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New kinetic model of coal tar hydrogenation process via carbon number component approach

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HIGHLIGHTS

- A kinetic model based on carbon number component approach is developed.
- Product streams are represented by the structural matrix at a molecular level.
- A transformation method is developed for interrelating properties and composition.
- Both the kinetic model and the transformation method present good prediction effect.

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ABSTRACT

Hydrogenation technology is an important chemical upgrading process for low quality oil such as coal tar. Kinetic modeling for hydrogenation process remains a challenging task because of the large amount of compounds and complex reactions involved. Therefore, a new systematic methodology is proposed in this study to characterize mixture streams for the kinetic modeling of coal tar hydrogenation. The methodology incorporates both lumped method based on boiling point to represent feedstock and a carbon number-based component approach in the form of a structural matrix to characterize products at a molecular level. A mathematical transformation model is built for interrelating the bulk properties and molecular composition of products. A detailed kinetic model for coal tar hydrogenation is constructed based on the reaction pathway networks between lumped feedstock and carbon number-based molecular product. Detailed molecular compositions of the products are obtained from experiments to provide a basis for estimating the parameters of the kinetic model. The proposed method is verified by experiment results, which are consistent with predicted values.

1. Introduction

The global energy demand is expected to increase by 40% from 2008 to 2030 at a rate of 1.5% per year [1]. Developing various alternative energy sources to ensure global energy security has strategic significance because of decreasing sources of petroleum fuel and rising fuel price. Coal tar is a byproduct of coal carbonization or gasification [2]. Coal tar output in China was estimated at more than 12 million tons in 2010 [3–6]. However, much of the coal tar was burned directly as crude fuel, causing significant resource waste and environment pollution. Therefore, coal tar hydrogenation, has received substantial attention as one of the most viable alternatives for converting heavy coal tar into lighter and more valuable clean fuel, such as gasoline and diesel.

Coal tar hydrogenation is the main processing technology for producing cleaner fractions, in which the process control is a significant factor for improving the quality of production. To accurately predict and control the process, an reliable and more detailed kinetic models must be developed with particular attention to design, simulation, and optimization of the hydrogenation process. Theoretically, the required kinetic model should consider all the elementary reactions occurring during hydrogenation [7], but practical application is impossible because of the complexity of the reaction mixture consisting of numerous components. Thus, existing modeling technologies of hydrogenation are primarily based on the lumped method [8–16], in which the complex mixture is usually divided into smaller groups of pseudo components with respect to their properties, such as boiling point, and

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structure. The lumping method is effective in predicting products distribution and optimizing operating conditions and the number of lumps is generally increased to improve the accuracy of lumped models. However, the models cannot capture the molecular composition of products and their corresponding physical properties, which are important indicators in product quality control. Thus, developing a more detailed kinetic model for coal tar hydrogenation on the basis of molecular level is required.

Molecular characterization of the reaction mixture is the basis for developing the molecular-based kinetic model. For instance, Peng et al. [17] proposed an approach to represent a complex mixture based on a molecular-type homologous series (MTHS) with homologous and carbon number. Subsequently, Yan et al. [18] incorporated the matrix into a heavy oil system and built a molecular model for the thermal cracking of heavy oil, which yields good results. In addition, two different algorithms were developed by Hudebine et al. [19] to generate a complex mixture of molecules from standardized petroleum analyses: a stochastic reconstruction technique and a reconstruction by information entropy maximization. Both approaches can be advantageously combined to effectively represent the molecular information of the mixture, and have also been applied to many complex systems, such as petroleum residue fractions and LCO gasoils. Oliveira et al. [7] extended the work of Hudebine and developed a kinetic modeling of vacuum residue hydroconversion based on a modified two-step molecular reconstruction algorithm, the model not only allows predicting the global information of the process, such as its yield structure and hydrotreating performances, but it also provides many molecular details throughout the reactor simulation.

In addition, several other molecular-based kinetics models for hydrogenation process have also been proposed [20–27]. However, most models have been developed and applied for heavy petroleum systems, few studies have focused on the molecular model of coal tar hydrogenation.

