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Quantitative correlations of cracking performance with physiochemical properties of FCC catalysts by a novel lump kinetic modelling method

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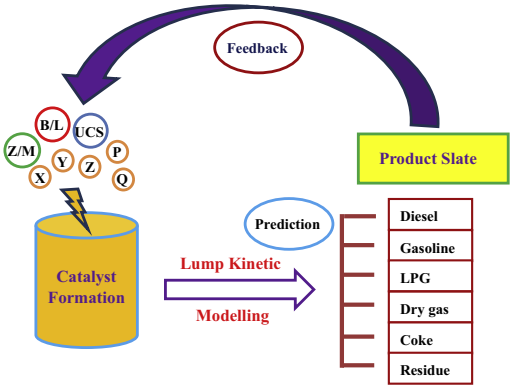
HIGHLIGHTS

- Quantitative correlations of cracking performance with physiochemical properties of FCC catalyst were studied.
- Three key property parameters of FCC catalyst were incorporated into a lump kinetic model for the first time.
- The catalyst property-included lump kinetic model was proved to be effective and reliable.
- Application of lump kinetic model was broadened in the field of catalyst selection and design.
- The new modelling method was expected to make the process of catalyst selection and design more theory-guided.

GRAPHICAL ABSTRACT



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ABSTRACT

The cracking performance determined by corresponding physiochemical properties of a FCC catalyst is usually one of the most important factors for catalyst selection and design. Thus, it is crucial to study the quantitative correlations of cracking performance with catalyst physiochemical properties. In this study, six commercial FCC catalysts were evaluated by cracking experiments on a fixed fluidized bed (FFB) and characterized of three key properties: zeolite to matrix specific surface area ratio (Z/M), total Bronsted to Lewis acid amount ratio (B/L) and zeolite unit cell size (UCS). Based on the experimental data, six 6-lump kinetic models were established for the six FCC catalysts. The three key property parameters were correlated with corresponding kinetic parameters of the six FCC catalysts, which leaded to the establishment and first report of a catalyst property-included lump kinetic model. The predicted data of product distribution exhibited good consistency with those experimental ones for two new FCC catalysts, and the relative errors were mainly below 10% for the catalyst property-included lump kinetic model. The new modelling method broadens the application of lump kinetic model in the field of catalyst selection and design, and in turn makes the process of catalyst selection and design more theory-guided.
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1. Introduction

The world refining industry has already been in the era of inferior and heavy oil, and the current state seems to being strengthened year by year [1–3]. Apart from hydroprocessing, fluid

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Nomenclature

a_j	concentration of lump j (kmol kg^{-1}) (oil gas)
C_C	weight percentage of coke on catalyst (%)
$f(A)$	catalyst deactivation function of heavy aromatics adsorption
$f(N)$	catalyst deactivation function of basic nitrogen poisoning
G_v	mass flow rate at cross profile (kg m^{-2} h^{-1})
k_A	adsorption coefficient of heavy aromatics, constant
k_j	rate constant of lump j (m^3 kg^{-1} h^{-1})
k_N	deactivation coefficient of basic nitrogen poisoning, constant
k_1~k_{12}	rate constants of the reactions between lumps (m^3 kg^{-1} h^{-1})
L	effective reactor length (m)
M_j	molecular weight of lump j (kg kmol^{-1})
$\overline{M}_w$	average molecular weight of the oil gas in reactor (kg kmol^{-1})
P	absolute pressure of reaction (kPa)
r_j	reaction rate of lump j (kmol m^{-3} h^{-1})
r_1~r_{12}	reaction rates between lumps (kmol m^{-3} h^{-1})
R	gas constant, 8.3145 (J mol^{-1} K^{-1})
S_{WH}	weight hourly space velocity (h^{-1})
t_c	catalyst residence time (s)
T	reaction temperature (K)
w_A	weight percentage of aromatics in feedstock (%)
w_{ASP}	weight percentage of asphaltenes in feedstock (%)
w_N	weight percentage of basic nitrogen in feedstock (%)
w_R	weight percentage of resin in feedstock (%)
x	reactor length at x cross profile (m)
X	dimensionless length
$y_{i,j}^{\exp}$	experimental data of lump j in experiment set i (%)
$y_{i,j}^{pre}$	predicted data of lump j in experiment set i (%)
yj	weight percentage of lump j (%)
$y1$	weight percentage of lump S (%)
$y2$	weight percentage of lump D (%)
$y3$	weight percentage of lump G (%)
$y4$	weight percentage of lump LPG (%)
$y5$	weight percentage of lump D_R (%)
$y6$	weight percentage of lump C_K (%)

