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Hydrodesulfurization and hydrodemetallization of different origin vacuum residues: New modeling approach

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HIGHLIGHTS

- The residue description gives a better differentiation of different origin residues.
- The chemical kinetic and Maxwell–Stefan equations are coupled in the catalyst.
- The diffusion limitation due to the molecule sizes improves the HDM prediction.
- The vanadium HDM seems to be controlled by the diffusion.

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ABSTRACT

In order to be able to upgrade the heaviest part of the crude oil one needs to remove several impurities, such as sulfur or metals. Residue hydrotreatment in fixed beds, under high hydrogen pressure can achieve high removal performances, with an industrial catalysts optimized staging. Despite the recent improvements, petroleum residues remain very difficult to describe and characterize in detail. Several kinetic models have been developed, but mostly they are feed dependant and their predictions are not satisfying for residues of different origins. Based on a recent study comparing residue properties and the differentiating physical–chemical properties responsible for reactivity (Ferreira et al., 2012), the present work develops a hydrotreatment kinetic model coupled with mass transfer in the catalyst which attempts to simulate the different residue performances. After estimation of kinetic parameters for a Iraqi residue (Buzurgan) with API gravity of 5, the model taking into account differences in residue characteristics, was validated for residues with API gravity close to Buzurgan one but shows increasing discrepancies with increasing API gravity.

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1. Introduction

Upgrading petroleum residue into lighter fractions is crucial to satisfy the increasing energetic demand. In addition, the available crude oils are becoming heavier and therefore the removal of impurities, as sulfur or metals is more necessary before converting. Residue upgrading processes produce either more distillates (low sulfur fuel oil) or residues suitable for the residue cracking units (RFCC). Among all residue upgrading processes, fixed bed hydro-treatment units are the most frequently used.

The residue fixed bed hydrotreatment process, Hyvahl™ developed by IFPEN in 1982 [2,3], consists of several trickle bed reactors in series, subdivided into two different reaction sections with specific catalysts. In each one of them. The first section

(HDM – hydrodemetallization) is intended to remove most of the metals and to slightly hydrocrack the asphaltenes. The second section (HDS – hydrodesulfurization) allows, with a deeper desulfurization function, the required sulfur levels to be achieved. Both sections operate at high hydrogen pressure and high temperatures. The understanding of chemical and physical phenomena in these reactors is a major challenge.

The heaviest fraction of oil contains a large polydispersity of molecular structures, which is very difficult to characterize precisely. A typical way to start residue characterization is by fractionation. The heaviest fraction, called asphaltenes, is obtained by precipitation using a paraffin [4]. The nature of asphaltenes is still a subject of much controversy [5–8]. It is nonetheless accepted that they are constituted of large size molecules and this phase possibly has a colloidal structure with an high concentration of impurities. Their hydrotreatment is then much more difficult than for lighter structures.

