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Dynamic modeling and simulation of hydrotreating of gas oil obtained from heavy crude oil

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ABSTRACT

This paper describes a dynamic heterogeneous one-dimensional model of trickle-bed reactor used for catalytic hydrotreating of oil fractions. The model takes into consideration the main reactions occurring in the hydrotreating process: hydrodesulfurization, hydrodenitrogenation, hydrodearomatization (mono-, di-, and polyaroamatics), olefins hydrogenation, and mild hydrocracking (gas oil, naphtha, and gases). Kinetic parameters were determined from experimental data obtained in an isothermal bench-scale reactor during hydrotreating of atmospheric gas oil coming from a heavy crude oil over a commercial CoMo catalyst. The developed model was used to predict the dynamic behavior of an industrial hydrotreating reactor within a wide range of reaction conditions. Changes in concentration, partial pressure, and temperature profiles are simulated and discussed as a function of reactor axial position and time. The simulation results obtained with the proposed dynamic model showed good agreement with experimental data.

1. Introduction

Catalytic hydrotreating (HDT) has become one of the fundamental processes in the petroleum-refining industry from technical, economic, and environmental points of view. The HDT process has been used for over 60 years to obtain fuels with improved quality and low polluting compounds content (sulfur, nitrogen, aromatics, etc.) and to fulfill the applicable legal norms of gas emissions. Nevertheless, since 2009 in the European Union automotive fuels have to meet the so-called ultra-low sulfur specifications (10 ppmw total sulfur in gasoline and diesel), which are probably to be applied worldwide [1]. Among other changes (i.e., new reactor design, use of new generation catalysts, etc.), these environmental restrictions will force the refineries to increase the severity in the operating conditions of the HDT reactor in order to match these more stringent specifications [2–4]. To reach this low sulfur content value is even more complicated when refinery feed is composed by high amount of heavy crude oil. Distillates, such as gas oil, coming from heavy petroleum are characterized by high content of impurities (sulfur, nitrogen, aromatics, etc.) exhibiting complex structure and refractory in nature. These new conditions will alter the performance of HDT commercial units; for instance, light hydrocarbons production, H_2 consumption, yield of liquid, temperature gradient in the reactor will be altered, among other consequences. One way to deal with this situation is either by detailed and extensive experimental program or by reactor modeling and simulation, which allows for having a deep understanding on the phenomena occurring in the HDT reactor with the main purpose of establishing the optimal operating conditions, catalyst formulation, process configuration, reactor design, feed selection, reactor internals design, effect of operating variables, combination with other emerging technologies, etc.

Among the different approaches for modeling chemical reactors sustaining HDT reactions, the most common are those that perform the analysis based on local average behavior of molecules (lump models), which generally were developed as pseudohomogeneous and heterogeneous reactor models on steady state [5–21], while studies on dynamic modeling and simulation with either pseudohomogeneous or heterogeneous reactor models are scarce [22–29], and nothing has been reported for modeling the hydrotreating of gas oil distilled from heavy petroleum.

The objective of the present contribution is to illustrate the application of a dynamic plug-flow heterogeneous one-dimensional trickle-bed reactor (TBR) model to obtain kinetic data from bench-scale experiments and their subsequent use to predict the unsteady state behavior of an industrial HDT reactor.