Greek symbols

ε	void volume fraction of the fluidized bed, dimensionless variable
ρ	oil gas density (kg m^{-3})
ρa_j	molar concentration of lump j (kmol m^{-3})
ρ_c	catalyst bed density (kg m^{-3})
$\varphi(C_C)$	catalyst deactivation function of coking
$\Phi_{c/o}$	weight ratio of catalyst to oil, dimensionless variable

Abbreviations

S	residue
D	diesel
G	gasoline
LPG	liquefied petroleum gas
D_R	dry gas
C_K	coke

catalytic cracking (FCC) is the most flexible and efficient process to convert inferior and heavy feedstock into large amounts of gasoline, diesel and light olefins [4,5]. As is well-known, catalyst plays an important role in FCC process and the change of its formulation could lead to significant differences in product distribution. Besides, compared with technical reform and plant revamp, replacement of catalyst is the most economical, swift and efficient way for FCC units to obtain a better product distribution. Nowadays, the global demand for FCC catalyst is ever increasing. According to the report [6] of IHS Chemical, demands for catalytic cracking catalysts are expected to grow 3% annually through 2017. Therefore, the selection and design of FCC catalysts of better performance are always urgent and profitable subjects.

It is without denying that the cracking performance of a FCC catalyst is determined by its physiochemical properties under given reaction conditions. Hence, to facilitate the selection and design of FCC catalysts, it is crucial to investigate the relation between physiochemical properties with cracking performance of the catalyst. Despite much attention has been paid to deal with such issue in several literatures, they were mainly based on empirical or semi-empirical research method of poor extrapolation effect and could not quantitatively describe such relations [7–11]. For instance, Scherzer [10] reviewed the correlation between catalyst formulation and catalytic properties with abundant examples and discussed the design philosophy of FCC catalyst. Likewise, in order to select proper catalyst for each FCC unit, Chen [11] analyzed the relations of unit cell size (UCS), rare earth content and zeolite to matrix specific surface area ratio (Z/M) with cracking performance. Actually, current process of selection and design of industrial catalysts (including FCC catalysts) is rather complicated and is mainly based on laborious experiments and incomplete, unsystematic empirical rules [12–14]. Besides, the process of selection and design of FCC catalyst is increasingly challenged by more inferior and heavy feedstock, diversified and fluctuating product demand as well as ever stringent environmental restrictions.

Compared with those empirical and semi-empirical research methods, kinetic modelling is a more theory-guided method to study the cracking performance of a catalyst where lump kinetic modelling is the most popular and well-developed one. Notably, based on lump kinetic modelling, several literatures were reported for the screening and selection of FCC catalysts [15–22]. De Lasa et al. [19] reported their work of 8-lump kinetic modelling and FCC catalyst selection using a self-designed riser simulator. Ouyang and Weng [20] established three 11-lump kinetic models for three different FCC catalysts and determined the optimal operating temperatures for each catalyst by comparison of their rate constants. Vieira et al. [21] studied the kinetic behaviors of three equilibrium FCC catalysts and found that kinetic constants associated with the cracking of heavy components correlated well with the surface area and the microactivity of the catalysts. Quintana-Solorzano et al. [22] developed four 5-lump kinetic models for four different FCC catalysts, quantified the relative importance of different reactions at particular operating conditions by combination of kinetic and concentration effects, and analyzed the relation between catalyst properties and cracking performance. All these open literatures were meaningful attempts to reveal the relation between catalyst properties and cracking performance by lump kinetic modelling, while they could not quantify the relation for lack of quantitative relation between catalyst properties and kinetic parameters. However, as a quite instructive work, Ancheyta-Juarez [23] successfully correlated the FCC feed composition parameters with lump kinetic parameters. Up until now, catalyst property effect on product distribution has not been quantitatively considered in reported lump kinetic models and there is no lump kinetic model

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