from different sources. The models are typically tailored to one system, usually describing only one type of feedstock.

Thus, our preceding work was primarily aimed at the development of the radical mechanistic model using automated RNG and the group contribution method for kinetic parameters estimation

[34,35]. Optimizing the relatively few group-contribution factors improved the model generalization, so that it is able to simulate substantially different feedstock types (*n*-alkanes, *i*-alkanes, cycloalkanes) and their behavior in the micro-pyrolysis reactor [36] at varied temperature (650–815 °C) and residence time (0.1–1.0 s). The next step in our effort for improved model generalization was to extend the model to simulating the pyrolysis experiments in two substantially different reactors, using only one shared set of generalized kinetic parameters, represented by group contribution factors. At the same time, the model ability to simulate pyrolysis of different structures, using the one generalized set of parameters, should be maintained.

While our approach included using the experimental data for more hydrocarbons [37], one compound had to be chosen as the key model substance. In the group of alkanes C_5H_{12} to $C_{12}H_{26}$ at about 780 °C, *n*-heptane gives the highest conversion and the highest yield of ethylene [38]. Therefore, *n*-heptane is particularly suitable for studies of kinetics and mechanisms of pyrolysis at different reaction rates, and in reaction systems [39,40]. Our previous work dealt with the study of pyrolysis of C_7 – hydrocarbons in the presence of steam in a flow reactor. Thus, in this study, *n*-heptane was selected as a key model feedstock because it is an excellent model compound for studying the cracking behavior of heavy naphtha fraction (90–180 °C). The kinetics of heptane pyrolysis is somewhat more complex than that of hexane reported previously [19], due to longer hydrocarbon chain and thus more opportunities for radical isomerization.

Several research groups published fundamental studies of *n*-heptane pyrolysis [7,41–48]. Appleby et al. [41] and Chakraborty [48] carried out the pyrolysis at high pressure. They supposed that the yields of ethane and propane increase with increasing pressure while the yield of ethylene decreases. Bajus et al. [45] investigated the pyrolysis of *n*-heptane in flow reactor at atmospheric pressure with the steam as inert. The pyrolysis at atmospheric pressure was also studied by Murata and Saito [42–44] and they also proposed the molecular model for the product distribution. Aribike and Susu [46,47] developed mechanistic model of *n*-heptane pyrolysis using the kinetic description of radical decomposition. They showed the mechanistic model is able to describe the behavior of *n*-heptane satisfactorily even under various experimental conditions (740–780 °C, 0.7–1.0 s residence time).

2. Experimental

The experimental data used in this work were obtained on two different reactors and experimental setups used by two co-operating research groups. Reactor A is a micro-reactor operated in a pulse regime, on-line connected to a multi-column system for detailed product separation by gas chromatography. A feedstock is introduced into the reactor in the liquid state into the stream of a nitrogen carrier gas. It is very quickly vaporized, so that a pulse of reaction mixture is formed, passes through the reactor non-diluted, and proceeds to the chromatograph analysis immediately after the reaction. The most important reactor characteristics are provided in Table 1 and more detail of the experimental method can be found elsewhere [49]. The key feature of the reactor A is very rapid operation and sample flexibility, that allowed an extensive set of pyrolysis data for a broad variety of hydrocarbon species to be measured [36]. Therefore, there is a substantial data base representing the effects of hydrocarbon structure variability on pyrolysis reactions. On the other hand, the micro-size of the reactor is also its most significant drawback. The temperature profile is determined somewhat less accurately along a very short reactor length and there may be some systematic error in the results. However, the sensitivity to structure variability is maintained and the data from

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