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8-Lump kinetic model for fluid catalytic cracking with olefin detailed distribution study

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ABSTRACT

Modeling fluid catalytic cracking (FCC) riser reactors is of significant importance in FCC unit control, optimization and failure detection, as well as development and design of new riser reactors. In this study, kinetic behavior of vacuum gas oil (VGO) catalytic cracking is studied by developing an 8-lump kinetic model to describe the product distribution. The feedstock and products are divided into eight lumps by reasonably simplifying reaction network, including VGO feed, diesel oil and gasoline, LPG, butylenes, propylene, ethylene, light gases, and coke. A time-on-stream non-selective catalytic activity equation is also assumed to model deactivation mechanism. Twenty-seven pairs of model kinetic parameters are estimated using two different optimization methods, namely: non-dominated sorting genetic algorithm II (NSGA-II), and chaotic particle swarm optimization (C-PSO) algorithm. Performances of both optimization methods are compared and C-PSO algorithm is selected as the superior method in terms of computation time and finding the global optimum. In the current research, based on validated estimated parameters of the preferred C-PSO method, the effects of some operating parameters on product yields distribution are investigated and discussed. This model can be used to predict the riser key products and their compositions with high degree of accuracy which may be especially useful for the conventional FCC processes with olefins production streams.

1. Introduction

1.1. Background information

Since the beginning of industrialization, the world energy consumption has been growing. The need for energy increases with economic and social developments. As long as energy inspires development among nations, demand for fossil energies increases as well. Considering slow progress rate of new energy systems, it is unlikely that, over the next few decades, fossil and oil energies possess a significantly small portion of the world consumption [1].

The oil industry has always adjusted its refining tool to the development of crude oil characteristics and usability, and fuel/petroleum products market. Consequently, demand for sever conversion of heavy feeds into light transportation fuels has been increasing quite swiftly since the mid-1990s. Development of heavy and extra heavy crude oils is financially profitable and politically mandatory to meet current and future fuel demands [1,2].

Among the highly required value of light runs of a refinery, global demand for olefins aims at strengthening prospects for refining and

producing petrochemical products. In chemical industry, light olefins (C₂ through C₅) like ethylene and propylene, are important intermediates and feedstock for production of plastics and rubbers, fuel components, and other valuable chemical products. Over the last decade, the need for olefins has grown more than 50% so that we are witnessing production of almost 25 trillion tons of ethylene per annum. With ongoing increase of the world population, demand for olefins is expected to increase even further. Obviously, an economical olefin producing process is required to meet these needs [3–5].

Until recently, light olefins have been mainly produced by steam crackers, during a process in which propylene and butylenes were recovered as side-products of ethylene production units. However, natural gas accessibility has converted ethane into a dominant feedstock for steam cracking in many regions, and resulted in removing the production of propylene and butylene from the units. Propylene is still a major feedstock for petrochemical plants, while butylenes have been essential for high-octane gasoline at alkylation units. This implies that other technological methods must be introduced in order to suffice growing demands, particularly in catalytic cracking units and consciously olefin production [5,6].

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FCC can generate propylene and butylene from fuel-oil and residual oils together with other fuel products (gasoline and gas-oils). Historically, FCC unit has been operating in two modes of maximum gasoline as well as maximum distillate, based on seasonal product requirements and refinery location. The main motive for FCC process improvement is the need for more olefins gas production and the reduction in demand of residual oils [5,6].

Process adaptations and commercial catalysts and additives ended in increased propylene and/or butylene yields. Currently, it has been suggested to increment light olefin yield and decrease either naphtha/LCO yield, depending on technology and operation changes. Replacing diesel fuels with gasoline also forces FCC technology to reduce its production to take advantage of lighter products. To this end, with emersion of reformulated gasoline standards in recent years, FCC unit has been growingly required to operate in maximum olefin production mode [5,6].

1.2. Scope of the current study

Technological evolution of FCC units is very fast due to importance of these units in global economy of refineries. As soon as difficulties relevant to reaction complexities were overcome, great progresses were made in fundamental aspects such as mechanism of cracking, kinetic modeling of cracking, and catalyst deactivation. On the other hand, operation in FCC units is subjected to permanent improvements because of product quality requirements, particularly for automotive fuels, and differences in feed composition required by the market.

Kinetic study of FCC units is of great importance for reaching an optimum operating condition, as well as evolution in design of new riser reactors. In this study, kinetic behavior of catalytic cracking of VGO over a commercial FCC catalyst is studied by developing an 8-lump kinetic model to describe the catalytic cracking reaction system for production of liquid fuels and various olefin gases. Model parameters are estimated using two different optimization methods and the predicted yields are in good agreement with experimental data in the literature. Finally, the effects of some key operating parameters on the product yields are investigated and discussed.