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Nomenclature

a_s	specific surface area of catalyst pellet ($\text{m}^2 \text{m}^{-3}$)	q^{max}	active site saturation concentration (mol m^{-3} of solid)
A_s	coefficient of the Scheibel correlation (-)	q^{site}	active site concentration (mol m^{-3} of solid)
b_i	thermodynamic Langmuir coefficient of the lump i ($\text{m}^3 \text{mol}^{-1}$)	q_i	concentration of the lump i in adsorbed phase (sites) (mol m^{-3} of solid)
C_i^p	concentration of the lump i in the fluid inside the pellet at equilibrium with the adsorbed phase (mol m^{-3})	Q_L	volumetric liquid flow rate ($\text{m}^{-3} \text{s}$)
C_i^f	concentration of the lump i in the extra granular fluid phase (mol m^{-3})	r_i^j	volumetric production reaction rate j of lump i ($\text{mol m}^{-3} \text{m}^{-2} \text{s}^{-1}$)
C_T	total concentration (mol m^{-3})	r_i	global volumetric surface production rate of lump i ($\text{mol m}^{-3} \text{m}^{-2} \text{s}^{-1}$)
D_{ij}^{eff}	effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	r_p	pore radius (m)
D_{ij}	Stephan-Maxwell binary lumps (ij) diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
D_{ij}^0	Stephan-Maxwell binary segment (ij) diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	R_c	catalyst pellet radius (m)
D_∞	bulk phase diffusion coefficient or translational diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	R_{coke}	coke molecules radius (m)
k	Boltzmann constant (J K^{-1})	R_h	molecule hydrodynamic radius (m)
k_j	kinetic constant of reaction j ($\text{m}^{-2} \text{s}^{-1}$ ou $\text{m}^3 \text{mol}^{-1} \text{m}^{-2} \text{s}^{-1}$)	S_c	section of the catalyst pellet (m^2)
k'_j	apparent kinetic constant of reaction j ($\text{m}^{-2} \text{s}^{-1}$)	S_{catalyst}	catalyst surface (m^2)
k_i^m	mass transfer coefficient of the lump i corresponding to the fluid phase (m s^{-1})	$S_{\text{initially available}}$	initially available surface of catalyst (m^2)
K_r	viscous drag coefficient of the considered lump (-)	$S_{\text{occupied,coke}}$	occupied surface of catalyst (m^2)
K_p	solute partition coefficient (-)	T	temperature (K)
L_c	length of the cylindrical pellet (m)	V_c	catalyst volume (m^3)
M_i	molecular weight of the lump i (kg mol^{-1})	$V_{p,\text{intragranularphase}}$	intra granular volume (m^3)
$M_{i,\text{GPC}}$	molecular weight of the lump i obtained by GPC (kg mol^{-1})	v_i^j	stoichiometric coefficient of the lump i of reaction j (-)
$M_{i(\text{Buzurgan}),\text{GPC}}$	molecular weight of the lump i obtained by GPC for Buzurgan (kg mol^{-1})	v_o^f	fluid velocity inside the reactor (m s^{-1})
$M_{i(\text{Buzurgan})}$	molecular weight of the lump i from Akbarzadeh works [26] for Buzurgan (kg mol^{-1})	v_i	molecular volume of the lump i ($\text{m}^3 \text{mol}^{-1}$)
nc	number of lumps (-)	v_o	molar volume of the elementary segment ($\text{m}^3 \text{mol}^{-1}$)
nd	number of deposits (adsorbed lumps) (-)	ε_i	extra granular porosity (-)
N_i	molar flux of the lump i ($\text{mol m}^{-2} \text{s}^{-1}$)	ε_p	intra granular porosity (-)
N_i^0	molar flux of the segment i ($\text{mol m}^{-2} \text{s}^{-1}$)	ϕ_i^p	volume fraction of the lump i in the intra granular solid phase (-)
N_{coke}	number of coke molecules (-)	ϕ_i^f	volume fraction of the lump i in the extra granular fluid phase (-)
n_{si}	number of segments of the lump i , comparing to the elementary volume (-)	ϕ_i^s	volume fraction of the coke, Vanadium or Nickel on the catalyst surface (-)
NR	number of reactions (-)	τ_R	catalyst tortuosity (-)
		ρ_i	density (kg m^3)
		η	viscosity of the fluid phase (Pa s)
		λ	ratio between pore and molecule hydrodynamic radius (-)

In parallel to the development of the process and understanding of the residue physical and chemical properties and reactivities, IFPEN has been working on the development of kinetic and catalyst deactivation models for both sections of the process [9–11]. These models give quite satisfying results, but were developed for specific Middle East residues and lack accuracy when tested to simulate residues of different origins. Alternative hydrotreatment models reported in the literature are based on heavy residues originating from other areas but are only tested for the specific residues for which they are developed and no general model is suggested [12–16].

The problem of such models is that their feed description is quite simple and that the model parameters such as kinetic constants, depend on the vacuum residue origin. To overcome such constraints, quite complex residue description models based on molecular reconstruction have been developed and can be found in the literature [17–19]. However, these models are so complex that, due to their computing time, they are almost never integrated in a complete kinetic model of residue hydrocracking and are of

very difficult practical application. Moreover, works of Ferreira et al. have introduced the diffusion limitation in the catalyst in order to describe the impact of molecules sizes on the hydrotreatment performances [20].

In the present work, based on the experimental works of Ferreira et al. [1], we introduce a new heavy residue feed description and consequent kinetic network. The aim is that model parameters should be independent of vacuum residue origin whilst the model itself remains as simple as possible. This description is then introduced into the reactor/kinetic model which includes the two sections of the process. After parameter estimation with a Iraqi residue, the model is validated with experimental results from three residues with different origins.

2. Experimental section

Vacuum residues with quite different characteristics, i.e. densities, sulfur, metals and asphaltenes content were selected and

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