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Feedstock molecular reconstruction for secondary reactions of fluid catalytic cracking gasoline by maximum information entropy method

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HIGHLIGHTS

- The FCC gasoline is simulated using a new combined method based on maximum information entropy method.
- Structural oriented lumping and Monte Carlo method are applied to create an initial molecular library.
- Maximum information entropy method is introduced to optimize the initial molecular library.
- The accuracy and convergence rate is significantly increased compared with traditional Monte Carlo method.

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ABSTRACT

A novel methodology of maximum information entropy theory combined with structure oriented lumping (SOL) and Monte Carlo (MC) method was developed to simulate the feedstock for secondary reactions of fluid catalytic cracking (FCC) gasoline at the molecular level. The SOL method was applied to represent the feedstock configuration framework; a molecular library consisting of a large ensemble of computational molecules was created by stochastically assembling structural increments using MC method; then, the maximum information entropy method (MIEM) was introduced to adjust the mole fractions of the structural increments in the molecular library to achieve a closer matching with the actual analytical characteristics. Three samples of catalytic cracking gasoline from the industrial FCC units of China were used to validate and evaluate the proposed method. The simulation results of the feedstock properties, such as the average molecular weight and the weight fractions of main components including paraffin, olefins, naphthenes and aromatics agreed well with the experimental data.

1. Introduction

Fluid catalytic cracking (FCC) is the most important technology to convert low-value heavy oils into more valuable blending stocks by the reactions named primary reactions, such as direct cracking, dehydrogenation, and condensation. However, the FCC gasoline obtained from the primary reactions is of low quality and with high olefin and sulfur, which fails to meet the current fuel quality standards. If gasoline and diesel produced in the primary reactions are upgraded through secondary reactions including cracking, hydrogen transfer, isomeration, aromatization, alkylation, condensation, etc., clean gasoline with a lower olefins content and a higher octane rate can be produced.

The secondary reactions of FCC gasoline are complex parallel-series reactions in carboniumion mechanism involving hundreds of components in different types and structures. Due to the lack of fundamental information on feedstock structures, simulation of the feedstock of such a complex system is very challenging. In order to predict the behavior of such complex mixtures under reaction conditions, one needs to characterize the chemical structure of these mixtures. Lumped strategy [1–3] has been developed to simplify the representation of composition. However, lumped kinetic models cannot provide the detailed cracking pathways and resulting chemical speciation as well as the time evolution of product distribution during the course of catalytic cracking process. Furthermore, lump models have poor extendibility for varying feedstocks and operating conditions, which limits their applications from a practical point of view. Quann [4] and Jaffe

Abbreviations: SOL, structure oriented lumping; MC, Monte Carlo; FCC, fluid catalytic cracking; MIEM, maximum information entropy method.

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[5] have developed a method called structure oriented lumping (SOL) to describe molecules and hydrocracking of heavy oil fractions with a notation of vectors, which allows a computer program to produce each molecule and to represent the reaction network. Martens [6,7] and Alwahabi [8] have reported a model for the hydrocracking of hydrogenated vacuum gas oil based on theoretical and mechanistic considerations. However, these molecular modeling requires a detailed information of feedstock structures, rate constants, and reaction pathways which are often inaccessible from a refinery process. Neurock et al. have developed a Monte Carlo residua construction technique by which petroleum molecules are stochastically constructed by random sampling of probability distribution functions [9]. Monte Carlo sampling makes it possible to provide a large ensemble of computational molecules whose properties are close to experimental values, and it merely requires common analytic data to simulate the reaction process. However, it cannot give a proper representation for each molecule like the molecule simulation methods do. Considering the characteristics of molecule methods and MC method, a method of SOL combined with MC method was employed to simulate the system of secondary reactions of FCC gasoline from molecular scale in our previous work [10]. However, numerous sampling and a very long simulation time are needed by using this combined MC method to obtain a satisfactory result because of the uncertainties of the stochastic sampling involved. Furthermore, the probability distribution function was determined by hypotheses, which may cause that some molecules are favored over others and also introduce some deviations [11,12].

The maximum information entropy method (MIEM) has become an effective tool for optimization problems. Based on the principle of MIEM, if only partial information concerning the possible outcomes is available, the probabilities are to be chosen so as to maximize the uncertainty on the missing information, which is represented by the Shannon's information entropy [13,14]. Therefore, the problem to obtain the most likely composition for molecular reconstruction can be treated as the one to locate the maximization of the information entropy [15,16]. Marin et al. studied on the molecular reconstruction of residual oil and naphtha with MIEM [13]. Pyl et al. reported a model on molecular reconstruction of naphtha based on MIEM and made a comparison between the multiple linear regression and neural network methods [17]. Verstraete et al. developed a model on molecular reconstruction of the light cycle oil fraction, Arabia light vacuum residue, and naphtha steam cracking feedstock based on MIEM [18,19]. However, this method requires a particularly well defined initial set of molecules, because the search of a solution will get increasingly computational-costly when the properties of the initial set of molecules are far away from the analytical data [19].

Given the above, the method by combining SOL and MC allows to create computational molecules that roughly approach the feedstock properties, however, it needs numerous sampling and computation steps to achieve a satisfactory correspondence; while the MIEM could easily obtain an optimum mixture with properties that are quite close to the analytical data, however, a well-defined initial set of molecules will be required. A new approach integrating these three methods together would provide an appropriate initial set of molecules for MIEM and at the same time simplify the calculation process of MC.

Towards this end, a novel method of MIEM combined with SOL and MC is developed to simulate the feedstock of secondary reactions of FCC gasoline at the molecular level in this work. Three samples from three different industrial FCC units in China are used to evaluate the strength of this method.

2. Properties of feedstock

Three samples of catalytic cracking gasoline used in this work were taken from the industrial FCC units of China. Their basic properties are shown in Table 1 [10].

3. Simulation process

The simulation framework of the proposed methodology is given in Fig. 1. The method involves three main steps. The first step is to build the configuration framework of the feedstock using structure oriented lumping (SOL) method. Here, the feedstock was represented by a two dimensional matrix D in which each row represents a molecule and the row number is the number representing the molecules. The second step is to create a molecular library containing computational molecules that constructed by SOL. To create each molecule vector, the random sampling of Monte Carlo (MC) method will be used, which provides a large ensemble of calculated molecules whose properties will be compared with the experimentally measured values. The construction of a set of representation molecules is accomplished by rigorous assembly of different structural features or increments [10]. In the third step, the mole fractions of the structural increments contained in the molecular library are adjusted by the maximum information entropy method (MIEM) to achieve a better matching with the desired characteristics, e.g., the average molecular weight. The method's build-up is described in more details in the following sections.

3.1. Feedstock configuration framework by SOL

For structure oriented lumping method, a molecular type (e.g., PONA) is subdivided into the basic structural increments. A

Table 1
Properties of the feedstock used in the experiments.

Gasoline number		No. 1	No. 2	No. 3
Density 293 K/kg·m^{-3}		705.8	732.4	741.1
Elemental composition/wt%	C	86.30	86.39	86.45
	H	13.59	13.46	13.44
	S	1.034×10^{-3}	1.427×10^{-3}	9.51×10^{-4}
	N	2.0×10^{-5}	9.2×10^{-5}	5.0×10^{-5}
Hydrocarbon composition/vol%	P	36.1	30.7	28.2
	NA	13.7	9.4	9.3
	A	15.0	18.1	19.3
	O	35.2	41.8	43.2
Boiling range/K	IBP	312.5	310	312
	10%	326	330.5	331
	50%	353.5	370.8	372
	90%	407	434	439
	FBP	439	459.8	468