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Modeling the deactivation by metal deposition of heavy oil hydrotreating catalyst

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ABSTRACT

Modeling the deactivation of heavy oil hydrotreating catalyst was carried out by using a pore plugging model. Experimental data were obtained at constant temperature of 385 °C, pressure of 9.8 MPa, LHSV of 0.25 h and 5000 scf H_2/bbl oil. Kinetics was derived from experimental data collected at short times-on-stream (TOS) whereas data affected by pore plugging by metal deposition was obtained between 200 and 2200 h TOS. The model employed was capable of predicting with confidence the profiles of diminution of metal removal (nickel and vanadium) at short and long values of time-on-stream.

1. Introduction

The study of the hydrotreating (HDT) of heavy oils and residua is a formidable task due to the difficulty for obtaining reliable experimental information as well as the complex nature of those feeds and the large number of reactions occurring [1,2]. The collection of data over representative long-term experiments can be another insurmountable economical barrier for many researchers. Various works reported in the literature have dealt with studies on the kinetics of HDT of heavy feeds, however absence of the effect of deactivation phenomenon is noticeable. From the industrial point of view modeling the catalyst performance at long times-on-stream (TOS) is more valuable than at short TOS. Several HDT processes use fixed-bed reactor for hydrotreating purposes [3]. In that type of reactor undesirable loss of catalyst activity is observed as function of TOS.

Traditionally the deactivation phenomenon has been divided in three stages: early deactivation due to coke deposition (SOR: start-of-run), middle stage deactivation due to loss of sites by poisoning and pore-plugging by metal-sulfide deposits (MOR: middle-of-run), and total loss of activity by severe diffusional resistances due to almost total pore plugging (EOR: end-of-run), that reduces the activity at such a lower value that unavoidable unit shut down is carried out [4–7].

Most of the reported studies have been conducted with commercial catalyst at first hours of TOS and kinetic parameters are lumped with initial rapid deactivation factor. Modeling that deactivation period has been reported by others [8–10]. Some approaches use experimental information to determine parameters of semi-empirical models but simulations are only valid within the range of operation variables and parameters have not always physical meaning [11–13], hence limited applications of such models is devised. On the other hand, considering simple reactions various approaches to model HDT catalyst deactivation have been proposed. The end of life of catalyst, i.e. EOR although valuable is not of enough interest to be modeled with confidence. However studies on middle stage of catalyst deactivation seem to be very useful because during this period is when the catalyst is employed in the industrial practice. Predicting the performance of catalyst for long TOS by using models with tuning parameters is almost impossible. Thus it seems that more fundamental modeling of deactivation during middle stage is necessary. Some approaches have been used for predicting catalyst life [14,15] but the effect of metal deposits was not taken into account and in some cases very long times were necessary in order to tune the empirical constants.

Among the several reported models for predicting the performance of HDT catalyst in middle stage the one developed by Oyekunle and coworkers [16,17] is a suitable approach for representing the growing of metal-sulfide deposits within the catalyst pore due to hydrodemetallization (HDM) reaction [18].

Thus the aim of this work is to apply the pore plugging model due to metal-sulfide compounds deposition to predict the performance of catalyst for HDM of heavy oil during long time-on-stream

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Nomenclature

A_1	Riazi's correlation parameter
A_2	Goto and Smith's correlation parameter
B	matrix for orthogonal collocation
B_1	Riazi's correlation parameter
C	reactant concentration
C_A	reactant concentration of A species
C_{A0}	reactant concentration at entrance of reactor system
D	bulk diffusion
D_r	restrictive diffusion coefficient
d_p	catalyst diameter
d_t	reactor diameter
i	degree of polynomial
k	reaction rate constant
K	reaction rate constant per unit of surface area
L	characteristic catalyst particle size
LHSV	liquid hourly space-velocity
M_{ms}	molecular weight of metal-sulfide compounds
n	reaction order
N_A	molar flow across circle area
P	pressure
r_{mol}	molecular radius of metal-bearing compounds
r_p	instantaneous pore radius
S	cross-flow area
t	Time
T	absolute temperature
T_0	boiling temperature of the lightest compound in the feed mixture
T_{mean}	mean absolute temperature
u_L	linear liquid velocity
v	molar liquid volume
cwt	cumulative weight fraction
z	position within pore

