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Kinetic model development and simulation of simultaneous hydrodenitrogenation and hydrodemetallization of crude oil in trickle bed reactor

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ABSTRACT

One of the more difficult tasks in the petroleum refining industries that have not been considered largely in the literature is hydrotreating (HDT) of crude oil. The accurate calculations of kinetic models of the relevant reaction scheme are required for obtaining helpful models for HDT reactions, which can be confidently used for reactor design, operating and control. In this work, an optimization technique is employed to evaluate the best kinetic models of a trickle bed reactor (TBR) process utilized for hydrodenitrogenation (HDN) and hydrodemetallization (HDM) that includes hydrodevanadization (HDV) and hydrodenickelation (HDNi) of crude oil based on pilot plant experiments. The minimization of the sum of the squared errors (*SSE*) between the experimental and estimated concentrations of nitrogen (N), vanadium (V) and nickel (Ni) compounds in the products is used as an objective function in the optimization problem to determine the kinetic parameters.

A series of experimental work was conducted in a continuous flow isothermal trickle bed reactor, using crude oil as a feedstock and the commercial cobalt–molybdenum on alumina (Co–Mo/γ-Al_2O_3) as a catalyst.

A three-phase heterogeneous model based on two–film theory is developed to describe the behaviour of crude oil hydroprocessing in a pilot–plant trickle bed reactor (TBR) system. The hydroprocessing reactions have been modelled by power law kinetics with respect to nitrogen, vanadium and nickel compounds, and with respect to hydrogen. In this work, the gPROMS (**g**eneral **PRO**cess **M**odelling **S**ystem) package has been used for modelling, simulation and parameter estimation via optimization. The model simulations results were found to agree well with the experiments carried out in a wide range of the studied operating conditions. The model is employed to predict the concentration profiles of hydrogen, nitrogen, vanadium and nickel along the catalyst bed length in three phases.

1. Introduction

The technologies for upgrading petroleum fractions are some of the most important processes in the refining industry because of the growing market demands for different crude oil derivatives and decreasing availability of light oils [1]. Therefore, it is essential to increase the productivity of distillates with high quality. Among these technologies, hydrotreatment operation, which has the capacity for increasing the distillates production and to remove the impurities such as sulfur, nitrogen, metals (Ni and V) and asphaltenes [2].

The presence of nitrogen compounds in crude oil or oil fractions has a detrimental effect for refining industries. Nitrogen compounds are responsible for catalyst poisoning and reducing catalyst activity. Furthermore, nitrogen compounds have toxic effects on the storage stability of oil products and affect the colour of oil products [3]. Andari et al. [4] have shown the impact of nitrogen and sulfur compounds through their studies of Naphtha, Kerosene and Diesel oils derived from Al-Kuwait crude oil and they proved that these compounds showed unwanted influence on the stability of fuel in addition to the environmental pollution. Kaernbach et al. [5] confirmed that the nitrogen compounds significantly affect the catalyst activity through their works on the vacuum residue.

The metallic compounds in crude oil have also been of great interest to researchers in this area because of the problems caused by these compounds. The existence of metallic compounds in crude oil and its fractions has harmful effects. These compounds have a very bad influence on the HDT efficiency, plug the pores of catalysts used, cause rapid deactivation for the hydroprocessing catalyst, where they tend to deposit on the catalyst, and seem to act to reduce HDT activity by decreasing catalyst surface area [6–8]. Also, the presence of vanadium and nickel in addition to iron and copper affects the activity of cracking catalysts and causing an

