



Short communication

Modeling of kinetic-based catalyst grading for upgrading shale oil hydrogenation



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HIGHLIGHTS

- The shale oil hydrogenation was upgraded at different catalysts grading schemes.
- Model of kinetic-based catalyst grading for shale oil hydrogenation was developed firstly.
- The catalysts grading schemes for shale oil hydrogenation were optimized.

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ABSTRACT

In this work, shale oil hydrogenation was upgraded in a two fixed-bed reactors to maximize light fraction with ultra-low sulfur and nitrogen. Three types of catalyst grading for shale oil hydroprotection, hydrofining, and hydrocracking were investigated to evaluate the hydrogenation performance. A lumping kinetic model of hydrodesulfurization, hydrodenitrification, and hydrocracking based on catalysts grading was established for the first time. Model parameters were determined using the Levenberg–Marquardt optimization algorithm. Results revealed that the model could accurately predict the removal ratios of sulfur, nitrogen, and desired product yields in shale oil hydrogenation under different catalyst grading. Thus, the model can be used for optimization of catalyst stacking to meet the requirements of hydrogenation products.

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1. Introduction

The growing concern on diminishing petroleum resources and rising fuel price has led to the development of various alternative energies to ensure global energy security [1,2]. Shale oil is a primary alternative energy that has received widespread attention in recent years because of its globally huge reserves of over 4.7 billion tons [3]. Shale oil is an unstable and extremely complex mixture of compounds with high heteroatom content, hence the desire for a suitable technology to upgrade shale oil. Shale oil hydrogenation currently attracts much pursuit because of its capacity to convert low-quality shale oil into valuable clean fuels, such as gasoline and diesel.

A number of studies on catalysts, technological conditions, and kinetic modeling for shale oil hydrogenation have been reported [4–6]. Landau et al. [7] developed a novel catalyst for Israeli shale

oil hydrogenation, which successfully reduced sulfur and nitrogen concentration in hydrogenation products and met the requirement for further hydrogenation. Luik et al. [8–10] systematically investigated the catalytic hydrotreatment of different fractions of Kukersite oil in a laboratory batch autoclave filled with Co–Mo and Ni catalysts, especially focusing on the influence of different operating conditions (temperature and hydrogen pressure) on the products properties. The experimental results from the hydrogenation also showed a remarkable improvement on the density, heteroatoms, and unsaturation degree of the hydrogenated distillate. Besides, the kinetic model for batchwise hydrogenation of shale oil explored by Johannes et al. [9] was effectively applied to the quantitative evaluation of catalysts and initial oils. Moreover, Tang et al. [11] currently reported that the lumping kinetic of hydrodesulfurization (HDS) and hydrodenitrification (HDN) were developed for the Chinese Huadian shale oil hydrogenation, in which the predictions showed a good agreement with the experimental data. Other studies on the upgrading of shale oil hydrogenation were also published. However, no information could be found regarding the

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Nomenclature

r	reaction rate (h^{-1})	k_{3N}	reaction rate constants of HDN in the HC catalyst bed (h^{-1})
w	mass fraction of heteroatom in shale oil, ($\mu\text{g/g}$)	y_1	volume fraction of HP catalyst (%)
k	apparent reaction rate constant (h^{-1})	y_2	volume fraction of HF catalyst (%)
X	heteroatom removal ratio (%)	y_3	volume fraction of HC catalyst (%)
$C_{i,F}$	mass fraction of each lump i in HF catalysts (%)	Abbreviations	
$C_{i,C}$	mass fraction of each lump i in HC catalysts (%)	HDS	hydrodesulfurization
$W_{inlet,s}$	mass fraction of sulfur in the feedstock ($\mu\text{g/g}$)	HDN	hydrodenitrification
$W_{outlet,s}$	mass fraction of sulfur in the product ($\mu\text{g/g}$)	HC	hydrocracking
LHSV ₁	LHSV in the HP catalyst bed (h^{-1})	HP	hydroprotecting
LHSV ₂	LHSV in the HF catalyst bed (h^{-1})	HF	hydrofining
LHSV ₃	LHSV in the HC catalyst bed (h^{-1})	LHSV	liquid hourly space velocity
k_{1S}	reaction rate constants of HDS in the HP catalyst bed (h^{-1})	RSS	residual sum of squares
k_{2S}	reaction rate constants of HDS in the HF catalyst bed (h^{-1})	Subscripts	
k_{3S}	reaction rate constants of HDS in the HC catalyst bed (h^{-1})	S	sulfur compound
k_{1N}	reaction rate constants of HDN in the HP catalyst bed (h^{-1})	N	nitrogen compound
k_{2N}	reaction rate constants of HDN in the HF catalyst bed (h^{-1})	i	lump component i