Subscripts

0	initial
f	feed
p	product
r	restrictive
t	instantaneous

Greek symbols

α	geometry parameter
Γ	the gamma function
γ	ratio of instantaneous pore radius to initial pore radius
δ	metal-sulfide thickness within catalyst pore
€	metal sulfide molecules per molecule of reactant
ε_0	bed void fraction
ε_L	dynamic liquid holdup
ζ	dimensionless intra-particle position
η	effectiveness factor
λ	ratio of molecule radius to pore radius
μ	dynamic liquid viscosity
ρ_{ms}	metal-sulfide compound density
ρ_{oil}	heavy oil density
τ	dimensionless time
ϕ	Thiele modulus
χ	dimensionless reactant concentration

in middle stage deactivation period and to predict the changes in activity for longer times. Kinetic parameters are derived from experimental information and transport properties are estimated with correlations recommended in the literature.

2. The model

2.1. Mass balances

The model employed to describe the pore plugging of the catalyst due to deposits of metal-sulfide species is that developed by Oyenkule et al. [16,17]. The following assumptions were done:

i. Irreversible HDM reaction (*HC-Metal* → *HC*-free metal).
ii. Power-law kinetic model.
iii. Constant hydrogen concentration due to its presence in excess.
iv. No resistances to mass transfer between fluid and catalyst particle.
v. Cylindrical pores.
vi. Loss of activity due to reduction of pore size.
vii. Isothermal particle with constant size and shape.
viii. Plug-flow reactor model.
ix. Negligible pressure drop.
x. No vaporization of feed due to its heaviness.

The mass balance within the pore (Fig. 1) is as follows:

$$-N_A|_z S + N_A|_{z+\Delta z} S + k\overline{C_A^n} S\Delta z = -\frac{\partial C_A}{\partial t} S\Delta z \tag{1}$$

where concentration over-bar means average reactant concentration in the volume element.

After dividing by cross-flow section (S) and Δz and taken the corresponding limit:

$$\frac{\partial N_A}{\partial z} + kC_A^n = -\frac{\partial C_A}{\partial t} \tag{2}$$

The following form of Fick's first law is assumed [19]:

$$-D\frac{\partial C_A}{\partial z} = N_A \tag{3}$$

Substitution of Eq. (3) in Eq. (2) produces:

$$D\frac{\partial^2 C_A}{\partial z^2} - kC_A^n = \frac{\partial C_A}{\partial t} \tag{4}$$

The following dimensionless variables are used:

$$\chi = \frac{C_A}{C_{A0}} \quad \zeta = \frac{z}{L} \quad \tau = \frac{tD}{L^2} \quad \phi = L\sqrt{\frac{kC_{A0}^{n-1}}{D}}$$

After proper application of chain rule, Eq. (4) is transformed to:

$$\frac{\partial \chi^2}{\partial \zeta^2} - \phi^2\chi^n = \frac{\partial \chi}{\partial \tau} \tag{5}$$

The size of molecule bearing metal-sulfide compounds can restrict the diffusivity of species [9,20–22], so that this restriction was taken into account by using Eq. (6):

$$D_r = D(1-\lambda)^4 \tag{6}$$

where $\lambda = (r_{mol}/r_p)$

Hence the mass balance (Eq. (5)) takes the following form [16]:

$$\frac{\partial \chi^2}{\partial \zeta^2} - \phi_r^2\chi^n = \frac{\partial \chi}{\partial \tau_r} \tag{7}$$

With initial conditions:

$$\text{At} \quad \tau_r = 0 \quad \chi = \chi_{\max} \quad \forall_\zeta | \chi \in (0, 1],\ \chi = 1,\ \chi = 0$$