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Nomenclature

a	dimensionless number
a_L	gas–liquid interfacial area, cm^{-1}
a_S	liquid–solid interfacial area, cm^{-1}
A_C	surface area, cm^2
A_j^0	pre-exponential factor for reaction j, $(mol/cm^3)^{1-n}\,(cm^3/g\ s)\,(mol/cm^3)^{-m}$
API	American Petroleum Institute
$C_{H_2}^L$	concentration of hydrogen in the liquid phase, mol/cm^3
C_i^L	concentration of i compound in the liquid phase, mol/cm^3
$C_{H_2}^S$	concentration of H_2 in the solid phase, mol/cm^3
C_i^S	concentration of i compound in the solid phase, mol/cm^3
De_i	effective diffusivity of i compound in the pores of catalyst, cm^2/s
d_c	diameter of cylindrical catalyst particle, cm
$D_{H_2}^L$	molecular diffusivity of H_2 in the liquid, cm^2/s
D_K	Knudsen diffusivity, cm^2/s
D_i^L	molecular diffusivity of i compound in the liquid, cm^2/s
DR	reactor diameter, cm
d_s	diameter of spherical catalyst particle, cm
EA_j	activation energy for j process, J/mol
G_L	liquid mass velocity, $g/cm^2\ s$
h_{H_2}	Henry's coefficient for hydrogen, MPa cm^3/mol
k_j	reaction rate constant for j reaction, $(mol/cm^3)^{1-n}\,(cm^3/g\ s)\,(mol/cm^3)^{-m}$
$K_{H_2}^L$	gas–liquid mass transfer coefficient for hydrogen, cm/s
$K_{H_2}^S$	liquid–solid mass transfer coefficient for H_2, cm/s
K_i^S	liquid–solid mass transfer coefficient for i compound, cm/s
L	length of particle, cm
L_c	length of cylindrical catalyst particle, cm
LHSV	liquid hourly space velocity, h^{-1}
m_j	order of reaction of hydrogen in reaction j
n_j	order of reaction of i compound in reaction j
Mw	molecular weight, kg/kg mole
p	reactor total pressure, psia
$P_{H_2}^G$	partial pressure of hydrogen, MPa
r	particle radius, cm
r_g	pore radius, cm
r_j	chemical reaction rate of j reaction per unit mass of the catalyst, $mol/g\ s^{-1}$
R	universal gas constant, J/mol K
S_g	specific surface area of particle, cm^2/g
S_p	total geometric external area of particle, cm^2
SSE	sum of square errors
$Sp.gr_{15.6}$	specific gravity of oil at 15.6 °C
T	reaction temperature
T_{meABP}	mean average boiling point, °R
TBR	trickle bed reactor
u_g	velocity of the gas, cm/s
u_L	velocity of the liquid, cm/s
v	volume, cm^3
V_g	pore volume per unit mass of catalyst, cm^3/g
V_{H_2}	molar gas volume of H_2 at standard conditions, Nl/mol
V_p	total geometric volume of catalyst, cm^3
z	reactor bed length, cm

Greek letters

ρ_B	bulk density of the catalyst particles, g/cm^3
ρ_L	liquid density at process conditions, lb/ft^3
$\rho_{15.6}$	density of oil at 15.6 °C, g/cm^3
ρ_{20}	density of the oil at 20 °C, g/cm^3
ρ_o	density of oil at 15.6 °C and 101.3 kPa, lb/ft^3
ρ_p	particle density, g/cm^3
η_j	catalyst effectiveness factor j reaction
ε	void fraction of the catalyst bed
μ_L	liquid viscosity at process conditions, mPa.s
υ_C^L	critical specific volume of liquid feedstock, cm^3/mol
υ_C^i	critical specific volume of i compound, ft^3/mol
υ_L	molar volume of liquid feedstock, cm^3/mol
υ_i	molar volume of i compound, cm^3/mol
λ_{H_2}	solubility coefficient of H_2, Nl kg^{-1} MPa^{-1}
$\Delta\rho_P$	pressure dependence of liquid density, lb/ft^3
$\Delta\rho_T$	temperature correction of liquid density, lb/ft^3
ϕ_i	Thiele Modulus i compound
θ	particle porosity
τ	tortuosity factor

Superscripts

0	degree
G	gas phase
H_2	hydrogen
L	liquid phase or gas–liquid interface
S	solid phase or liquid–solid interface
i	compound (crude oil, H_2, N, V or Ni)

Subscripts

0	at the first reactor length
c	cylindrical
f	at the final reactor length
g	gas
H_2	hydrogen
i	compound (N, V, Ni or H_2)
j	reaction (HDN, HDV or HDNi)
L	liquid
s	spherical

increase in the level of coal deposited. Also, the presence of these compounds, especially vanadium in the fuel used in the high power machines as gaseous turbines lead to the formation of some sediment on the turbine, which can lead to the change in balance [9,10]. Furthermore, the ash resulting from the combustion of fuels containing sodium and particularly vanadium reacts with refractory furnace linings to lower their fusion points and hence cause their destruction [3].

The process of crude oil hydrotreating is a new challenge and new technology which has not been considered previously, where all hydrotreating processes are carried out on each oil cuts separately, and not on the full crude oil (i.e. after the separation of crude oil to its derivatives, such as gasoline, kerosene, light and heavy gas oil). This means that a large amount of the impurities, namely, sulfur, nitrogen, metals, aromatics and asphaltenes will be deposited at the bottom of the atmospheric and vacuum distillation column. In addition, hydrotreating process each section separately is fairly easy due to the ability to control the reaction, the knowledge of physical and chemical properties, kind of reaction and its condition. Hydrotreating of crude oil is regarded as a big and difficult challenge since crude oil involves a lot of compounds and multiple phases, in addition to difficult structures. Additionally, hydrotreating of crude oil in the existence of asphaltenes that contain a large amount of these impurities, especially metals that close the active sites on the catalyst is one of the more difficult and significant problems. The expected benefits of directly hydrotreating crude oil are increasing of middle distillates productivity due to conversion of heavy compounds and long molecules that