The current study highlights the development of a detailed kinetic model for coal tar hydrogenation process based on the carbon number component approach. A structural matrix that contains different molecular classes and carbon number groups was used to represent the molecular compositions of the product resulting from coal tar hydrogenation. A mathematical transformation model was also developed to interrelate product properties and molecular composition. The objective of the established model is to predict the molecular yields and bulk properties of the products to improve the design, simulation, and optimization of the required process.

2. Composition representation of coal tar hydrogenation system

2.1. Feedstock-lumped division

Coal tar feedstock is a complex mixture consisting of paraffins, olefins, naphthenes, aromatics, and heteroatom compounds. The complete molecular composition of the mixture is difficult to determine even by the most advanced analytical techniques. Hence, three conventional methods, namely, bulk property, compound class [28], and average structural parameter characterizations [29,30], are largely used to characterize the hydrocarbon mixtures. The bulk property characterization method combines the bulk properties with the distillation data of the entire stream to generate boiling point cuts and properties, such as density and API gravity. This method is largely used in commercial software packages, such as ASPEN-PLUS, PRO II, and HYSYS, in which a hydrocarbon mixture is only characterized into pseudocomponents and viewed as pure components. The compound class characterization method describes the components of a mixture based on the chromatographic separation technique, a typical example of which is the SARA method [28]. Yet the molecular composition of a mixture is not well-defined because the compound classes are defined by their solubility characteristics. The average structural parameter characterization method represents the complex mixture based on the functional groups and structural parameters, such as the number of aromatic rings, carbon/hydrogen ratio, and weight percentage of carbon atoms in the CH_2 groups. Two examples of this method include the Brown–Ladner method [29] and functional group analysis by linear programming [30].

Due to coal tar is treated as a peculiar material and often fractionated based on its boiling point, thus the bulk property characterization method was selected in this study to describe the coal tar feedstock that is represented by boiling range. Moreover, Dai et al. [31] also demonstrated in our previous works that the feed can be lumped into four groups, namely Lump 1 [>300 °C], Lump 2 [250–300 °C], Lump 3 [20–250 °C], and Lump 4 [20–200 °C]), and the corresponding model presented adequate prediction of product yields distribution that suitable for coal tar hydrogenation systems.

In addition, a large amount of complex reactions is involved during coal tar hydrogenation. The main products resulting from these reactions include cracked gas, gasoline, diesel, and asphalt. According to experimental analysis, cracking gas mainly consists of hydrogen sulfide, nitrides, alkanes and other hydrocarbons with less than 5 C. Gasoline and diesel, which are viewed as desired products, basically represent hydrocarbons from 5 C to 23 C, with the distillation temperature ranges corresponding to 50–200 °C and 200–400 °C respectively. The remainder with distillation temperature more than 400 °C is a kind of black sticky liquid, being termed as asphalt because the heavy fraction components are hardly available despite the use of modern analytical instruments. Analysis results of coal tar hydrogenation showed that the diesel and gasoline yields reached 96% under optimal conditions, whereas the asphalt and cracked gas yields are relatively low. This finding indicates that the kinetic reaction of diesel and gasoline are far more prevalent than that of cracked gas and asphalt.

2.2. Representation of products based on the structural matrix

A systematic carbon number component approach based on the structural matrix is proposed to represent the mixture on a molecular level. The matrix incorporates the main information of products, i.e. the molecular classes and carbon number groups [17], as shown in Fig. 1 in Supporting information. The columns in the matrix are homologous series for different molecular classes existing in the complex mixture, for instance P, O, N, A represent distinct series corresponding to paraffins, olefins, naphthenes, and aromatic hydrocarbons, while the rows represent the different carbon number groups, i.e., the molecular size of the components. The species of the molecular classes and the size of carbon numbers may vary for different mixtures represented. In addition, the pure molecules with the same carbon number in a homologous series are grouped into a carbon number component as a matrix element, thereby considerably reducing matrix complexity. For example, Fig. 2 shows a homologous series of one-ring aromatic compounds, during which the four isomers with the same eight-carbon number are viewed as a carbon number component 1A8. Therefore, the matrix elements represent the mass or molar percentage of either a single molecule or a lump of all possible structural molecular isomers [32]. Hydrocarbon heteroatoms in mixture, such as nitrogen and sulfur compounds, are also incorporated in the structural matrix. The matrix containing enough composition information of products provide a basis for accurately modeling the kinetic of hydrocarbon conversion process based on the reaction pathway network.