1.3. Literature review

Commercial FCC feedstock commonly contains thousands of chemical components with a wide range of boiling temperatures. Detail description of kinetic behavior of such a complex mixture is a rather difficult task, though Gates et al. [7] tried to identify chemical reactions important to catalytic cracking. Thus, lumping of oil streams is essential to understand the kinetic modeling. Needless to say that a model which include underlying chemistry, i.e. single event method, is the most progressive approach to catalytic cracking owing to its fundamental characteristic. However, since a large number of parameters is necessary for detailed characterization of the feed, this method is still not widely applicable [8].

Generally, two basic techniques are available in lumping of catalytic cracking of heavy oils. The first one is lumping molecules into various distillation cuts called “pseudo-species” which considers chemical reactions between lumps. The lumps are often the feedstock and the final cracked products, such as gasoline, light cycle oil, light gases, and coke. The second approach is lumping different products according to main chemical characteristics such as paraffins, olefins, naphthenes, and aromatics. Using this approach, important data, including the reaction type (cracking, condensation, hydrogen transfer) and stoichiometry, are involved. It is worthwhile to mention that the second approach might be used to describe the pathways of various reactions [9].

To model the cracking kinetics, Weekman and Nace [10] separated FCC feedstock and products as three lumps: feedstock, gasoline (with a boiling range of $C_5 - 210^\circ\text{C}$), remaining butanes (C_4 's), dry gas, and coke. They also presented a predicting kinetic model for FCC riser.

Evaluations of the model kinetic parameters were carried out using the experimental data. This model was able to predict gasoline yield. However, it was not capable of predicting coke yield as a distinct component.

Prediction of coke is of importance as coke combustion in regenerator provides heat demanded for endothermic reactions of cracking in the riser reactor. Later, Yen et al. [11] and Lee et al. [12] developed a four-lump kinetic model in two distinct papers in which coke was considered as a separate lump added to the model of Weekman and Nace [10]. The model is still helpful because of its simplicity, easy formulation, solving of kinetics, energy and material equations. This simple lumping method to model the kinetics was further developed by various scholars by increasing the number of lumps in the models. Efforts made in this direction include: five-lump model proposed by Larocca et al. [13] and Ancheyta-Juarez et al. [14], six-lump model by Takatsuka et al. [15] and Xiong-Kai et al. [16], eight-lump model by Kraemer et al. [17], ten-lump model by Coxson and Bischoff [18], Jacob et al. [19] and Du-Yupeng et al. [20], eleven-lump model by Zhu et al. [21] and Huixin et al. [22], twelve-lump model by Oliveira [23] and Zong G. et al. [24], thirteen-lump model by Sa et al. [25], and nineteen-lump model by Pitault et al. [9]. Table 1 summarizes the published papers on the FCC lumping schemes.

1.4. Process description

FCC process, today, is still playing a major role as the heart of an advanced chemical refinery. The primary process is targeting the upgrading of low value heavy petroleum streams, such as fuel oil and VGO, into higher value cleaner fractions, mainly transportation fuels (such as gasoline, jet fuel, and diesel) as well as C_3 - C_4 olefins.

The process flow diagram of a side-by-side FCC unit is displayed in Fig. 1. Steam and VGO are heated to 316 – 427°C and are fed by the bottom of the reactor (riser), which is a long vertical pipe. The regenerated high temperature catalyst at 649 – 760°C also enters the bottom of the riser.

The main reactor is the riser where endothermic reactions of cracking occur. Residence time is usually between 2 and 10 s in the riser. Gaseous products flow from the top of the riser into the fractionator, while some heavy liquid hydrocarbons together with catalyst flow back into the disengaging zone. Hot steam is injected to the stripper section where the catalyst in oil is removed by some baffles installed inside the stripper. Oil strips from the catalyst in this way and the spent catalyst flows to the regenerator at 482 – 538°C . The coke, produced during cracking reactions inside the spent catalyst, is burned out by air

Table 1
Information of the published papers on FCC lumping schemes.

Number of kinetic lumps	Author(s)	Year of publication	Ref. No.
3	Weekman and Nace	1970	[10]
4	Yen et al.	1988	[11]
4	Lee et al.	1989	[12]
5	Larocca et al.	1990	[13]
5	Ancheyta-Juarez et al.	1997	[14]
6	Takatsuka et al.	1987	[15]
6	Xiong-Kai et al.	2015	[16]
7	Xu Ou-guan et al.	2006	[26]
8	Kraemer et al.	1991	[17]
10	Jacob et al.	1976	[19]
10	Coxson and Bischoff	1987	[18]
10	Du-Yupeng et al.	2015	[20]
11	Zhu et al.	1985	[21]
11	Huixin et al.	1995	[22]
12	Oliveira	1987	[23]
12	Zong G. et al.	2010	[24]
13	Sa et al.	1995	[25]
19	Pitault et al.	1994	[9]

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