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Nomenclature

a_L	gas–liquid interfacial area per unit reactor volume, cm_I^2/cm_r^3
a_S	liquid–solid interfacial area per unit reactor volume, cm_S^2/cm_r^3
A',b'	empirical constants for Bondi's correlation, dimensionless
Cp_f	specific heat capacity of f phase, $J/(g_f K)$
C_i^L	molar concentration of component i in the bulk liquid phase, mol_i/cm_L^3
C_{SLi}^S	molar concentration of compound i at surface of solid covered by liquid phase, mol_i/cm_L^3
d_{pe}	equivalent particle diameter, cm_S
D_{ei}^L	effective fickian diffusivity in liquid phase of compound i inside porous solid, $cm_L^3/(cm_S\,s)$
D_{Mi}^L	molecular diffusion coefficient of compound i in the liquid phase, $cm^3{}_L/(cm_S{\cdot}s)$
$E_{a,j}$	activation energy for j reaction, J/mol_i
f_w	catalyst wetting efficiency, $cm_{S,wet}^2/cm_S^2$
F	objective function to be optimized, mol_i/cm_L^3 or g_i/g_{Total}
G_{mL}	superficial mass flow velocity of liquid phase, $g_L/(cm_r^2\,s)$
h_{LS}	heat transfer coefficient for liquid film surrounding the catalyst particle, $J/(s\,cm_S^2\,K)$
H_i	Henry's law coefficient of component i, $MPa\,cm_L^3/mol_i$
$k_{1,2,3}$	intrinsic reaction rate constants for mild HCR reactions, $(mol_i/cm_L^3)^{1-n}(1/s)$
$k'_{app,j}$	apparent reaction rate constant for heterogeneous reaction j, $(cm_L^3)^{m+n}/[mol_i{}^{(m+n-1)}\,g_S\,s]$
$k'_{in,j}$	intrinsic reaction rate constant for heterogeneous reaction j, $(cm_L^3)^{m+n}/[mol_i{}^{(m+n-1)}\,g_S\,s]$
$k_{0,j}$	frequency factor for reaction j, $(mol_i/cm_L^3)^{1-n}(1/s)$
$k'_{0,j}$	frequency factor for heterogeneous reaction j, $(cm_L^3)^{m+n}/[mol_i{}^{(m+n-1)}\,g_S\,s]$
k_i^S	liquid–solid mass transfer coefficient of compound i, $cm_L^3/(cm_S^2\,s)$
K_{Li}	overall gas–liquid mass transfer coefficient of compound i in the liquid phase, $cm_L^3/(cm_I^2\,s)$
K_j	equilibrium constant for j (=$HDA_{Poly/Di/Mono}$) reaction, dimensionless
K_{H_2S}	adsorption-equilibrium constant of H_2S on catalyst active sites, cm_L^3/mol_{H_2S}
$K_{0,j}$	pre-exponential factor for equilibrium constant of reaction j, dimensionless
K_{0,H_2S}	pre-exponential factor for adsorption-equilibrium of H_2S, cm_L^3/mol_{H_2S}
L_B	length of catalyst bed, cm_r
m,n	reaction order, dimensionless
MW_L	molecular weight of liquid phase, g_L/mol_L
N_{RL}	number of reactions in the liquid phase, dimensionless
p_i^G	partial pressure of component i in the bulk gas phase, MPa
r_j^L	rate of reaction j per unit of volume in the liquid phase, $mol_i/(cm_L^3\,s)$
r'^L_j	rate of reaction j per unit of catalyst mass in the liquid phase, $mol_i/(g_S\,s)$
R	gas law constant, $J/(mol_i\,K)$
S_p	total geometric external surface area of catalyst particle, cm_S^2
t	time, s
T_f	temperature of f phase, K
u_f	superficial velocity of f phase, $cm_f^3/(cm_r^2\,s)$
V_p	total geometric volume of catalyst particle, cm_S^3
w_i	weight fraction of compound i in the liquid phase, g_i/g_L
Y_i	weight fraction for mild HCR reactions, g_i/g_{Total}
z	axial reactor coordinate, cm_r

Greek symbols

$\Delta H_{ads,H_2S}$	adsorption enthalpy of H_2S, J/mol_{H_2S}
$\Delta H_{R,j}^L$	heat of reaction j in the liquid phase, J/mol_i
$\in_B$	catalyst bed void fraction, $cm_{(G+L)}^3/cm_r^3$
$\in_S$	catalyst particle porosity, $cm_{(G+L)}^3/cm_S^3$
ε_f	external holdup of f phase, cm_f^3/cm_r^3
$\eta_j{}^L$	catalyst effectiveness factor of reaction j in the liquid phase, dimensionless
ρ_B	catalyst bed density, g_S/cm_{cat}^3
ρ_f	density of f phase at process conditions, g_f/cm_f^3
$\upsilon_{i,j}{}^L$	stoichiometric coefficient of component i in reaction j in the liquid phase, dimensionless
ζ	catalyst bed dilution factor, $cm_{cat}^3/(cm_{cat}^3 + cm_{inert}^3)$
ϕ_S	shape factor (=surface area of a sphere of equal volume/solid surface area), dimensionless
Φ_j^L	Thiele modulus of reaction j in the liquid phase, dimensionless
τ	tortuosity factor for catalyst particle, cm_L/cm_S

Subscripts

app	apparent
calc	calculated
CH_4	methane
Di	diaromatics
exp	experimental
f	phase (gas, liquid or solid); final or outlet condition
G	gas phase
GO	gas oil
HC	hydrocarbon
HCR	hydrocracking reaction
HDA	hydrodearomatization reaction
HDN	hydrodenitrogenation reaction
HDS	hydrodesulfurization reaction
HGO	olefins hydrogenation reaction
H_2	molecular hydrogen
H_2S	hydrogen sulfide
i	component index
in	intrinsic
I	gas-liquid interface
j	reaction index
k	experiment index
L	liquid phase
Mono	monoaromatics
N	nitrogen compound
Naph	naphthenes
NH_3	ammonia
O	olefins
Poly	polyaromatics
S	sulfur compound; solid phase; condition at external surface of catalyst particle
0	initial or inlet condition; reference condition