mathematical modeling of different catalyst grading approaches for performance optimization of shale oil hydrogenation.

Loading of catalyst grading is the key aspect of fixed-bed hydrogenation technology. Appropriate grading ratio is beneficial in enhancing catalyst activity and working life, as well as improving the quality of desired products [12]. Grading ratio is usually determined through experimental screening and artificial selection, which require a huge number of experiments with strong subjectivity and arbitrariness. Lei et al. [13] recently proposed a kinetic model approach based on catalyst grading that could predict hydrogenation effectiveness on different loading of catalysts grading. However, this model lacked the validation and is mainly applied for residual oil hydrogenation system. Moreover, modeling of kinetic-based catalyst grading for optimization of shale oil hydrogenation has been given little attention.

The current work systematically investigated shale oil hydrogenation in fixed-bed reactors by using different loading of catalysts grading. A lumping model for HDS, HDN, and hydrocracking (HC) kinetics based on various types of catalyst grading was established and also validated to optimize hydrogenation by predicting the appropriate catalyst stacking ratio.

2. Experimental

Shale oil distillate fraction, with boiling temperature below $360\text{ }^\circ\text{C}$ was used as feedstock, and its properties are summarized in Table 1. The shale oil demonstrated high sulfur and nitrogen features.

Hydrogenation catalysts were loaded combining laboratory synthesized hydroprotecting (HP), hydrofining (HF), and hydrocracking catalysts in series. The composition and its property characterization of each catalyst are shown in Table 2. All catalysts were pre-stabilized for more than 24 h under the required operating conditions.

Shale oil was hydrogenated in a two-stage fixed bed with bench-scale units, as shown in Fig. 1. Each stage reactor has an internal diameter of 15 mm and an entire length of 110 mm, detailed description of the experimental setup and procedure can be found elsewhere [14,15]. A series of hydrogenation tests was performed

under various catalyst grading schemes (Table 3) to evaluate the effect of catalyst grading on hydrogenation performance. The operating conditions for shale oil hydrogenation were optimized, as follows: reaction temperature: $380\text{ }^\circ\text{C}$; Pressure, 8 MPa; Liquid hourly space velocity (LHSV), 0.4 h^{-1} ; and H_2/oil , 1600.

The hydrogenation products were separated using a distillation device. The obtained cracking gas was analyzed using online gas chromatography, whereas the liquid products were characterized by their yield, density, and distillation range, and by C, H, S, and N analyses. The analyzed data provide a detailed basis for modeling the kinetic-based catalyst grading of shale oil hydrogenation.

3. Model approach

As shown in Fig. 1, the reaction section consisted of HF and HC reactor in series. The reactions in first reactor filled with HP and HF catalysts mainly involve HDS, HDN, and mild HC. In the second reactor loading only HC catalysts with mainly function of HC and partial HDS, HDN [16]. The HP catalysts are primarily used to intercept solid particles and remove parts of impurity in the feedstock,

Table 1
Feedstock characteristics.

Characteristics	Feedstock
Density (g/cm^3)	0.8892
Viscosity (mPa s)	16.23
<i>Elemental analysis (wt%)</i>	
C	80.39
H	11.03
O	5.85
N	1.98
S	0.75
H/C molar ratio	1.65
<i>Distillation range ($^\circ\text{C}$)</i>	
IBP	80
10%	179
50%	293
90%	358
95%	360

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